ISOTOPIC EXCHANGE REACTIONS IN ACETIC
ANHYDRIDE AND ANHYDROUS ACETIC ACID

by

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ISOTOPIC EXCHANGE REACTIONS IN ACETIC ANHYDRIDE AND ANHYDROUS ACETIC ACID

INTRODUCTION

GENERAL. Some of the properties of acids and bases have been recognized and used from very ancient times, and interest in defining and characterizing these classes of substances has been apparent for more than four centuries. Nevertheless, there is still some controversy, as evidenced by the five major concepts of acid-base phenomena which still exist (42, p.1).

A large number and variety of experimental approaches have been applied to studies of acid-base and associated phenomena. They have included conductivity measurements, titration procedures (particularly with indicators), determinations of solubilities, studies of displacement reactions, and isolation of end products of reactions. Since the turn of the century, extensive investigations which have been carried out in non-aqueous, ionizing solvents have contributed much to development in this field (5, p.13).

There is in progress in this department at
the present time an integrated program for investigation of such phenomena in non-aqueous, ionizing solvents by using radioactive tracer procedures. This involves determining the rates of isotopic exchange of solutes with such solvents, and with other solutes dissolved in them, as a function of various experimental conditions. This report represents work, some of it of a more or less exploratory nature, which has been carried out within the framework of this larger program. The solvent systems investigated have been those of acetic anhydride and anhydrous acetic acid.

Before details of the work are presented, it may be pertinent and of interest to review very briefly the historical development of concepts of acid-base phenomena and non-aqueous solvent systems.

HISTORICAL BACKGROUND. It has been pointed out by Muir (44, p. 239) that the long history of the terms acid, base, and salt has been subject to a tyranny of words, phrases, and over-simplified analogies. For example, when Scheele labeled his new discovery "dephlogisticated marine acid," it was accepted as an acid for years by those who worked with it. Laviosier named "dephlogisticated air" oxygen and, using the terminology of the alchemists,
called it the "acidifying principle" of all acids. This concept had many adherents for nearly half a century, although it occasionally had to be stretched somewhat in order to cover data obtained in the laboratory. After he had shown that all acids do not contain oxygen, Davy reached the rather far-sighted conclusion in 1814 that acidity depended upon "peculiar arrangements" of various "substances" rather than upon the presence of any one particular elementary substance. However, the "acidifying principle" was revived again in 1838 when Liebig defined acids as compounds of certain radicals with replaceable hydrogen. His views, with slight refinements, were considered satisfactory by most chemists until recent times.

Near the end of the nineteenth century, van't Hoff and Arrhenius endeavored to teach chemists that in aqueous solutions of acids, bases, and salts the molecules, or at least part of the molecules, were separated into charged particles, and that reactions in solutions were reactions of these charged particles or ions. In fact, Arrhenius believed that, "One may even go so far as to assert that only ions can react chemically." (44, p.498)
With the advent of the Arrhenius theory of dissociation, acids and bases became substances which gave up hydrogen and hydroxyl ions, respectively, in water solutions. This concept was gradually adopted by most chemists and constituted the water theory (or, Arrhenius theory) of acids and bases. It was a completely satisfactory theory only as long as no attention was directed to non-aqueous solvents and acid-base systems in these solvents. As early as 1896, however, it was observed that basic behavior is possible in such non-aqueous solvents as aniline, in which hydroxyl ions are not present (27, p.783).

Beginning in 1897, an extensive series of investigations of liquid ammonia was begun by Franklin and his co-workers (23, pp.1-339). Their research demonstrated a large number of striking resemblances between the unusual properties of liquid ammonia and water. For example, ammonium and amide ions were found to be comparable to hydrogen and hydroxyl ions in their properties and reactions.

This work led to the development of an ammonia or nitrogen system of compounds comparable to the ordinary oxygen or water system, and to a concept called the solvent theory of acids and bases.
A number of other non-aqueous solvents attracted attention during this period and were frequently considered as parent substances for solvent systems comparable to those of ammonia and water. In many cases the analogies included substances such as methane and were carried to an extreme. The interest in a wide variety of non-aqueous protonic solvents, such as hydrogen sulfide, hydrogen fluoride, ammonia, and water, eventually contributed to the third modern concept of acids and bases—the one-element proton theory developed by Bronsted and Lowry (42, pp.6-9).

This theory differs from the more common Arrhenius definition primarily in that any substance which gives up a proton or hydrogen ion in solution is an acid and any substance which takes up a proton is a base. There are several important differences between this view and the older theory. For example, a substance can be an acid or a base regardless of its charge; that is, it can be either a compound or an ion. Although an acid still requires hydrogen, the term "base" is thus no longer limited to the hydroxyl ion. Finally, the terms "salt" and "neutralization" have no part in this concept.
The development of a number of non-protonic solvent systems, such as that of liquid phosgene (24, p.71), led to efforts to extend the proton theory to include "proton-like" ions. According to this idea, acids should no more be confined to substances containing labile hydrogen than bases should be restricted to compounds forming hydroxyl ions. In the phosgene system, for example, the behavior of carbonyl and chloride ions is analogous in many respects to that of hydrogen and hydroxyl ions, respectively, in the water system.

The electron theory of acids and bases proposed by Lewis is a more fundamental view of acid-base phenomena than the concepts described above and, unlike them, is independent of any particular ion or solvent. According to this theory, an acid is a molecule or ion which can accept an electron pair, and a base is a molecule or ion which can donate a pair of electrons. Neutralization is then defined as the formation of a covalent compound between an acid and a base. Although this explanation was first suggested by Lewis in 1923, he did not elaborate upon it until 1938 (40, pp.293-313).

The fifth current theory of acids and bases
is the positive-negative theory of Usanovich (42, p.13). It defines an acid as a substance which can yield cations or combine with anions, and a base as a substance which can give up anions or combine with cations. A number of objections to this theory have been expressed by Luder (42, p.13).

**NON-AQUEOUS SOLVENT SYSTEMS.** The non-aqueous solvent systems of liquid ammonia, liquid sulfur dioxide, acetic anhydride and anhydrous acetic acid will be discussed briefly because they are the ones to which isotopic investigations have been directed.

**Liquid ammonia.** Of non-aqueous, ionizing solvents, liquid ammonia has been the most extensively investigated. These studies have made very important contributions to synthetic inorganic and organic chemistry, to theoretical chemistry (serving, for example, as the experimental basis for the Bronsted-Lowry and Lewis concepts), and to the organization and systematization of nitrogen chemistry (5, pp.13-17).

Although several earlier workers accumulated experimental data which showed that liquid ammonia is an unusual solvent in which chemical reactions can be readily carried out, it was not until 1896 that its
striking resemblance to water was first noted (23, p.10). Prior to that time, the success of Arrhenius' work had led to the tacit assumption that only water could be used as a solvent for ionic reactions.

The research of Franklin and others has since shown that self-ionization occurs to a limited extent in liquid ammonia just as it does in water.

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

The ammonium and amide ions may be considered analogous to the hydronium and hydroxyl ions. Thus, for example, ammonium chloride and sodium amide are, respectively, an acid and a base. The phenomena of solvation and solvolysis, as well as characteristic acid-base reactions such as neutralization, amphoterism and reaction with metals to form hydrogen have also been found to be similar in the ammonia and water system. It was the existence of a large variety of such analogies in the liquid ammonia and water system that caused Franklin to formulate the ammonia system of acids, bases, and salts, and a scheme of nomenclature for describing these derivatives and their reactions (22, pp.285-317).
The success of the solvent theory in the case of liquid ammonia encouraged investigations of a large number of other non-aqueous solvents, both protonic and non-protonic. Some of the protonic substances also considered to a greater or lesser extent as parent compounds and reaction media were hydrogen sulfide, hydroxylamine, hydrazine, alcohols, hydrogen halides, and acetic acid.

**Sulfur dioxide.** Although sulfur dioxide was studied as an ionizing medium almost as early as liquid ammonia, the solvent theory was first applied to a non-protonic solvent in 1925 when Germann (24, p. 71) showed that typical acid-base reactions could be carried out in liquid phosgene. He also found, for example, that the slightly conducting, pure phosgene gave carbon monoxide and chlorine as products of electrolysis, indicating the existence of a water-like self-ionization:

\[
\text{COCl}_2 \rightleftharpoons \text{CO}^{++} + 2\text{Cl}^-
\]

or

\[
\text{COCl}_2 \rightleftharpoons \text{COCl}^+ + \text{Cl}^-
\]

"Acids," such as aluminum chloride, were found to form isolable solvates when dissolved in the liquid and gave solutions which reacted with metals to form
gaseous carbon monoxide, just as hydrogen can be displaced by metals in aqueous acid solutions.

Although Germann formulated a scheme of acid-base nomenclature corresponding to these observations, it was not well accepted until slightly modified and simplified by Cady and Elsey (12, pp. 1425-1428), who then applied it to the liquid sulfur dioxide system.

The very poor conductance of pure, liquid sulfur dioxide indicates that it undergoes a slight amount of self-ionization according to the following mechanism.

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

According to the nomenclature of Cady and Elsey, an acid of this system is one which increases the concentration of the cations formed according to this equation. Thionyl chloride was proposed as such an acid, assuming that its dissociation to give thionyl ions upon solution in sulfur dioxide is as follows:

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

Similarly, a salt such as caesium sulfite or tetramethylammonium sulfite, when ionized in solution, should act as a base by increasing the concentration
of sulfite ions. The following reaction was then given as a typical neutralization reaction in solvent sulfur dioxide.

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

Most of the experimental evidence for the above reactions has been obtained in a series of investigations by Jander and his co-workers (33, pp.209-306). Their work has been primarily concerned with conductivity studies and reactions such as those of displacement. The results have shown, for example, that (1) a solution of thionyl chloride in sulfur dioxide has a slightly greater conductivity than the pure solvent, (2) neutralization reactions between acids and thionyl chloride and tetramethylammonium sulfite can be studied by conductimetric titrations, (3) amphoteric behavior is demonstrated by the fact that aluminum sulfite will dissolve readily in a sulfur dioxide solution containing either an acid or a base, and (4) displacement reactions, such as the formation of thionyl bromide and potassium chloride from thionyl chloride and potassium bromide, can take place. Such observations led Jander's group to conclude that thionyl and sulfite ions do exist in
solutions of "acids" and "bases" of this system. Some doubt is cast upon this conclusion, however, by data obtained in recent radioactive tracer studies (35, pp.3052-3055), which will be discussed later.

**Anhydrous acetic acid.** Although some work had been done by a number of earlier workers, systematic investigations of acetic acid as a water-like, ionizing solvent did not begin until 1928 when Davidson and his co-workers began a series of investigations which soon showed that a sufficiently large variety of acids, bases, and salts is soluble in acetic acid to justify its consideration as the parent substance of a solvent system (17, pp.1890-1894). Since that time, a great number of metathetical reactions have been studied in this solvent and many have been found to occur as readily in it as in water. Extensive studies of those involving "neutralization" have been made and have since proved useful in analytical chemistry where acetic acid has been used as a solvent for titrations involving very strong acids and very weak bases (9, pp.374-375).

Numerous conductivity and cryoscopic studies have shown that electrolytes dissolved in this solvent are only weakly ionized and that even the
strongest bases are incompletely dissociated at high dilutions (36, p.1008)(1, pp.2877-2879). Kolthoff and Willman have shown by conductivity and indicator studies that the order of decreasing strength of bases in acetic acid is KAc > NH₄Ac > BaAc₂ > NaAc > LiAc > SnAc₂ > MgAc₂ > BiAc₃ > PbAc₂ > HgAc₂.

