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High Frequency Titrations In Liquid Ammonia

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HIGH FREQUENCY TITRATIONS IN LIQUID AMMONIA

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by

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CHAPTER I

A STATEMENT OF THE PROBLEM

An extensive literature has been established on the use of high frequency conductometric methods in chemical analysis and research. The fact that the instruments respond to chemical changes without having electrodes immersed in the reacting solutions has attracted the attention of many investigators. Until the last few years, practically all of the investigations were concerned with aqueous solutions, with the exception of measurements of dielectric constants.

There seemed no logical reason for not extending the use of the high frequency instruments to the study of Bronsted acid-base reactions, organic syntheses, rates of reaction, and the other commonly studied aspects of non-aqueous chemistry. A few early works were published with regard to esterifications and the titration of weak acids in organic solvents; but no extensive reports were forthcoming on the general utility of high frequency titrimetry in non-aqueous systems until the paper of Grove and Jeffery (1960). Since 1960, an increasing interest has been shown in non-aqueous use of high frequency titrimeters, as will be shown in the next chapter.

It seemed only a matter of time until someone would perform the research necessary to allow the use of solvents which could be kept in the liquid state (at atmospheric pressure) only at low temperatures. The classical example of such a solvent is liquid ammonia which boils at -33.4°C., but a great deal of work has been done in other low temperature solvents such as sulfur dioxide, hydrogen cyanide and hydrogen fluoride. A major obstacle to the use of such low temperature liquids with high frequency titrimeters was the lack of a suitable cell; one which could maintain the low temperature necessary to preserve the liquid state for the protracted periods of time required to perform titrations.

Thus, it was the purpose of the present investigation to develop a cell which would permit the use of high frequency titrimeters for studying low temperature, nonaqueous solvents--specifically ammonia. On the assumption that a suitable cell could be constructed, a further aspiration of the research was to investigate the response of high frequency titrimeters to a sufficient number of liquid ammonia reactions to show that an attractive area of chemical research had been exposed by the development of the cell.

CHAPTER II

HIGH FREQUENCY TITRIMETERS

History. The earliest work on equipment suitable for high frequency studies of chemical systems was that of Blake (1933), although Jensen and Parrack (1946) are often given the credit. In his early work, Blake seemed primarily interested in the physics of the equipment and its response to aqueous solutions of electrolytes rather than to titrations. At a later date he turned his attention to the application of the apparatus to chemical studies, and published one of the two existing books devoted exclusively to high frequency titrations and instruments (Blake, 1950; and Cruse and Huber, 1957).

But even though high frequency methods were suggested by Blake some thirty years ago, little interest in these methods was shown until the pioneer work of Jensen and Parrack at Texas A and M College (1946) resulted in an explosive, world-wide development. It is interesting to note that the initial manuscript of Jensen and Parrack contained no reference to the work of Blake and was apparently prepared independently of any influence of Blake's earlier efforts.

In the sixteen years that have elapsed since Jensen and Parrack's first paper, over two hundred papers have

been published on high frequency titrimetry, including several reviews; and no major scientific country in the world has failed to produce work on the subject. The first commercially available instrument, the E.H. Sargent Company's Jensen and Parrack High Frequency Titrator, was based on the design of the Jensen-Parrack instrument; and the most recently developed instrument was the Sargent-Jensen Model HF High Frequency Titrimeter. Thus the stature of the research team of Jensen and Parrack as the prime developers of high frequency titrimetry has been well demonstrated, and the consensus among reviewers of instrumental methods was that the Texas work, rather than that of Blake, triggered the outpouring of research that followed the 1946 publication.

Design and Construction. The essential features of a high frequency titrimeter consisted of three main components: the oscillator which supplied the high frequency field, the solution cell which interacted electronically with the oscillator, and the detector which measured variations in some parameter of the oscillator caused by changes in the cell. In 1954, two excellent articles (Sherrick, Dawe, Karr and Ewen; and Reilley) reviewed the modifications that had been investigated with respect to each of the three mentioned components and established a theoretical basis for their design. Blaedel and Malmstadt (1950) postulated that the

loading mechanism by which the cell interacted with the
oscillator involved capacitance changes almost exclusively;
and also, extended the range of frequencies to 350 megacycles.
By 1958, a well written, simplified description of the equip-
ment was available in a textbook (Willard, Merritt, and
Dean) on instrumental methods. The discussion developed for
this dissertation has drawn largely on these references in-
order to outline the fundamental features of a high frequency
titrimeter.

Willard, Merritt and Dean (1958) point out that:

A current alternating at frequencies exceeding
1 megacycle per second affects the conductance and
capacitance of a solution placed within the field. The
vessel containing the solution is placed in the field of
an inductance coil or between the plates of a capacitor
carrying the high frequency current. Since the induct-
ance coil or the capacitor is part of the high frequency
oscillator circuit, any changes in the composition of the
solution will be reflected as changes in the frequency
of the oscillator or changes in the plate and grid
currents and voltages.

The essential parts of an oscilator have been shown
in the schematic diagrams of Figure 1. In part 1a, the three
components of a simple oscillator have been arranged. The
condenser's capacitance, C, was in parallel with the coil's
inductance, L, and some sort of resistive components, R.
The resistive components were inherent in both C and L. At
resonance, the oscillator current surged back and forth
through the resistance as the condenser was discharged
through the coil, and the frequency of the back and forth
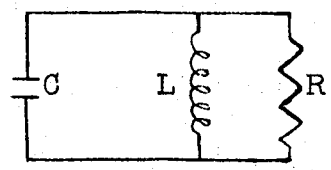
a.   Fundamental oscillator circuit
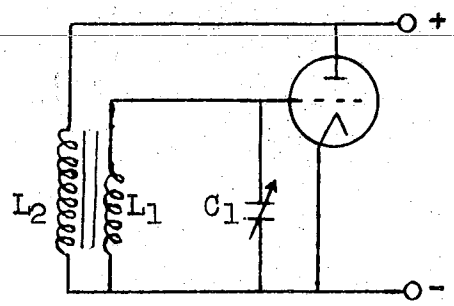
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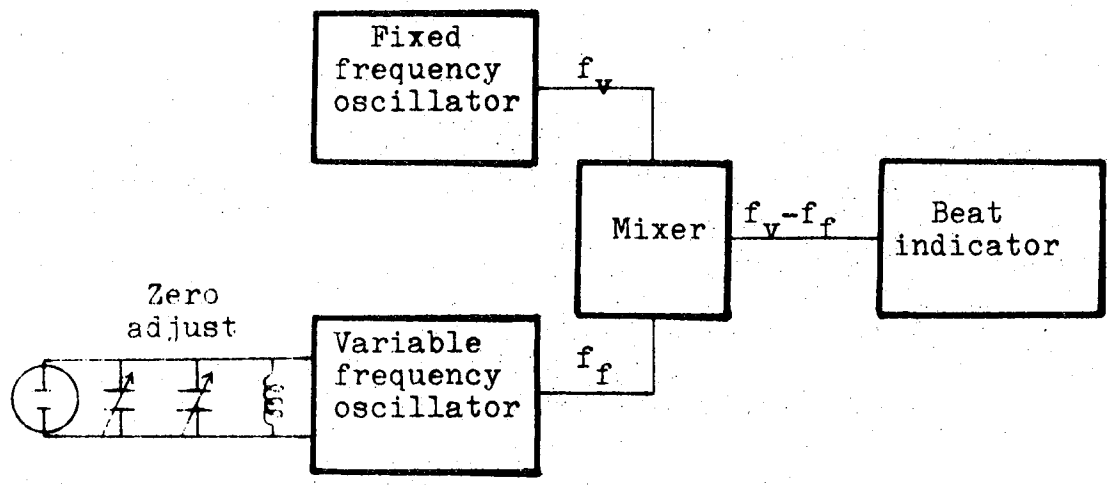
c.   A beat-frequency titrimeter

Figure 1.   High frequency oscillator schematic diagrams.

motion was given by the relationship

$$f = \frac{1}{2 \pi \sqrt{LC}}$$

Thus, was established the fundamental frequency of the oscillator in a high frequency titrimeter, usually designed to operate in the 2-500 megacycle per second region of radio waves.

In Figure 1b, the schematic diagram of a tuned-grid oscillator circuit has been shown as a modification of the la circuit. The use of an electronic tube to amplify the resonant current of the oscillator allowed the decaying effects on the current, due to the resistance, to be counter-acted. The use of two inductances L_1 and L_2, on a common core, made it possible to design a system that would continue oscillating indefinitely at some pre-selected resonant frequency. In Figure 1b, the inductance, L_2 has been shown in the plate circuit of the tube and the oscillator induc-tance, L_1, in the grid circuit; but in other instrumental designs L_1 has been placed in the plate circuit.

A variation on the oscillator circuits shown in Figure la and lb was developed by Johnson and Timnick (1956) who replaced the coil (inductor) with a coaxial half-wave line, permitting operation at frequencies up to 130 mega-cycles per second. Operation at higher frequencies made

possible the use of higher concentrations of reagents in the cell.

The titration cell has been incorporated into the oscillator circuit as a part of either the coil or the capacitor; but, in either case, the net effect of such a cell at high frequencies was to alter the capacitance of the resonant circuit. Such changes in the oscillator's capacitance were reflected in changes in (a) the resonant frequency of the oscillator, (b) the grid current, (c) the plate current, or (d) some combination of all of these variables. For example, Jensen and Parrack's original titrimeter used a milliammeter to measure plate current in the range of 15 to 20 megacycle per second.

A distracting difficulty associated with many of the early instruments was a tendency for the output signal to drift with time due to instrument warm-up, aging of the electronic components, or spatial variations between components as a result of inadequate mechanical rigidity of the system. These problems were minimized by the development of beat-frequency instruments of the type diagramed in Figure 1c. In such instruments, two oscillators that generated nearly identical frequencies were coupled so that their output resulted in a lower beat-frequency signal. The cell was associated with only one of the oscillators, and that oscillator also contained sensitive variable capacitors.

Typically, one of the variable capacitors was used to establish a zero point when the cell was a part of the system, but before any reaction took place. After the reaction took place, a second variable condensor was used to return the electronic system to its original zero point "beat"; and this condensor was equipped with a calibrated dial which gave an indication of the magnitude of the change that occurred in the cell.

Both the CF-120 High Frequency Titrimeter (Clinkscales and Frye, 1960) and the Sargent Model V Chemical Oscillimeter (Sherrick, Dawe, Karr, and Ewen; 1954), the instruments used in this investigation, are of the beat-frequency type; but the methods used to measure their signal output are different.

Cell design has been a major concern of several investigators and was a significant phase of this investigation. However, it was considered desirable to discuss the detailed design of cells in the same chapter (IV) used to describe the cell actually built for use in this research.

The final aspect of the general problem of designing a high frequency titrimeter was related to the technique of measuring the output of the oscillator-cell combination. As mentioned above, microammeters have been used, as well as some devices to determine the beat-frequency. In the later category were oscilloscopes (Fischer and Fisher, 1952) and

matching signal generators for those instruments utilizing
only one oscillator circuit. Researchers have reported
using wheatstone bridges (Mori, Hyodo, and Murakami; 1950),
and Johnson and Timnick (1956) used a polarograph in con-
junction with their previously mentioned 130 megacycle per
second instrument. The most sophisticated approach to the
measurement of the instrument signal was the use of a record-
ing potentiometer by the staff of E.H. Sargent and Co.
(1954) and by Musha, Ito, and Takeda (1952).

Many other investigators have made specific improve-
ments in some detail of a high frequency titrimeter, but to
elaborate on each contribution was beyond the scope of this
introductory chapter; especially when an excellent compila-
tion was made in Scientific Apparatus and Methods (1957),
the house organ of E.H. Sargent and Company. Cruse and
Huber (1957) gave a table summarizing the type of instrument,
the type of oscillator, the parameters measured, the type of
cell, the frequency, and the original literature references
for high frequency titrimeters reported to that date; and
only a few new instruments have been reported since.
The more interesting of the newer reports were Conseiller
and Courteix (1958), Tarnay and Juhaz (1958), Clinkscales and
Frye (1960), Kimura (1961), Pungor (1960), Ermakov (1960),
Groubert and Caillon (1960), and Lorenz (1960). Some other
recent references were listed in Chemical Titles, but neither

the original journal nor a chemical abstract was available to permit an evaluation of the significance of the research; Mukherjee (1957), Musha and Takeda (1957), Mai (1961), Vakhtel and Chernyakina (1961), Matsuda and Matsuda (1961), Gorokhovskii, Samitov, and Tremasov (1960), and Kashima (1960).

Applications to Aqueous Systems. Because the present research was primarily concerned with nonaqueous reactions, the prior art of aqueous studies was satisfactorily reviewed by the previously mentioned Scientific Apparatus and Methods article (E.H. Sargent and Company, 1957). The investigations had covered a tremendous range of chemical activities including acid-base titrations (of all degrees of acid and base strengths), binary and ternary analyses, analytical methods for determining metals and their complexes, ester-ification, saponification, chromatography end points, precipi-tations, water hardness, chelate reactions, reaction rates, and on-stream control of industrial processes.

Newer research was considered of greater interest in the present investigation, and the literature since 1957 has been reported more exaustively than that of the earlier period.

Clinkscales (1957) built a heterodyne type, 120 mega-cycle per second instrument and demonstrated its effectiveness

by performing conventional acid-base titrations, dielectric
measurements and salt-response experiments. The apparatus
was also suggested as a suitable instrument for student use
in undergraduate analytical chemistry courses (Clinkscales
and Frye, 1960).

Mandel'berg and Zarinskii (1958) obtained a Russian
patent for an "Appartus for high frequency titration and for
determination of the concentration of solutions."

Nakano, Ishikawa, and Shibata (1958) found that the
presence of sodium carbonate accounted for the cross-over of
the response curves of sodium chloride and sodium hydroxide.

A titrimeter operating at the unusually high frequency
of 500 Mc. per second was developed by Paucek (1958) and
found suitable for titrations in the .05 M to .1 M range of
ionic salt concentrations.

Titration curves for barium, silver and sodium ions
were reported by Barbi (1951).

Soils and humus were analyzed by means of a 420 mega-
cycle per second instrument in the work of Pavel and
Zazvorka (1958).

Johnson and Neale (1961) studied high frequency
effects in polyelectrolytes.

The "determination of codeine and salicylic acid in
an aqueous environment" was performed with "high frequency
currents" in the research of Kalinowski (1961).

Anikin, Kirpichev, and Gordeev (1961) investigated
the absorbtion of the energy of a high frequency electric
field by aqueous and alcoholic solutions of alkaline earth
chlorides.

The high frequency titration of mercaptans was
reported by Mukherjee and Roy (1961).

An extensive series of researches has been carried
out in Hungary under the direction of Pungor. Papers bearing
only his name appeared on the development of a 130 megacycle
per second instrument (1959), the oxidation of chlorpro-
mazine (1960), and a review of high frequency methods (1962).
Pungor and Balazas reported that the 130 megacycle per second
instrument was useable for titrating hydrochloric acid and
acetic acid at concentrations of one and twenty gamma per
milliliter, respectively; and cations were titrated in concen-
trations of two gamma per milliliter for silver nitrate
and ten gamma per milliliter for barium acetate. Pungor,
Tacacs, and Scherr-Bruzer (1960) investigated the use of
their high frequency titrimeter to test the stability of
pharmaceutical injection solutions, chlorpromazine and
vitamin C, in sealed ampules. Pungor and Zappi (1959)
developed a method for the "rapid determination of aluminum,"
and in the same year reported again on an investigation of
aluminum complexes. Pungor continued his extensive work in
the field of high frequency titration by again collaborating

with Balazs (1962) in a study of the use of methyl glucamine standard solution for a titration of cations with a "high frequency end-point indicator."

Macro amounts of "fluoride" were determined by steam distillation in conjunction with high frequency titration in the investigation of Calkins (1962).

Applications to Nonaqueous Systems. As in the case of applications to aqueous systems, the Sargent (1957) review article contained an excellent summary of the developments to that date. The use of dielectric properties to evaluate the composition of mixtures of organic solvents occupied the attention of most early investigators. The methods were initially concerned with binary systems but soon became sufficiently sophisticated to handle ternary systems and binary systems containing added electrolytes. Some work was done on solids, especially with a view toward the determination of moisture content. Many titrations were performed in nonaqueous solvents such as benzene, alcohols, acetic acid, dimethylformamide, phenol, and pyridine. Some work on rates of reactions were reported, especially in connection with the formation and hydrolysis of esters.

Since the 1957 review article, increased efforts have been expended on the study of nonaqueous research with high frequency titrimeters. The recent literature has been summarized

in this dissertation as a convenient source for future
investigators.

A series of rate studies has been performed at the
University of the Pacific by students of Dr. H.G. Frye.
Lowry (1958) investigated the kinetics of the pyridine
catalyzed esterification of acetic anhydride with ethanol,
Lewis (1959) extended these studies by his work on the acetic
anhydride-isobutanol system, and Abraham (1961) explored the
propionic anhydride reactions with 1-propanol and 2-propanol.

Conseiller and Courteix (1958) used a two megacycle
per second crystal oscillator of their own design, along with
some unique cells, to titrate organic bases with perchloric
acid in a solution that used acetic acid as the solvent.
Methanol-benzene solutions of sodium methylate were also used
as a titrant for organic acids. Caffeine was said to be
titrated with a relative precision of 1 per cent.

A valuable report on the suitability of solvents for
the titration of acids and bases was published by Grove and
Jeffery (1960), using acetonitrile, ethylenediamine, and
butyl amine for the titration (both conductometric and high
frequency) of ammonium iodide, 3,5-dinitrobenzoic acid,
potassium methoxide and tetrabutylamine hydroxide. It was
concluded that the best solvents were those with relatively
high dielectric constants and very weakly basic properties.

Groubert and Caillon (1960), using modified high frequency instruments, studied the dielectric properties of ethylene glycol and diacetone alcohol.

Several recent articles have appeared for which no detailed information is available, except the title. Matsuda and Matsuda (1961) released a paper entitled "Quantitative analysis of halogen of alkyl tin halides by high frequency titration," Simonyi and Tokar (1961) used aluminum halide alcoholates to titrate nonaqueous solutions, Golub and Golodets (1961) investigated lead iodide complexes in nonaqueous solvents, Kirilyuk and Miskidzhyan (1961) analyzed the mechanism of electrolytic dissociation in non-aqueous systems. Cruse (1961) used high frequency titration methods to analyze organic compounds. Ershov and Pokrovskaya (1961) titrated cresol isomers. Caley and Hubboush (1961) determined the composition of organic liquids by titrating them with water (with alcohols and aromatic hydrocarbons as solvents). Anakin, Kirpichev, and Gordeev (1961) investigated the absorption of high frequency energy by alcoholic solutions of alkaline earth chlorides. And finally, Fujishima and Takeuchi (1962) reported a "Rapid determination of trace carbon in metals, by using high frequency condensers of submerging type."

CHAPTER III

A SUMMARY OF LIQUID AMMONIA PROPERTIES AND REACTIONS

Physical and Chemical Properties. Excellent reviews
have been written on liquid ammonia and its reactions (Watt,
1950; Audrieth and Kleinberg, 1953), the most recent being
a chapter in the paper-bound book by Sisler (1961). For
the purpose of this investigation, the more significant
physical and chemical properties of liquid ammonia have
been summarized in Table I; and the general reactions
that occur in liquid ammonia have been reviewed with
specific examples noted which have possible application to
high frequency work.

The solubility of a chemical compound in liquid
ammonia plays an important part in its selection for study,
so a composite list of solubilities was assembled from
the above review articles. Table II summarizes general
qualitative solubility information on inorganic compounds,
and Table III, summarizes general qualitative solubility
information on organic compounds. In general it has been
noted that organic species tend to be more soluble in liquid
ammonia than in water; but for inorganic compounds the con-
verse was true. Reactions occuring in liquid ammonia have
been classified in various ways in review articles. Some of
the sub-divisions used were: Metathetical, Aminolysis,

TABLE I

SOME USEFUL PROPERTIES OF LIQUID AMMONIA

Melting point, $^{\circ}$C.	-77.74
Boiling point, $^{\circ}$C.	-33.35
Heat of Fusion, cal. per mole	1352
Heat of Vaporization, cal. per mole	5581
Dielectric Constant	
$\quad$ -60°C.	26.7
$\quad$ -34°C.	22
Heat of Formation (gas), cal. per mole	-11,040
Critical Temperature, $^{\circ}$C.	133.0
Density	
$\quad$ liquid (-33.4°C.), g. per cc.	.677
$\quad$ gas (-34°C.), mg. per cc.	.863
Specific Conductance (-35°C.), mho	
$\quad$ distilled from sodium	1×10^{-11}
$\quad$ in apparatus with stopcock grease	1×10^{-8}
$K_{ion} = (NH_4^+)(NH_2^-)$, (-50°C.)	1.9×10^{-33}
Ionization Potential, e.v.	10.154
Viscosity (-34°C.), poise	2.558×10^{-3}

TABLE II

SOLUBILITIES OF CLASSES OF INORGANIC COMPOUNDS
IN LIQUID AMMONIA

Alkali amides	Soluble, except for lithium and sodium salts.
Alkali metals	Soluble
Ammine-metal cations	Soluble. Those cations most highly aquo-solvated tend to show greatest solubility in liquid ammonia.
Ammonium salts	Soluble, except for the salts of insoluble oxy-anions listed below (NH_4NO_3, NH_4CNS and NH_4OAc are "ammono-deliquescent.")
Arsenates	Insoluble
Carbonates	Insoluble
Halides	Soluble, with increasing solubility as atomic number of halide increases. Exceptions: Most fluorides, $CaCl_2 \cdot 2H_2O$ and $ZnCl_2$.
Nitrates and nitrites	Soluble
Oxides and hydroxides	Insoluble
Perchlorates	Soluble
Persulfates	Soluble
Phosphates	Insoluble
Sulfates and sulfites	Insoluble. Ammonium sulfate forms a soluble 3-ammoniate.
Sulfides	Insoluble
Thiocyanates	Soluble

TABLE III

SOLUBILITIES OF CLASSES OF ORGANIC COMPOUNDS IN LIQUID AMMONIA

Acid amides	Soluble
Alcohols and phenols	Small molecules are soluble.
Aldehydes and ketones	Moderately soluble, most aldehydes react and some ketones.
Alkanes	Insoluble
Alkenes and alkynes	Low solubility
Alkyl halides	Small molecules are soluble and react with increasing speed as halide size increases.
Amines	Solubility decreases from primary to secondary to tertiary and all decrease with increasing molecular weight.
Aromatic hydrocarbons	Benzene and toluene are soluble, solubility decreases with molecular weight.
Carboxylic acids	Form ammonium salts, of which small molecules are soluble.
Esters	Small molecules are soluble and react.
Ethers	Et_2O is moderately soluble, large molecules become insoluble.
Nitroalkanes and nitroaryls	Soluble and react
Nitrogen bases	Soluble
Sugars and alkaloids	Soluble
Sulfonic acids	Form soluble ammonium salts.

Ammonolyses, Ammonolytic, Ammono Acids, Ammono Bases, and Metal-Ammonia Solutions. For the purpose of this investigation, reactions were classified to emphasize their general application to chemical processes, rather than to the special interests of researchers in liquid ammonia, with the ultimate aim of drawing the attention of other investigators to the utility of high frequency titrimetry. The sub-divisions were Oxidation-Reduction, Acid-Base Titrations, Rate of Reactions, and Organic Synthesis. As with all such classifications, some reactions were difficult to limit to one sub-division and the actual assignment was arbitrary.

Oxidation-Reduction Reactions in liquid ammonia have been studied most intensively from the viewpoint of using the reducing properties of solutions of alkali and alkaline earth metals in liquid ammonia. The most obvious reactions to investigate were between the metal and liquid ammonia itself, but such reactions were generally slow unless catalyzed by finely divided transition metals such as iron.

$$2M^I + 2NH_3 \xrightarrow{\text{Fe}} 2M^+ + 2NH_2^- + H_2$$
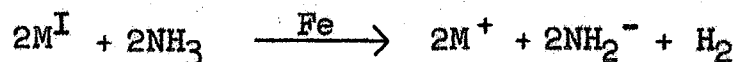
Watt (1950) reviewed the literature of metal ions reduced by M^I and M^{II} metals in liquid ammonia, and discussed the results in terms of four possible outcomes:

Depending on the metal produced, it may (a) undergo reduction to lower oxidation states, (b) catalyze the reaction between alkali or alkaline earth metal and solvent, (c) react with the amide formed catalytically or, (d) participate in no further reactions.

It was interesting to note that the presence of the iodide ion in a reducible metal salt seemed to prevent that metal from catalyzing the formation of amides.

The reduction of inorganic anions has been studied less intensively than the reduction of cations, but the process generally consisted of either lowering the oxidation state of an ion, as in the case where NO_2^- was reduced to NO_2^{--}, or the formation of multiple negative ions, as when S_x^{--} was reduced to both S^{--} and $S_{(x-1)}^{--}$. The second phenomenon was more frequently reported than the first.

An idea of the scope of the reactions with chemical elements was given by Sisler (1961) who listed the products obtained by reactions of alkali metal-ammonia solution reductions of O_2, S_8, Se, Te, P, As, Sb, Bi, Ge, Pb, and Hg.

Solutions of alkali metals in liquid ammonia have been used to reduce a large number of acids (Audrieth and Kleinberg, 1953). The basic nature of the liquid ammonia solvent enhanced the dissociation of even extremely weak acids and hence promoted the reduction of such acids to a greater extent in liquid ammonia than would have been the case in less basic solvents. In fact, some species that

ordinarily were considered bases were reduced as acids by alkali metals in liquid ammonia. For example, each of the NH_2 groups in sulfamide supplied a hydrogen atom with the resultant formation of $SO_2(NH)_2^{--}$ and H_2. Some typical acid species reduced by M^I in liquid ammonia were: NH_4^+, GeH_4, PH_3, AsH_3, NH_3, urea, hydrazine, organic acids, phenols, and alcohols.

The literature on the use of the ammonium ion for synthesizing inorganic chemicals was covered intensively by Watt (1950), and Table IV has generalized much of the information he presented.

Many typical reduction reactions encountered in aqueous and nonaqueous chemistry also occurred with M^I and M^{II} solutions in liquid ammonia. Oxides and halides were reduced to free metals. The oxidation state of the central metal ion in complexes was lowered, as in the case where $Ni(CN)_4^{--}$ was reduced to give $K_4Ni(CN)_6$, an unusual compound containing zero-valent nickel. Hydrocarbon ions were prepared by the reduction of acetylenes and alkyl halides. Metal to metal bonds were created by reducing alkyl tin halides. And as a final example, electrochemical oxidation-reduction processes were utilized in liquid ammonia in the preparation of solutions of aluminum and beryllium metals.