The conductivity of such electrolytes in acetic acid is markedly increased by the addition of even very small amounts of water (36, p.1008). This is presumably due to an increase in the dielectric constant of the medium, which would, of course, decrease the stability of ion pairs and triplets normally formed by the electrolytes.

Several investigations have been made of the phenomenon of amphoterism in acetic acid solutions. Salts for which such behavior has been demonstrated include the acetates of zinc (21, pp.519-527) (39, pp.3340-3342), copper (19, pp.1341-1357), and lead (18, pp.4524-4525)(38, p.142). The solubilities of these acetates are very markedly increased by the alkalimetal acetates or ammonium acetates, all of which act as strong bases in this solvent. This is analogous, formally at least, to the behavior of the hydroxides of these metals in aqueous solutions when
a strong base is added.

Plumbous acetate exhibits an anomalous behavior in acetic acid just as it does in aqueous solutions. In contrast to the very slight solubilities of zinc and copper acetates, for example, it is soluble to the extent of 17 mole per cent at 25° C (18, pp. 4524-4525) which is even greater than that observed for the acetates of the alkali metals. However, plumbous acetate is a much poorer conductor in acetic acid than are the alkali metal acetates, and, according to Davidson and co-workers (20, pp. 1523-1527), must be considered only very slightly dissociated. These investigators also found that the increase in conductivity resulting from dissolving plumbic acetate in acetic acid is so slight that this solute is apparently "altogether non-ionic in character." In support of this conclusion, they found that, whereas the solubility of plumbous acetate increases with increasing concentration of sodium acetate, the solubility of the plumbic salt decreases upon addition of the strong base.

This behavior appears to be an exception to the usually analogous behavior of the acetic acid and water systems, since in the latter Pb(0H)₄ gives a number of plumbates in which the tetravalent state of lead is even more stable than in the dioxide (49, p. 603).
Davidson and his co-workers, however, consider the behavior of plumbic acetate to be simply an example of the "salting out" of a non-electrolyte (20, p.1527).

**Acetic anhydride.** Investigations of this substance as an ionizing solvent have not been as extensive as those of acetic acid. Most of the work has been that of Usanovich (52, p.4540)(53, p.6444) and Jander (33, pp.307-341). The slight specific conductivity of the pure substance (2x10^-7 to 5x10^-7 ohm^-1 at 25°C) (33, p.309) is presumably due to the water-like self-ionization

$$(\text{CH}_3\text{CO})_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}^+ + \text{CH}_3\text{COO}^-.$$  

According to solvent system nomenclature, such compounds as acetyl chloride, acetyl bromide, acetyl thiocyanate and acetyl sulfide are, therefore, acids in this system, and acetates are bases.

The relatively high dielectric constant of this solvent probably accounts for the fact that most salts and the acetates of the alkali and alkaline earth metals are fairly strong electrolytes in this solvent. For instance, the equivalent conductance of a 0.001 M potassium acetate solution at 25°C is 26 ohm^-1 in acetic anhydride (33, p.315). In contrast
to this, however, the acetates of the more acidic elements, such as silicon, tin and arsenic, are very weak electrolytes.

A number of metathetical reactions which are formally analogous to those of the water system have been investigated in this solvent (33, pp.307-341) (43, pp.159-171)(53, p.644). For example, neutralizations of alkali metal acetate solutions by the addition of such "acids" as acetyl chloride have been followed conductimetrically. Not all such acids of this system undergo these reactions extremely rapidly, however. Usanovich has reported that when a solution of sodium acetate is titrated with one of acetyl chloride, the color of the indicator used changes only very slowly because of the slow ionization of the "acid" (53, p.644). Jander followed this neutralization conductimetrically and found that the conductivity varies for some time after each addition of the acetyl chloride (33, p.325). However, his explanation of this behavior is simply that supersaturated solutions of sodium chloride are readily formed.

APPLICATION OF RADIOACTIVE TRACERS. A few non-aqueous solvents, such as liquid ammonia, liquid sulfur dioxide, and glacial acetic acid, have, as
indicated above, commanded most of the attention of investigators in the past. Although these are probably the ones most conveniently studied and the results are perhaps of the most utility, there are a number of other non-aqueous, "water-like" solvents which have also been investigated. Table 1, page 18 indicates the large variety of such substances.

It should be noted that there is already some evidence to show that the dissociation of pure ionizing solvents in the water-like manner indicated in this table may not occur in some cases. For example, cryoscopic studies have shown (26, p.2552) that most of the dissociation of pure nitric acid occurs by the self-dehydration

$$2\text{HNO}_3 \rightleftharpoons \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O}$$

rather than by the self-ionization mechanism

$$2\text{HNO}_3 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{NO}_3^-.$$ 

Other cryoscopic work has shown that a similar situation exists in pure sulfuric acid (25, p.2516). Although part of the self-dissociation occurs according to the equation
Table 1.
Non-Aqueous Ionizing Solvents

<table>
<thead>
<tr>
<th>Solvent and supers /ionized</th>
<th>Reference</th>
<th>Melting point °C</th>
<th>Boiling point °C</th>
<th>Dielectric constant</th>
<th>Typical acid</th>
<th>Typical base</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$</td>
<td>(23, pp. 1-339)</td>
<td>-77.7</td>
<td>-33.4</td>
<td>22.7(-50°)</td>
<td>$\text{NH}_4\text{Cl}$</td>
<td>$\text{NaNH}_2$</td>
</tr>
<tr>
<td>$2\text{SO}_2 \rightleftharpoons \text{SO}^{++} + \text{SO}_3^-$</td>
<td>(33, pp. 209-307)</td>
<td>-75.7</td>
<td>-10.02</td>
<td>13.8(14.5°)</td>
<td>$\text{SOCl}_2$</td>
<td>($\text{CH}_3)_4\text{N}_2\text{SO}_3 \cdot \text{SO}_2$</td>
</tr>
<tr>
<td>$2\text{HOAc} \rightleftharpoons \text{H}_2\text{OAc}^+ + \text{OAc}^-$</td>
<td>(17, pp. 1890-1894)</td>
<td>16.7</td>
<td>118.1</td>
<td>6.25(20°)</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$\text{K(\text{CH}_3\text{COO})}$</td>
</tr>
<tr>
<td>$\text{Ac}_2\text{O} \rightleftharpoons \text{Ac}^+ + \text{OAc}^-$</td>
<td>(33, pp. 315-341)</td>
<td>-73.1</td>
<td>140</td>
<td>20.5(20°)</td>
<td>$\text{CH}_3\text{COCl}$</td>
<td>$\text{K(\text{CH}_3\text{COO})}$</td>
</tr>
<tr>
<td>$2\text{I}_2 \rightleftharpoons \text{I}^+ + \text{I}^-$</td>
<td>(34, pp. 321-338)</td>
<td>113.6</td>
<td>183.0</td>
<td>12(130°)</td>
<td>$\text{ICl}$</td>
<td>$\text{KI}$</td>
</tr>
<tr>
<td>$2\text{H}_2\text{S} \rightleftharpoons \text{H}_3\text{S}^+ + \text{HS}^-$</td>
<td>(58, pp. 237-250)</td>
<td>-85.5</td>
<td>-60.4</td>
<td>9.05(-78°)</td>
<td>$\text{HCl}$</td>
<td>($\text{C}_2\text{H}_5)_3\text{NH}$</td>
</tr>
<tr>
<td>$2\text{HCN} \rightleftharpoons \text{H}_2\text{CN}^+ + \text{CN}^-$</td>
<td>(33, pp. 120-169)</td>
<td>-13.35</td>
<td>25</td>
<td>123(15.6°)</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$\text{KCN}$</td>
</tr>
<tr>
<td>$\text{SeOCl}_2 \rightleftharpoons \text{SeOCl}^+ + \text{Cl}^-$</td>
<td>(51, p. 167)</td>
<td>8.5</td>
<td>179.4</td>
<td>46(20°)</td>
<td>$\text{FeCl}_3$</td>
<td>$\text{KCl}$</td>
</tr>
<tr>
<td>$\text{CCl}_2 \rightleftharpoons \text{COC}^+ + \text{Cl}^-$</td>
<td>(24, pp. 24)</td>
<td>-104</td>
<td>8.2</td>
<td>4.3(22°)</td>
<td>$\text{AlCl}_3$</td>
<td>$\text{CaCl}_2$</td>
</tr>
<tr>
<td>$2\text{HF} \rightleftharpoons \text{H}_2\text{F}^+ + \text{F}^-$</td>
<td>(50, pp. 213-235)</td>
<td>-83</td>
<td>19.5</td>
<td>83.5(0°)</td>
<td>$\text{KF}$</td>
<td>$\text{KCl}$</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^-$</td>
<td>(2, pp. 369-370)</td>
<td>-11.2</td>
<td>21.1</td>
<td>2.56(15°)</td>
<td>$\text{NOCl}$</td>
<td>($\text{Et}_2\text{NH}_2\text{NO})$</td>
</tr>
<tr>
<td>$\text{NOCl} \rightleftharpoons \text{NO}^+ + \text{Cl}^-$</td>
<td>(11, p. 1964)</td>
<td>-61.5</td>
<td>-5.8</td>
<td>18.2(12°)</td>
<td>$\text{NOCl}$</td>
<td>$\text{KCl}$</td>
</tr>
</tbody>
</table>
In deciding upon which non-aqueous solvents to study by tracer techniques several criteria have been applied in reducing the large number of possibilities. For example, the melting and boiling points must be suitable for experiments using conventional vacuum line techniques at convenient temperatures. The solutes and solvents should be readily prepared and purified. Suitable radioisotopes must be obtainable and the radiochemical preparations should be reasonably straightforward.

Up to the time of the work described here, only liquid ammonia and sulfur dioxide had been studied as ionizing solvents by using isotopes. In the case of liquid ammonia, Nyman and co-workers (46, p.1034) dissolved $\text{N}^{15}$-labeled ammonium chloride in liquid ammonia, then evaporated off the solvent and determined its $\text{N}^{15}$ content. Their shortest run required seven minutes to evaporate off the ammonia at $33^\circ \text{C}$ after the ammonium chloride had dissolved. Complete exchange had occurred within this period of

\[2\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{SO}_4^+ + \text{HSO}_4^-\]
They are continuing this investigation, using different techniques, in order to determine which of the following two mechanisms is involved in this proton exchange.

\[
\begin{align*}
(1) & \quad \text{NH}_4^+ + \text{NH}_3 &\rightleftharpoons & \text{NH}_3^+ + \text{NH}_4^- \\
(2) & \quad 2\text{NH}_3 &\rightleftharpoons & \text{NH}_4^+ + \text{NH}_2^-
\end{align*}
\]

In this laboratory, Johnson, Norris, and Huston have studied exchange rates of "acids" and "bases" in liquid sulfur dioxide (35, pp.3052-3055). This work has shown that the "base" tetramethylammonium pyrosulfite exchanges extremely rapidly with the solvent. This could be interpreted as resulting from exchange of sulfite ions from the ionization of the pyrosulfite with sulfite ions produced by self-ionization of the solvent. However, on the basis of investigations by Huston (31, pp.3049-3051) and Nakata (45, pp.635-638), Johnson, et al., have proposed that a direct interaction takes place between solvent and sulfite, the solvent acting as an acid, in the Lewis sense, and accepting an oxide ion from the sulfite base in the following manner:

\[
\text{SO}_3^- + \text{SO}_2 \rightleftharpoons \text{SO}_2 + \text{SO}_3^-
\]
Labeled sulfur in the "acids," thionyl chloride and thionyl bromide, was found to undergo an extremely slow rate of exchange, if any at all, with solvent sulfur dioxide. These results, in conjunction with other evidence (6, pp.243-287), indicate that in at least some instances the sulfur dioxide system of chemistry proposed by Jander (33, pp.209-307) requires modification. In particular, ionic mechanisms, especially those involving his proposed water-like, self-ionization of the solvent, may have been over-emphasized.

Since the liquid ammonia and sulfur dioxide systems have already been the subject of tracer investigations, acetic acid is, perhaps, the most logical solvent for additional work of this nature. In contrast to sulfur dioxide, for instance, it is a protonic solvent. Like sulfur dioxide, it has a very low dielectric constant (6.25 at 25° C). It differs from liquid ammonia in being an acidic rather than a basic solvent, as well as in having a much lower dielectric constant. Its low specific conductivity (0.5-0.8x10^-8 ohm^-1 at 25° C) (36, p.1008) indicates that self-ionization occurs only to a small extent. As previously mentioned, it is a good
solvent for a number of salts, although such solutions have very low equivalent conductances due to association of the ions into pairs or triplets, or to complex ionization, or to both (36, p.1008).

The melting and boiling points of the material make it convenient for use with vacuum line apparatus. The isotopes used (carbon-14 and radium D) are readily available and the radiochemical preparations are relatively simple. A satisfactory procedure also exists for purifying the solvent and for determining its purity.

There are a number of interesting questions concerning the acetic acid system for which it was hoped this research with radioactive carbon and lead would provide answers. In general, these are concerned with the validity of one of the main criticisms which has been directed at solvent system theories: over-emphasis on ionic mechanisms (42, p.13). For example, considering the very slight degree of ionization of plumbous acetate in acetic acid, as indicated by previously mentioned conductivity and cryoscopic studies, it was felt that the exchange of acetate ions between this solute and the solvent might occur at a reasonably slow rate. In that case, several worthwhile
lines of investigation would be opened. For instance, in addition to kinetic studies at various temperatures, the effect of the addition of traces of water could be determined and the results possibly correlated with such factors as the hydrogen bonding and dielectric constant of the solvent.

A determination of the exchange rate of sodium acetate was also considered worthwhile. If it were more rapid than the plumbous acetate exchange, the addition of the alkali acetate to an acetic acid solution of presumably amphoteric lead acetate might be expected to increase the exchange rate of the latter through an equilibrium such as

\[ 2\text{NaOAc} + \text{Pb(OAc)}_2 \rightleftharpoons \text{Na}_2\text{Pb(OAc)}_4 \]

which the work of Lehrman (38, p.142) has indicated.

Since, as discussed previously, lead tetracetate has been reported to be a non-electrolyte in solvent acetic acid, experiments comparable to those described above for the diacetate would also be worthwhile, since exchange might reasonably be expected to be measurably slow.

Other interesting solutes for which measurable exchange rates were considered at least a possibility
were boron acetate, which is also reportedly a covalent compound (48, p.612), and iodine triacetate.

Sidgwick has pointed out that the only evidence for the existence of plumbic ions in acetic acid is the work of Hevesy and Zechmeister (29, pp.410-415)(30, pp.151-153), who found that labeled lead ions from plumbous acetate exchange at an immeasurably rapid rate with those from plumbic acetate when these two solutes are dissolved in glacial acetic acid. These investigators do not give all of the conditions of their experimental work, such as times of exchange, temperature, purity of the solvent and counting procedure. However, it is indicated that the runs were made at higher temperatures, for relatively long periods of time, and with ordinary glacial acetic acid. It, therefore, seemed worthwhile to repeat this investigation with better control of such experimental factors. The exchange of radioactivity between plumbous and plumbic acetates would, of course, require the interchange of two electrons. Outside of the Hevesy and Zechmeister work, only a very few such exchange reactions have been reported, and none of these have been in
non-aqueous solvents (55, p.23).

A study of the acetic anhydride solvent system by tracers is, in one respect, more intriguing than a similar study of acetic acid, because $^{14}C$ can be used for studying the acids, as well as the bases, which have been proposed for this solvent. Thus, in addition to making the same types of studies with bases as those previously described for solvent acetic acid, it appeared worthwhile to investigate the exchange rate of acetyl chloride with acetic anhydride. The formal resemblance of this acid to thionyl chloride (which exchanges extremely slowly, if at all, with solvent sulfur dioxide) made such a study of particular interest. The system is a more attractive one for investigation than that of liquid sulfur dioxide–thionyl chloride, in that only one chlorine atom is involved. The results are consequently likely to be unambiguous.

In the case of "base" solutes, one exchange study has been reported (48, p.3050). The exchange of solid sodium acetate with acetic anhydride was found to occur very rapidly (55% randomization in twenty minutes). Since this rate of exchange was remarkably great, considering the insolubility of sodium acetate in this solvent, it seemed worthwhile to repeat this
experiment, as well as carrying out the homogeneous experiments previously mentioned.

An investigation of the rate of isotopic exchange of labeled acetic acid with solvent acetic anhydride (as well as the reverse case) would possibly indicate whether the self-ionization of non-aqueous solvents is as vital a factor in reactions of acids and bases in these systems as has been commonly believed. In other words, if acetic acid and acetic anhydride self-ionize appreciably they might very well exchange rapidly with each other—subject, of course, to the assumption that the acetic acid molecules would ionize more or less as readily in acetic anhydride as in pure acetic acid, and vice versa.
EXCHANGE REACTIONS IN ANHYDROUS ACETIC ACID

EXPERIMENTAL OUTLINE. The isotopic exchange rates of three bases (sodium acetate, plumbous acetate, and plumbic acetate) with acetic acid of the highest possible purity were determined. One of the main reasons for choosing these three solutes was the fact that they differ appreciably in their physical and chemical behavior in acetic acid. Thus, as previously discussed, sodium acetate is a strong base in this system; plumbous acetate may exhibit amphoteric behavior; and, plumbic acetate is apparently a non-electrolyte.

Unexplainable variations in experimental results from preliminary sodium acetate exchange studies indicated that an isotope effect might be operative in the wet combustion of acetates or acetic acid. Since the wet combustion method has also been commonly used by other workers for oxidation of labeled acetates (8, p.998)(41, pp.192-199)(47, p.660), experiments were performed to find whether or not it is subject to such an effect and, if so, to what degree.

Following this, investigations were made of the plumbous acetate-acetic acid, acetic anhydride-acetic acid, and plumbous acetate-plumbic acetate-acetic
acid systems to find whether or not measurable exchange rates existed in any of these cases. Radioactive lead (ThB and RaD) was used to label the plumbous acetate exchange involving the two valence states of lead.

**EXPERIMENTAL PROCEDURE.** In all the experimental work described here great care was used to prepare anhydrous reagents and to make the runs in such a way that these hygroscopic materials were exposed to the least possible amount of moisture. This was ordinarily accomplished by using high vacuum techniques. Where these were not feasible (in making weighings or transferring salts, for instance,) a dry box was used in which the air was thoroughly dried by passing it through calcium chloride and barium perchlorate columns. The conventional vacuum system used gave vacua of better than $10^{-5}$ mm Hg. "Apiezon N" grease was used wherever stopcocks or ground joints were required.

The radioactive carbon used in this work was obtained from the Atomic Energy Commission as BaCO$_3$. The radium D was obtained from the Canadian Radium and Uranium Corporation of New York City in a solution of lead nitrate of high specific activity.
The labeled carbon compounds used were converted to barium carbonate for radioassay. This was then plated on copper planchets according to the procedure of Dauben, et al., (16, p.828) and counted, using a Berkeley scalar having an end window counter (Tracerlab Model TGC-2, (2.0 milligrams per square centimeter of mica)). Self-absorption corrections from an empirically determined curve were used.

All counting samples from experiments involving radioactive lead were mounted as lead chromate because this is one of the very few lead compounds which is sufficiently insoluble to be precipitated from an acetate solution. Lead dioxide, which was used by early workers (29, pp.410-415) (30, pp.151-153), was tried but not found to be as suitable.

The counting procedure for radioactive lead did not differ materially from that used for the radiocarbon except that it was necessary to make at least two counts at separate times (standardizing with a Tracerlab RaD standard) and to use a shield of aluminum to keep polonium alpha particles from reaching the counter tube.

In practice, the lead chromate labeled with
RaD had a secular equilibrium activity of 534 counts per minute per milligram (corrected to zero thickness). Usually, ten to fifteen milligrams of material, with perhaps one-half the secular equilibrium activity, were counted. Although an experimental self-absorption curve was used, the correction was, in most cases, less than three per cent.

**Radium D as tracer.** Radium D is more convenient than thorium B for labeling lead because its long half-life (22 years) means that only one Pb(OAc)₂ preparation is required. Both isotopes of lead (ThB and RaD) are usually counted by means of the beta rays from their daughters. While a preparation labeled with ThB will almost certainly be in secular equilibrium with its daughter, ThC, (half-life of 60.5 minutes) when counted, this is not at all certain when RaD is used, since RaE has a half-life of 5.0 days.

In other words, a preparation containing RaD may contain more or less than the secular equilibrium quantity of RaE. For instance, it is interesting to note that practically no RaE was carried down when Pb(OAc)₂ was crystallized from glacial acetic acid, while, on the other hand, the RaE was precipitated completely when Pb(OAc)₄ was hydrolyzed.
in water to give PbO$_2$.

Though it has been done (59, pp.1739-1744), it is neither necessary nor practical to wait the period of about a month required for a RaD preparation to attain secular equilibrium. The equilibrium activity may be calculated by counting the same sample several days apart and using the equation

$$\frac{N_{\text{max.}} - N_1}{N_{\text{max.}} - N_2} = e^{(\Delta t)(5.78 \times 10^{-3})}$$

- $N_{\text{max.}}$ = number of counts at secular equilibrium,
- $N_1$ = initial number of counts observed at time $t_1$,
- $N_2$ = number of counts observed at a later time $t_2$.

The above equation can be derived from that for the growth curve, $N = N_{\text{max.}} (1 - e^{-\lambda t})$, where the constant, $\lambda$, is equal to $5.73 \times 10^{-3}$ days$^{-1}$. As a matter of convenience, the expression $e^{(\Delta t)(5.78 \times 10^{-3})}$ was plotted as a function of $\Delta t$. A possible alternative to the above procedure would be to make use of the fact that during any one half-life the amount of daughter element progresses one-half of the distance to secular equilibrium, regardless of where the
starting point may have been.

**Preparation of carboxyl-labeled sodium acetate.** The procedure used was that described by Claycomb, et al. (54, pp.45-48). Approximately 200 mg of BaCl$_4$O$_3$ were acidified in an evacuated system and the evolved CO$_2$ allowed to react with an excess of methyl magnesium iodide in ether. After hydrolysis with sulfuric acid, the ether was distilled off and silver sulfate added. The acetic acid was then separated by steam distillation and very carefully titrated to the phenolphthalein end point with standard sodium hydroxide solution.

Yields of 61 and 82 per cent, based upon the carbon dioxide, were obtained in the two preparations made by this method.