Jolly (1956) pointed the way to calculating redox potentials for liquid ammonia half-reactions, based on the thermodynamic treatment of standard potentials in aqueous

TABLE IV

PRODUCTS FORMED BY THE REDUCTION OF AMMONIUM SALTS
BY ALKALI OR ALKALINE EARTH METALS
IN LIQUID AMMONIA

Salt	Products in Addition to H_2
NH_4X	M^IX and $M^{II}X_2$
NH_4NO_3	$M_2^I NO_2$ (no H_2 formed)
NH_4N_3	$M^I N_3$ and $M^{II}(N_3)_2$
NH_4CN	$M^{II}(CN)_2 \cdot 2NH_3$
$(NH_4)_2S$	$M_2^I S$ and $M^{II}S$
NH_4OAc	$M^I OAc$
$NH_4SO_3NH_2$	$M^I SO_3NH_2$
$NH_4SC_6H_5$	$M^I SC_6H_5$
NH_4ClO_4	$M^I ClO_4$

solution. The more generally useful values calculated by Jolly were rearranged to provide Table V which may be used to predict reactions in liquid ammonia in a manner analogous to the use of standard potential tables in aqueous chemistry.

The more recent investigations on oxidation-reduction reactions in liquid ammonia have been reviewed in all issues of Chemical Titles. Jortner (1961) discussed the interaction of cations and electrons in metal-ammonium solutions. Reinaecker and Roloff (1961) prepared catalytically active nickel. Two Russian articles related to studies of oxygen in metal-ammonia solutions; Makarov and Skovnin described the "solubility of potassium ozanide in liquified ammonia (the ammonia-potassium trioxide system)." and Nevzorov (1961) investigated the "polarization and transport of oxygen in liquid ammonia." Ugi and Bodesheim (1961) reduced both iso-nitriles and alkaline earth metals. Evers and Filbert (1961) measured the volume expansion of sodium-in-ammonia solutions. Tsou, Du, and Xue (1961) used sodium to reduce insulin and its benzyl derivaties. Emeleus and Mackay titrated sodium with phosphine, arsine, stibine and germanes. The "Infra-red Spectra of marginally metallic systems. Sodium-ammonia solutions." were obtained by Beckman and Pitzer (1961). Sodium-ammonia solution was also used by Kocor and Kotlarek (1961) to reduce 2,6- and 1,5-dihydroxynaphthalene ethers. Berns, LePoutre, Bockelman, and Patterson studied the salt

TABLE V

OXIDATION POTENTIALS IN LIQUID AMMONIA AT 25°

Couple	E^{O}_{Acid}, volts	E^{O}_{Base}, volts
$Li = Li^+ + e^-$	2.34	2.70
$Ba = Ba^{++} + 2e^-$	2.2	----
$Ca = Ca^{++} + 2e^-$	2.17	2.83
$K = K^+ + e^-$	2.04	2.04
$e^-_{(am)} = e^-$	1.95	1.95
$Na = Na^+ + e^-$	1.89	2.02
$Zn = Zn^{++} + 2e^-$	0.54	1.8
$Ni = Ni^{++} + 2e^-$	0.1	1.3
$Fe = Fe^{++} + 2e^-$	0.0	----
$Cu = Cu^+ + e^-$	-0.36	1.3
$Cu = Cu^{++} + 2e^-$	-0.40	----
$Ag = Ag^+ + e^-$	-0.76	1.0
$I^- = \frac{1}{2}I_{2(s)} + e^-$	-1.26	-1.26
$Cl^- = \frac{1}{2}Cl_{2(g)} + e^-$	-1.91	-1.91
$F^- = \frac{1}{2}F_{2(g)} + e^-$	-3.50	-3.50

effect of sodium chloride in sodium-ammonia solution. Lithium-ammonia solution was used by Schaub and Weiss (1961) to form steroid enolate anions from conjugated unsaturated ketones. Foster and Mackie (1962) measured the absorption spectra of substituted polynitrobenzenes in an investigation of the interaction of electron acceptors with bases. Hueckel and Jennewein (1962) reduced and methylated 1-methyl naphthalene. A reaction for the separation of hydrogen peroxide in a liquid ammonia medium was reported by Miranov, Dzyatkevich, and Vovchenko (1961). And finally, Ichniowski and Clifford (1961) reported a "Polarographic study of chromium (III) in ammonia solvents (Divers/liquids)."

An extensive series of articles on the properties of metal-ammonia solutions was written by Paoloni in the period 1960-1961. These reports summarized thermodynamic measurements in 1960; and electrochemical properties, spectroscopic and photochemical data, theoretical interpretations, and electronic structure, all in 1961.

Acid-Base Titrations in liquid ammonia usually have involved the ammonium ion as the acidic species. Liquid ammonia exerted a "leveling" effect on the acid strength of any proton donor which dissolved, in a manner analogous to the comparable aqueous phenomenon which generated hydronium ions. Audrieth and Kleinberg (1953) described liquid ammonia

as being "more an acid-leveling than an acid-differentiating
solvent," pointing out that the percentage ionization of
acids is much less in liquid ammonia than in water because
of the lower dielectric constant of the ammonia. Typically,
the conversion of an acid into the ammonium ion has been
represented by the equation:

$$NH_3 + HX \longrightarrow NH_4^+ + X^-$$
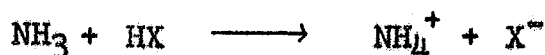
It was furthermore pointed out that no abnormal ionic
mobility has been observed for the "hydrogen ion" associated
with the ammonium ion in liquid ammonia, even though the
"hydrogen ion" associated with the hydronium ion in aqueous
solutions has displayed enhanced mobility. The conductances
of the ammonium ion in ammonium salts have been shown to lie
in the same range as those of the alkali metal ions in their
corresponding salts. Equivalent conductance at -33°C, is
between 300 to 340 for all such salts in liquid ammonia.

The Bronsted concept of acids has permitted the
inclusion of organic amido and imido derivatives in the list
of acids that can exist in liquid ammonia. As was pointed
out earlier in this chapter, species such as urea exhibit
sufficiently acidic properties to be reduced by active
metals. In the Bronsted sense, solvated metallic ions also
have displayed acidic properties. The amido complexes of
silver, copper and zinc (Sisler, 1961) were ammine complexes

which had lost protons to strong bases. For example:

$$Ag(NH_3)_2^+ + 2 \; :B^- \longrightarrow Ag(NH_2)_2^- + 2 \; H:B$$

The strongest base that has been reported in liquid ammonia is the amide ion, which is much stronger than the hydroxide ion. Thus liquid ammonia made available reactions that required stronger bases than were possible in water. An interesting example was shown in the reaction where acetylene was involved in an acid-base reaction with the amide ion, with the result that a stable solution of acetylide ion was formed:

$$HC{\equiv}CH + :NH_2^- \longrightarrow HC{\equiv}C:^- + :NH_3$$
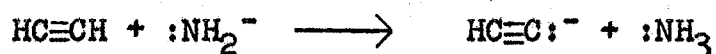
The existence of strongly basic alkyl ions has been reported (Watt, 1950) as a result of reactions between RX and metal-in-ammonia solutions. Such R^- species could not exist in aqueous solutions, but in liquid ammonia they have been used to form alkyl organic metallic compounds.

For purposes of titration, the most common reaction encountered in liquid ammonia, comparable to neutralizing a strong acid with a strong base in aqueous chemistry, has been between ammonium ions and amide ions:

$$NH_4^+ + NH_2^- \longrightarrow 2 \; NH_3$$
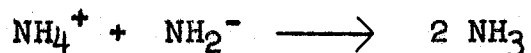
Rates of Reaction have been studied only to a limited extent in liquid ammonia, as evidenced by the fact that the most recent review (Sisler, 1961) made little specific mention of quantitative studies. However, the literature of liquid ammonia was replete with qualitative indications of varying rates of reaction, often not explicitly stated by an author whose main interest was in another aspect of the problem under investigation.

The outstanding pioneer in the study of the physical chemical properties of liquid ammonia, C.A. Kraus (1953), pointed out the need for definitive studies on catalysts that cause M^I and M^{II} metals to react with ammonia to form amides. He suggested that any finely divided surface could act as a catalyst, although oxides and metals were known to be especially effective. The amide reaction was usually a source of difficulty at low metal concentrations, and may have competed with a desired redox syntheses.

Another indication of competitive rates was implied in those investigations which described the yields of several products that resulted from a particular reaction. For example, Audrieth and Kleinberg (1953) described the action of liquid ammonia on halogenated hydrocarbons. In general, iodides were stated to be most easily subjected to solvolysis with the resultant formation of amines and ammonium iodide; but at the boiling point of liquid ammonia, even the

reactions of iodides were "rather slow." Further, in discussing the ammonolysis of specific compounds, it was noted that both primary amines and secondary amines were formed, with the relative amount of the primary amine being larger when the alkyl group was larger (10 per cent RNH_2 from n-amyl bromide and 90 per cent RNH_2 from n-dodecyl bromide).

These authors also reviewed the ammonolysis reactions for esters and reported items of potential interest from the standpoint of rates:

> The extent of ammonolysis is definitely dependent upon the nature of the ester. For instance, ethyl esters of formic, acetic, propionic, valeric, caprylic and phenylacetic acids undergo no appreciable reaction when allowed to stand with liquid ammonia at -33°C. for a period as long as 24 hours. The ethyl esters of mono-, di-, and trichloracetic acid give quantitative yields of corresponding amides under the same conditions. Ethyl oxalate is rapidly and completely converted to oxamide. Ethyl malonate also undergoes ammonolysis quite rapidly.

Rate studies, begun concurrently in Russia by Shatenshtein and the U.S.A. by Audrieth, were performed on the ammonium ion catalysis of a larger number of esters, but the ammonolysis was carried out at temperatures above the boiling point of ammonia. Watt and his students at the University of Texas, in the early 1940's, found that all electrolytes acted as catalysts for the ammonolysis of organic halides, but again the work was at elevated temperatures.

A survey of the literature published in the past two

or three years has been undertaken with the help of Chemical
Titles. No great increase in the volume of research related
to kinetic studies was noted, although the research on liquid
ammonia of the three early investigators, mentioned previously
has continued. Watt and Vaughn (1961) reported evidence for
a "trans" effect in the octahedral spin-paired cobalt (III)
complexes as a result of their investigation of the mechanism
of electrodeposition of cobalt in liquid ammonia.
Shatenshtein and Ranneva (1961) considered the factors affect-
ing the mechanism and partial rate of deuterium exchange in
both dimethyl aniline and liquid ammonia; and Shatenshtein
(1962) published an article entitled "Mechanism of the pro-
tophilic substitution of hydrogen in aromatic compounds by
means of hydrogen isotope exchange with liquid ammonia."
A typographical error was undoubtedly present in the spelling
of Shatenshtein's name in the report by Astafev, Rabinovich
and Schatenshtein (1961), that described the mechanism by
which potassium amide initiated styrene polymerization in
liquid ammonia.

Tesi and Audrieth (1960) strayed somewhat from the
study of rates of reaction but maintained their interest in
liquid ammonia by the "Quantitative determination of some
halogens and halogenides of phosphoronitrile by means of
metallic sodium in liquid ammonia."

Haul, Ihle, and Schierholz (1961) reported on deuterium exchange between hydrogen and liquid ammonia, using potassium amide as a catalyst. Shimo, Wakamatsu, and Inoue (1961) studied the solvent catalyzed alkylation of active methylene groups in liquid ammonia.

Organic Synthesis. The Sisler (1961) review, classified those organic and organo-metallic reactions that had been studied into five categories; (1) metathesis reactions which took advantage of solubility characteristics of substances to prepare compounds such as metal alcoholates, (2) and (3) reactions of ammono acids and bases (previously discussed in this chapter under the heading Acid-base titrations), (4) reactions of metal-ammonia solutions (previously discussed in this chapter under the heading Oxidation-reduction reactions), and (5) ammonolyses.

Some of the ammonolysis reactions mentioned by Sisler were previously discussed in this chapter under the heading Rates of reaction, for example the reaction of alkyl halides to form amines. The other large class of reactions surveyed was that of the esters which were usually converted to acid amides. Reactions of ammonia with nitriles and with the unsaturated hydrocarbon portions of esters were discussed also.

In general, the Sisler review seemed weaker in the

discussion of organic reactions than in its treatment of other reactions in liquid ammonia. Therefore, the review of the recent literature on the reactions of organic species in liquid ammonia was allowed to over-lap Sisler's work and include all of the researches reported in Chemical Titles.

A relatively large number of the investigations of organic chemistry in liquid ammonia took advantage of the reducing properties of metal-ammonia solutions and some of those were mentioned earlier in this chapter under the other headings; but, in general, such reactions have been reiterated in this section of the chapter for the convenience of the reader chiefly interested in organic chemistry. Organo-metallic references have been included in this section also.

A pair of articles has appeared on using the reducing powers of metal-in-ammonia solutions for opening rings in organic compounds and for syntheses. Suquet and Schmitt (1960) used ethanol and lithium in liquid ammonia for "opening the heterocycle of some alkylphenol thiazines at the nitrogen. . ." Tomita and Ujiie (1961) cleaved some heterocycles containing sulfur and oxygen by means of alkali metals in liquid ammonia.

Ugi and Bodensheim (1961) reduced isonitriles. Sodium in liquid ammonia was used by Tsou, Du, and Xue (1961)

to reduce insulin and its benzyl derivatives. Shimo and
Wakamatsu (1961) synthesized dl-glutamic acid by the Michael
reaction of acetamidomalonic acid and acetamidocyanoacetic
acid derivative with acrylic acid derivative. Kocor and
Kotlarek (1961) reported the reduction of 2,6-and 1,5-di-
hydroxynapthalene ethers by sodium. Reports related to the
synthesis of steroids involved hydrophenanthrene and hydro-
chrysene derivatives, as synthesized by Nagata, et al.,
(1961), and the lithium-ammonia reduction of conjugated
unsaturated ketones by which Schaub and Weill (1961) formed
"steroid enolate anions." Shimo, Wakamatsu, and Inoue (1961)
reported on "solvent catalyzed alkylations of active methy-
lene groups in liquid ammonia." Shatenshtein (1962) discuss-
ed the mechanism of the protophilic substitution of hydrogen
in aromatic compounds by means of hydrogen isotope exchange
with liquid ammonia. Absorption spectra of substituted
polynitrobenzenes in liquid ammonia were discussed by Foster
and Mackie (1962). Huckel and Jennewein (1962) reduced and
methylated 1-methyl napthalene. Phenanthrene was reduced
with sodium by Mejer (1961). And finally, mention should be
made of the fact that Reinaecker and Roloff (1961) prepared
catalytically active nickel by reduction in liquid ammonia.
(The preparation of catalytic nickel, although an inorganic
reaction, was thought to be of chief interest to organic
chemists interested in the hydrogenation of organic

compounds.)

In connection with organo-metallic compounds, Behrens has participated in the investigation of the addition of metallic carbonyls to liquid ammonia with an article (Behrens and Hagg, 1961) on the binuclear metal compounds of chromium and molybdenum and with two papers on dihydrogenhexacarbonyl-dinickelate (-1) (Behrens and Lohoefer, 1961; and Behrens, Zizlsperger, and Rauch, 1961). Behrens and Zizlsperger (1961) reported on the reactions of nickel carbonyl with liquid ammonia and with sodium borohydride in liquid ammonia.

Applications to High Frequency Titrimetry. The factors which determined the selection of particular liquid ammonia reactions for study by high frequency methods fell into two categories; and, although the gross features of these categories were apparent, it was believed that some of the less obvious aspects were of sufficient interest to warrant discussion and exemplification.

1. Titrations in which ionic species were precipitated would have caused large changes in instrument response and would have given sharp end points as the capacitance of the cell decreased suddenly.

    Some metathesis and neutralization reactions belonged to this category; but of even greater interest were the reactions of a conducting

species with the solvent. For example, in an
earlier portion of this chapter, it was mentioned
that the highly ionic sodium-ammonia solution was
converted (when catalyzed) to a suspension of
insoluble sodium amide with hydrogen gas bubbling
out of the mixture, as shown in equation (1).

$$2 \text{ Na} + 2 \text{ NH}_3 \longrightarrow 2 \text{ NaNH}_2 + \text{H}_2 \qquad (1)$$

During the time that the sodium concentration
exceeded the response limits of the titrimeter,
no decrease in cell capacitance would have been
observed, but as the sodium concentration decreased
to within the sensitive range of the titrimeter,
the instrument readings would have decreased,
along with the sodium concentration, until the
"no response" pattern of insoluble sodium-amide
was obtained as a constant reading. A titration
curve like the one shown in Figure 2a would have
resulted from such a reaction. The reaction of an
alkali metal to give a soluble amide, for example
potassium, probably would not have resulted in a
"useable" titration curve.

The time required for a given weight of sodium
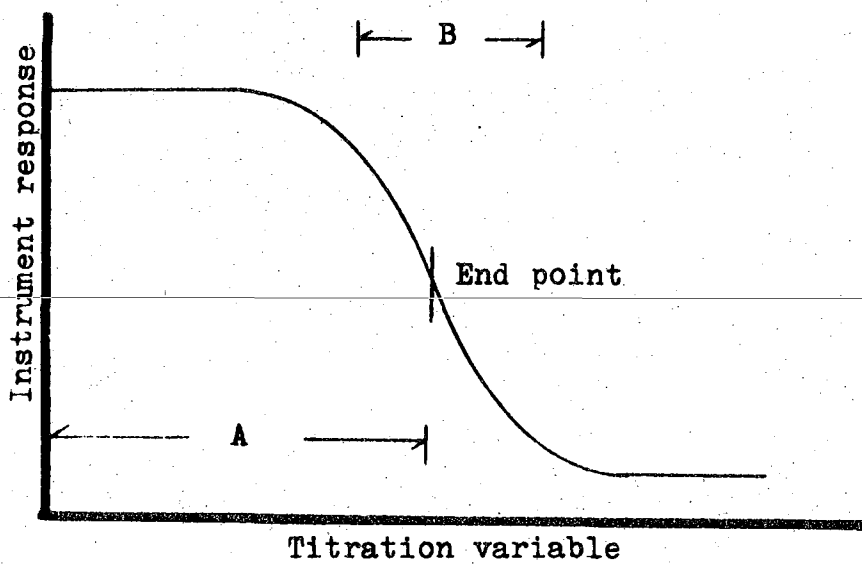
a. Reactions resulting in decreased cell capacitance.
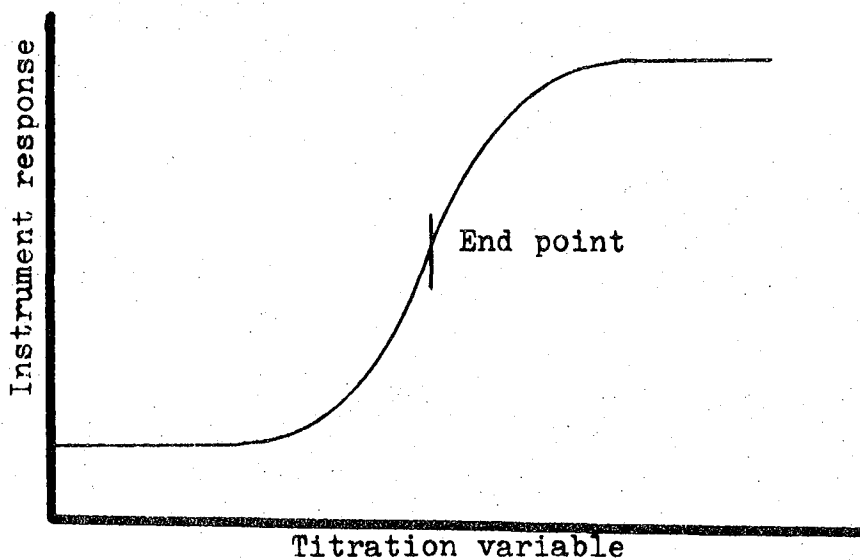
b. Reactions resulting in increased cell capacitance.

Figure 2. Characteristic high frequency titration curves.

to reach the "end-point" could have been measured
(part A of the titration curve) and used to cal-
culate rate constants for the reaction; or the
portion of the titration curve that represents the
maximum change in instrument response (part B of
the titration curve) could be followed by an auto-
matic recorder to give a sensitive indication of
time versus sodium metal concentration, again
permiting the calculation of rate constants.

Metatheses and neutralization reactions would
result in a curve like that of Figure 2a only in
those cases where some of the reactants were ionic
and all of the products of the reaction were
either insoluble or non-ionic. Many reactions
that at first seemed to be of these types would
have had sufficient ionic concentration remaining
after the end point to exceed the response limits
of the titrimeter and, therefore, would have been
difficult to work with unless the concentrations
of reagents were carefully controlled. Equation
(2) has been written to represent a neutralization
reaction that would result in curve 1a; and
equations (3) and (4) have been written to repre-
sent a comparable neutralization reaction and a
metathesis difficult to follow by means of high

frequency titrimetry, even though there would be
fewer ions present after reaction than before.
In the equations, solid substances of low solu-
bility have been underlined and soluble species
have been shown in ionic form.

$$2K^+ + 2NH_2^- + \underline{(NH_4)_2SO_4} \longrightarrow \underline{K_2SO_4} + 4NH_3 \qquad (2)$$

$$K^+ + NH_2^- + NH_4^+ + I^- \longrightarrow K^+ + I^- + 2NH_3 \qquad (3)$$

$$Ba^{++} + 2NO_3^- + 2NH_4^+ + S^{--} \longrightarrow \underline{BaS} + 2NH_4^+ + 2NO_3^- \qquad (4)$$
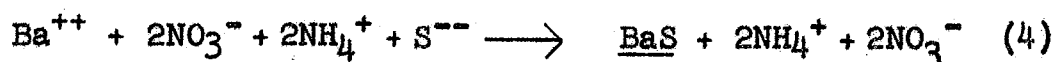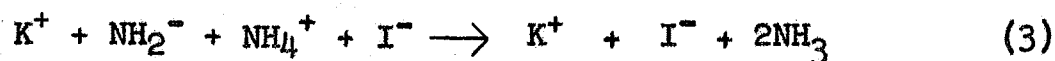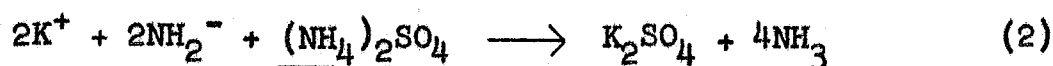
2. Titrations in which insoluble substance react to
   form soluble, ionic species would have resulted
   in large changes in instrument response and would
   have given sharp end points as the capacitance of
   the cell increased suddenly. A similar change
   would have occurred in those cases where a non-
   ionic substance reacted with the solvent (or some
   other non-ionic molecule) with the formation of
   ionic products. In such instances, a curve like
   the one in Figure 2a would have resulted.

   Neutralization reactions could have resulted
   in curve 2a, if the original acid or base was
   insoluble and the final solution contained a

soluble salt. However, if either the reacting acid or the base was insoluble and the resulting salt was also insoluble no titration curve would have been obtained. Similarly, if both the reacting acid and base were soluble and the resulting salt also soluble, no titration curve would have resulted. Equation (5) has represented a neutralization reaction that would have resulted in the type curve shown in Figure 2a. The part of the curve that was generated subsequent to the end point was essentially the salt response curve for the salt formed in the reaction.

$$NaNH_2 + NH_4^+ + I^- \longrightarrow Na^+ + I^- + 2 NH_3 \qquad (5)$$

The solvolysis reactions of alkyl halides would have resulted in the formation of curves like 2b. A generic substance has been shown undergoing such a reaction in equation (6).

$$RX + 2 NH_3 \longrightarrow RNH_2 + NH_4^+ + X^- \qquad (6)$$
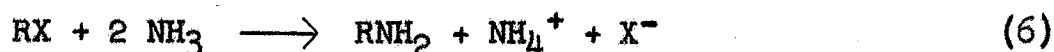
However, these reactions have been catalyzed by ammonium ion, and it would have been possible to use such a large concentration of the catalyst

that no titration curve would result.

Titration curve 2b could have been used for rate studies in a manner analogous to the use made of curve 2a. The reaction up to the end point could have been timed, or the section of the curve with rapidly increasing instrument response could have been recorded to get an accurate indication of the concentration changes versus time.

The discussion presented in this section of the chapter has been limited to those reactions in which large changes occured in the concentration of ions, and the present investigation has been designed to investigate such changes. By the careful selection of the substances involved in a particular type of reaction so that the solubility and ionic changes result in large instrument response, it has seemed possible to study a variety of reactions involving acid-base neutralizations, oxidation-reductions, rate studies and organic synthesis.

No doubt more subtle changes in instrument response also would have had interest. Presumably the high frequency titrimeter could have responded to dielectric changes less drastic than those represented by molecule-to-ion conversions; for example, the solvolysis of an ester to an acid amide. A preliminary investigation of the capacitance changes in the hf-cell by the addition of high dielectric, non-ionic

molecules to liquid ammonia could have been a step toward the study of such reactions.

CHAPTER IV

A TITRIMETER CELL SUITABLE FOR USE AT LOW TEMPERATURES

Design. The arrangement of electrodes in cells used in conventional room-temperature high frequency studies has been investigated by many researchers, and a survey of the efforts suggested three major design categories as indicated in the schematic drawing of Figure 3. The unusual designs of Conseiller and Courteix (1958) have been largely ignored by other investigators.

The decision was made to modify the design shown in Figure 3c, by enveloping it in an evacuated Dewar-type glass jacket; (1) in order to keep a uniform separation between fixed concentric electrodes, and (2) in the belief that the dielectric material between the electrodes was being subjected to more uniform stress than was possible with designs 3a or 3b.