The sodium acetate solution was dehydrated, without the appreciable loss of acetic acid from hydrolysis which occurs if the water is evaporated off by heating, by placing it in a flask connected by ground joints to one end of a large, evacuated U-tube having a similar flask immersed in liquid air at the other end. The cooling caused by sublimation kept the sodium acetate frozen, thus avoiding any bumping. After dehydration was apparently complete,
a small amount of very dilute acetic acid was added to neutralize any sodium hydroxide which might be present and the solution was again dehydrated. It was found necessary to slowly heat the flask with the sodium acetate up to 100° C in vacuo near the end of the dehydration in order to be sure of making the acetate anhydrous in a reasonable length of time. The dehydrated material, over which a vacuum of less than 10⁻⁵ mm Hg could be held, was kept in an oven at 110° C until used.

Preparation of anhydrous acetic acid and acetic anhydride. Since anhydrous acetic acid is extremely hygroscopic, the purification problem is primarily that of removing small amounts of water. Melting points which have been obtained for acetic acid prepared by the various methods reported in the literature vary considerably and many were uncorrected. The acetic acid used in the present investigation was purified by the procedure of Hess and Haber (26, pp. 2205-2209). This method involves fractional distillations, followed by fractional crystallizations, and yields material having a melting point of 16.635° ± 0.005° C (corr.). They found that it was necessary to work with relatively large amounts of the acid, avoiding any exposure to
In this work, 1950 ml of Baker and Adamson 99.5% acetic acid was fractionated in a "D0-2" distilling column having thirty plate sections.¹ Fourteen hundred ml of residue, boiling at 117.7° C, were combined in a dry atmosphere with 1200 ml of residue obtained by a similar fractional distillation with 2250 ml of starting material. Seven hundred milliliters of the 2600 ml of combined residues was then distilled off, leaving a residue boiling at 118.1° C, and having a melting point of 16.54° C. Sixteen hundred milliters of this material were then distilled off and fractionally crystallized.

The crystallizations were carried out in a stoppered, three liter, round-bottom boiling flask which was packed in ice and shaken mechanically. After all but about 200 ml or less of the acetic acid had crystallized, the flask was quickly dried, transferred to a dry box and the mother liquor decanted. After melting the crystals the procedure was repeated.

After five fractional crystallizations, the melting point of the crystalline residue had risen to

¹. Glass Engineering Laboratories, Belmont, California.
16.63 ± 0.01° C (corr.) and did not change with subsequent crystallizations. A mercury thermometer calibrated by the Bureau of Standards was used for taking the melting points according to the procedure of Hess and Haber.

The flask of pure acetic acid was placed in a dry box and the material forced by means of compressed air into dry 25 and 50 ml flasks having necks with break-off tips for later vacuum line manipulation. The acid entered the flasks through very small side arms which were then closed by means of small corks and sealed off in a flame immediately after removal of the flasks from the dry box.

Pure acetic anhydride, boiling at 140.0° C was obtained by fractional distillation in the column previously described. Precautions were taken to protect it at all times from any contact with atmospheric moisture. It was collected in thoroughly dried flasks similar to those used for storing acetic acid. These were then sealed in the manner described above for acetic acid.

Sodium acetate-acetic acid exchange reaction. The procedures used in preliminary exchange runs were found to be subject to several errors and will
be described only briefly.

A small amount of labeled, anhydrous sodium acetate was weighed out and introduced through a small side arm into a large tube (2 cm in diameter and 15 cm long) connected to the vacuum line. This side arm was quickly stoppered and then sealed off with a torch. The tube containing the sodium acetate also had three other arms. The first of these contained pure acetic acid and was connected to the tube through a break-off tip. The other two arms were used for collecting samples of acetic acid distilled from the sodium acetate by cooling them in liquid air.

In making a run, this system was evacuated, the acetic acid frozen in liquid air, and the break-off tip connecting it to the tube with the sodium acetate smashed by means of a glass-enclosed magnetic breaker. After the air in the acetic acid compartment had been pumped out, the acetic acid was melted and poured on the sodium acetate by tilting the apparatus. It was necessary to freeze the sodium acetate solution in liquid air in order to be sure of getting all of the acetic acid transferred into it from the arm with the break-off tip. The solution of acetic acid and sodium acetate thus obtained was then melted, carefully shaken, and a sample of pure
solvent distilled from it into one of the side arms by cooling the arm in liquid air. Another sample was collected from the solution later by cooling the second side arm, while keeping the first distillate cooled in an ice-salt bath to prevent any appreciable amount of it from distilling off.

Both side arms were then broken off and the acetic acid in them and in the residual solution neutralized with sodium hydroxide solution. After dehydrating the resulting solution in a vacuum, samples of the dry sodium acetate were converted to barium carbonate by a wet combustion procedure and radioassayed.

This exchange procedure was not entirely satisfactory for several reasons. For instance, after the break-off tip had been smashed and the air with the acetic acid removed, it was necessary to melt the acetic acid before pouring it. During the appreciable amount of time required for this, the solvent was found to distill into the readily soluble sodium acetate in sufficient amounts to give it a moist appearance. This, together with the delay caused by the necessity of transferring the last portion of the acetic acid to the salt by freezing the acetate solution, made it impossible to make
rapid exchange studies, or to establish the time of the exchange reaction with any accuracy. Also, leaving the first distillate from the radioactive solution until after the second distillate had been collected before removing it was not a satisfactory arrangement. Finally, it was necessary to rebuild the apparatus for each run.

Since this preliminary work indicated the possibility of (1) a very rapid but measurable rate of exchange, and (2) an isotope effect in the wet combustion of sodium acetate or acetic acid, two new sets of apparatus were made. The first was to permit more rapid studies of exchange reactions, and the second was to divide the CO$_2$ from wet combustions into two fractions for radioassay and determination of whether or not an appreciable isotope effect existed (i.e., whether or not unlabeled acetates are oxidized more rapidly than labeled ones). The exchange apparatus is shown in Figure 1 on the following page. Figure 2, page 43 shows the combustion set-up.

The apparatus shown in Figure 1 was evacuated and flamed-out as thoroughly as possible over a period of at least an hour before each exchange run in which it was used. It was then placed in a dry box and a
FIGURE I. APPARATUS FOR EXCHANGE REACTIONS.
small amount (about 20 mg) of labeled sodium acetate and an ampoule containing about 2 ml of very pure acetic acid were placed in the bottom of tube "A."
The device was then reassembled and placed on the vacuum line. After it had been evacuated, CO₂ which had been allowed to stand several weeks in a flask containing some anhydrous magnesium perchlorate was admitted to give a pressure of 20 mm Hg. Following this, the apparatus was closed by stopcock "S2" and removed from the vacuum line.

The ampoule was crushed by a slight rotation of the breaker arm "C" in the ball and socket joint "S2." It was found that spattering of the solvent occurred in the crushing process unless CO₂ was

---

2. The breaker consisted of a piece of heavy capillary tubing (approximately 5 mm diameter) sealed to a piece of glass tubing of a size which fitted snugly inside the male half of the ball and socket joint. The ends of this tubing and the joints were sealed together as indicated. It was found that a considerable force could be applied to the breaker tip without breaking the seal at "C." The small knobs on the capillary tubing were ground off nearly flat and prevented the breaker from slipping off the ampoule. The Teflon washer, "D," was cut to fit very tightly into the space between the capillary tubing and the ground joint. This prevented any radioactive solution or water from getting into the very narrow space between the inside and outside walls during the run or while the apparatus was being cleaned.
present to increase the pressure slightly. The CO$_2$

essentially eliminated this difficulty.

The sodium acetate dissolved almost immedi-
ately in the acetic acid. The solution was carefully
shaken for a short time and a small amount of the
solvent then distilled through one of the 8 mm
stopcocks, "Sl," into a small receiving tube attached
to a ball and socket joint, "Bl." The stopcock was
then closed and the distillate removed. When necessary,
a second sample was collected in the same manner just
described by using the other arm. The distillates
were neutralized and the water then removed from the
salt, without hydrolysis, by using a high vacuum.$^3$
Following this, the acetate was converted to barium
carbonate by using the apparatus shown in Figure 2,
page 43. (When used for this purpose, only one arm
of the apparatus was actually used.)

3. It was found that this could be carried out
readily without using liquid air. The solution
was placed in a 35/25 ball and socket male
joint which had been sealed off at the end.
This was attached to a manifold to which
other similar joints were attached. By cool-
ing one of these other joints in a Dewar flask
full of chopped ice, nearly all of the water
was distilled from the salt solution without any
"bumping." The remainder was removed by using
liquid air as the coolant.
Isotope effect in wet combustions. Modifications of wet combustion equipment described in the literature (14, pp. 38-41) were used in preliminary studies, but were found to be unsatisfactory for the present work. This was primarily because of the difficulty with which blanks due to carbon dioxide from the air and sulfur trioxide from the Van Slyke-Folch oxidizing fluid were eliminated. Such blanks were found to be negligible in runs made with the apparatus in Figure 2 on the following page.

4. The Van Slyke oxidizing fluid is ordinarily prepared by heating a mixture of 66 ml of fuming sulfuric acid (20-30% SO$_3$), 33 ml of syrupy phosphoric acid and 6 grams of chromium trioxide up to 150°C and holding it at 140-150°C for approximately fifteen minutes in order to drive off excess sulfur trioxide and dissolve the chromic anhydride. An oxidizing mixture prepared in this manner slowly loses its strength and a new solution is usually prepared after about a week. It has been found in this work that the solution is better prepared by heating the two acids together at 160-180°C until SO$_3$ evolution ceases, then cooling to 140-150°C and adding the chromic anhydride in a finely powdered form. A short period of shaking of the solution is sufficient to dissolve the oxide. (Definite decomposition was found to occur when the solution was prepared by heating the mixture of acids and anhydride to 140-160°C as recommended by Armstrong, et al. (4, pp. 531-533)). This procedure has the advantage that the solution can be heated sufficiently to prevent evolution of any substantial amount of SO$_3$ during combustions, without causing it to lose its oxidizing strength. A solution prepared in this manner has been found satisfactory for use after standing nearly two months.
FIGURE 2. WET COMBUSTION APPARATUS.

B1 - Ball & Socket Joint, 35/25
F - Four-way Stopcock, 10 mm bore
The combustion of a sample of sodium acetate in investigating the isotope rate effect was carried out in the following manner. A sample of labeled sodium acetate of approximately 50 mg was placed in the 50 ml flask "C" of the apparatus in Figure 2. The set-up was then connected to an aspirator through stopcock "S2" and evacuated by closing stopcocks "S1" and "S3" and turning the four-way stopcock "F" to each of the side arms in turn. (Stopcock "S3" and the 19/38 joint were lubricated by a mixture of syrupy phosphoric and phosphorous pentoxide; the other stopcocks and joints were lubricated with "Apiezon N" grease.) The large stopcock "F" was opened to the left side, 25 ml of saturated barium hydroxide solution placed in the left cup "J," stopcock "S1" opened slowly and the solution filtered through the medium fine, sintered glass disc into the left tube "G." "S1" was then closed, stopcock "F" opened to the right arm and the procedure repeated. Stopcocks "S1" and "S2" were then closed and 20 ml of oxidizing fluid allowed to flow slowly through "S3" into the combustion flask. This flask was then heated by a very small flame with occasional shaking. The barium hydroxide solution was stirred by a magnetic stirring bar.
After approximately the desired amount of BaCO$_3$ had been precipitated in tube "G" at the right arm, the combustion flask was opened to the left arm by turning "F" and the combustion completed. It was found that a total period of ten to fifteen minutes of heating was required. The solution was then allowed to stand for fifteen or twenty minutes, while stirring the barium hydroxide solution, in order to absorb all of the CO$_2$.

Blanks due to SO$_3$ from the combustion precipitating as BaSO$_4$ were eliminated in the following way. Stopcock "F" was turned so that both side arms were closed off. Stopcock "S2" was then opened, the combustion flask replaced by another exactly similar flask except that it had a sintered glass disc at the bottom of the cup "A." "Apiezon N" grease was used on the stopcock and joint of this flask. It was evacuated, 25 ml of saturated barium hydroxide solution filtered into it through stopcock "S3," stopcocks "S2" and "S3" closed and "F" opened to the right (or left) arm of the apparatus. Dilute hydrochloric acid was then slowly added to the barium carbonate precipitate in this arm through stopcock "S1." When all of the CO$_2$ thus formed had been absorbed by the hydroxide solution in "C," this flask was
quickly removed and the barium carbonate filtered off on a sintered glass filter crucible. The precipitate was thoroughly washed, first with CO₂-free water, then alcohol. Following this, the flask was washed, returned to the apparatus and the last half of the above procedure repeated. The precipitates were dried at 100°C, then counted.

Figure 3(a), page 47, shows a plating arrangement that was found to be convenient for centrifuge plating very thin samples evenly.⁵ (It was observed that thin deposits were usually rough and non-uniform when prepared by the usual procedure of heating with an infra-red heat lamp.) In this device, the brass cap "D" was machined to fit the Teflon ring "P" tightly and to hold it against the Tracerlab copper planchet "A." The cylinder "E" was made to fit into a standard centrifuge cup holder at the top and was machined as shown at the bottom to fit snugly against a planchet at "B." Any slipping of the planchet while the cap was screwed on or off was prevented by a small ridge "C."

⁵. Hutchens, et al. (32, pp.41-44), reported a different device and procedure for centrifuge plating. These were designed for heavy, infinite-thickness planchets, however, and a considerable amount of time is required.
FIGURE 3. (a) DEVICE FOR CENTRIFUGE PLATING. (b) ARRANGEMENT FOR SEPARATIONS BY FRACTIONAL CRYSTALLIZATION.
In use, the device was assembled as indicated, warmed slightly under a heat lamp, a few drops of a dilute suspension of barium carbonate placed on the planchet and then centrifuged until the ether-alcohol mixture had evaporated from the carbonate deposit. The time required depended, of course, upon the amount of the suspension used. If small amounts were used the evaporation was usually complete within a few minutes.

Plumbous acetate-acetic acid exchange reaction. Anhydrous plumbous acetate was prepared by the method of Davidson and Chappell (18, pp. 4524-4525), with the following modifications. After four recrystallizations of Pb(OAc)$_2$ from dilute acetic acid, approximately one gram of it was dehydrated by the vacuum technique previously described for sodium acetate. Following this, the salt was moistened by a small amount of anhydrous acetic acid and the acid then distilled off in a vacuum. After desolvation was apparently complete, the salt was slowly heated to 100° and kept there two days. Any remaining trace of acetic acid was distilled into liquid air. Plumbous acetate prepared in this manner had a melting point of 202-203° C. The m.p. reported by the above workers was 204° C.
The pure plumbous acetate was labeled by using the apparatus shown in Figure 4. The procedure was as follows. Any water adsorbed in the first half of the system was evacuated through a stopcock initially attached at "Cl." The end of tube "E" was closed by a rubber stopper during this evacuation. Air was then admitted at "Cl" and ten milligrams of high specific activity sodium acetate placed in "D." After approximately one gram of lead acetate had been transferred to "G" through the opening at "H," the tubing at that point was heated and sealed off as indicated.

The anhydrous acetic acid in "A" was frozen by liquid air, the break-off tip "B" smashed with the glass-enclosed breaker and the system again evacuated through "Cl." The system was sealed off at that point, as shown, and approximately one ml of acetic acid then distilled into "D" to be activated by the sodium acetate. Both "A" and "D" were cooled by liquid air, and the flask "A" was sealed off by heating at the constriction "E1."

The labeled acetic acid in "D" was distilled through the glass wool at "Fl" onto the lead acetate
FIGURE 4. APPARATUS FOR LABELING COMPOUNDS BY EXCHANGE REACTIONS.
in "G," and the section containing "D" then pulled off by heating at "E2." The solution of lead acetate in "G" was left overnight to be sure that exchange with the labeled acetic acid occurred.

The second half of the apparatus was now evacuated through a stopcock at "C2" and sealed off as shown by the dotted line. The tip at "B" was broken and approximately 0.15 ml radioactive acetic acid distilled through glass wool at "F2" and into each of the small (approximately one ml) ampoules, "J1." The excess was distilled into "L," which was then sealed off at "E4." Each of the ampoules was removed by heating at "I" (after freezing the acetic acid in liquid air) and tube "G," containing labeled lead acetate was sealed off at "E3."

6. The wool used at "F1" was found to be necessary to catch very fine particles of sodium acetate which were otherwise swept over near the end of the distillation.

7. It was found that by removing the ampoules at "I" there was much less danger of ruining a whole run as a result of one of the ampoules cracking during the cooling or heating operations. The necks of these acid ampoules were later sealed off individually, after they had been used to volumetrically estimate the amount of liquid present by inverting the ampoule.
The procedure used in investigating the exchange reaction between plumbous acetate and solvent acetic acid was essentially the same as that given for sodium acetate and acetic acid.

**Plumbic acetate-acetic acid exchange reaction.** Plumbic acetate was prepared by the method in which red lead is allowed to react with a mixture of acetic anhydride and glacial acetic acid (10, p. 47). One hundred fifty grams of the dry lead oxide were slowly added to 270 g glacial acetic acid and 90 g of acetic anhydride in a 500 ml, three-neck flask equipped with a thermometer and mercury-sealed stirrer. The lead tetracetate was filtered off on a glass filter, quickly recrystallized from hot glacial acetic acid containing five percent acetic anhydride and again filtered. The precipitate was washed five times with the hot acetic acid-acetic anhydride solution, then quickly transferred to a 125 ml standard taper flask. Most of the solvent was evaporated off and the solvated salt then slowly heated to 100° and held at that temperature overnight in order to insure complete removal of the acetic acid and acetic anhydride. The melting point of this material was 176-180° C. The m.p. in the literature is 175-180° C. (10, p. 47).
Two analyses were carried out by adding water to weighed samples of the tetracetate, filtering off and weighing the lead dioxide, and titrating the acetic acid formed. Found (average): PbO$_2$, 54.13%; (CH$_3$-CO)$_2$O, 45.93. Calculated: PbO$_2$, 53.95%; (CH$_3$-CO)$_2$O, 46.05.

Since the tetracetate is extremely hygroscopic, it was subsequently handled only in a dry box in which the air had been thoroughly dried by calcium chloride and barium perchlorate drying columns, and after each run the flask in which the acetate was stored was evacuated.

The activation of this plumbic salt for exchange experiments with acetic acid was accomplished by a technique similar to that described in detail above for plumbous acetate.

Radioactive acetic acid was distilled into a tube containing 200 mg of plumbic acetate. After allowing about twelve hours for exchange between the acetate and acetic acid to occur, all of the acid was distilled off in a high vacuum, as previously described, and the tube containing the pure, labeled plumbic acetate then sealed off.

The exchange reaction occurring between the
tetracetate and acetic acid was investigated in the same apparatus, and by the same procedure as that described above for the sodium acetate and plumbous acetate experiments. More shaking was required to get all of this relatively slightly soluble salt dissolved.

**Acetic anhydride-solvent acetic acid exchange reaction.** In this experiment the acetic anhydride solute was labeled by a vacuum technique similar to that previously described. Pure, inactive anhydride was distilled into sodium acetate of high specific activity, then into small ampoules which were sealed off with long necks as described for the preparation of labeled acetic acid.

The arrangement shown in Figure 3(b), page 47, was used for carrying out the exchange reaction and for separating the two compounds by fractional crystallization. The section of tubing containing the sintered glass disk was 10 mm in diameter.

A heavy mercury-in-glass breaker and an ampoule each of acetic acid and acetic anhydride were placed in the large end of the filter tube and this part of the tubing then sealed off as near to the sintered glass as possible. The set-up was
evacuated through a stopcock sealed to the small end and this end also pulled off as shown.

The completed arrangement was shaken carefully until the mercury weight had broken both ampoules. After thorough mixing had occurred the tube was placed in a 25° C constant temperature bath. At the end of the exchange run the solution was fractionally crystallized by shaking the large end of the tube in a bath at 12° C. When crystallization was apparently complete the solution was cooled to 0° in an ice bath, then quickly transferred to a refrigerated centrifuge and the acetic anhydride (m.p. - 73.1°) separated from the frozen acetic acid (m.p. ± 16.63°) by centrifuging it through the sintered glass into the glass tip shown in the drawing. The tube was then quickly removed from the centrifuge and the tip containing the acetic anhydride snapped off at its junction with the larger tubing. It was transferred to a weighing bottle, weighed, and the pure anhydride titrated with sodium hydroxide solution. Following this, the empty tip and weighing bottle were again weighed.

The methods which have been proposed (33, p.310) for the analysis of acetic acid-acetic anhydride
mixtures were not suitable for this work where subsequent radioassay is required. The filtrate titrations did not give results consistent with the radioassays. This may have been because of a weighing error due to moisture condensing on the ice-cold glass tip. Since the equivalent weight of the anhydride is not greatly different from that of the acid, a small error of this type in the initial weight would markedly affect the titration results.

Pb(II) - Pb(IV) exchange reaction. The ThS which was used as the radioactive tracer in preliminary experiments was prepared in the following manner.

Fifty grams of thorium nitrate were dissolved in about 200 cc of water. Small amounts of nitric acid and inactive Pb(OAc)_2 were added and PbS precipitated with H_2S. The sulfide was then filtered off on a small, medium fine filter and dissolved with 5 cc of concentrated HCl.

A second 5 cc portion of the acid was washed through the filter to be sure of dissolving all of the PbCl_2. The precipitation and solution processes were then repeated.

To the above solution, 6 N NaOH (chloride free) was added until the alkaline end point of malachite
green was reached (pH of 13) and basic lead carbonate precipitated by adding 0.5 g NaHCO₃. This carbonate was filtered, dissolved in 10 cc of HAc (1:1) and again precipitated. The precipitate was dissolved, 0.5 g of C.P. Pb(OAc)₂·3H₂O added, and basic lead carbonate reprecipitated. This precipitate was thoroughly washed with water, then absolute alcohol, and, finally, sucked dry.

The basic lead carbonate was dissolved in 1:1 HAc and boiled to remove the CO₂ formed. The excess acetic acid and water were distilled off by using liquid air and the high-vacuum arrangement described for previous experiments. After the apparently dry Pb(OAc)₂ had been slowly heated up to 100° while in this apparatus and held at that temperature for more than an hour, it was transferred to a vacuum desiccator.

The radiochemical purity of this preparation was shown by the half-life of 10.6 hours observed when the lead was radioassayed as PbCl₂. Only two exchange experiments were possible with this preparation because of the short half-life.