The size of the electrodes was arrived at in consultation with Dr. H.G. Frye (1961) on the basis of his experience with both the 120 megacycles per second instrument built as the University of the Pacific (Clinkscales and Frye, 1960) and the commercially available 5 megacycles per second Sargent Model V Chemical Oscillometer. The final dimensions were chosen to give a cell that responded to each of these available instruments, and the result is shown schematically
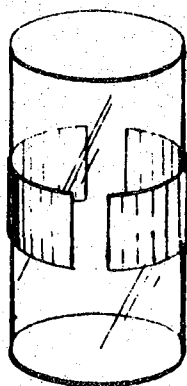
a. Curved electrodes

b. Side and bottom electrodes
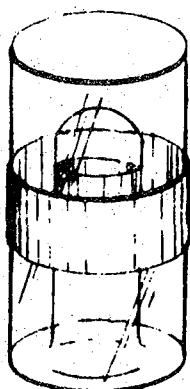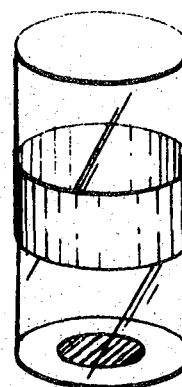
c. Concentric-band electrodes

Figure 3.   Three main types of cells used with high
            frequency titrimeters.

in Figure 4.

Construction. The glass walls of the cell consisted
of conventional pyrex tubing with the inside cylinder being
twenty-five millimeters, inside diameter, and the middle
cylinder being forty-five millimeters, inside diameter. The
outside cylinder was seventy-five millimeters, inside diam-
eter. The copper electrodes were cut from twenty gauge
copper sheet and silver soldered into twenty-five millimeter
wide bands of the appropriate diameter to allow a firm fit
against the respective glass surfaces. Stranded eighteen
gauge copper wire was silver soldered to each electrode, and
each piece of stranded wire was also silver soldered to
twenty-four gauge tungsten wire which was the portion of the
electrical lead that passed through the outside glass wall of
the cell. The use of tungsten minimized the problems inherent
in making a vacuum-tight glass-to-wire seal, but tungsten was
not suitable for the entire lead because its stiffness would
have caused undesirable shifting of the electrodes during the
process of annealing the glass portion of the cell. After
the electrodes were in place and the leads brought through
the glass wall, the bottom of the outside glass cylinder was
rounded off and attached to a piece of twelve millimeter,
inside diameter, heavy-walled glass tubing suitable for
attachment to the vacuum pump. The cell was annealed and the
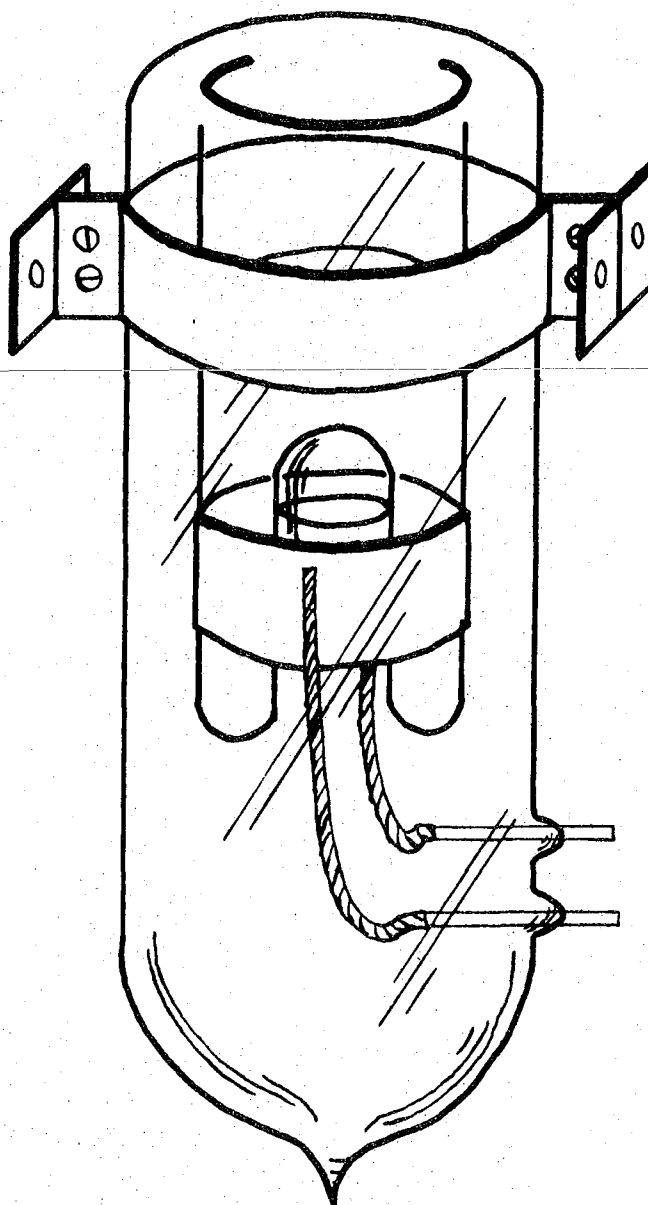
Figure 4. The hf-cell for low temperature studies with
high frequency titrimeters.

electrodes were cleaned of copper oxide with dilute nitric acid. The pressure in the Dewar section of the cell was reduced to 10^{-6} millimeters of mercury, and the bottom tube was sealed off. The cell held approximately fifty milliliters when filled to the top of the inner cylinder and 125 milliliters brim full.

The resulting low temperature cell was labeled the hf-cell as a conveniently short name, suggestive of both its originators and its function.

In order to attach the hf-cell to both the CF-120 Titrimeter and the Model V Chemical Oscillometer in a manner that would minimize the effects of extraneous electrical and magnetic fields, the cell was mounted in a silver plated brass cylinder, recovered from war surplus radar equipment. The eighteen gauge brass ground-ring, shown in Figure 4, was designed to serve also as a suspending support which centered the hf-cell in the cylindrical shield, as shown in Figure 5. The tungsten wires projecting from the outside wall of the hf-cell were soldered with electrical grade tin solder to stranded wires leading to a bakelite case equipped with banana prongs arranged to plug directly into the CF-120 Titrimeter. Alligator clips from these banana prongs to the coaxial cable input of the Model V Chemical Oscillometer permitted convenient interchange of the hf-cell between the two instruments.

Figure 5.   The hf-cell in its metallic shield.

When used at room temperatures, no particular atten-
tion was given to the problem of sealing the brass cylindri-
cal shield so as to keep condensed moisture away from the
tungsten leads. However, at temperatures representing the
liquid range of ammonia, all openings in the cylinder were
sealed with plastic electrical tape or rubber cement.
This seal included the cylinder-to-glass section where the
top of the hf-cell extends from the shield. Glass tubes of
calcium sulfate drying agent were loosely plugged at each end
with glass wool and taped inside and to the bottom of the
shield, thus keeping to a minimum the vapor pressure of water
in the sealed-off space.

Cell Capacitance Calculations. The mathematical
relationships pertaining to the design of cells compatible
with a particular oscillator were thoroughly described by
Sherrick, Dawe, Karr and Ewen (1954), and have not been
summarized in this dissertation. The same authors developed
equations for calculating the cell constants of concentric-
band cells, analogous to the hf-cell; and the pertinent
relationships have been organized in Table VI for conven-
ient reference.

The entire group of equations rests on the assumption
that the capacitance of the cell was equivalent to a single
parallel plate condenser where the metal plate areas were

TABLE VI

SUMMARY OF EQUATIONS FOR CALCULATING CELL CONSTANTS,
CAPACITANCE, AND DIELECTRIC CONSTANTS IN
HIGH FREQUENCY RESEARCH

Equation Number	Relationship*	Comment
4-1	$$C = \frac{C_g C_s}{C_g + C_s}$$	For determining the total capacitance of the system.
4-2	$$C = \frac{C_g C_o}{C_g + C_o}$$	A special form of 4-1 with air or a vacuum in the cell.
4-3	$$K = \frac{C_g + S\left(\frac{C_g}{C_o} + 1\right)}{C_g - S\left(\frac{C_o}{C_g} + 1\right)}$$	For the determination of dielectric constants from instrument dial units.
4-4	$$\frac{C_o}{C_g} = \frac{S_2(K_1-1)-S_1(K_2-1)}{K_1 S_1 (K_2-1)-K_2 S_2 (K_2-1)}$$	For getting C_o/C_g to use in 4-3 with nonionic systems.
4-5	$$\frac{C_o}{C_g} = \frac{S_W}{K_W(S_{KCl} - S_W) - S_{KCl}}$$	For getting C_o/C_g to use in 4-3 with ionic systems.
4-6	$$S = \frac{A(K-1)}{1 + BK}$$	For calculating dielectric constants from scale units without C_o/C_g.

* Symbols have been described in the dissertation.

separated by two kinds of dielectric material: (1) the glass walls between the metal rings, and (2) the fluid in the annular space of the cell. Because the two glass walls were constant in thickness and dielectric constant, the total capacitance (C) was considered as that of two capacitance in series, one of the capacitances being fixed (C_g) and the other variable (C_s). When the cell contained air (ideally a vacuum) with a dielectric constant (K) of one, the total capacitance was given the notation C_0. The term S was used, with an appropriate subscript, to represent instrument scale readings. Thus S_1 and S_2 stood for two different instrument dial values in a particular experimental determination using solutions with dielectric constants of K_1 and K_2 respectively. Similarly, the S_{KCl} and S_W represented instrument dial values taken with potassium chloride solution and water. In order to convert instrument dial values to absolute capacitance units, the various cell constants needed to be evaluated by comparison with a standard condenser.

Attention has been called to the qualitative difference of the instrumental response obtained in systems of low dielectric constant and that obtained in ionic solutions. Equations 4-4 and 4-5 have been developed to allow determinations to be made in either type of system.

Equation 4-6 involved two generalized constants A and B. By measuring the S values of two different known

dielectric liquids, simultaneous equations were set up which permitted calculation of A and B. Once established, the values of A and B were used to determine K for other liquids in subsequent measurements. The use of equation 4-6 resulted in the avoidance of a calculation of C_o/C_g. In actuality A is equal to C_o and B is equal to C_o multiplied by the term

$$(\frac{1}{C_g} - w^2 L)$$

which includes effects caused by the inductance (L) of the system and the frequency of the instrument $(w = 2\pi f)$.

CHAPTER V

THE PREPARATION OF REAGENTS

Liquids. The liquids used in this investigation were
water, methanol, ethanol, acetone, carbon tetrachloride,
1-iodopropane, benzene and ammonia. The details regarding
source, purity and special treatment have been given for each
substance.

Water from the distilled water tap in the laboratory
was redistilled in glass equipment without a fractionating
column and stored in a glass-stoppered borosilicate bottle
equipped with an "ascarite" tube to minimize re-solution of
carbon dioxide.

Methanol was purchased from Matheson, Coleman and Bell.
The "absolute, ACS Analyzed Reagent" was stored in a glass
stoppered borosilicate bottle and used without further treat-
ment.

Ethanol was purchased from Commercial Solvents Company.
The anhydrous product (tax-free, 200 proof) was transferred
from the original five gallon container, stored in glass
stoppered borosilicate bottles, and used without additional
treatment.

Acetone was obtained from a stock room bottle that
was not the original container. The liquid was stored
several hours over freshly heated silicon dioxide drying

agent and distilled in glass equipment without a fractionating column. The middle 80 per cent fraction of the sample, distilling at 57°C. (uncorrected), was stored in a glass-stoppered borosilicate bottle. Wash-grade acetone, of no special purity, was used to make the CO_2 slurries.

Carbon tetrachloride was obtained from a stock room bottle which contained no information regarding its source. The material was stored for several days over freshly heated silicon dioxide drying agent and redistilled in glass equipment without a fractionating column. The middle 80 per cent portion of the sample, distilling in the range 74.5 - 76.0°C. (uncorrected), was stored in a glass-stoppered borosilicate bottle.

The 1-iodopropane, obtained from Matheson, Coleman and Bell, was used without additional treatment. The boiling point range was given as 100-102°C.

Benzene was withdrawn from a bottle in the stock room which was not the original container. The liquid was dried several hours over freshly heated silicon dioxide drying agent, and distilled in glass equipment without a fractionating column. The middle 80 per cent portion, boiling in the range 80.0 - 80.5°C. (uncorrected), was stored in a glass-stoppered borosilicate bottle.

Ammonia was purchased from the Braun-Knecht-Heimann Division of the Van Waters and Rogers Company. The

refrigeration grade, anhydrous material was delivered in a
350 pound pressurized tank (96 p.s.i.g. at 60°F.) equipped
with an X-type dip-stick outlet valve. By rotating the tank
to the appropriate side it was possible to remove either
liquid or gaseous NH_3. All of the liquid ammonia used as a
solvent in the present research was drawn from the cylinder
as a gas and condensed (carbon dioxide-acetone slurry) into a
glass vessel containing pieces of sodium metal. The inlet
tube of the glass vessel was arranged so that incoming gas
was bubbled through a solution of sodium-in-ammonia and the
space around the inlet tube was packed with glass wool.
Thus, the glass vessel served as a "scrubber" for the incoming
ammonia gas. After a sufficient quantity of gaseous ammonia
was condensed for a titration, the liquid was allowed to
warm up and pass from the "scrubber" to the hf-cell in the
gas phase. The purified ammonia gas was re-condensed into
the hf-cell by means of a cold finger filled with a carbon
dioxide-acetone slurry.

The "scrubber" served as a purifier of incoming
gaseous ammonia, even after its own supply of metal-in-
ammonia solution had been lost as a result of ammonia evapora-
tion. The unreacted sodium metal from the sodium-in-ammonia
solution was deposited over the entire surface of the glass
wool, resulting in the exposure of "make-up" ammonia gas to a
large surface area of sodium metal. The "make-up" gas was

occasionally required to adjust the amount of liquid ammonia in the hf-cell to the desired volume.

The ammonia inlet train included a graduated cylinder fastened to the cold finger by means of new, black-rubber pressure tubing. Occasionally, the gas evaporating from the "scrubber" was condensed into the graduated cylinder in order to obtain an accurate liquid volume measurement. In those instances, the liquid was poured from the graduated cylinder through the rubber tubing and into the hf-cell. At no time was there any residue in the hf-cell that would suggest materials had been leached out of the rubber tubing by the liquid ammonia, but no specific tests were performed to prove that such was the case.

Solids. Most of the solids consisted of salts and the treatment was determined largely by the detailed properties of the particular compound. A large group of recently purchased, freshly opened, non-hygroscopic salts were merely stored in dessicators over anhydrous calcium sulfate. For convenience, salts of that type have been listed in groups according to source so as to avoid a tedious repetition of the procedures used in working with them. Salts requiring special treatment have been discussed individually.

Lithium fluoride and sodium bromide were obtained as "Certified Reagents" from the Fischer Scientific Company.

The K and K Laboratories supplied rubidium chloride, 99.8 per cent; rubidium bromide, 99.8 per cent, caesium chloride, 99 per cent, and caesium iodide, no per cent purity given.

Ninety nine per cent pure cobalt trifluoride was purchased from A.D. Mackay.

Baker and Adamson supplied reagent grade A.C.S. potassium chloride crystals; reagent grade potsssium fluoride (anhydrous, granular); reagent grade A.C.S. potassium bromide crystals; reagent grade A.C.S. sodium fluoride powder; reagent grade A.C.S. cupric nitrate crystals; reagent grade cupric bromide; and reagent grade granular ammonium sulfate.

Anhydrous calcium sulfate, "Drierite," was the product of the W.A. Hammond Drierite Company.

The J.T. Baker Chemical Company was the source of C.P. chromium fluoride powder; "Baker's Analyzed", C.P. cadmium containing 99.2 per cent of the hexahydrate.

A few materials were stored in bottles that were not the original containers; and therefore, the original purveyor was not determinable. The general appearance of the compounds suggested that they were reasonably pure, so no attempt was made to purchase new supplies with precisely known purities. Substances in this category were; sodium iodide, sodium metal (approximately one pound extruded chunks,

stored under xylene), potassium metal (stored under toluene), sodium chloride (labeled U.S.P.), and antimony trifluoride (a student preparation).

The only available ammonium iodide contained a brown iodine impurity which was washed out with carbon tetrachloride. The resulting white granules were dried in a vacuum desiccator over anhydrous calcium sulfate.

Ammonium fluoride was prepared by neutralizing aqueous HF (stored in a wax bottle) with concentrated reagent grade ammonium hydroxide. The resulting solution was filtered through paper and evaporated to dryness at room temperature in a vacuum desiccator.

Silver iodide was prepared by adding a slight excess of tenth molar aqueous silver nitrate to a concentrated solution of ammonium iodide. The resulting yellow precipitate was filtered out on a fritted glass funnel and washed successively with one molar ammonia, distilled water, and acetone. The product was dried at reduced pressure in a vacuum desiccator over anhydrous calcium sulfate.

CHAPTER VI

THE USE OF THE HF-CELL WITH THE CF-120 TITRIMETER

Titrimeter Modifications and Operation. The mounted
and shielded hf-cell was designed to connect, by means of
three banana plugs, directly into the titrimeter, replacing
the plastic cell and the associated cell holder described
in the Clinkscales (1957) University of the Pacific thesis.

Two minor changes were made in the output detection
section of the instrument. The ear-phones were replaced with
a Heathkit Laboratory Oscilloscope, with the beat-frequency
being fed into the vertical input; and the National "one
thousand-to-one" dial, which had become defective, was re-
placed with a somewhat less sensitive dial obtained from
war-surplus radar equipment. The replacement dial had
approximately a two hundred-to-one ratio. The exact ratio
between the fine and coarse dials was not considered important,
because only the difference between successive readings was
used in plotting the final titration or response curves.

Reproducibility of readings of the fine dial was
investigated by repeatedly turning the dial clockwise and
counter-clockwise past the resonance point. On the basis of
about 200 readings, the reproducibility was found to be plus
or minus three. When the coarse dial was changed and an
attempt was made to set it back to the place from which it

was moved, without watching the oscilloscope, the repro-
ducibility averaged plus or minus eleven fine-dial units,
with an ocasional variation of as much as twenty-five fine
dial units. However, when the oscilloscope was watched, it
was possible to set the fine dial at any desired point and
adjust the instrument by means of the coarse dial until the
resonance pattern appeared on the oscilloscope. This was
interpreted to mean that only the reproducibility limitations
of the fine dial were of significance in the operation of the
CF-120 Titrimeter.

The titrimeter signal on the oscilloscope was capable
of being adjusted to a thin-lined, practically flat ellipse
with the long axis symmetrically oriented around the
horizontal zero-line of the oscilloscope. When resonance
was almost established, the signal line broadened in the
vertical direction to a maximum determined by the setting of
the variable resister in the output of the CF-120 Titrimeter.
At the exact point of resonance, the oscilloscope signal
suddenly collapsed to practically zero and then, just as
suddenly, returned to maximum as the dial was turned past the
point of resonance.

The circuit of the CF-120 Titrimeter generated
harmonic resonances which caused the oscilloscope to go
through the same rise-fall-rise pattern as did the funda-
mental resonance. The harmonic resonances appeared when the

dial was turned either clockwise or counter-clockwise from the fundamental resonance, but the extent of the vertical rise of the oscilloscope signal was considerably less than the rise obtained for the fundamental resonance. By adjusting the fundamental resonance to give a full scale vertical rise just prior to the resonance dip, a rise of thirty-four units on the Heathkit Oscilloscope picture tube, it was possible to estimate the intensity of the harmonic resonances by measuring the extent of their vertical broadening. Two categories of harmonic resonances were observed, those of medium intensity, giving essentially a half-scale rise of about fifteen to twenty units, and those of weaker intensity, generating a rise of six to eight units. After some practice with the instrument no difficulty was experienced in deciding when the fundamental resonance was being observed.

Response Patterns. When the hf-cell was plugged into the CF-120 Titrimeter and an attempt was made to follow the changes in all of the resonances, both fundamental and harmonic, as the cell was filled with liquid, a bewildering sequence of changes occured as the level of the liquid increased. Both harmonic and fundamental resonances appeared on the oscilloscope at a particular liquid level, and these changed systematically as the liquid level rose. Eventually however, when the hf-cell was filled to a point past the

lower edge of the ground ring, a particular fundamental resonance, with its associated harmonics, became stablized. Figure 6 shows the filling pattern observed with water and acetone. (Acetone was chosen for work at room temperature because it had a dielectric constant approximately the same as liquid ammonia at its boiling point). The filling pattern for the acetone below thirty milliliters was omitted to increase the legibility of the figure, but it closely paralled that of water.

No significance has been attached to these patterns below the forty milliliter or "full" level of the hf-cell. Above the "full" level, the presence of harmonics along with the fundamental resonance made it imperative that the operator of the instrument follow a particular signal throughout the course of an experimental determination.

It was apparent that the hf-cell should be filled with at least forty-five milliliters of liquid in order to give signals at a constant dial reading, but in practice, stirring the contents of the hf-cell required at least seventy-five milliliters of liquid. Thus, experimental difficulty was not created by the fluctuating response pattern obtained when the cell was partially filled.

An interesting application of these filling pattern data was envisioned when a large dial change was expected in a particular determination. In some cases, for example if
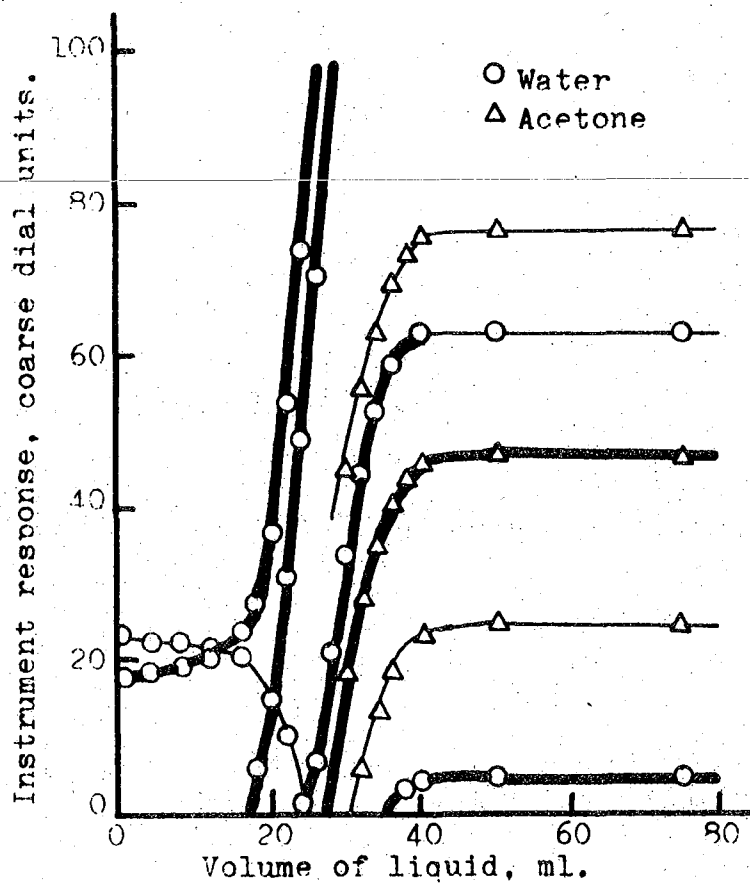
Note: The width of the curve represents the relative
intensity of the resonant response.

Figure 6. CF-120 Titrimeter response pattern when the
hf-cell is being filled with water or acetone.

acetone was the solvent, it was desirable to follow the
increase in the weak harmonic rather than the fundamental so
as to leave more "room" on the dial for dial increases occur-
ing during the experiment.

Experimental Results. The capacitance of the hf-cell
was too large to permit the use of significant amounts of
ionic substances in aqueous solutions. When attempts were
made to study ionic solutions, the CF-120 Titrimeter ceased
to resonate in a manner that could be followed by the
oscilloscope. From the operators point of view, the harmonic
being tracked on the dial went off scale and no other
harmonic respnances appeared at any point of the dial.
Suddenly, the signal just ceased to exist. To a degree, the
same problem was encountered even when a liquid with a lower
dielectric constant than water was used as the solvent; but
oscillation could be maintained if, rather than ionic sub-
stances, some low-dielectric material was added to the
solvent.

The results obtained with the addition of water to
methanol and acetone have been summarized in Figure 7. The
choice of these solvents reflects the fact that their
dielectric constants bracket that of liquid ammonia at its
boiling point.