Experiments with RaD were carried out in the following manner. A small ampoule of high specific
activity lead nitrate solution from the Canadian Radium and Uranium Corporation was frozen, the tip snapped off and the solution transferred to a flask for dilution. Approximately 0.025 millicurie (containing less than 0.075 mg of lead) was pipetted into 23 g of Pb(OAc)\(_2\)·3H\(_2\)O and this was dissolved in about 15 cc of boiling, dilute acetic acid. The solution was cooled to produce crystallization and about one-half of the recovered product was then dissolved in ordinary glacial acetic acid. The acid was then removed by distillation to liquid air in a high vacuum.

The methods used in making exchange runs were similar to those of Hevesy and Zechmeister (29, pp. 410-415)(30, pp. 151-153), with certain important exceptions which will be noted. In general, the procedure was to, (1) dissolve labeled lead(II) acetate and inactive lead(IV) acetate in anhydrous acetic acid, (2) separate the two salts by one of the methods to be mentioned later, and (3) radioassay the two compounds. All work which required exposure of the very hygroscopic plumbic acetate and acetic acid to air, including weighings, were carried out in the dry box previously described. Details of the
experiments performed are summarized in Table 5, page 66.

In all experiments except No. 7, the very pure acetic acid previously described was used. Sufficient water was added to No. 7 by means of a tuberculin syringe to make the solvent one per cent water. Particular pains were taken in run No. 10 to duplicate the procedure used by Hevesy and Zechmeister.

The procedure of both Zintl and Rauch (55, pp.1739-1744) and of Hevesy and Zechmeister were used to separate Pb(II) and Pb(IV). In the table, "aqueous-acid" means that the solution of plumbic and plumbous acetates in glacial acetic acid was poured into water and the PbO₂ and Pb(OAc)₂ separated by centrifugation and filtration. "Aqueous-basic" means that 5 ml of the acetic acid exchange solution were poured into 50 ml of 16 N KOH which had been made free of carbonate by shaking with solid Ba(OH)₂, followed by centrifugation. Although the resultant plumbite and plumbate ions are soluble and stable in the presence of each other in strong alkali and do not undergo exchange of lead (59, pp.1739-1744), a transitory, brown precipitate was generally observed. This was presumably lead dioxide. The color was
especially noticeable in run No. 10.

The plumbite-plumbate solution was brought to boiling in a standard taper Erlenmeyer flask and 5 millimoles of solid Ba(OH)$_2$ added. The flask was shaken mechanically for half an hour and the contents then centrifuged. The precipitate (a mixture of barium carbonate, barium hydroxide and barium plumbate) was washed three times with 12 N carbonate-free KOH by centrifugation. Excess 6N HNO$_3$ was then added to form PbO$_2$. As in all other runs, this was washed, converted to PbCl$_2$ with concentrated HCl and, after boiling, the solution was diluted, heated, and K$_2$Cr$_2$O$_7$ added. If necessary, a few drops of chloride-free NaOH were added in order to secure precipitation of lead chromate. This was always precipitated from an acidic solution.

"Crystallization" means that the (rather concentrated) solution in glacial HAc was cooled to 30°C and Pb(OAc)$_4$ filtered and washed once with glacial acetic acid. It was then added to water and the resultant PbO$_2$ treated as above.

EXPERIMENTAL RESULTS. The data in Table 2 on the next page show that very rapid exchange occurs between solvent acetic acid and all three of the
## Table 2
Exchange of "Bases" with Acetic Acid

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOAc</td>
<td>1*</td>
<td>1.3</td>
<td>150</td>
<td>5 min.</td>
<td>84.1</td>
<td>95.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.12</td>
<td>12</td>
<td>3 min.</td>
<td>83.2</td>
<td>81.4</td>
</tr>
<tr>
<td>Pb(OAc)$_2$</td>
<td>3</td>
<td>0.15</td>
<td>30</td>
<td>2.5 min.</td>
<td>9.4</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.17</td>
<td>30</td>
<td>3 min.</td>
<td>10.2</td>
<td>10.4</td>
</tr>
<tr>
<td>Pb(OAc)$_4$</td>
<td>5</td>
<td>0.19</td>
<td>32</td>
<td>3 min.</td>
<td>6.7</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.21</td>
<td>33</td>
<td>5 min.</td>
<td>7.2</td>
<td>7.5</td>
</tr>
</tbody>
</table>

* Preliminary run.
acetates studied (sodium acetate, plumbous acetate and plumbic acetate). Since only a few minutes elapsed from the time the solvent first contacted the salt until a sample was distilled off for counting, it seems unlikely that refinements in the procedure would change these results.

In contrast to the rapid reactions above, a measurably slow exchange between solute acetic anhydried and solvent acetic acid is indicated by the data in Table 3, page 63. A semi-logarithmic plot of these results is shown on page 64 to show the general trend of the reaction and to give an idea of the half-time of the exchange (roughly ten hours). The data could not be expected to strictly follow a simple exponential law, since concentrations of the solutions necessarily varied somewhat because of the difficulty of duplicating exactly the amounts of solute and solvent sealed into the ampoules used in successive runs. Typical results obtained from a large number of combustions made in establishing the fact that an isotope rate effect exists in the wet combustion of metal acetates, or acetic acid, are given in Table 4, page 63. They show that incomplete combustions of acetic acid in obtaining samples of barium carbonate for counting can cause errors of as much as three or four per cent.
### Table 3
Exchange of Acetic Anhydride with Solvent Acetic Acid.

<table>
<thead>
<tr>
<th>Run</th>
<th>Time</th>
<th>Milliequivalents HOOAc</th>
<th>Ac₂O</th>
<th>Sp. Act. (c/min/mg)</th>
<th>Exchange* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25 min</td>
<td>43</td>
<td>37</td>
<td>372</td>
<td>10.6</td>
</tr>
<tr>
<td>2</td>
<td>3 hr</td>
<td>35</td>
<td>41</td>
<td>292</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>41 hr</td>
<td>32</td>
<td>66</td>
<td>593</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>111 hr</td>
<td>47</td>
<td>37</td>
<td>194</td>
<td>27</td>
</tr>
</tbody>
</table>

* On basis of experimentally-determined specific activity of 314 c/min/mg for Ac₂O before exchange reaction experiment.
** Using total activity calculated from activities of two fractions.

### Table 4
Isotope Effect in Oxidation of Acetic Acid.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fr. 1</td>
<td>Fr. 2</td>
<td>Fr. 1</td>
<td>Fr. 2</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>34.8</td>
<td>107.7</td>
<td>82.4</td>
<td>86.0</td>
<td>97.0</td>
</tr>
<tr>
<td>2</td>
<td>92.4</td>
<td>127.3</td>
<td>81.7</td>
<td>86.9</td>
<td>96.2</td>
</tr>
<tr>
<td>3</td>
<td>101.0</td>
<td>110.4</td>
<td>78.7</td>
<td>83.1</td>
<td>98.4</td>
</tr>
<tr>
<td>4</td>
<td>39.1</td>
<td>160.2</td>
<td>77.5</td>
<td>80.5</td>
<td>97.0</td>
</tr>
<tr>
<td>5</td>
<td>83.6</td>
<td>122.3</td>
<td>75.4</td>
<td>82.3</td>
<td>94.1</td>
</tr>
</tbody>
</table>

Av. 96.5 ±1.1

* Sodium acetate used in runs 1 and 2 had a different specific activity than the material used in the last three runs.
Table 5, on page 66, summarizes the investigation of the exchange reaction between plumbous acetate (labeled with RaD) and plumbic acetate in solvent acetic acid. The results show that the exchange, if any, is very slow, except when caused by the separation procedure. (In the "Crystallization" separation runs, some of the exchange indicated is probably due to incomplete removal of all the plumbous acetate-acetic acid solution from the precipitated plumbic acetate. The latter was washed only once with pure acetic acid after it had been filtered off on a glass filter.)
Table 5. Plumbous Acetate-Plumbic Acetate Exchange Reaction.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Time (min.)</th>
<th>Temp. (°C)</th>
<th>HAc (cc)</th>
<th>Pb(OAc)$_2$ (mmoles)</th>
<th>Pb(OAc)$_4$ (mmoles)</th>
<th>Separation Method</th>
<th>Specific Activity Pb(II)</th>
<th>Pb(IV)</th>
<th>Exchange (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>25-30</td>
<td>25</td>
<td>0.060</td>
<td>0.055</td>
<td>Aq.-acid</td>
<td>47.6</td>
<td>51.6</td>
<td>104</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>5</td>
<td>0.153</td>
<td>0.162</td>
<td>Aq.-acid</td>
<td>13.8</td>
<td>13.1</td>
<td>97.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>0.159</td>
<td>0.159</td>
<td>Aq.-base</td>
<td>530</td>
<td>6.0</td>
<td>2.2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>80±10</td>
<td>1.47</td>
<td>1.30</td>
<td>Crystal</td>
<td>503</td>
<td>2.7</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>80±5</td>
<td>0.920</td>
<td>0.767</td>
<td>Crystal</td>
<td>516</td>
<td>6.6</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>0.903</td>
<td>0.785</td>
<td>&quot;</td>
<td>530</td>
<td>4.4</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>0.514</td>
<td>0.513</td>
<td>Aq.-acid</td>
<td>254</td>
<td>252</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Crystal</td>
<td>516</td>
<td>1.0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4 hr.</td>
<td>80 ±1</td>
<td>0.903</td>
<td>0.782</td>
<td>Aq.-base</td>
<td>475</td>
<td>25.7</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>&quot;</td>
<td>0.514</td>
<td>0.513</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Runs 1, 2: ThB tracer; all others, RaD.

Runs 1, 2: Activities of both Pb(II) and Pb(IV) determined; in all other runs, activity of Pb(II) taken from self-absorption curve of original PbAc$_2$, minus activity of Pb(IV).

Runs 1-4: Dissolved Pb(OAc)$_4$ in small volumetric first, then added Pb(OAc)$_2$; exchange was induced by water when dilute solutions of Pb(OAc)$_2$ and Pb(OAc)$_4$ poured into it, i.e., no true rapid exchange rate exists.

Run 5: Pb(OAc)$_2$ and Pb(OAc)$_4$ dissolved separately in solvent; solutions then combined in one arm of apparatus which contained thermometer.

Run 6-10: Solvent added to mixture of two salts in tube with standard taper thermometer.
EXCHANGE REACTIONS IN ACETIC ANHYDRIDE

EXPERIMENTAL OUTLINE. Sodium and plumbous acetates are only very slightly soluble in acetic anhydride. However, Ruben, et al., have reported that rapid exchange occurs in the heterogeneous sodium acetate-acetic acid system (48, p. 3050). Their experiment was repeated, since it was found during a preliminary preparation of labeled anhydride by exchange with active sodium acetate that the rate of the exchange was apparently less than that which they observed.

The exchange reaction of the "acid," acetyl chloride, and the "base," plumbic acetate, with solvent acetic anhydride were investigated. The solvent was labeled in the first case and the rate of exchange determined by removing the acetyl chloride by vacuum distillation and checking it for activity. In the exchange study of the acetate, it was the salt which was labeled.

8. Jander reports conductivity studies involving 0.01 M NaOAc solutions at room temperature (33, p. 315). In the present work, the solubility of this acetate was found to be less than 0.003 M, even at 50° C.
Since plumbic acetate, in contrast to the plumbous acetate, was found to be soluble (6.3 g per 100 ml of acetic anhydride at 25° C), it was possible to study the exchange reaction of the plumbic acetate and acetic anhydride in a homogeneous system.

Finally, since the exchange of acetic anhydride with solvent acetic acid had been found to be slow, it seemed of interest to find whether or not the same result would be obtained if the situation were reversed, i.e., acetic anhydride used as the solvent for acetic acid. This was determined by exchange runs in which it was found that the solute, acetic acid, could be extracted from the acetic acid-acetic anhydride solution by using ice-cold water.

EXPERIMENTAL PROCEDURE. In general, the apparatus and the techniques used in the investigation of solvent acetic anhydride were the same as those employed in the acetic acid experiments.

Acetyl chloride-acetic anhydride exchange reaction. The acetic anhydride for this work was labeled by a procedure very similar to that previously described (page 49), using high specific activity sodium acetate. The pure anhydride was first distilled onto the acetate, then into ampoules.
Approximately 20 ml of Fisher's C. P. acetyl chloride was transferred, in a dry box atmosphere, to a small, dry flask having a break-off tip, and the inlet to this flask was then sealed off. After distilling off half of the acetyl chloride, 0.15 ml of the remaining material was distilled into each of five small ampoules, which were then sealed and removed by the method described on page 49.

The apparatus diagrammed in Figure 5 was used to make the exchange reaction and to separate the solute and solvent.

The standard taper tip of the 19/38 male joint shown in Figure 5 was drawn down and sealed off at one end as shown. A glass-enclosed breaker and ampoules of labeled acetic anhydride and acetyl chloride were then enclosed in this joint by sealing off the other end after evacuating. The ampoules were crushed by the breaker and the tube placed in a 0°C bath until the exchange run was completed.

The fractionating column devised for separating the solute and solvent was similar, in some respects, to one reported by Craig (15, p.444). The central tube was made from thin-walled, 10 mm Pyrex and was almost completely surrounded by a thin,
FIGURE 5. APPARATUS FOR EXCHANGE REACTION, OF ACETYL CHLORIDE WITH ACETIC ANHYDRIDE, FOLLOWED BY FRACTIONAL DISTILLATION.
smooth sheet of aluminum foil. It was further insulated by the vacuum jacket. The tube "E" was used as a condenser and was filled with a Dry Ice and acetone mixture. A small, approximately 0.2 ml cup, "F" was sealed to the tip of "E." Samples of distillate were removed from this cup by means of a long, thin pipette admitted through the 10/30 standard taper joint. The column was evacuated through "J" to the desired pressure by means of a set-up like the one described by Carney (13, p.109). Dry air was admitted through "I" by turning the stopcock "H" before collecting a sample of distillate.

The separation procedure was as follows. The reaction tube containing the acetyl chloride-acetic anhydride solution was inserted into the ground joint of the dried and assembled fractionating column. The system was carefully evacuated and then closed off from the vacuum line by turning stopcock "H." The tip of the reaction tube was broken off by rotating it past the constriction at "B," and the bulb "D" was cooled in liquid air to condense all of the solution down into it. The column was then sealed off at "C" and the pressure in the column regulated, by means of the vacuum system attached at "J," to give a suitable
pressure (approximately 15 mm Hg). "p" was surrounded by a water bath and the solution prevented from bumping by means of a magnetic stirring bar.

The purity of the acetyl chloride separated from solvent acetic anhydride by this apparatus was checked by titrating the distillate samples (or aliquots of them) with a standard solution of mercuric nitrate using sodium nitroprusside as the indicator and making a blank correction. The first sample of distillate collected in each run was found to be 100% acetyl chloride.

**Plumbic acetate-acetic anhydride exchange reaction.** This experiment using labeled lead acetate was carried out by exactly the same procedure as that described for the exchange of this substance with acetic acid (page 52).

**Sodium acetate-acetic anhydride exchange reaction.** This exchange differed from others involving metal acetates in that the system was a heterogeneous one because of the very slight solubility of the labeled solute. The anhydrous sodium acetate used was material which had been prepared in a finely divided state by dissolving it in pure acetic acid and then subliming the acid off in a vacuum. (Ten mg of sodium acetate
treated in this way occupies a volume comparable to that of several hundred milligrams of ordinary, crystalline material.) During the exchange run the apparatus was carefully shaken to insure complete mixing of the solid material with the solvent.

**Acetic acid-acetic anhydride exchange reaction.** The following procedure was devised in an exploratory effort to determine whether or not a measurable rate of exchange might be expected in this system.

A small ampoule containing approximately 0.15 ml of acetyl anhydride was placed in a male standard taper joint which had been pulled down and sealed off at the end so that its shape resembled that of a 15 ml centrifuge tube. Two milliters of pure acetic anhydride were then added by means of a calibrated, automatic pipette. The ampoule was quickly crushed with a glass rod, a standard taper cap placed on the reaction tube and the solution mixed by careful shaking. The tube was then sealed in a sheet of paraffine to keep out any moisture and placed in a bath at 0° C.

At the end of the desired exchange time, the tube was opened, the solution transferred to a 15 ml, graduated centrifuge tube (to avoid trouble with
glass particles later in the separation) and 5 ml of ice water added. The tube was then stoppered and shaken vigorously for twenty seconds. It was centrifuged for approximately fifteen seconds and the lower anhydride layer separated from the acetic acid-water layer by means of a medicine dropper with an elongated tip.

The two solutions (each containing approximately one milliliter) were neutralized with sodium hydroxide solution and the resulting sodium acetate samples converted to barium carbonate and counted.

The last run of this experiment was varied in several respects. Approximately 0.4 ml of labeled acetic acid and 5 ml of acetic anhydride were used. Two milliliters of this solution were removed at the end of two hours and another 2 ml at the end of five hours. Each of these two samples was then handled as described above, except that the shaking was done by a mechanical shaker and the centrifuging was carried out at 0° C. The radioassays of the resulting samples indicated that more complete separation was accomplished by this method.

EXPERIMENTAL RESULTS. The data in Table 6 below show that very rapid exchange occurs between labeled metal acetates and solvent acetic anhydride
at room temperature, even in a heterogeneous system.
In the first run with plumbic acetate, the exchange was apparently not quite complete at the end of five minutes. However, since the tetracetate did not dissolve immediately, this was probably the result of a few particles of the material being temporarily washed up on the wall of the reaction tube during the initial shaking, and thus not getting dissolved until after further agitation of the solution. Another possibility is that when the ampoule was crushed a small amount of the solvent was spattered and then distilled off without having had an opportunity for exchange. To prevent this, the reaction mixture was quickly frozen in liquid air to condense all of the solvent down upon the salt in the second run.

### Table 6

<table>
<thead>
<tr>
<th>Solute</th>
<th>Milliequiv. of Solute</th>
<th>Exch. Time</th>
<th>Spec. Act. (c/min/mg)</th>
<th>Exch. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAc</td>
<td>5.9</td>
<td>35</td>
<td>25 min</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dist. 11</td>
<td>(0.8g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Res. 4.6</td>
<td></td>
</tr>
<tr>
<td>Pb(OAc)₄</td>
<td>0.30</td>
<td>25</td>
<td>5 min</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dist. 11</td>
<td>(1.0g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Res. 82</td>
<td></td>
</tr>
<tr>
<td>Pb(OAc)₄</td>
<td>0.18</td>
<td>22</td>
<td>6 min</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dist. 8.9</td>
<td>(0.5g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Res. 95</td>
<td></td>
</tr>
</tbody>
</table>
The data in Table 7, below, indicate that the exchange of the "acid," acetyl chloride, and solvent acetic anhydride is slow, although it does occur. The calculations are based on the total experimental activity, since the original activity of the acetic anhydride was different in each of the three runs. These data are plotted semi-logarithmically in Figure 6, page 77. Since there were variations in the concentrations in different runs, the data from this experiment would not be expected to follow a simple exponential rate curve. This work was more or less of an exploratory nature to determine whether the rate of exchange was slow enough to make detailed kinetic studies feasible in this system. Since the half-time is of the order of ten hours, such studies would apparently be possible, by varying the procedure. For example, a number of distillate samples should probably be collected at intervals from one reaction mixture by using conventional vacuum techniques. Perfect separation would not be essential since, in contrast to the acetic acid-acetic anhydride system, accurate analyses are readily possible.
Table 7
The Exchange Reaction between Acetyl Chloride and Acetic Anhydride.

<table>
<thead>
<tr>
<th>Time</th>
<th>Milliequivalents</th>
<th>Millieq.</th>
<th>Specific Activities (c/min/mg)</th>
<th>Exchange (per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ac₂O</td>
<td>AcCl</td>
<td>Distilled</td>
<td>Res.</td>
</tr>
<tr>
<td>10 min</td>
<td>40</td>
<td>2.0</td>
<td>1.55</td>
<td>2.4</td>
</tr>
<tr>
<td>4.25 hr</td>
<td>58</td>
<td>2.5</td>
<td>1.88</td>
<td>18.8</td>
</tr>
<tr>
<td>36 hr</td>
<td>67</td>
<td>2.1</td>
<td>0.75</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Table 8, page 78, summarizes seven runs made in studying the acetic acid-solvent acetic anhydride exchange. The initial specific activity of the labeled acetic acid which was used in calculating the fraction exchange in each run was determined by averaging the values obtained from dividing the total apparent activity involved in each run by the milliequivalents of HOAc used. In Runs 6 and 7, mechanical shaking was used during the separation by the extraction procedure, and the reaction mixtures were kept at 0°C during the centrifugation. The data indicate that this resulted in more complete extraction of the labeled acetic acid by the water. They also suggest that appreciable apparent zero-time exchanges are involved to a varying degree in some of the runs because of incomplete separation of the labeled material.
Figure 6. Exchange of acetyl chloride with solvent acetic anhydride at 0°C.

Figure 7. Exchange of acetic anhydride with solvent acetic acid at 25°C.
Table 8

Exchange Reactions between Acetic Acid and Solvent Acetic Anhydride.

<table>
<thead>
<tr>
<th>Run</th>
<th>Time</th>
<th>Millimoles used*</th>
<th>Millimoles **OAc-</th>
<th>Specific Activity</th>
<th>Exchange (Per Cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 min</td>
<td>21</td>
<td>3.5</td>
<td>21</td>
<td>126</td>
</tr>
<tr>
<td>2</td>
<td>35 min</td>
<td>&quot;</td>
<td>2.7</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>3.75 hr</td>
<td>&quot;</td>
<td>3.0</td>
<td>17</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>7.25 hr</td>
<td>&quot;</td>
<td>2.8</td>
<td>22</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>40 hr</td>
<td>&quot;</td>
<td>2.6</td>
<td>21</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>2 hr</td>
<td>20</td>
<td>2.9</td>
<td>23</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>5 hr</td>
<td>20</td>
<td>2.9</td>
<td>23</td>
<td>25</td>
</tr>
</tbody>
</table>

* Estimated volumetrically.

** Volume of Ac₂O layer was measured and the assumption was made that it contained no HOAc or H₂O.
A semi-logarithmic plot of the results of this experiment are given by Figure 8, page 80. The curve indicates that the exchange occurs at a measurably slow rate with a half-time of the order of five and one-half hours. The observed scattering of the points is to be expected, in view of the small variations in concentrations and the nature of the procedure required for separating the two reactants.
FIGURE 8. EXCHANGE OF ACETIC ACID WITH SOLVENT ACETIC ANHYDRIDE AT 0° C.
WET COMBUSTION ISOTOPE EFFECT. The work reported here has shown that an isotope rate effect definitely exists in wet combustions of labeled acetates, or acetic acid, and that, unless combustions of labeled acetates are carried to completion, the specific activities found may be several per cent low. The nature of the combustion procedure and of the counting technique used is such that a more detailed study of the isotope effect involved does not appear worthwhile.9

METAL ACETATES AND ACETIC ACID. The very rapid rate of exchange which has been found to occur between labeled acetates, or "bases," and acetic acid suggests rapid ionization of these compounds. (This would be in agreement with the appreciable equivalent conductivities which have been thoroughly studied for most acetates in these two solvent systems.)