In Figure 8, the results have been shown of an attempt
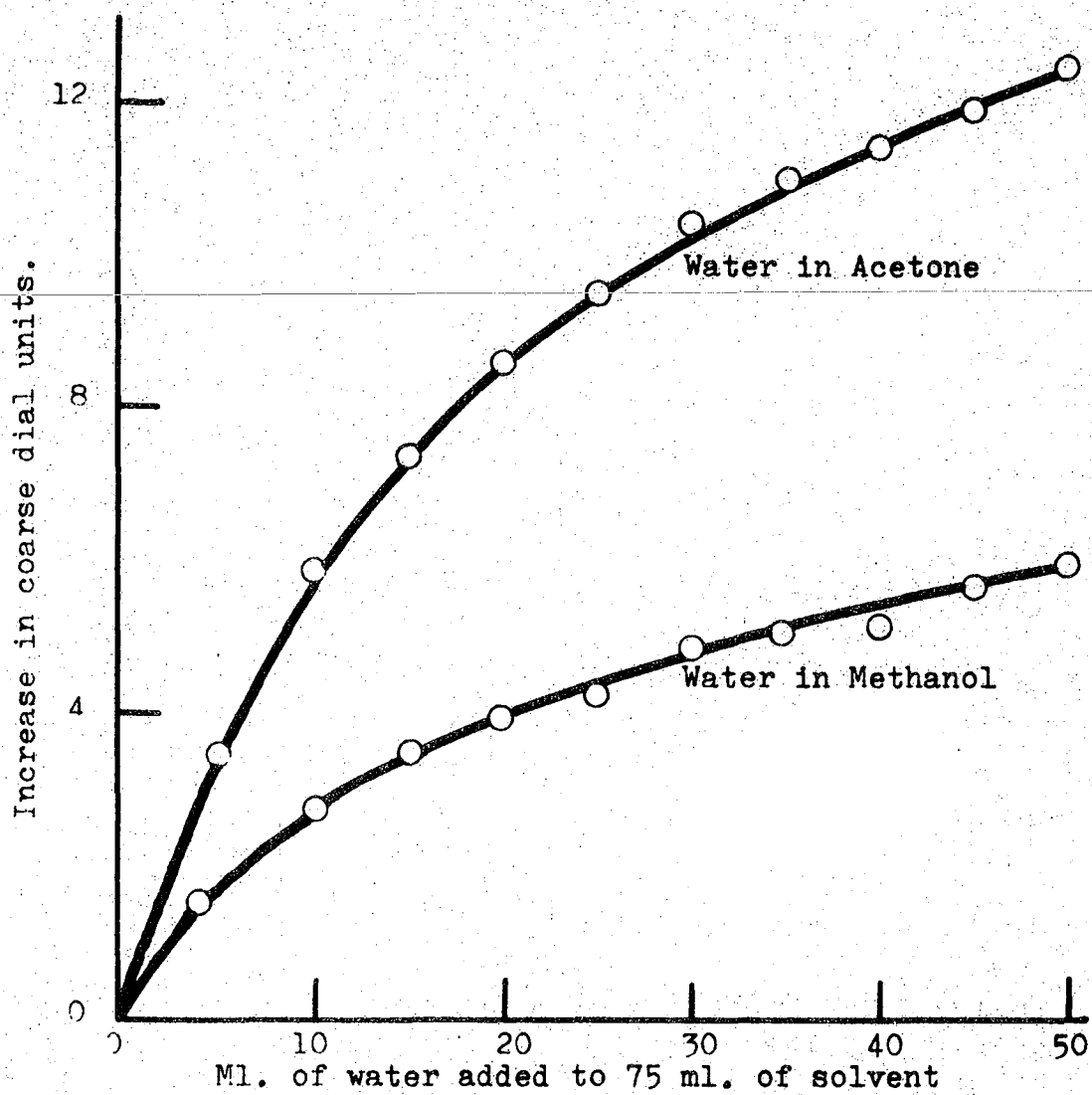
Figure 7. Response curve of water in acetone and methanol, using the hf-cell and the CF-120 Tritrimeter.
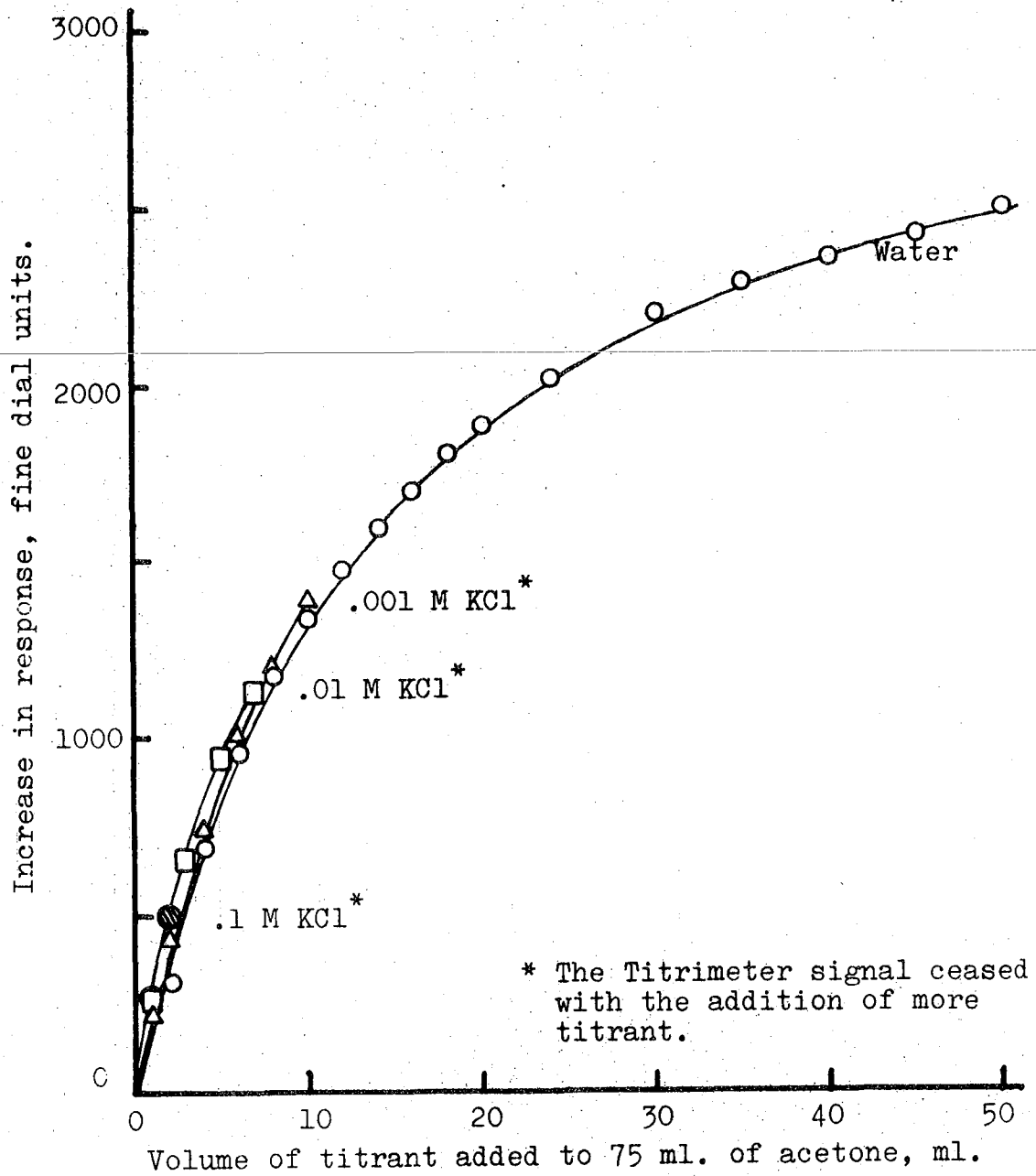
Figure 8. CF-120 Titrimeter response curves for aqueous KCl and for water added to acetone in the hf-cell.

to add a salt to a solvent such as acetone which has a low dielectric constant in comparison with water. Aqueous solutions of potassium chloride contained sufficient water to keep the salt in solution in the acetone; but, the CF-120 Titrimeter ceased to oscillate when any significant amount of salt was added. The titration curve with pure water was included for comparative purposes. The low ionic concentrations permissible and the inherent undesirability of working with a three component mixture caused an abandonment of this type of investigation.

The use of salts which dissolved directly in the acetone, without requiring the solubilizing effect of water, was considered a more promising area of study. The addition of acetone solutions of cadmium iodide to pure acetone was investigated and the results have been presented in Figure 9. The equipment arrangement permitted the slow evaporation of acetone during the titration, and the resultant temperature change caused significant changes in instrument response. By knowing the slope of the response-temperature curve (to be discussed later), it was possible to correct the raw data as shown for the .0100 M CdI_2 titration, but the uncorrected curve was omitted to improve the legibility of the Figure.
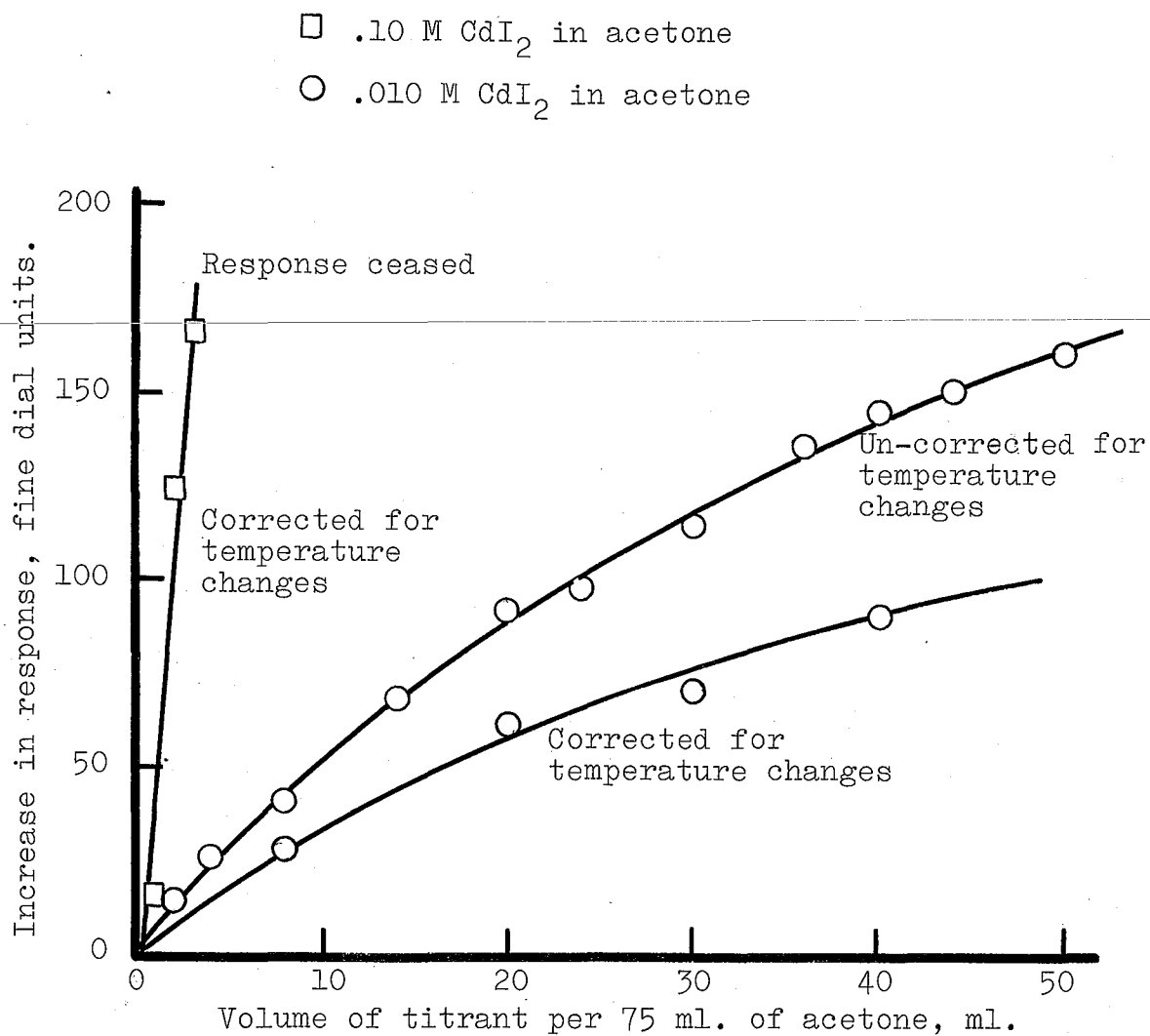
Figure 9. CF-120 Titrimeter response to acetone solutions of CdI_2 added to acetone in the hf-cell.

Because of the low tolerance for ionic compounds, displayed even when acetone was the solvent, it was decided not to attempt to use liquid ammonia in the hf-cell with the CF-120 Titrimeter, at least until considerable experience was obtained with the ammonia and hf-cell and the less sensitive Sargent Model V Chemical Oscillometer.

Comments on instrument operation. One aspect of the operation of the CF-120 Titrimeter was uncovered that conflicted with the information supplied by Clinkscales (1957) who indicated that the voltage supply was set at about 300 volts. In this investigation, the coarse dial of the CF-120 Titrimeter was set at thirteen, the hf-cell was filled with air, and the fine dial was used to establish resonance at different voltage settings. The strongest response was obtained when the voltage was 190 volts, and this gave a corresponding power supply current of about twenty-six milliamperes. All of the data reported in this dissertation were obtained with the power supply set at 190 volts.

Instrument warm-up was not necessary for the protracted periods of time suggested by previous investigaters. Lowry (1958), Lewis (1959) and especially Abraham (1961) turned the CF-120 Titrimeter on several hours before they used it, stating that the purpose of the long warm-up was to minimize instrumental drift during an experiment. For the present

investigation, the tubes were all checked and those that appeared sub-standard, in any way, were replaced. In Figure 10, the change in instrument response with time has been plotted, using the hf-cell filled with seventy-five milliliters of water. Little drift occured except during the first few minutes of operation.

Temperature fluctuations, occuring in the hf-cell during a titration, were reflected in the instrument response, as shown in Figure 11 and Figure 12. The slope of the instrument response-temperature curve for fine dial readings was found to be minus twenty-seven fine dial units per degree when acetone was the liquid (Figure 11). A less sensitive measurement (Figure 12) was obtained for the coarse dial units, but these data were interesting because they permitted a rough comparison of the surprisingly different slopes of the instrument response-temperature curves of acetone and water. The slopes were -.09 and -.03 coarse dial units per degree, respectively.
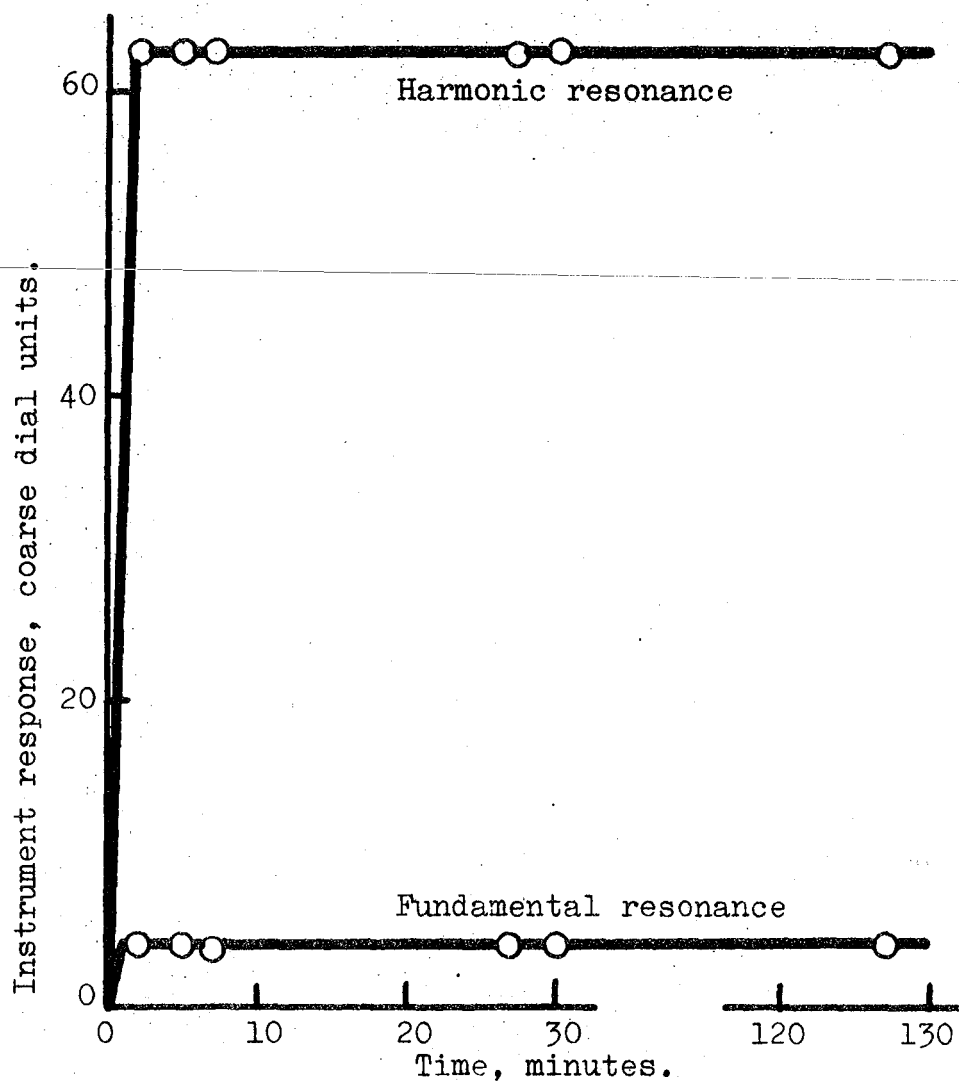
Figure 10. The effect of warm-up time on the response
    of the CF-120 Titrimeter with the hf-cell and 75 ml.
    of water.
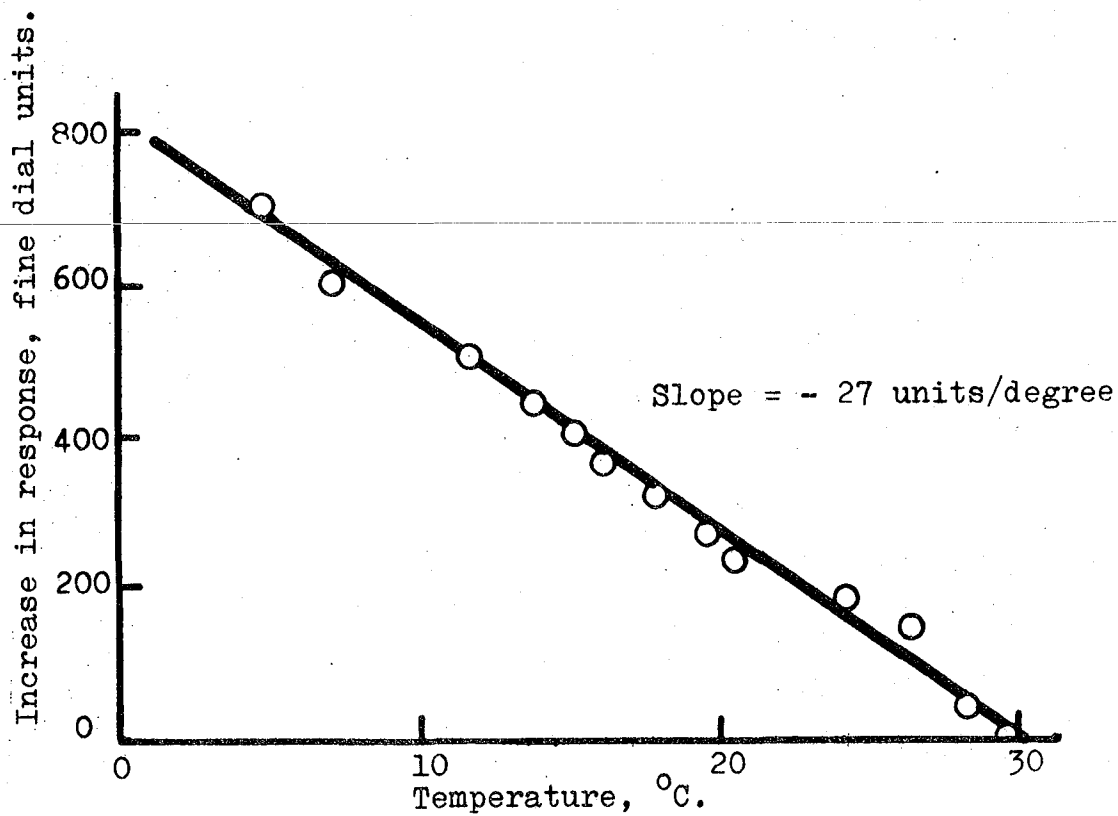
Figure 11. The effect of temperature on the response of
the CF-120 Titrimeter, using the hf-cell and 75 ml.
of acetone.
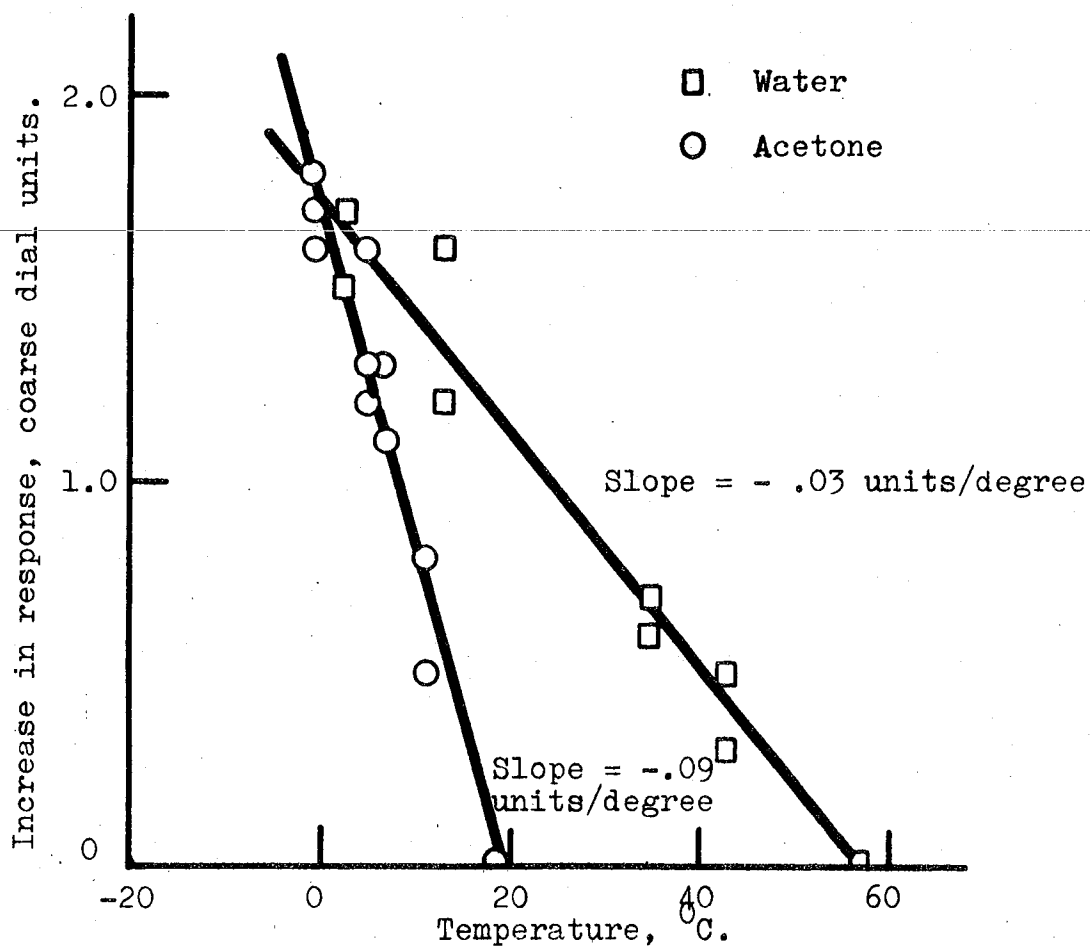
Figure 12. A comparison of the response-temperature
relationship of water and acetone, using the CF-120
Titrimeter and hf-cell with 75 ml. of liquid.

CHAPTER VII

THE USE OF THE HF-CELL WITH THE SARGENT
MODEL V CHEMICAL OSCILLOMETER

<u>Titrimeter Modification and Operation</u>. The major modification of the Model V Chemical Oscillometer consisted of replacing the conventional titration cell with the hf-cell and the auxiliary apparatus needed to work with liquid ammonia.

The hf-cell was attached by means of the three banana plugs projecting from the circular, black-plastic box, visible in Figure 5. One of the threaded couplings was removed from the transmission cable, supplied as standard equipment with the chemical Oscillometer; and alligator clips were soldered to the core-wire and to the outside, woven shield. The alligator clips were attached to the two banana plugs leading to the hf-cell electrodes. A separate wire, with an alligator clip on each end, was used to ground the third banana plug to the metal shell of the oscillometer. To add rigidity to the connection between the hf-cell and the Chemical Oscillometer and to shield the connections against external electrical and magnetic effects, a cylinder of copper gauze was taped to the black box and around the transmission cable. Also, the gauze was grounded to the Chemical Oscillometer chassis.

The equipment needed to fill the hf-cell with liquid ammonia, to keep the system stirred and at constant temperature, to add solid or liquid samples, and to aspirate the hf-cell contents have been shown schematically in Figure 13.

The cold-finger was filled with a solid carbon dioxide-acetone slush to condense ammonia into the hf-cell. After the desired quantity of ammonia had condensed, excess solid carbon dioxide was removed from the cold-finger and small pieces were re-added at intervals in order to keep the hf-cell contents at the boiling point of liquid ammonia.

The temperature of the acetone in the cold-finger varied from -36°C. to -42°C. depending on the experimental conditions, but in all cases it was possible to maintain the temperature of the hf-cell contents within ± .1°C. of -33.4°C., the boiling point of liquid ammonia.

During many of the experiments, an A.S.T.M 33C thermometer, -38° to +42°C., was used to determine the temperature of the hf-cell contents, but it was found equally feasible to observe the manometer and adjust the cold-finger temperature to give a pressure of one atmosphere in the hf-cell. Variations in atmospheric pressure were not sufficient to affect the boiling point of the liquid ammonia more than the ± .1°C.; and, therefore, the thermometer was not used in some of the experiments; reliance being placed on the observation of the manometer.
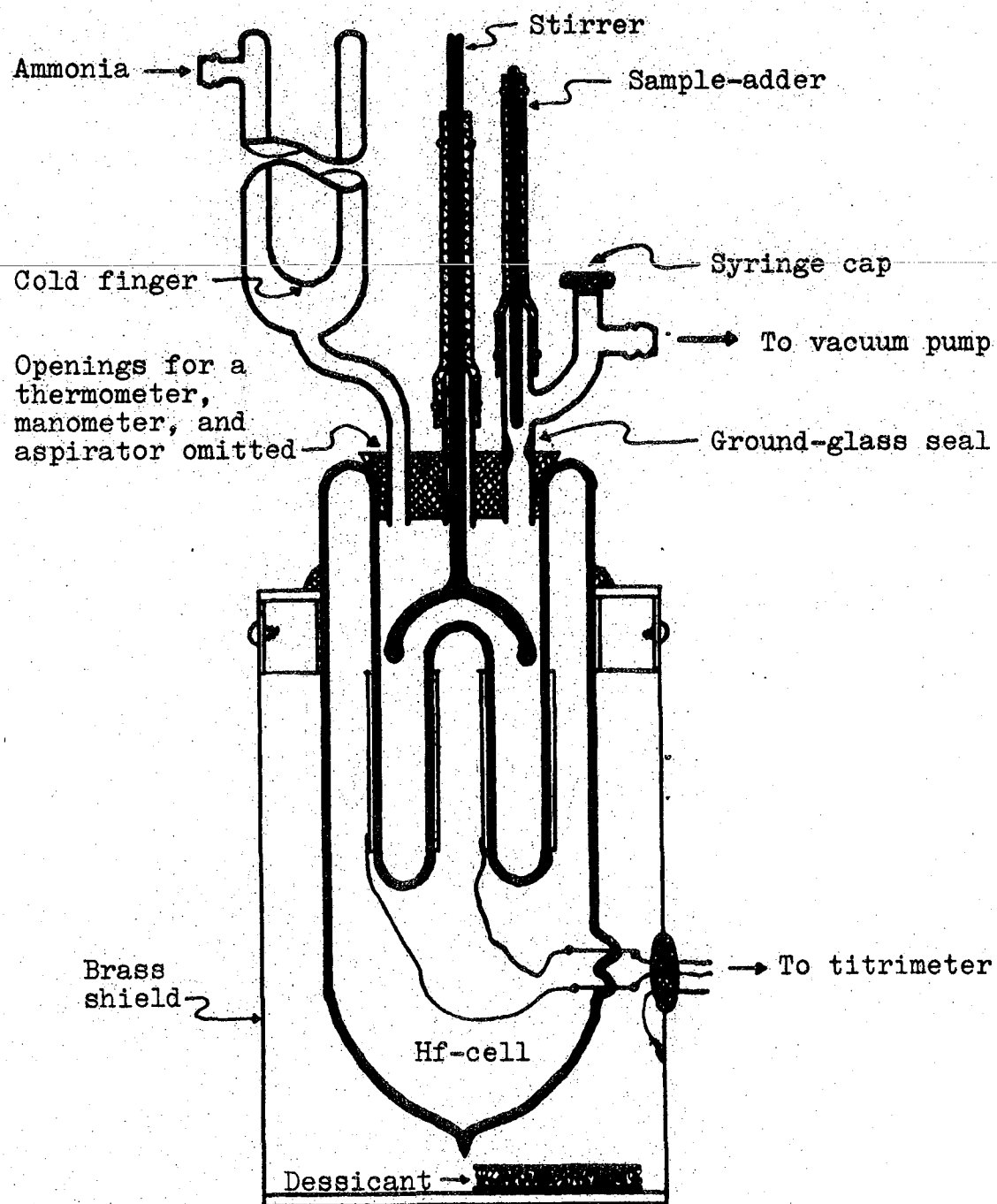
Figure 13. A schematic diagram of the shielded hf-cell, equipped for use with liquid ammonia.