9. Bigeleisen, et al., have recently concluded that even the most precise counting techniques can hardly be expected to give more than qualitative information in this type of investigation (7, pp. 760-764). They have shown that mass spectrometic methods are capable of giving a precision which is a whole order of magnitude greater.
However, (as pointed out below) the evidence does not necessarily demand such an explanation.

Since earlier conductimetric and cryoscopic studies had shown that sodium and plumbous acetates are electrolytes in solvent acetic acid (although the plumbous salt is a very weak one), rapid exchange for these two solutes was not too surprising. In the case of plumbic acetate, however, it was felt that if exchange of acetate ions proceeded via ionization it might very well be at a measurably slow rate, since this compound behaves like a non-electrolyte and as though it were completely non-ionic in character (20, pp. 1523-1527).

An alternative to exchange through ionization might be the formation of an intermediate complex involving the higher covalences which are possible for lead. The fact that no evidence at all has been found for acetoplumbates militates against this. Since boron acetate, which has also been described as a covalent compound (49, p. 612), would possibly form an acetate complex less readily than the lead because of the small size of the boron atom, it would be interesting to check the exchange rate of this compound with acetic acid. Further information as to whether
such complex formations do play an important part in the rapid exchanges observed in this work might be obtained in this way.

METAL ACETATES AND ACETIC ANHYDRIDE. The 4.6% exchange observed in a period of twenty-five minutes in the heterogeneous sodium acetate-acetic anhydride system is appreciably less than the 52%, twenty-minute exchange reported by Ruben, et al., for a similar experiment. The concentrations of the reactants were essentially the same in both cases. As previously mentioned, special efforts were made in the present work to obtain very finely divided sodium acetate, and the exchange solution was vigorously agitated. It, therefore, appears that the slower rate observed here was not the result of a surface effect or lack of mixing. The acetic anhydride used by Ruben and co-workers may have contained sufficient acetic acid to affect the exchange rate which they observed, since it boiled at 138.5-139.5° (compared to the 140.0° b.p. of pure acetic anhydride). It is also likely that an appreciable amount of sodium hydroxide was formed by hydrolysis during their evaporation of labeled sodium acetate to dryness preparatory to making a run. (This was avoided in
the present study by subliming off the water in a vacuum.)

The very rapid exchange observed between labeled lead tetracetate and acetic anhydride suggests that rapid ionization occurs in this solvent, just as in acetic acid. No conductimetric or other studies of this system have been reported.

ACETIC ACID AND ACETIC ANHYDRIDE. If the exchange of metal acetates proceeds via ionization, the ions formed could exchange with the solvent in either of two ways: (1) through the assumed self-ionization of the solvent; (2) by reaction with un-ionized solvent molecules. In other words, the situation is comparable to that of the liquid ammonia experiments described on page 20. In connection with this question, the slow exchanges which were found to occur in acetic acid-acetic anhydride solutions are of interest. Although a number of unknown factors make it speculative, it would seem that if rapid self-ionizations of the pure solvents did occur, as indicated by their specific conductivities, more rapid exchange of acetate ions might be expected in solutions of one in the other. The fact that the exchange is slow regardless of which solvent is in excess, may
represent further evidence for the view of Bateman, Hughes and Ingold (6, pp.243-247), and of Johnson, Huston and Norris (35, pp.3052-3055), that self-ionizations of non-aqueous solvents may not be as important to their solvent behavior as commonly believed.

ACETYL CHLORIDE AND ACETIC ANHYDRIDE. The results of this experiment show conclusively that the exchange reaction is a slow one, indicating that this "acid" ionizes very slowly in solvent acetic anhydride. This view agrees with that of Usanovich (53, p.6444), who found that when a solution of sodium acetate in acetic anhydride is titrated with acetyl chloride the indicator changes color only very slowly.

It is also interesting to compare these results with those from investigations which have been made with the "acids," thionyl chloride (35, pp.3052-3055) (33, pp.209-307) and nitrosyl chloride (1, p.1297) (2, pp.369-370) (3, p.3211), of the liquid sulfur dioxide and dinitrogen tetroxide solvent systems. For thionyl chloride, Johnson, Norris and Huston (33, pp.3052-3055) found that ionization according to the frequently proposed equation

\[ \text{SOCl}_2 \rightleftharpoons \text{SO}^{++} + 2\text{Cl}^- \]
apparently does not occur, since labeled sulfur in this acid does not exchange with solvent dioxide. In this case, however, as previously pointed out, the situation is complicated by the presence of two chlorine atoms and further work is being done to find out to what extent the following ionization occurs.

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

For nitrosyl chloride and acetyl chloride, the situation is simplified to some degree by there being only one chlorine to consider.

Extensive investigations of the liquid dinitrogen tetroxide system were recently carried out by Addison and his co-workers. They have concluded from physical measurements (bond length, dipole moment, and others) that liquid NOCl itself is at least partially dissociated into NO\(^+\) and Cl\(^-\) ions, but that dissolving the compound in liquid N\(_2\)O\(_4\) does not influence this dissociation to any particular degree (3, p. S214). In other words, unlike the case of an acid such as HCl in water or ammonia, NOCl is no more reactive as an acid in N\(_2\)O\(_4\) than in a solvent such as CCl\(_4\). Further, they find that the reaction of NOCl with a metal in the solvent N\(_2\)O\(_4\) to give off NO
gas may possibly occur by two different mechanisms—by reacting with NO ions and by direct interaction with nitrosyl chloride molecules.

A number of conductimetric studies concerned with the nature of non-aqueous solvents, such as those of the above "acids," have been reported. In many cases it seems doubtful whether or not the increase in conductivity which has been observed upon adding a solute to the pure, very slightly conducting solvent is significant. For example, pure sulfur dioxide at -19° C is reported to have a specific conductivity of 8x10^{-7} ohm^{-1}, while a 0.1 M solution of SOCl₂ has a conductivity of 11x10^{-7} ohm^{-1} (33, p.214). Similarly, the conductivity of pure acetic anhydride is supposed to be 2x10^{-7} to 5x10^{-7} at 25° C (33, p.309) and that of a 0.1 M solution, 2.5x10^{-7} at 25° C (33, p.315). The possibilities for reaching erroneous conclusions concerning the extent and importance of ionization in non-aqueous solvents from this method of investigation are, therefore, quite evident when one considers the very hygroscopic, unstable nature of the majority of these non-aqueous solvents.

Thus, the results of the present isotopic exchange investigation are consistent with the evidence obtained by a number of other methods.
(conductimetric work, titrations and physical measurements, for example) in showing that, although "bases" of these various solvents are rapidly ionized (analogously to bases of the water system), concepts of rapid ionization and emphasis on ionic mechanisms such as have been proposed by Jander and others for the corresponding "acids" require at least some modification.

PLUMBOUS ACETATE-PLUMBIC ACETATE. The slow exchange of labeled lead atoms between these two solutes is in direct contradiction to the observations of Hevesy and Zechmeister (29, pp.410-415)(30, pp.151-153). The slowness is probably the result of one or both of two things--slow ionization of one or both of the compounds, or slow electron exchange between the lead ions. Since the rapid exchange found to occur between the lead acetates and acetic acid indicates that at least some lead ions are probably present in solution, the second possibility seems the most likely. Electron exchange could, of course, occur without ionization, but the acetate groups which would otherwise surround the central atoms might be expected to be of an insulating nature. If so, the transfer of electrons would be hindered (55, pp.25-27).
Although the mechanisms of electron exchange are not at all well understood, it is commonly believed that two-electron exchanges do not occur nearly as readily as one-electron exchanges. (In fact, only four such reactions have been found to occur—excluding the plumbous-plumbic case.) According to the views of several investigators, two-electron transfers would have to take place in one-electron stages (55, p. 26). In the case of exchange between plumbous and plumbic lead ions, no intermediate oxidation state is known and hence a stepwise exchange would not be possible. (The compound Pb$_2$O$_3$, which apparently involves an intermediate oxidation state, has been shown by Zintl and Rauch (59, pp. 1739-1744) actually to consist of equal amounts of divalent and tetravalent lead.)

It is impossible to state exactly what was responsible for the extremely rapid exchange which Hevesy and Zechmeister reported. They give actual details for only one of their experiments—that involving the separation of the plumbous and plumbic ions at the end of a run by an aqueous method. When this procedure was duplicated in the present work, exchange
was observed. Further work, however, showed that it was only an apparent exchange and was due to the separation procedure used. When a crystallization procedure was employed (one for which Hevesy and Zechmeister give no details) the exchange was found to be extremely slow or nonexistent.

Essentially all electron exchange reactions which have been studied have been carried out in aqueous solutions. Weiss has quite recently proposed a theory based upon the water, or oxygen, in such solutions playing an important part in an intermediate redox reaction to account for such exchanges (57, p.1066). It is quite possible that the glacial acetic acid used by Hevesy and Zechmeister contained some impurity which acted in a similar way to cause exchange since, according to their papers, ordinary glacial acetic acid was apparently used without any further purification. It has been shown in this work, however, that the exchange which they observed was not caused by a small amount of water being present as an impurity. A water effect was suspected, because Hevesy and Zechmeister mention filtering their exchange solution to clear it of turbidity. It was found that when 1% of water was present in a solution
of the acetate, the solution was turbid. However, it did not result in a rapid exchange in the present investigation.

It would seem to be of some interest to investigate other possible electron-transfer exchange reactions in non-aqueous solvents such as those which have been discussed above. This would be particularly true of those involving one-electron transfers. It might be anticipated that the results of such work would contribute to our understanding of the relative importance of the factors which govern rates of electron-transfer reactions. Myers and Prestwood have recently concluded (55, p.27) that, at the present time, even a qualitative discussion of these factors is hampered by the small amount of information available in this field.
SUMMARY

1. The exchange of acetate ions between labeled sodium, plumbous, and plumbic acetates and acetic acid as a solvent occurs immeasurably rapidly at room temperature.

2. An isotope rate effect occurs in the wet combustion of acetates. The CH$_3$-C$^{12}$O$^-_-$ ions are oxidized more rapidly than the CH$_3$-C$^{14}$O$^-_-$ ions.

3. The exchange of solid, labeled sodium acetate with acetic anhydride as the solvent is surprisingly rapid at room temperature, but is much slower than previously reported.

4. Labeled plumbic acetate exchanges very rapidly with acetic anhydride as a solvent at room temperature.

5. Acetyl chloride exchanges at a measurably slow rate with labeled, solvent acetic anhydride when present in a mole ratio of about 1:12 AcOCl:Ac$_2$O at room temperature.

6. Labeled acetic anhydride exchanges slowly with solvent acetic acid when present in mole ratios of 1:5 to 1:13 Ac$_2$O:H$_2$OA at room temperature.
7. Labeled acetic acid exchanges slowly with solvent acetic anhydride when present in a mole ratio of approximately 1:7 $\text{HOAc}:\text{Ac}_2\text{O}$ at 25°.

8. Lead(II) acetate, labeled with ThB or RaD, exchanges with inactive lead(IV) acetate very slowly, if at all.
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