Solid samples were added to the liquid ammonia in the hf-cell as individual crystals or pellets, weighed to the nearest .1mg. The space above the ground-glass seal of the "sample-adder" was evacuated with a Welch Duo-Seal pump and refilled with air passing through an anhydrous calcium sulfate drying tube. (In cases where the solid was something like sodium metal, capable of reacting with dry air, the evacuated space was filled with helium.) The rubber cap was removed, the sample quickly added, and the cap replaced. Any moist air admitted with the sample was re-evacuated and the chamber was again filled with dry air (or helium). On lifting the glass rod to open the ground-glass seal, the sample fell into the hf-cell.

Liquids were added by inserting a syringe needle through the rubber cap above the ground-glass seal and injecting a suitably sized liquid aliquot which fell into the hf-cell when the glass rod was lifted. For small samples, the hold-up around the glass seal was so large that the "sample-adder" was replaced by a short length of straight glass tubing topped with a gum rubber cap suitable for use with a syringe. Thus, it was possible to inject the sample directly into the hf-cell and, if desired, to have the tip of the syringe needle below the surface of the liquid ammonia.

The stirring rod entered the hf-cell through a glass sleeve which was filled with Dow Corning Stopcock Grease

Silicone Lubricant. To improve the ability of the seal to resist pressure variations within the hf-cell, a twenty centimeter length of rubber tubing was used to extend the glass sleeve, and the diameter of the tubing was such that a small torque was required to turn the stirring rod, even when lubricated with the silicone grease. During an experiment the rubber tubing temperature would rise to about $50^{\circ}C.$; but by careful selection of its diameter and by keeping plenty of silicon grease between the glass and the rubber, a seal was obtained that would withstand a vacuum of about 200 mm. of Hg and a pressure of about 50 mm. of Hg. During the extremes of pressure encountered when the hf-cell was being filled with ammonia or aspirated to remove the products of a reaction, the stirrer was stopped and the rubber tubing was wired to the glass stirring rod.

After the completion of an experiment in the hf-cell, the contents were aspirated into an adjoining vessel and the liquid ammonia was recovered by condensing it in the "scrubber." The hf-cell and its associated apparatus was cleaned, rinsed with acetone, and reassembled for the next experiment. Prior to re-filling the hf-cell with ammonia, the system was dried by being evacuated to below .1 mm. of Hg.

During the cleaning process it was possible to visually inspect the hf-cell to see if any undissolved

residues remained from solid samples added during the previous experiment. Most of any precipitate formed during a reaction was sufficiently finely divided to be aspirated with the liquid ammonia.

The operation manual for the Sargent Model V Chemical Oscillometer was written before the "Internal Reference" capacitance was added to the instrument. Thus, the procedure used in this experiment was slightly different than that described in the manual. Rather than using the hf-cell (empty or full of liquid ammonia) to establish a zero-point on the instrument dial, the "Internal Reference" was used to establish the zero-point. By returning the instrument to the "Internal Reference" after each reading, the zero-point was kept independent of instrument drift; and reproducible instrument response was obtained within $\pm$ 1 scale unit.

When the Sargent Recorder was used in conjunction with the Chemical Oscillometer, the "Internal Reference" could not be used to establish the zero reference without sacrificing Recorder sensitivity. In such cases, the procedures described in the operation manual were followed exactly.

The Sargent Cell Compensator was available as an accessory for use with nonionic solutions. The Cell Compensator consisted of a calibrated variable inductance in series with any cell used with the Chemical Oscillometer.

By filling a cell with a solution which exerted the maximum
response anticipated in an experiment, it was possible to
set the Cell Compensator so that the full scale, 32,000 units,
of the Chemical Oscillometer was being used. When the Cell
Compensator was used with ionic solutions, the Chemical
Oscillometer ceased to oscillate at such a low ionic concen-
tration that no practical advantage resulted.

Preliminary Studies. Prior to working with liquid
ammonia, the response characteristics of the hf-cell were
investigated briefly with water and acetone.

In Figure 14, the response of the Chemical Oscillometer
to aqueous solutions of a strong acid (HCl), a weak acid
(HOAc), and a soluble salt (KCl) were shown using the hf-cell;
and the resulting curves were completely analogous to the
curves obtained with the commercially available cells
supplied by the instrument manufacturer. The shape of the
hf-cell response curve was the same as for the Sargent cell,
but the magnitude of the response was decreased. For strong
electrolytes in the hf-cell, the region of maximum response
was obtained with concentrations of two to four millimoles
per liter of aqueous solution, depending on the ionic species.
Weakly dissociated substances such as acetic acid failed to
demonstrate a region of maximum response.
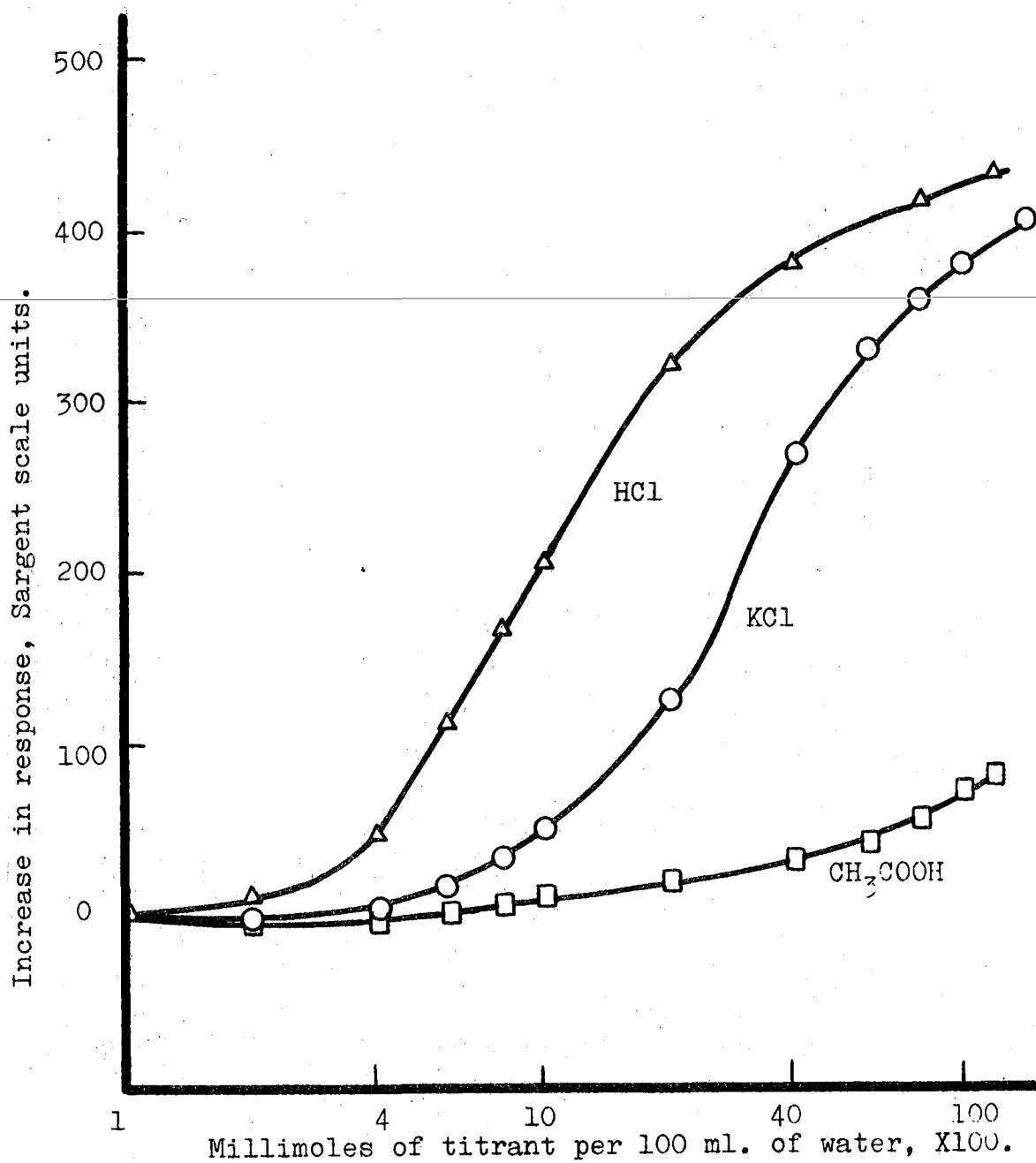
Figure 14. Response curves for hydrochloric acid,
    potassium chloride, and acetic acid added to water,
    using the Sargent Chemical Oscillometer and hf-cell.

A titration of 5×10^{-4} M HCl with .0100 M NaOH was performed in the hf-cell, and the results have been shown in Figure 15. The end point obtained from the titration curve did not agree well with the visual end point obtained with phenolphthalein, but the shape of the curve was typical for such titrations in conventional cells. Had the concentrations of the solutions used for the titration been selected to be in the region of maximum response, a greater correspondence between the visual and experimental end points would have been obtained. A ten-fold increase in the concentrations of the solutions would have been about right.

The response curves of an ionic substance, CdI_2, and of a non-ionic substances, H_2O, in acetone have been shown in Figures 16 and 17 respectively. The region of maximum response for CdI_2 occurred at about 6×10^{-5} mole fraction of salt. With water, no inflection point was observed in the response curve; and the resulting plot was typical of plots obtained with non-ionic species in the Sargent cell, especially when the Sargent Cell Compensator was used to increase the effective capacitance of the hf-cell.

The curve resulting from the nonaqueous titration of CdI_2 with NH_3 (both compounds dissolved in acetone) has been plotted in Figure 18 and compared with the curve that resulted when NH_3 was added to pure acetone. An interesting plateau was observed in the CdI_2 curve, and represented a
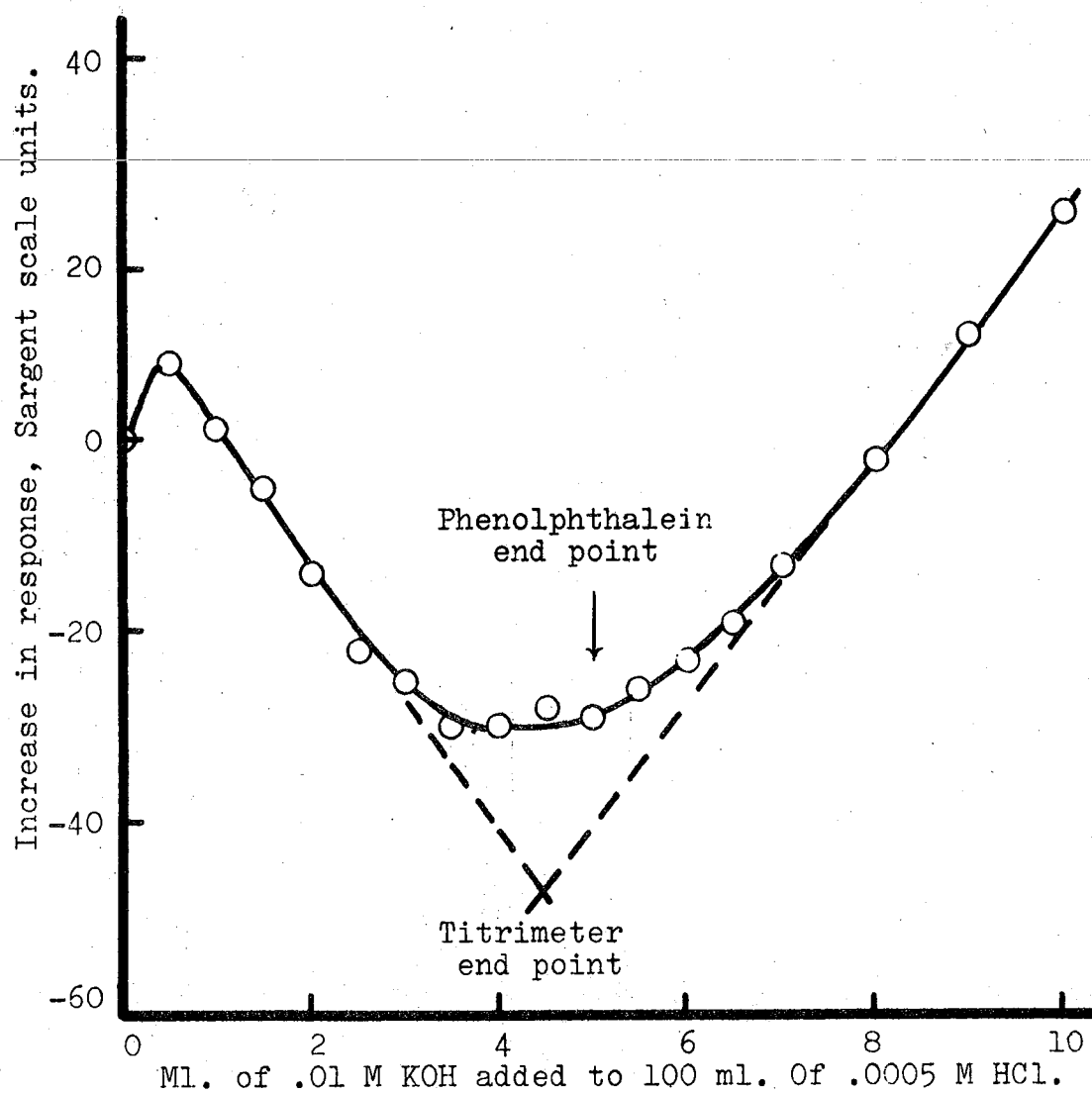
Figure 15. Titration of hydrochloric acid with potassium hydroxide in aqueous solution, using the Sargent Model V Chemical Oscillometer and the hf-cell.
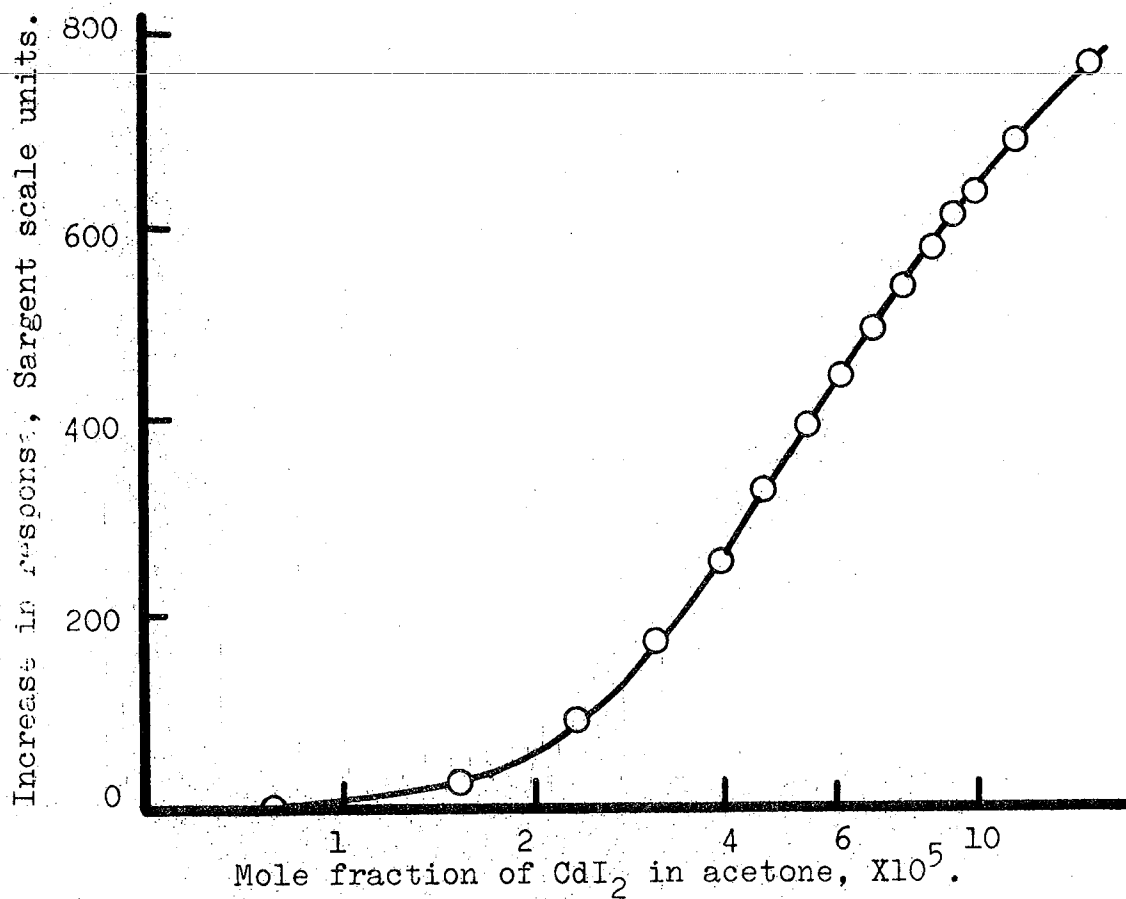
Figure 16. The response curve for cadmium iodide in acetone, using the Sargent Model V Chemical Oscillometer with the hf-cell.
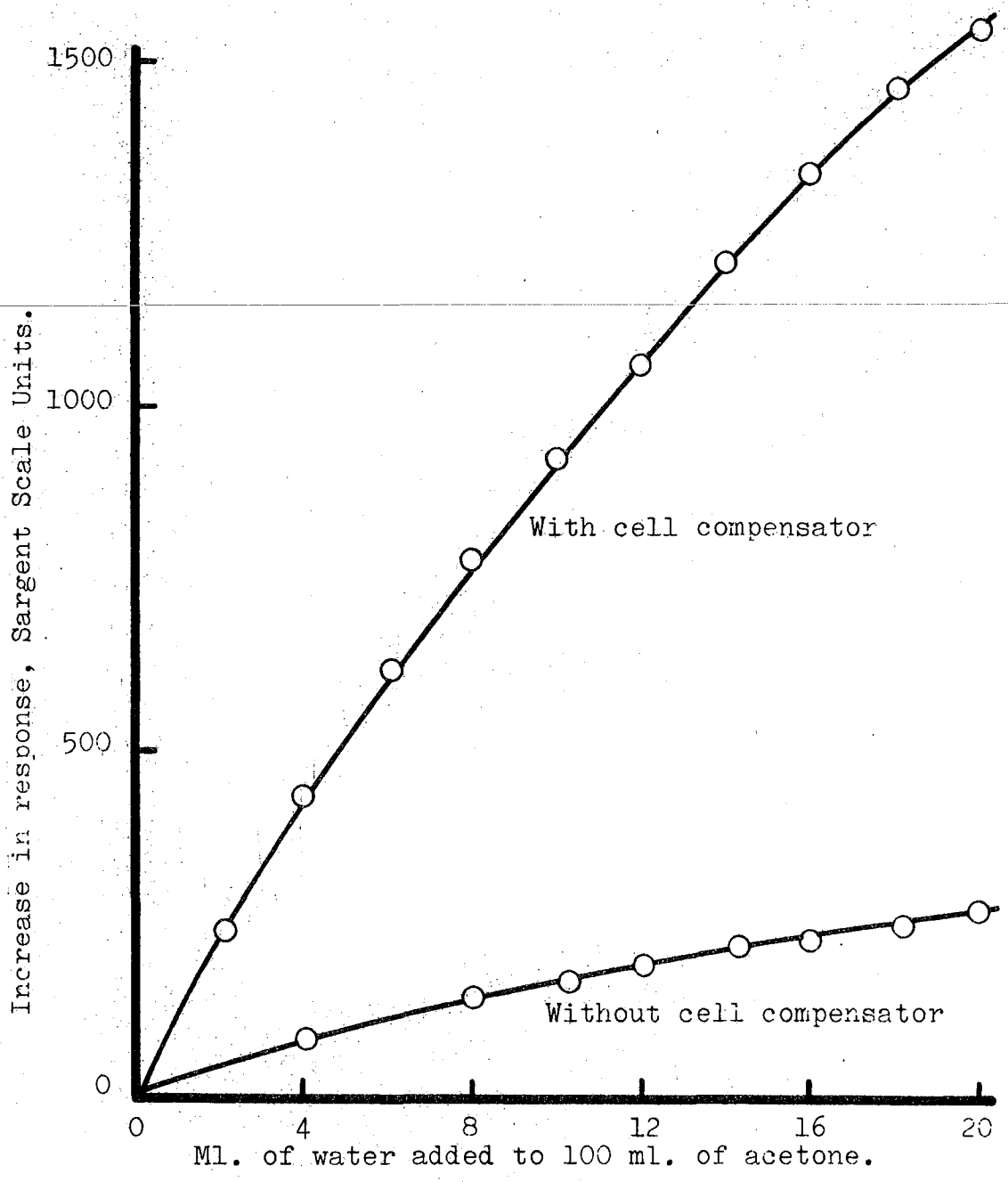
Figure 17. The titration of acetone with water, using
the Sargent Model V Chemical Oscillometer and hf-cell.
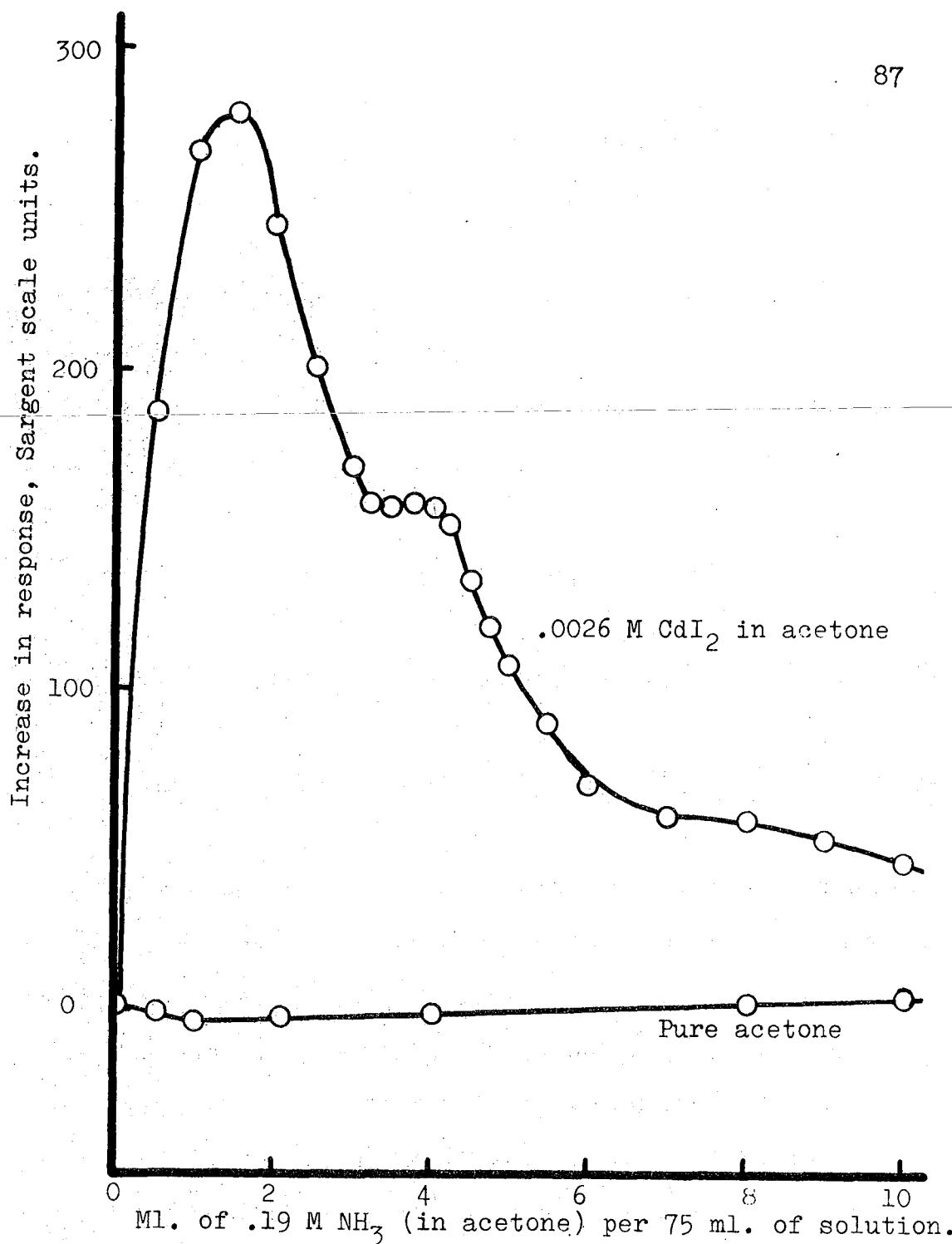
Figure 18.   Titration of CdI$_2$ with ammonia, in acetone, using the Sargent Chemical Oscillometer and f-cell.

response that did not appear when an identical titration
was performed with an Industrial Instruments, Inc.
Conductance Meter.

Presumably the initial CdI_2-in-acetone solution was
dissociated into Cd^{++} and $Cd(I_4)^{--}$, and at least three reac-
tions could have been predicted to occur with ammonia, as
shown in equations (7), (8) and (9).

$$Cd^{++} + CdI_4^{--} + 4\ NH_3 \longrightarrow Cd(NH_3)_4^{++} + CdI_4^{--} \tag{7}$$

$$Cd^{++} + CdI_4^{--} + 4\ NH_3 \longrightarrow 2\ Cd(NH_3)_2I_2 \tag{8}$$

$$Cd^{++} + CdI_4^{--} + 8\ NH_3 \longrightarrow 2\ Cd(NH_3)_4^{++} + 4\ I^- \tag{9}$$
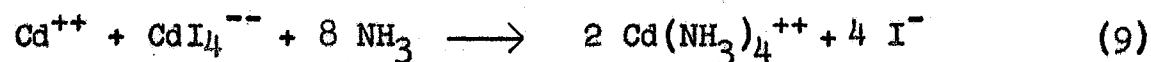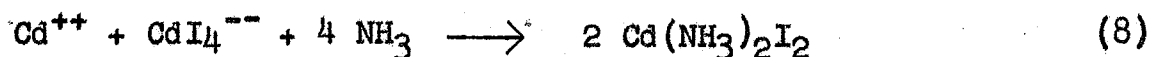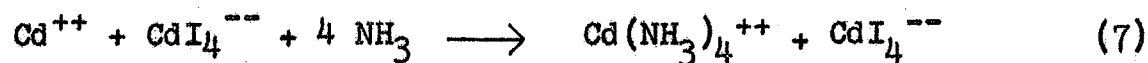
Equation (7) would have been expected to give only a slight
decrease, if any, in instrument response as the ammonia was
added, and equation (8) would have been expected to give a
large decrease in response. Thus, neither (7) or (8)
"explained" the shape of the titration cruve. Also, the
product of equation (8) would have been anticipated to be
insoluble, but no precipitate appeared at any stage during
the titration. Equation (9) would have been expected to give
the largest initial increase in response that was observed

experimentally, but (9) would not have "explained" the plateau. Several other equations could have been written to represent interactions between ammonia and the ions of CdI_2 solutions, and perhaps the plateau was the result of a more subtle reaction that occurred between partially solvated cadmium (II) or iodocadmium (II) ions. This question has been discussed further in the next chapter.

Preliminary studies in liquid ammonia consisted of determining the instrument response caused by the addition of water and methanol to liquid ammonia. It was believed that some species might be added to the liquid ammonia as water or methanol solutions, and hence it was considered desirable to be able to estimate the effect caused by these solvents alone. The response curves have been given in Figure 19.

A cursory investigation of the effect of temperature on the response of the Chemical Oscillometer indicated that corrections due to the small, normal, temperature variations from the boiling point of the liquid ammonia were less than the reproducibility of the instrument scale itself. Thus, no calibration curve relating temperature to instrument scale was prepared.

Response Patterns in Liquid Ammonia. The largest group of compounds for which response curves were obtained was the alkali metal halides. It was hoped that variations
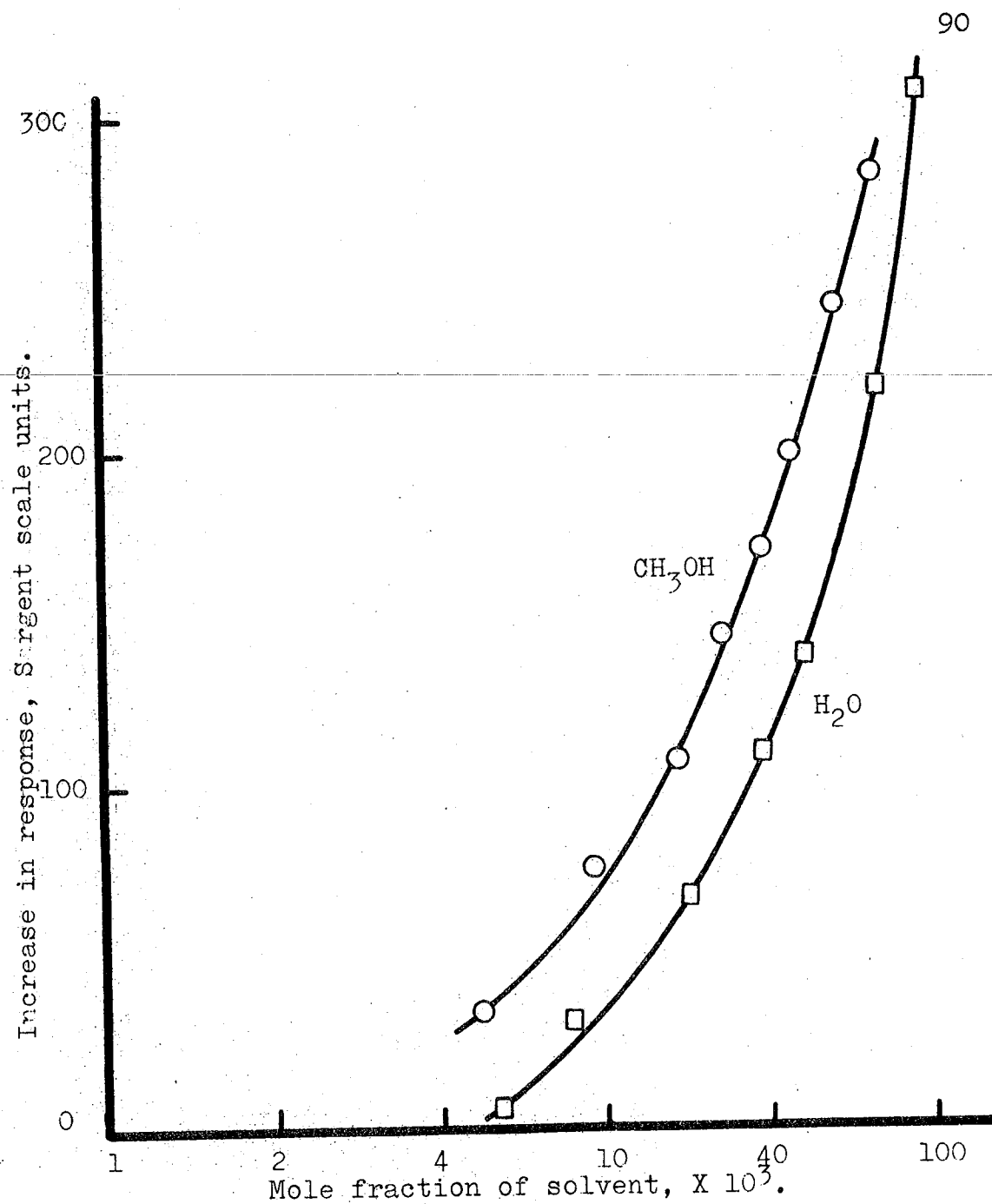
Figure 19. Titration of liquid ammonia with water and methanol at -33 °C., using the Sargent Model V Chemical Oscillometer and the hf-cell.

in the instrument response curves would have significance
for determining molar conductivities and ion mobilities in
liquid ammonia. The response curves for the chlorides have
been presented in Figure 20, and those for the potassium
halides in Figure 21. The response curves for additional,
miscellaneous alkali metal halides have been grouped together
in Figure 22, and the data for assorted ammonium salts,
silver iodide, cupric bromide, and sodium and potassium
metals were plotted in Figure 23.

The outstanding feature of the response curves was the
remarkable similarity of all the salts. In each case, the
maximum response of the Chemical Oscillometer occurred at
approximately 1×10^{-5} mole fraction, equivalent to .006
molal or .009 molar solution. Neither the extreme differ-
ences in formula weight nor the effect of multivalent ions
seemed to make a difference. Only in the case of the soluble
alkali metals was the sensitivity significantly different,
being of the order of $.5 \times 10^{-5}$ mole fraction; and the
mobility expected of the ammoniated electrons present in such
solutions would have led one to predict such an increased
instrument response.

The failure of the response curves to demonstrate
systematic variations in proportion to the molecular weights
of the alkali metal salts was disappointing. At first
glance, Figure 21 seemed to suggest that the size of the
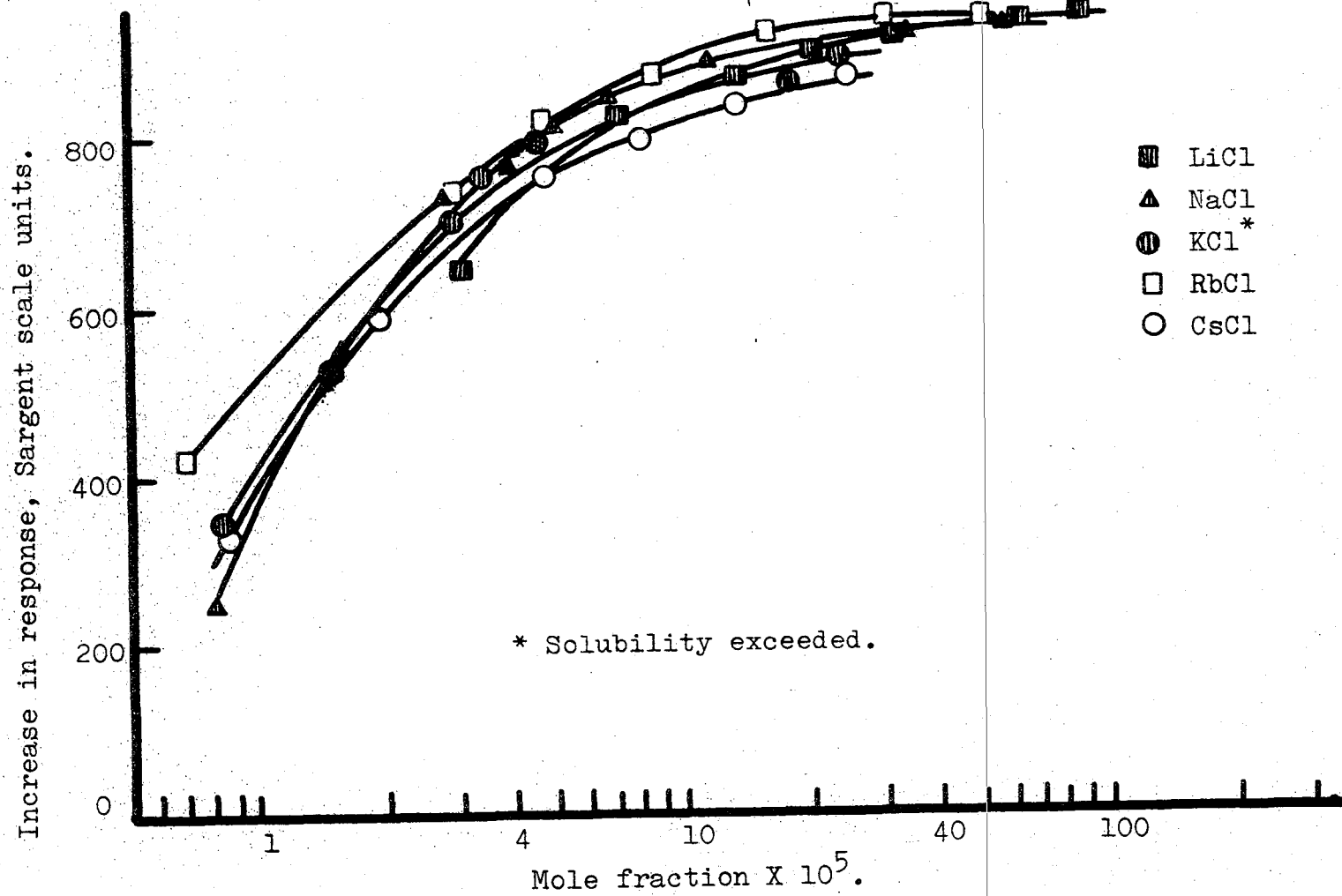
Figure 20. The response curves of alkali metal chlorides in liquid ammonia at
-33° C., using the Sargent Model V Chemical Oscillometer and hf-cell.

Note: The solubility of KCl was exceeded, and KF was so insoluble that no response increase was observed.
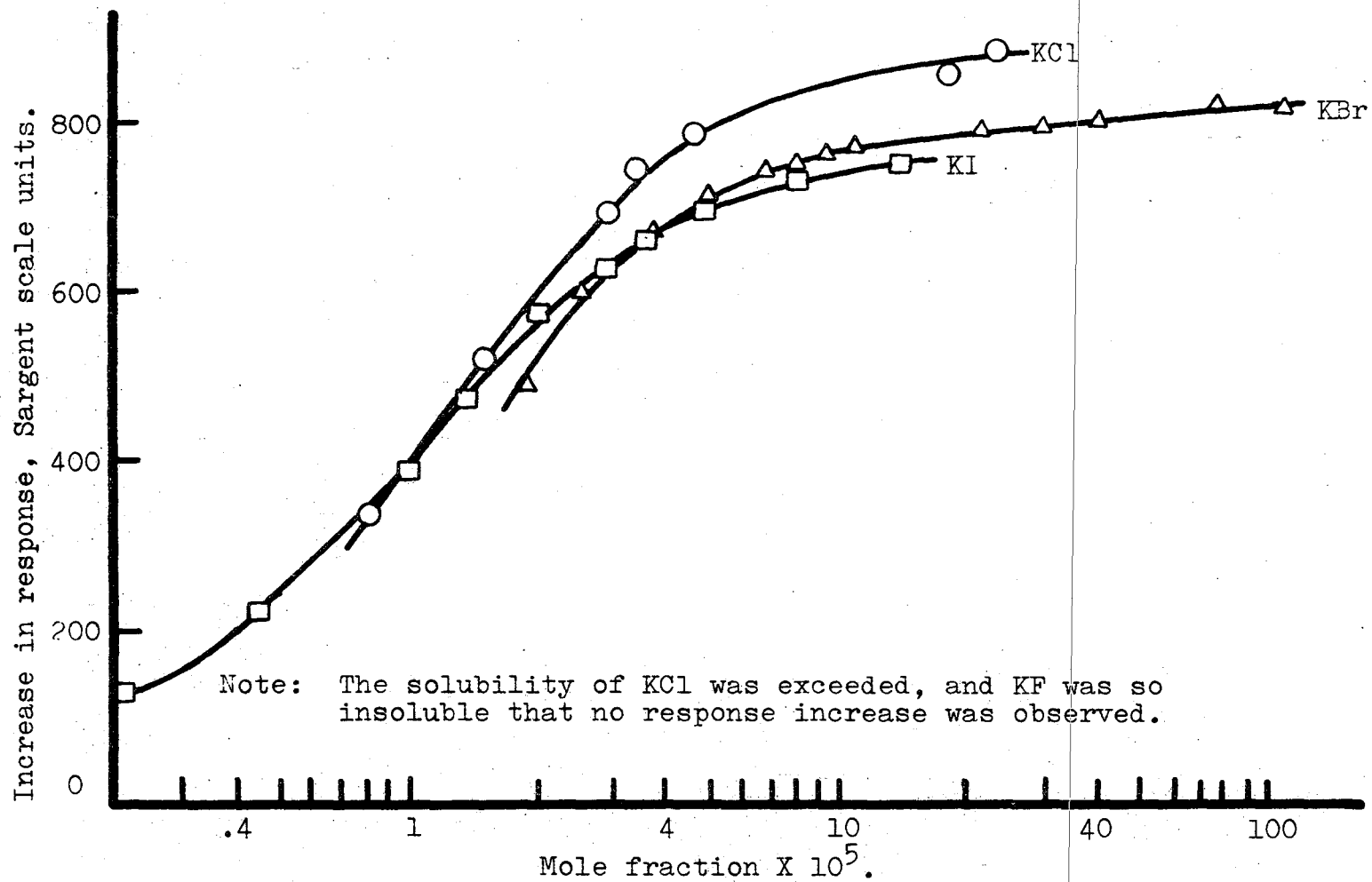
Figure 21. Response curves of the potassium halides in liquid ammonia at $-33°C$., using the Sargent Model V Chemical Oscillometer and hf-cell.
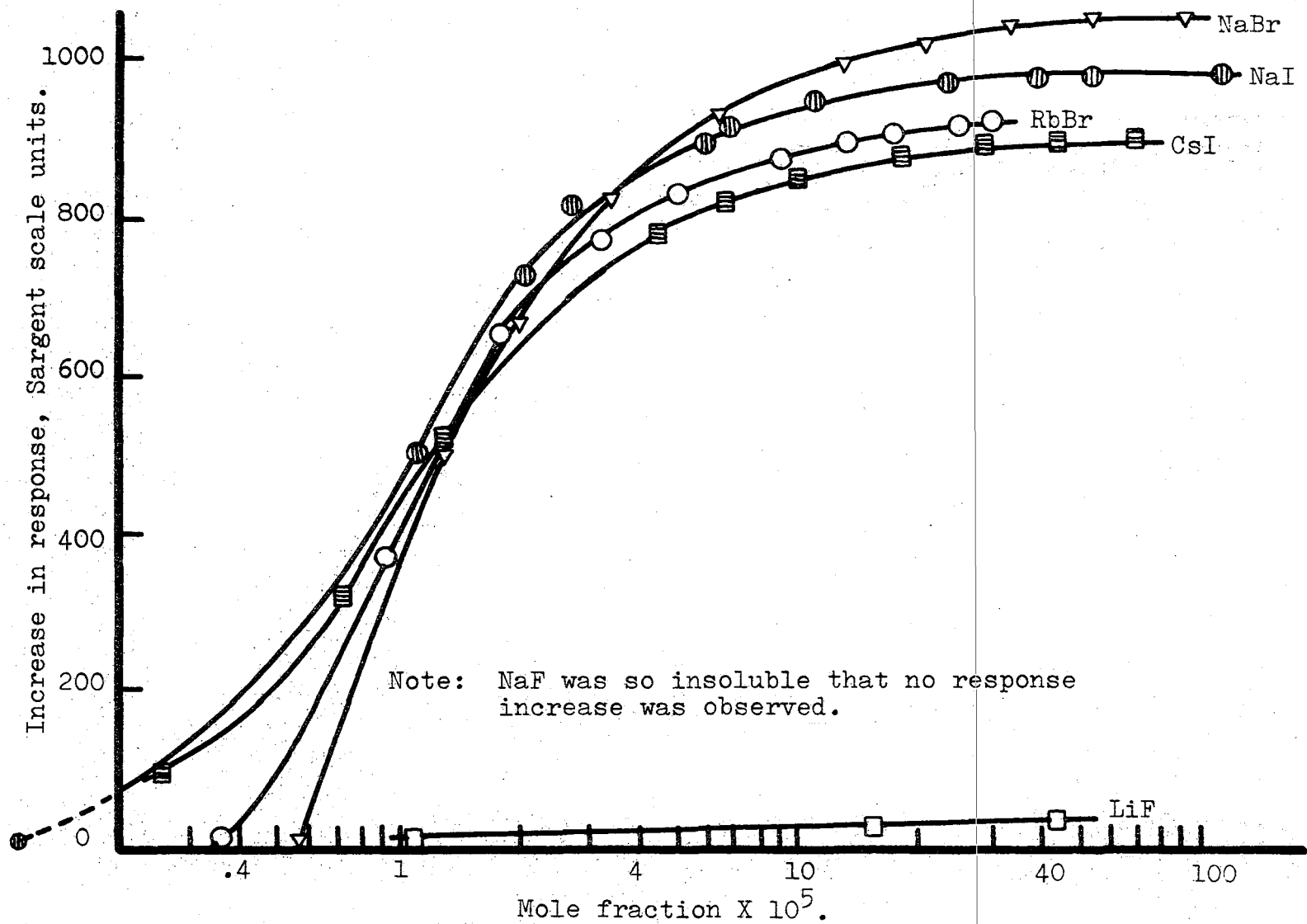
Figure 22. Response curves, $M^I X$, in NH_3 at $-33°C$., Chemical Oscillometer, hf-cell.

Note: NaF was so insoluble that no response increase was observed.

Note: CuF_2 and $(NH_4)_2SO_4$ were so insoluble that no increased responses were observed.
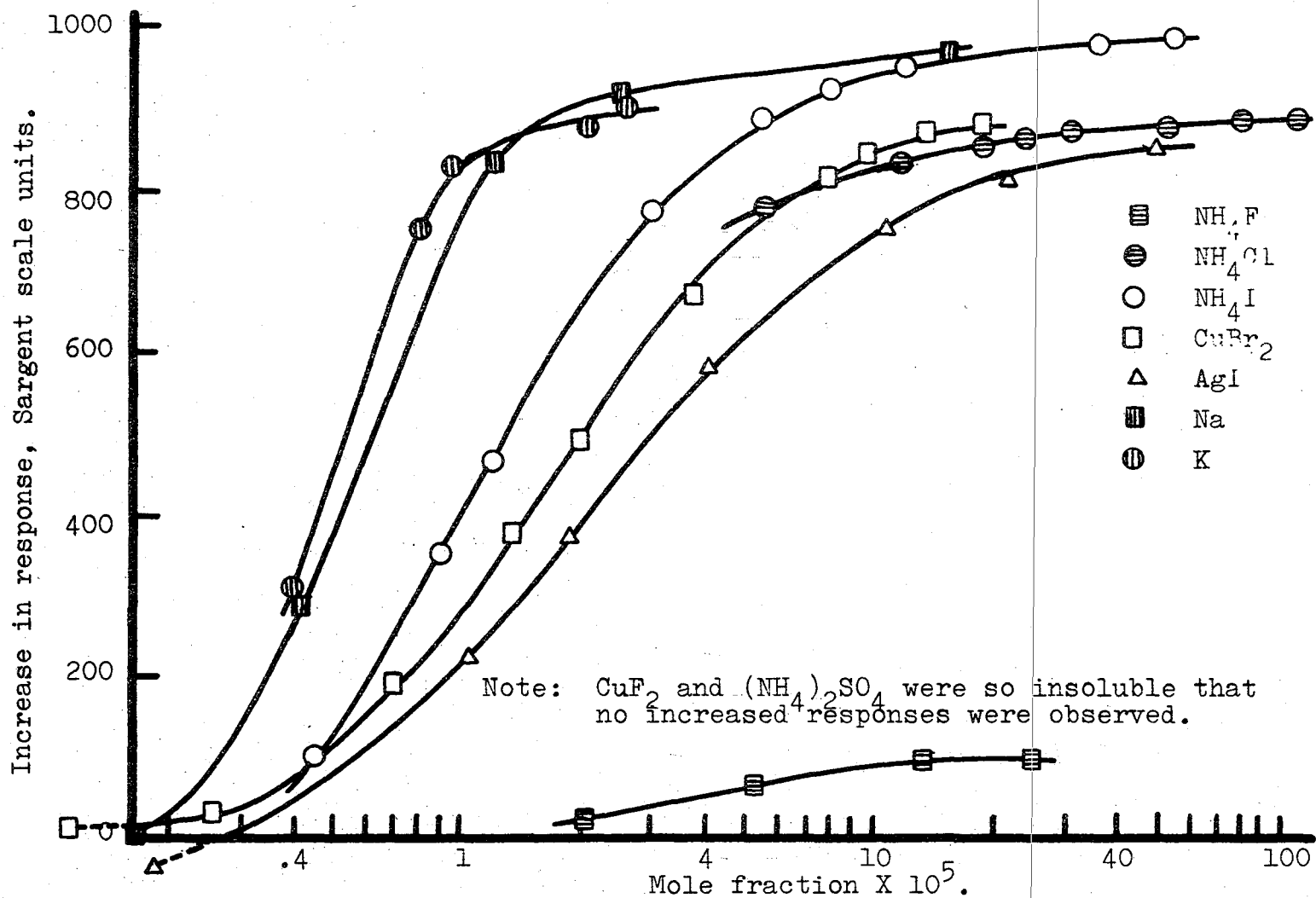
Figure 23. Response curves for selected ammonium salts, copper(II) salts, silver(I) iodide, and sodium and potassium metals in liquid ammonia at $-33°C.$, using the Sargent Chemical Oscillometer and hf-cell.

negative ion in such salts played a role in the high frequency response caused by the salts, but closer scrutiny of the data in other Figures, suggested that the results shown in Figure 21 were fortuitous rather than consistent.

The low "apparent" response of lithium fluoride (Figure 22) and ammonium fluoride (Figure 23) was not a valid indication of low instrument response to solutions of the salts. Rather, the low response resulted from the failure of the salts to dissolve very much, and the increase in the response with concentration probably reflected a slow rate of solution for the solids added to the liquid ammonia.

The response curves of the alkali metals were drawn from data which is subject to qualification. As pellets of metal were added to the liquid ammonia, a large instrument response was obtained. However, the pellets immediately began to react with the liquid ammonia; and before successive pellets could be added to get an accumulative response, the response due to the first pellets had partially faded. The method finally used to get the response curves for sodium and potassium involved adding pellets of different size, reading the response, and letting the response drop back to zero before the next pellet was added. Thus, each point on the response curve for sodium and potassium represented the response to a single addition rather than to an accumulation of dissolved substance.

Even so, some error (neglected when plotting the Figure) was present due to the reaction of part of the pellet during the time the remainder of the pellet dissolved. Fortunately, the amides formed by the reactions of the metals with the ammonia were insoluble and caused no residual response. The reaction of alkali metals with the solvent has been discussed further in a later section of this chapter.

Experimental Results of Chemical Reactions in Liquid Ammonia. The reaction of 1-iodopropane with liquid ammonia was investigated to see if products of the reaction would invoke sufficient instrument response to permit rate studies. The primary reaction to be expected was:

$$n\text{-}C_3H_7I + 2 NH_3 \longrightarrow n\text{-}C_3H_7NH_2 + NH_4^+ + I^-$$

although little instrumental response was anticipated from the formation of an amine, the generation of the salt was expected to result in sufficient response to permit the reaction to be followed.

Experimentally, ten microliters (.102 mmole) of 1-iodopropane was injected into 100 ml. of liquid ammonia at its boiling point. The final mole fraction of ammonium iodide was 2.6×10^{-5} and, based on the response curve for ammonium iodide, the increase in instrument response should

have approximated 740 Sargent Model V Chemical Oscillometer scale units.

The rate of reaction was so slow that it was not practical to supervise it throughout the entire process. At the suggestion of Dr. W.H. Wadman (1962), the increase in instrumental readings were plotted against the reciprocal of the time of reaction so that an extrapolation to zero would represent the response increase at infinite time. These data were used to prepare Figure 24, and the response increase of 705 scale units obtained when the reciprocal of time was extrapolated to zero seemed reasonably close to the anticipated value of 740. The half-life of the reaction was calculated to be 380 minutes on the basis of the 740 value for a maximum increase in response at the "completion" of the reaction.

The rate of reaction of an alkali metal with the solvent to form amides was investigated with sodium and potassium. Earlier in this chapter, mention was made of the difficulties involved in obtaining a response curve for sodium. According to Jolly (1960), a solution of sodium in liquid ammonia should have been stable unless a catalyst (iron (III) nitrate) was added. This was substantiated by the fact that sodium-ammonia solutions remained stable for many hours in the "scrubber" section of the apparatus used in the present investigation. However, when small pieces of sodium were added to ammonia in the hf-cell, the intense, dark blue
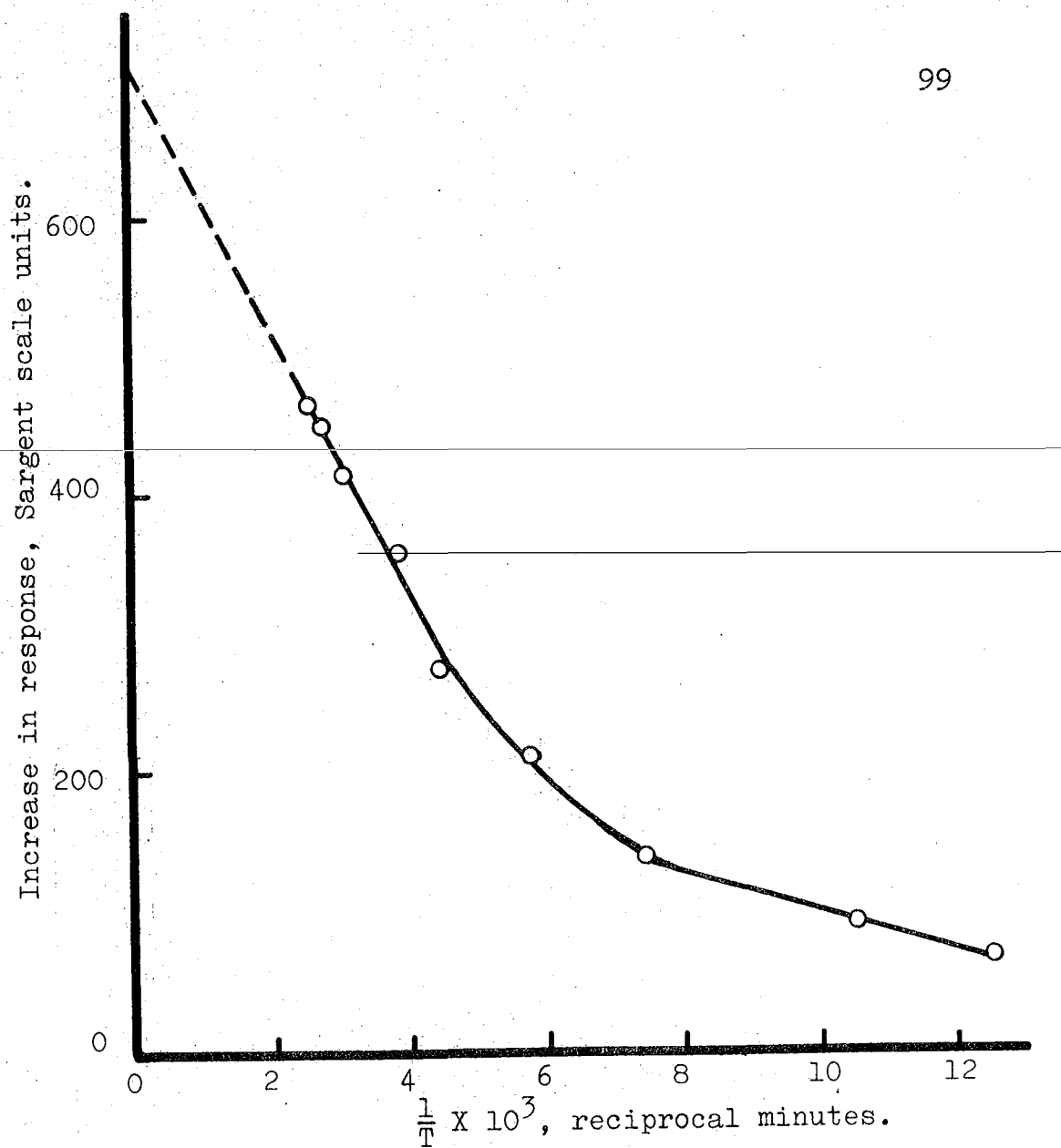
Figure 24. The ammonolysis with time of 1-iodopropane in liquid ammonia at -33 °C., using the Sargent Model V Chemical Oscillometer and hf-cell.

color, initially present, faded away in a matter of minutes. When the dark blue solution was aspirated out of the hf-cell, the color remained for several hours at 78°C., the temperature of the dry-ice-slurry.

An initial assumption, that the high frequency energy of the Chemical Oscillometer was causing the reaction, was disproved by the fact that the blue color faded just about as fast with the instrument turned off as when it was turned on. The phenomena were further investigated by adding Dow Corning Stopcock Grease to the flask into which the blue solution was aspirated. Even at -78°C., the blue color was discharged over night. Thus, it seemed likely that the silicon grease used to lubricate the stirrer was catalyzing the reaction between sodium metal and liquid ammonia.

Rate studies of amide formation in potassium-in-ammonia solutions were aided by the use of the Sargent Recorder. As different sized pieces of metal were added to boiling liquid ammonia in the hf-cell, the course of the reaction was followed by means of the recorded change in instrument response as a function of time.

The decay curves resulting from several additions of metal have been superimposed in Figure 25. The immediate "loss" of the first few potassium pellets was attributed to reactions of the alkali metal with traces of water absorbed on the walls of the hf-cell and on its accessory equipment.
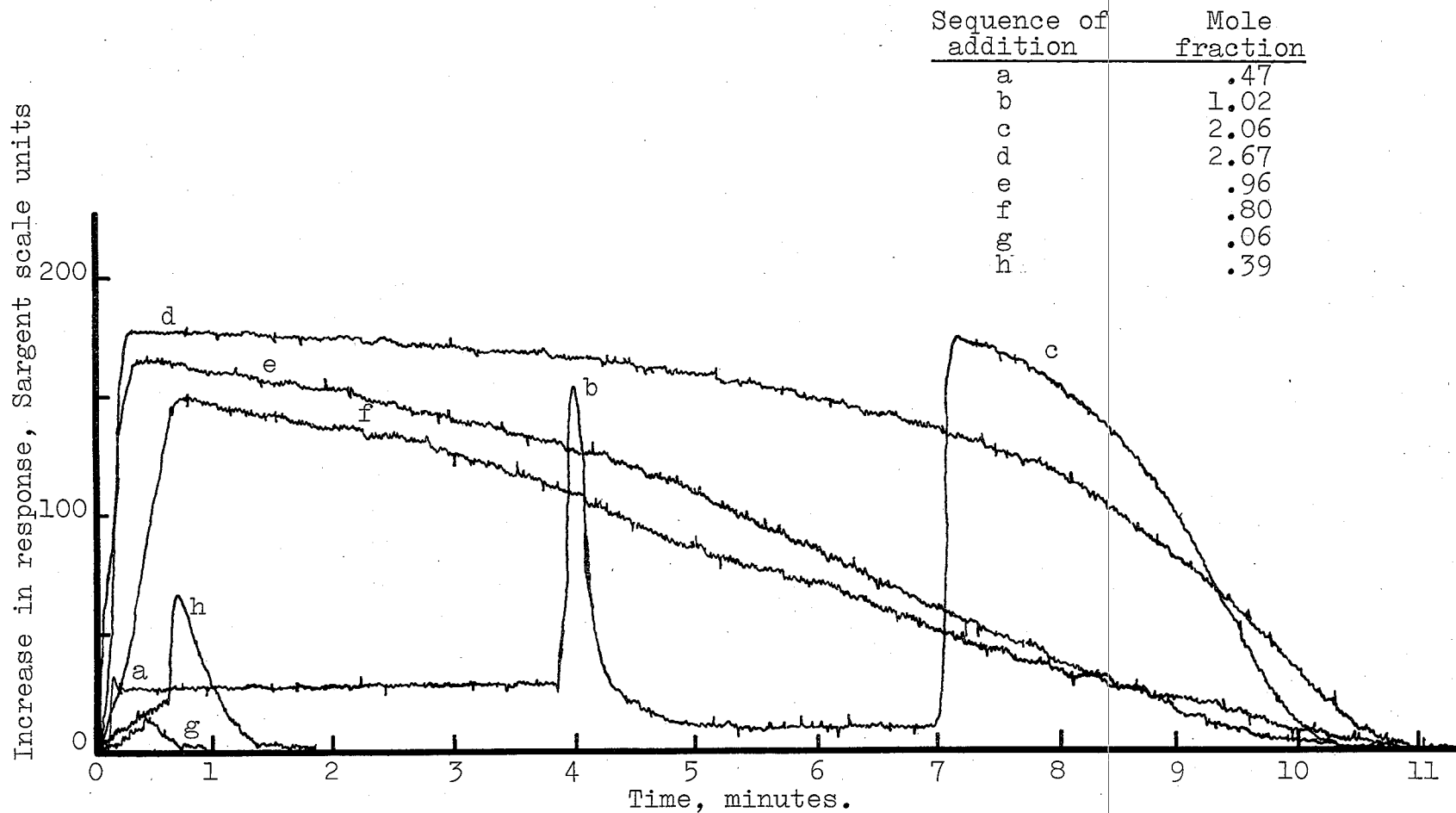
Figure 25. The effect of time on the reaction of potassium with liquid ammonia
at -33°C. as shown by the change in response of the Sargent Model V
Chemical Oscillometer with the hf-cell.

This was somewhat surprising because the entire system was pumped out for several hours with the Welch Duo-Seal Vacuum Pump (less than .1 mm. of Hg with a CO_2-acetone slurry trap), but no other explanation of the rapid removal of the potassium has been forthcoming.

In Figure 25, the time required for the response to decrease to its initial value was a function of the size of the potassium pellet. No catalyst was added, but it was assumed that silicon grease was causing the same effect on the potassium-ammonia reaction that it displayed in the sodium-ammonia reaction. It was interesting to note that the use of potassium metal for this study would not have been predicted from a study of the literature which stated that potassium amide was soluble in liquid ammonia (whereas sodium and lithium amides were "insoluble"). As a point of fact, however, KNH_2 was so insoluble that it generated no instrument response, whatsoever, in the Chemical Oscillometer with the hf-cell. Rate constants for the potassium-ammonia reaction were not calculated because of uncertainty about the degree of catalytic effect exerted by the silicon grease and about the exact size of the potassium pellets (to be discussed further in a later paragraph).

Preparatory to the reduction of metallic cations with sodium and potassium, some qualitative solubility studies were performed. It was considered desirable to have a

soluble metallic fluoride so that the products of the reduction reaction, the reduced metal and the alkali metal fluoride salt, would be insoluble and thus cause a decrease in instrument response during the reaction. However, the fluorides of copper(II), antimony(III), chromium(III), and cobalt(II) were insoluble in boiling liquid ammonia. The SbF_3 seemed to react, as evidenced by its color change from yellow to white, but the white product was insoluble.

Copper(II) fluoride was also insoluble in water, but it did dissolve in concentrated aqueous ammonia. Hence, two milliliters of water was added to the hf-cell containing a suspension of 361 mg. of copper(II) fluoride in 100 ml. of liquid ammonia at its boiling point. The increase in the response of the Chemical Oscillometer was no more than would have been expected from the addition of the water to pure ammonia and there was no change in color suggesting that the water had caused the copper salt to go into solution. Therefore, attempts to get a metallic fluoride into solution with liquid ammonia were abandoned.

A liquid ammonia solution of copper(II) bromide was treated with an excess of sodium metal at -33°C. The concentrations were well above those that could be followed by the Chemical Oscillometer, but it was hoped that a qualitative indication of the reduction of copper(II) cation to the metal would suggest further work at suitable concentrations.

A black precipitate formed, from which the ammonia was removed. The black residue partially dissolved in water to give a blue solution characteristic of the tetramminecopper-(II) ion. All of the water-insoluble, black residue dissolved in sulfuric acid except for a tiny portion which dissolved in nitric acid. Apparently the exceedingly small amount of copper metal formed by the reducing action of the sodium was sufficient to catalyze the reaction between the remaining sodium and the ammonia to give sodium amide which, in turn, precipitated most of the copper(II) ion as cupric amide. No further attention was given these reactions of copper compounds.

In Chapter 3, it was noted that the iodide ion promoted smooth reduction of metallic cations by alkali metal-liquid ammonia solutions. Therefore, an attempt was made to reduce silver iodide with potassium metal. A preliminary trial at relatively high concentration of silver iodide (1.9 mmole of AgI in 100 ml. liquid NH_3, treated with .055 mmole of K) resulted in a black precipitate which did not dissolve in sulfuric acid, but did dissolve in nitric acid. The unreduced, yellow silver iodide was admixed with the black silver metal after the liquid ammonia was evaporated from the system.

In an effort to use the Chemical Oscillometer and hf-cell to follow the silver iodide-potassium metal reaction, the procedure was repeated using 43.7 mg. of AgI (.018 mmole)

and "titrating" it with small pellets of potassium metal. Figure 26 summarizes the results. The Chemical Oscillometer response increased 340 scale units when the silver iodide was added to 90 ml. of liquid ammonia. Such an increase reflects the fact that the silver iodide concentration in ammonia was in the region of maximum response-sensitivity, as indicated by the response curve presented earlier. The decrease in response caused by the first few potassium pellets was not fully understood because the loss of silver iodide should have been counterbalanced by the gain in potassium iodide.

$$Ag(NH_3)_2^+ + I^- + K \longrightarrow K^+ + I^- + \underline{Ag} + 2\ NH_3$$
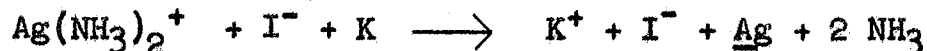
An explanation of the failure of the excess amounts of potassium, added at the end of the experiment, to cause an increased instrument response (in excess of that caused by the silver iodide alone) was aided by the observation that the blue color of the metal-ammonia solution was never present. Apparently the silver metal catalyzed the amide forming reaction of ammonia with the excess potassium to the extent that there never was developed a significant concentration of metallic potassium in ammonia. It was observed that the black, flocculent silver metal made it difficult to ascertain the presence of the blue metal-ammonia in the reaction
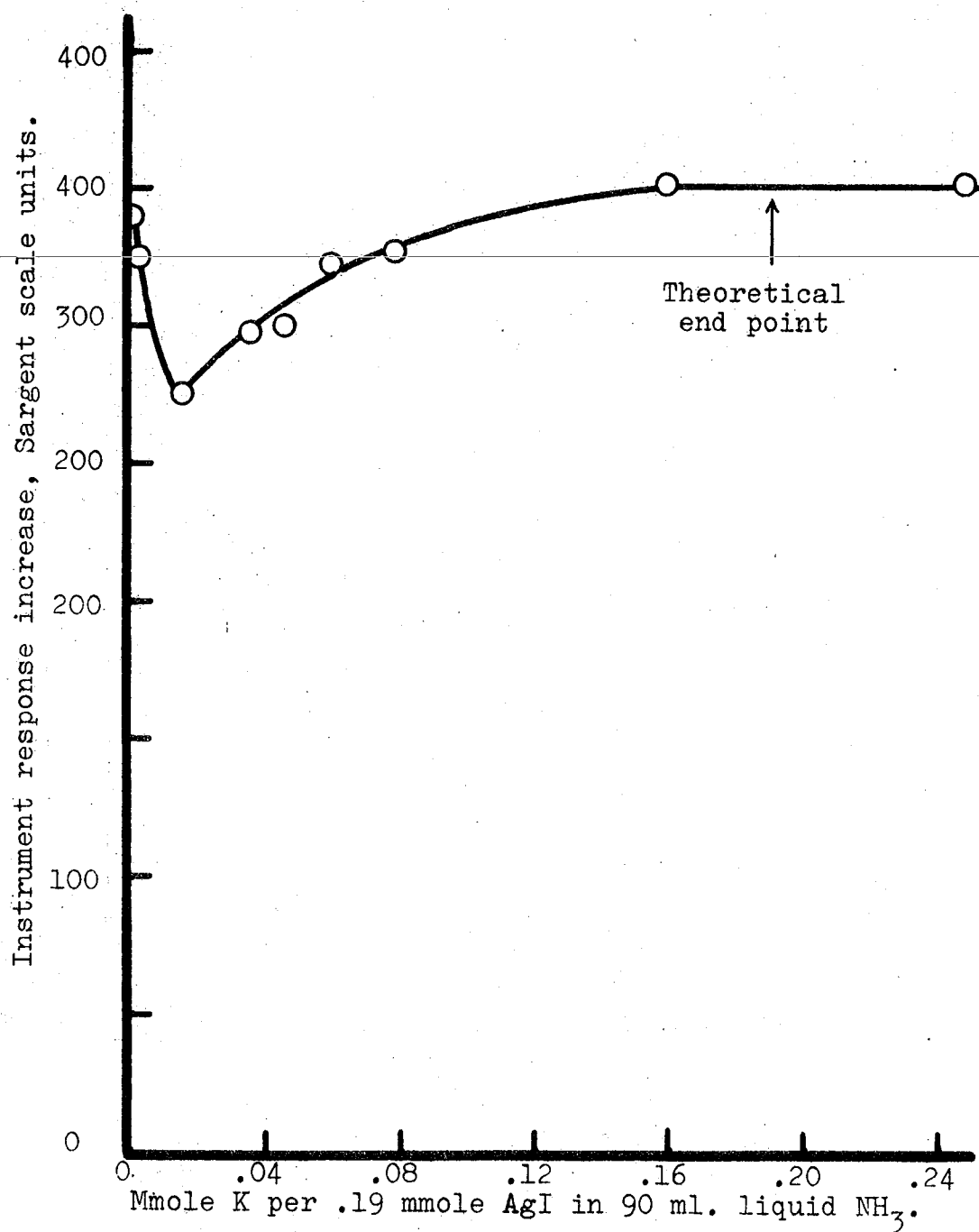
Figure 26. The reduction of silver(I) iodide by potassium
    in liquid ammonia at $-33°C.$, using the Sargent Model V
    Chemical Oscillometer and the hf-cell.

mixture. Only by turning off the stirrer, so that the silver metal could settle away from the top portion of the mixture, was it possible to observe the absence of the blue color.

The final reaction studied in this investigation involved the addition of a strong acid, ammonium iodide, to a suspension of an insoluble base, potassium amide. The results have been plotted in Figure 27. The potassium amide suspension (.45 mmoles in 90 ml. liquid NH_3) resulted from the experiment performed with potassium in liquid ammonia (Figure 24). Weighed pellets of ammonium iodide were added until the instrument response ceased to increase. The resulting curve was, in essence, the response curve for potassium iodide up to the theoretical end point, followed by the response curve for ammonium iodide.

An unfortunate choice of titration indicator and technique resulted in the difficulty alluded to earlier with regard to the determination of the size of the pellets of sodium and potassium metals. As each pellet was added to the hf-cell, one of identical size (as judged by eye) was placed in a small flask and saved for titration with .0100 M hydrochloric acid, using phenolphthalein as the indicator. Thus the results were erroneous to the extent that the metals absorbed carbon dioxide from the air during the time between the addition of the pellet to the flask and the titration. Under ordinary laboratory conditions, the error introduced
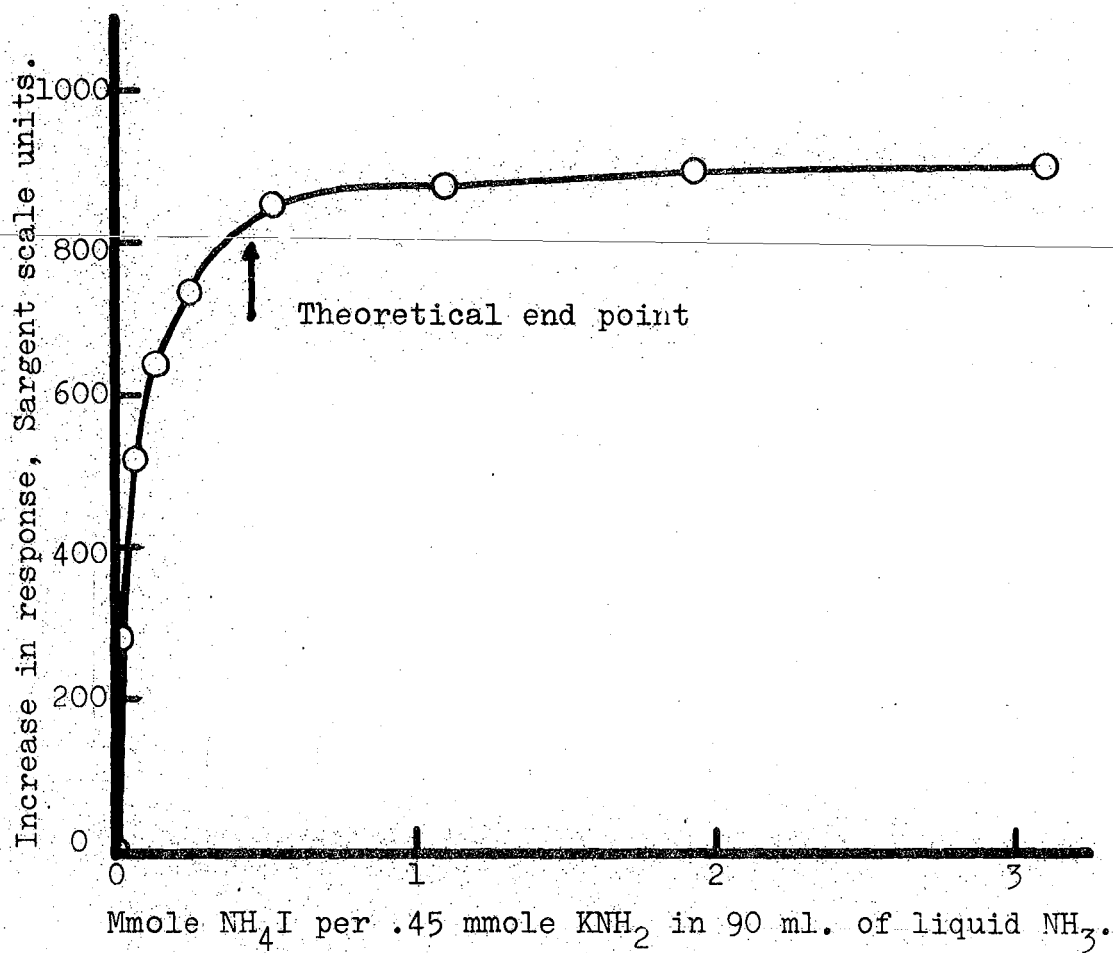
Figure 27. The titration of potassium amide with ammonium iodide in liquid ammonia at -33 °C., using the Sargent Model V Chemical Oscillometer and hf-cell.

by carbon dioxide contamination might have been ignored as
small compared with the error introduced by the visual
selection of "identical" pellets (an error estimated to be
less than 10 per cent); but in the laboratory used for the
present investigation, the use of carbon dioxide-acetone
slurry in the cold-finger was undoubtedly responsible for a
much higher than ordinary carbon dioxide concentration. A
better experimental approach would have been to add the
pellet of alkali metal to an excess volume of acid, and then
to back-titrate the excess amount of acid. The unreliability
with regard to the size of the alkali metal pellet in no way
invalidated conclusions regarding the usability of high
frequency titrimetry to the study of the reactions of such
metals in liquid ammonia. The important consideration was
whether or not sufficent response would occur to justify
further study, not the precise end point of the reaction.

CHAPTER VIII

SUMMARY AND SUGGESTIONS FOR FUTURE STUDY

Summary. Chemical reactions in liquid ammonia at -33.4°C. have been investigated successfully by means of high frequency titrimetry. The Sargent Model V Chemical Oscillometer was used in conjunction with a specially designed titrimeter cell, containing electrodes built inside of an evacuated Dewar-type jacket. Details of the design and construction of the special cell, called the hf-cell, were presented.

As an indication of response sensitivity, the response curves of a group of fourteen alkali metal halides were determined, and the salt concentration at which maximum sensitivity occurred was about 1×10^{-5} mole fraction for each salt, equivalent to a molality of .006 or a molarity of .009. Additional response curves were obtained for sodium and potassium metal, copper(II) bromide, silver(I) iodide, ammonium fluoride and ammonium iodide. All of the response curves demonstrated maximum response sensitivity essentially like that of the alkali metal salts except in the case of sodium and potassium metals which exhibited a maximum response sensitivity at about $.5 \times 10^{-5}$ mole fraction. Response curves were obtained also for the addition of water

and of methanol to liquid ammonia.

The uncatalyzed rate of ammonolysis of an alkyl halide, 1-iodopropane, was investigated and the reaction was found to have a half-life of approximately 380 minutes and to result in a predictable response change in the titrimeter.

Attempts to study the reduction of copper(II) bromide with sodium metal resulted in the precipitation of copper(II) amide, but the reduction of silver(I) iodide was achieved with potassium metal. With the proper choice of silver(I) iodide concentration, the reaction caused response changes in the high frequency titrimeter.

The rates of reaction of sodium and potassium metals with the liquid ammonia solvent were investigated, aided by the use of the Sargent Recorder in the case of potassium. The time required for potassium to react with the ammonia was a function of the initial concentration of the metal. There was evidence that the reaction of sodium (and, presumably, potassium) with ammonia was catalyzed by silicon grease.

The acid-base titration of insoluble potassium amide with ammonium iodide was performed to demonstrate that the response changes of the titrimeter could be used to follow the neutralization reaction, even though no inflection in the titration curve was obtained at the end point.

The suitability of the hf-cell for use with the CF-120 High Frequency Titrimeter, designed and built at the

University of the Pacific, was briefly investigated by studying the response curves of water, methanol, aqueous potassium chloride, and an acetone solution of cadmium iodide when acetone was used as the solvent. The CF-120 Titrimeter was incapable of generating a beat-frequency signal when highly ionized solutions were placed in the hf-cell, apparently because the hf-cell had too large a capacitance.

A titration of an acetone solution of cadmium iodide with an acetone solution of ammonia in the Sargent Model V Chemical Oscillometer and hf-cell suggested that there may be interesting areas of study in nonaqueous chemical reactions other than those of liquid ammonia.

Suggestions for Future Study. An important area of investigation remains that of cell design. It would be desirable to have a cell in which electrodes were interchangeable so that the capacitance of the system could be easily changed to accomodate titrimeters which have different frequencies of operation.

Rates of studies of ammonolysis reactions, comparable to that of 1-iodopropane, appear to have considerable interest. The effects of changes in alkyl configuration, halide, and catalysts would seem susceptible to intensive investigation, in situ. A type of ammonolysis not studied in this investigation, but closely akin to the 1-iodopropane

reaction, would involve esters. For example, I.W. Davies (1962) suggested that the ammonolysis of diethyl phthalate would have the interesting possibility of forming either the di-acid amide derivative or the imide (or both?).

The titration of strong acids with strong bases does not appear to have much interest. However, the development of cells with greater sensitivity and of titrimeters operating at higher frequencies might permit the step-wise titration of successively weaker acids in polybasic species such as sulfamide.

The reactions of metal-in-ammonia solutions appear to have great interest, in spite of the extensive work that has already been reported on such systems. More exacting experimental conditions may be required in such studies and a dry-box, an all-glass vacuum line and hf-cell, and a liquid-nitrogen trapped vacuum-pump would seem indicated. Dr. G. Julian (1962) suggested the use of commercially available alkali metal-mineral oil emulsions, diluted with additional mineral oil, as an improved method of adding small quantities of such metals to the liquid ammonia in the hf-cell.

A small, but important, area of research would involve the determination of solubilities of ionic species in liquid ammonia. Surprisingly often; the present literature is wrong or misleading. The high frequency titrimeter is extremely sensitive to the presence of dissolved ions, and

remarkably insensitive to the presence of dispersed, but undissolved, ionic substances.

The plateau observed in the cadmium iodide-ammonia titration in acetone would seem deserving of additional investigation. The use of a recording infrared spectrophotometer to determine the changes in the concentration of un-complexed ammonia might give a clue to the nature of the species responsible for the plateau.

BIBLIOGRAPHY

BIBLIOGRAPHY

Abraham, C.J., "A Kinetic Study of the Base Catalyzed Ester-
    ification of Propionic Anhydride with Isopropyl and
    n-propyl Alcohols using a High Frequency Oscillometer."
    Unpublished Master's thesis, University of the Pacific,
    Stockton, California, 1961.

Anikin, A.G., Kirpichev, E.P., and Gordeev, I.V., "Adsorption
    of the Energy of a High Frequency Electric Field by Aque-
    ous and Alcoholic Solutions of Alkaline Earth Chlorides."
    Vestnik Moskov. Univ., Ser. II, Khim., 16, 23(1961).

Astafev, I.V., Rabinovich, E.A., and Schatenshtein, A.I.,
    "Mechanism of Potassium Amide Initiation of Styrene Poly-
    merization in Liquid Ammonia." Uysokmolekulyarne
    Soedineniya, 3, 555(1961).

Audrieth, L.F. and Kleinberg, J., "Non-Aqueous Solvents."
    John Wiley and Sons, Inc., New York, 1953.

Balazs, L. and Pungor, E., "Use of Methyl Glucamine (1-deoxy-
    1-methylaminosorbitol) Standard Solution in the Case of
    Acid Titrations with a High Frequency End-Point Indicator."
    Microchim. Acta, 2, 309(1962).

Barbi, G., "New Device for Radio-Frequency Conductometric
    Measurements Using Nonimmersed Electrodes." Ricera Sci.,
    27, 1438(1957).

Beckman, T.A. and Pitzer, K.S., "Infrared Spectra of Margina-
    lly Metallic Systems, Sodium-Ammonia Solutions." J. Phys.
    Chem., 65, 1527(1961).

Behrens, H. and Lohoefer, F., "Chemistry of Metal Carbonyls
    in Liquid NH_3. Dihydrogenhexacarbonyldinickelate (-1)."
    Chem. Ber., 94, 1391(1961).

_____, and Hagg, W., "Chemistry of Metal Carbonyls in
    Liquid Ammonia. Binuclear Metal Compounds of Chromium
    and Molybdenum." Chem. Ber., 94, 312(1961).

_____, Zizlsperger, H., and Rauch, R., "Chemistry of Metal
    Carbonyls in Liquid NH_3. Dihydrogenhexacarbonyldinickel-
    ate(-1)." Chem. Ber., 94, 1497(1961).

Behrens, H. and Zizlsperger, H., "Metal Carbonyls in Liquid Ammonia. Reactions of Nickel Carbonyl with Liquid Ammonia and with Sodium Borohydride in Liquid Ammonia." J. Prakt. Chem., 14, 249(1961).

_____, and Ostermeier, J., "Behavior of Nonmetal Chalcogenides in Liquid Ammonia. Reactions of Silicon, Germanium, and Tin Sulfides in the Ammono System." Chem. Ber., 95, 487(1962).

Berns, D.S., LePoutre, G., Bockelman, E.A., and Patterson, A., "Salt Effect in Metal-Ammonia Solutions. Sodium Chloride in Sodium-Ammonia Solution at -33°C." J. Chem. Phys., 35, 1820(1961).

Blaedel, W.J. and Malmstadt, H.V., "High-Frequency Titrations. A study of Instruments." Anal. Chem., 22, 734(1950).

Blake, G.G., "Radiometric Condensers and Inductances." J. Roy. Soc. Arts (London), 82, 154(1933).

_____, "A Radiometric Condenser. Control of Oscillating Circuits by Radiant Heat." Electrical Review, 112, 434(1933).

_____, "Conductometric Analysis at Radio Frequencies." Chapman and Hall, Ltd., London, 1950.

Caley, E.R. and Habboush, A., "Determination of Composition of Solutions of Organic Liquids by Titration with Water. Application to Systems Composed of Aromatic Hydrocarbons and Lower Alcohols." Anal. Chem., 33, 1613(1961).

Calkins, R.C., "Determination of Macro Amounts of Fluoride by Steam Distillation and High Frequency Titration." Anal. Chem., 34, 837(1962).

Clinkscales, J.K., "A 120 Megacycle Self-Contained High-Frequency Titrimeter." Unpublished Master's thesis, College of the Pacific, Stockton, California, 1957.

_____, and Frye, H., "Building a High-Frequency Titrator for Instructional Use." J. Chem. Educ., 37, 304(1960).

Conseiller, Y. and Courteix, J., "High-Frequency Titrimetry. Use for Titrations in Anhydrous Media." Anal. Chem. Acta, 8, 166(1958).

Cruse, K., "Analysis of Organic Compounds by High Frequency Titration Methods." Z. Anal. Chem., 181, 180(1961).

———, and Huber, R., "High-Frequency-Titration." Verlag Chemie, GMBH., Weinheim/Bergstrasse, 1957.

Davies, I.W., Personal Communication, University of the Pacific, Stockton, California, 1961.

Egan, B.Z. and Shore, S.G., "Cryosopic Study of the Diammoniate of Diborane in Liquid Ammonia." J. Am. Chem. Soc., 83, 4717(1961).

Emeleus, H.J. and Kettle, S.F.A, "Sodium Derivatives of Stannane." J. Chem. Soc. (London), 2444(1958).

———, and MacKay, K.M., "Conductometric Titration of Sodium in Liquid Ammonia with Phosphine, Arsine, Stibine, and Germanes." J. Chem. Soc. (London), 2675(1961).

Ermakov, V.I., "Universal Apparatus for High Frequency Physico-Chemical Analysis and Titration of Solutions." Zhur. Fiz. Khim., 34, 2838(1960).

Ershov, B.P. and Borisov, I.G., "High-Frequency Titration. Determination of alpha-polyoxymethylene." Plasticheskie Massy, 11, 46(1961).

———, and Podrovskaya, V.L., "High Frequency Titration. Determination of the Cresol Isomers." Plasticheskie Massy, 7, 65(1961).

———, Pokrovskaya, V.L., and Druglow, S.P., "High-Frequency Titration. Determination of 1,2,4-and 1,2,5-Isomers of Xylenol." Plasticheskie Massy., 10, 58(1961).

Evers, E.C., "The Nature of Metal-in-Amine Solutions." J. Chem. Educ., 38, 590(1961).

———, and Filbert, A.M., "Volume Expansion of Sodium-in-Ammonia Solutions." J. Am. Chem. Soc., 83, 3337(1961).

Fischer, R.B. and Fisher, D.J., "Oscillographic Method for the Study of Solution Behavior at Radio Frequencies." Proc. Indiana Acad. Sci., 62, 160(1952).

Foster, R. and Mackie, R.K., "Interaction of Electron
    Accepters with Base Absorption Spectra of Substituted
    Polynitrobenzenes in Liquid-Ammonia." Tetrahedron, 18,
    161(1962).

Frye, H.G., Personal Communication, University of the Pacific,
    Stockton, California, 1961.

Fujishima, I. and Takeuchi, T., "Rapid Determination of Trace
    Carbon in Metals, by Using High-Frequency Condenser Elec-
    trode of Submerging Type." Bunseki Kagaku, 11, 420(1962).

Golub, A.M. and Goledets, G.I., "Iodide Complexes of Lead in
    Non-Aqueous Solvents." Ukrain. Khim. Zhur., 27, 141(1961).

Gorokhovskii, V.M., Samitov, U.U., and Tremasov, N.V.,
    "High Frequency Titration by the Method of Heterodyne
    Pulsations." Izvest. Vysshikh Ucheb. Zavedenii, Khem.
    I Khim. Teknol., 3, 805(1960).

Grossetti, E., "Rotational Mechanical Moments of Electrolyte
    Solutions in a Rotating High-Frequency Electric Field."
    Nuovo Cimento, 21, 395(1961).

Groubert, E. and Caillon, P., "Measurement of the Dielectric
    Properties of Substances at High Frequencies." J. Phys.
    Radium, 21 Suppl., 155A(1960).

Grove, E.L. and Jeffery, W.S., "A Study of Some Solvents as
    Media for the High Frequency Titration of Weak Acids."
    Talanta, 7, 56(1960).

Haul, R. and Blennemann, D., "Isotope Exchange Between Hydro-
    gen and Liquid Ammonia in the presence of Platinum
    Catalysts." Naturwissenschaften, 48, 644(1961).

_____, Ihle, H., and Schierholz, H., "Deuterium Exchange
    Between Hydrogen and Liquid Ammonia with Potassium Amide
    as a Catalyst." Chem. Ing. Tech., 33, 713(1961).

Hueckel, W. and Jennewein, C.M., "Reduction in Liquid Ammonia.
    Reduction and Methylation of 1-methyl-naphthalene in
    Liquid Ammonia." Chem. Ber., 95, 350(1962).

Ichniowski, T.C. and Clifford, A.F., "Polarographic Study of
    Chromium (III) in Ammonia Solvents (Divers/Liquids)."
    J. Inorg. Nuclear Chem., 22, 133(1961).

Jensen, F.W. and Parrack, A.L., "Use of High-Frequency Oscillators in Titrations and Analyses." Ind. Eng. Chem., Anal. Ed., 18, 595(1946).

Johnson, A.H. and Timnick, A., "Stable High Frequency Titration Apparatus in the 100-Mc. Frequency Range." Anal. Chem., 28, 889(1956).

Johnson, G.A. and Neale, S.M., "High Frequency Effects in Polyelectrolyte Solutions." J. Polymer Sci., 54, 229(1961).

Jolly, W.L., "Interpreting Liquid Ammonia Chemistry with Thermodynamics." J. Chem. Educ., 33, 512(1956).

_____, "Synthetic Inorganic Chemistry." Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1960.

Jortner, J., "Cation-Electron Interaction in Metal-Ammonia Solutions." J. Chem. Phys., 34, 678(1961).

Julian, G., Personal Communication, University of the Pacific, Stockton, California, 1962.

Kalinowski, K., "Titration with High-Frequency Currents with Application of Measuring Vessel of Electrolytic Condenser Type. Determination of Codeine and Salicylic Acid in Aqueous Environment." Acta Polon. Pharm., 18, 349(1961).

Kashima, T., "Nonaqueous Titration." Yukagaku, 9, 617(1960).

Kimura, E., "Automatic Chemical Balance Using High Frequency." Bunseki Kagaku, 10, 563(1961).

Kirilyuk, S.S. and Miskidzhyan, S.P., "Analysis of Current Conducting Non-aqueous Systems and Investigation of the Mechanism of Electrolytic Dissociation of the Compounds formed in Them." Ukrain. Khim. Zhur., 27, 180(1961).

Kocor, M. and Kotlarek, W., "Reduction of 2,6-and 1,5-Dihydroxynaphthalene Ethers by Sodium-Liquid Ammonia Solution." Bull. Acad. Polon. Sci., Ser. Sci. Chim., 9, 507(1961).

Kraus, C.A., "Fragments of Chemistry: Physical Properties of Metal Solutions." J. Chem. Educ., 30, 83(1953).

Lewis, C.H., "A Kinetic Study of the Reaction Between Acetic Anhydride and Isobutyl Alcohol Using a Chemical Oscillometer." Unpublished Master's thesis, College of the Pacific, Stockton, California, 1959.

Lorenz, W., "Impedance Measurement Arrangement for the Investigation of Electrode Reactions at High Frequency." Z. Phys. Chem. (Frankfurt), 26, 424(1960).

Lowery, W.E., "A Kinetic Study of the Base Catalyzed Esterification of Acetic Anhydride with Ethyl Alcohol Using a High Frequency Oscillometer." Unpublished Master's thesis, College of the Pacific, Stockton, California, 1958.

Mai, A.V. and Parlashkevich, N.Y., "High Frequency Apparatus for Conductometry and Titration." Plasticheskie Massy, 5, 52(1961).

Makarov, S.Z. and Sokovnin, E.I., "Solubility of Potassium Ozonide in Liquid Ammonia (The Ammonia-Potassium Trioxide System). Doklady Akad. Nauk S.S.S.R., 137, 612(1961).

Mandel'berg, I.R. and Zarinskii, V.A., "Apparatus for High Frequency Titration and for Determination of the Concentration of Solutions." USSR Patent No. 111, 724, (1958).

Matsuda, H. and Matsuda, S., "Quantitative Analysis of Halogen of Alkyl Tin Halides by High Frequency Titration." Kogyo Kagaku Zasshi, 64, 539(1961).

Mejer, S., "Phenanthrene Reduction by Sodium in Liquid Ammonia." Bull. Acad. Polon. Sci., Ser. Sci. Chim., 9, 773(1961).

Mironov, K.E., Dzyatkevich, B.S., and Vouchenko, T.I., "Reaction for the Separation of Hydrogen Peroxide in a Liquid Ammonia Medium." Izvest. Sibir. Otdel. Akad. Nauk S.S.S.R., 11, 130(1961).

Mori, R., Hyodo, T., and Murakami, Y., "Conductometric Titration with a High-Frequency Oscillator." Repts. Research Lab. Asahi Glass Co., 1, 76(1950).

Mukherjee, S.N., "High-Frequency Titrations." Sci. and Culture (Calcutta), 23, 53(1957).

Mukherjee, S.N., and Roy, B., "High Frequency Titration of Mercaptans." Sci. And Culture. (Calcutta), 27, 402(1961).

Musha, S., Ito, M., and Takeda, M., "Applied High-Frequency Wave Volumetric Analysis. III." J. Chem. Soc. Japan, Pure Chem. Sect., 73, 482(1952).

_____, and Takeda, M., "High-Frequency Analysis." Bunseki Kagaku, 6, 849(1957).

Nagata, W., Hirai, S., Terasawa, T., Kikkawa, I., and Takeda, K., "Total Synthesis of Steroids. Synthesis of Hydrophenanthrene as Hydrochrysene Derivatives." Chem. and Pharm. Bull. (Tokyo), 9, 769(1961).

Nakano, K., Ishikawa, S., and Shibata, S., "The Response Curves in High-Frequency Titration and Electric Conductance Curves of Sodium Chloride and Sodium Hydroxide." Nippon Kagaku Zasshi, 79, 531(1958).

Nevzorov, B.A., "Polarization and Transport of Oxygen in Liquid Ammonia." Zhur. Fiz. Khem., 35, 602(1961).

Paloni, L., "Solution of Alkali Metals in Liquid Ammonia. Thermodynamic Measurements." Gazz. Chim. Ital., 90, 1682(1960).

_____, "Solutions of Alkali Metals in Liquid Ammonia. Electrochemical Properties." Gazz. Chim. Ital., 91, 121(1961).

_____, "Alkali Metal Solutions in Liquid Ammonia, Spectroscopic and Photochemical Data, Diffraction of X-rays. Chemical Properties." Gazz. Chim. Ital., 91, 518(1961).

_____, "Alkali Metal Solutions in Liquid Ammonia. Theoretical Interpretation." Gazz. Chim. Ital., 91, 787(1961).

_____, "Solution of Alkali Metals in Liquid Ammonia. Electronic Structure of Type Presented in Sodium Solutions." Gazz. Chim. Ital., 91, 1062(1961).

Paucek, M., "High-Frequency Titrimeter (500 Mc)." Chem. Histy., 52, 1367(1958).

Pavel, L. and Zazvorka, M., "High-Frequency Titration of Soil Colloids." Sbornik Ceskoslov, akad, zemedel, ved., Rostlinna vyroba., 4, 1559(1958).

Pungor, E., "High-Frequency Titrimeter." Chem. Zvesti, 13, 823(1959).

_____, "Oxidation of Chlorpromazine and the Course of the Oxidation Followed with a High-Frequency Titrimeter." Pharm. Acta Helv., 35, 173(1960).

_____, "Formation of Some Metal Complexes by High-Frequency Titrimetry." Acta Chim. Acad. Sci. Hung., 25, 133(1960).

_____, "Injection-Solution Studies with a High-Frequency Titrimeter." Acta Pharm. Hung., 5, 193(1960).

_____, "Acid-Base and Iodometric Determinations with the High-Frequency Titrimeter." Magyar Kem. Folyoirat, 67, 11(1961).

_____, "Conductometry and Oscillometry." J. Electroanal. Chem., 3, 289(1962).

_____, and Zapp, E.E., "Rapid Determination of Aluminum with High Frequency Titration." Egypt J. Chem., 2, 81(1959).

_____, and Balazs, L., "Concentration Limits of High Frequency Titrimeters Working in the Region of 130 Mc." Magyar Kem. Folyoirat, 66, 128(1960).

_____, Tacacs, G., and Scherr-Bruzer, E., "Stability Testing of Solutions in Ampoules by Means of a High-Frequency Apparatus." Arch. Pharm., 293, 425(1960).

_____, Tacacs, G., and Scherr-Bruzer, E., "High-Frequency Titrimetric Study of Stability of Injection Solutions." Acta Pharm. Hung., 5, 196(1960).

Reilley, C.N., "High Frequency Methods.", Chapter 15 in "Instrumental Methods in Electrochemistry." Delahay, P., Interscience Publishers Inc., New York, 1954.

Reinaecker, G. and Roloff, B., "Preparation of Catalytically Active Nickel by Reduction in Liquid Ammonia." Z. Anorg. u. Allgem. Chem., 308, 263(1961).

Sargent, E.H. and Company., "Review of Oscillometric or High-Frequency Methods of Chemical Analysis." Scientific Apparatus and Methods, 9, 2(1957).

Schaub, R.E. and Weiss, M.J., "Formation of Steroid Enolate Anions by lithium-liquid Ammonia. Reduction of Conjugated Unsaturated Ketones." Chem. and Ind. (London), 49, 2003(1961).

Shatenshtein, A.I., "Mechanism of the Protophilic Substitution of Hydrogen in Aromatic Compounds by means of Hydrogen Isotope Exchange with Liquid Ammonia." Tetrahedron, 18, 95(1962).

————, and Ranneva, U.I., "Factors of the Partial Rate of Heat Exchange in Dimethylaniline and a Potassium Iodide Solution in Liquid Ammonia and the Mechanism of Basic Exchange." Zhur. Obshchei Khim., 31, 1432(1961).

Sherrick, P.H., Dawe, G.A., Karr, R., and Ewen, E.F., "Manual of Chemical Oscillometry." E.H. Sargent and Co., Chicago, 1954.

Shimo, K. and Wakamatsu, S., "New Synthesis of Amino Acids. Preparation of d,l-Glutamic Acid by the Michael Reaction of Acetamidomalonic Acid and Acetamidocyanoacetic Acid Derivative with Acrylic Acid Derivative in Liquid Ammonia." J. Org. Chem., 26, 3788(1961).

————, Wakamatsu, S., and Inoue, T., "Solvent Catalyzed Alkylations of Active Methylene Groups in Liquid Ammonia." J. Org. Chem., 26, 4868(1961).

Simonyi, I. and Takar, G., "Use of Aluminum Halide Alcoholate for Titration in non-aqueous Solutions." Acta Chem. Acad. Sci. Hung., 26, 495(1961).

Sisler, H.H., "Chemistry in Non-Aqueous Solvents." Reinhold Publishing Corp., New York, 1961.

Suquet, M.X. and Schmitt, J., "Opening of the Heterocycle of some Alkylphenothiazines at the Nitrogen by the use of Lithium and Ethanol in Liquid Ammonia." Bull. Soc. Chim., France, 2113(1960).

Tarnay, K. and Juhaz, E., "Determination of Concentrations by High Frequencies." Periodica Polytech., 2, 275(1958).

Tesi, G. and Audrieth, L.F., "Quantitative Determination of some Halogens and Halogenides of Phosphoro Nitrile by Means of Metallic Sodium in Liquid Ammonia." Gazz. Chem. Ital., 90, 1543(1960).

Tomita, M. and Ujiie, T., "Cleavage Reactions of Some Heterocycles Containing Oxygen and Sulfur by Alkali Metals in Liquid Ammonia." Yakugaku Zasshi, 81, 13(1961).

Tsou, C.L., Du, Y.C., and Xue, G.J., "Reduction of Insulin and its Benzyl Derivatives by Sodium in Liquid Ammonia and the Regeneration of Activity from the Reduced Product." Sci. Sinica (Peking), 10, 332(1961).

Ugi, I. and Bodesheim, F., "Reduction of Isonitriles and Alkaline Earth Metals in Liquid Ammonia." Chem. Ber., 94, 1157(1961).

Vakhtel, M.I. and Chernyakina, A.F., "Quantitative Determination of Furfurol by High Frequency Titration." Plasticheskie Massy, 2, 65(1961).

Wadman, W.H., Personal Communication, University of the Pacific, Stockton, California, 1962.

Watt, G.W., "Reactions of Inorganic Substances in Liquid Ammonia." Chem. Rev., 46, 315(1950).

_____, "Reactions of Organic and Organo Metallic Compounds with Solutions of Metals in Liquid Ammonia.: Chem. Rev., 46, 317(1950).

_____, and Vaughn, J.W., "Mechanism of Electrodeposition of Cobalt from Liquid Ammonia Solutions of Spin Paired Cobalt(III) Complexes. Evidence for a Trans Effect in Octahedral Complexes." J. Electrochem. Soc., 108, 351(1961).

Willard, H.H., Merritt, L.L., and Dean, J.A., "Instrumental Methods of Analysis." 3rd Edition, D. Van Nostrand Company, Inc., Princeton, N.J., 1958.

APPENDIX

EXPERIMENTAL DATA FOR FIGURE 6

Ml. water added to hf-cell	CF-120 Titrimeter, coarse dial units					
	Fundamental resonance				Harmonic resonance	
0	17.0				22.6	
4	18.0				22.1	
8	18.6				22.0	
12	20.00				21.3	
16	23.1				20.0	
18	27.2	5.2			----	
20	36.0	14.0			14.9	
22	53.5	30.5			9.4	
24	73.2	48.5			.2	
26		70.0	6.2			
28			20.6			
30			33.2			
32			43.5			
34			52.1			
36			58.3			
38				2.4		61.3
40				3.6		62.4
50				3.9		62.6
75				4.0		62.6

EXPERIMENTAL DATA FOR FIGURE 6 (continued)

Ml. acetone added to hf-cell	CF-120 Titrimeter, coarse dial units		
	Fundamental resonance	Harmonic resonance	
0 - 28	*	*	
30	17.4	43.9	
32	27.6	55.0	5.2
34	34.1	62.2	12.3
36	39.8	68.6	17.9
38	43.1	72.5	21.1
40	45.0	74.5	22.7
50	46.0	75.6	23.8
75	46.0	75.6	23.8

* Below 30 ml., the pattern for acetone closely resembled that obtained for water.

EXPERIMENTAL DATA FOR FIGURE 7

Ml. water in 75 ml. acetone	CF-120 Titrimeter		Ml. water in 75 ml. methanol	CF-120 Titrimeter	
	Coarse dial units	Increase		Coarse dial units	Increase
0	46.7	0	0	54.1	0
5	50.1	3.4	4	55.6	1.5
10	52.5	5.8	10	56.8	2.7
15	54.0	7.3	15	57.5	3.4
20	55.2	8.5	20	58.0	3.9
25	56.1	9.4	25	58.3	4.2
30	57.0	10.3	30	58.9	4.8
35	57.6	10.9	35	59.1	5.0
40	58.0	11.3	40	59.2	5.1
45	58.5	11.8	45	59.8	5.7
50	59.0	12.3	50	60.0	5.9

EXPERIMENTAL DATA FOR FIGURE 8

Ml. of water added to 75 ml. acetone	Increase in CF-120 Titrimeter response, fine dial units
0	0
2	305
4	693
6	955
8	1166
10	1335
12	1476
14	1589
16	1695
18	1804
20	1881
24	2008
30	2198
35	2290
40	2360
45	2425
50	2495

EXPERIMENTAL DATA FOR FIGURE 8 (continued)

Molarity of aqueous KCl	Ml. added to 75 ml. acetone	Increase in CF-120 Titrimeter response, fine dial units, hf-cell
	1	213
	2	427
.001	4	732
	6	1001
	8	1193
	10	1387
	1	252
	3	653
.01	5	938
	7	1473
	8	*
	1	257
.1	2	491
	3	*

* The CF-120 Titrimeter ceased to give a signal with the addition of more titrant.

EXPERIMENTAL DATA FOR FIGURE 9

Moles per liter	Ml. of titrant*	CF-120 Titrimeter response, fine dial units	
		temperature uncorrected	temperature corrected
	1	56**	16
.10	2	166**	124
	3	215**	166
	4	No response	---
	2	15	---
	4	26	---
	8	41	28
	14	68	---
	20	92	62
.010	24	98	---
	30	114	71
	36	136	---
	40	145	91
	44	151	---
	50	160	---

* CdI_2 dissolved in acetone added to 75 mol. of acetone.

** Not plotted in the figure.

EXPERIMENTAL DATA FOR FIGURE 10

Warm-up time, minutes	CF-120 Titrimeter response, coarse dial units with the hf-cell and 75 ml. water	
	Fundamental resonance	Harmonic resonance
2	3.9	62.6
5	3.8	62.6
7	3.7	62.5
27	3.8	62.4
30	3.9	62.7
127	4.0	62.6

EXPERIMENTAL DATA FOR FIGURE 11

Temperature, $^{\circ}C.$	Increase in CF-120 Titrimeter response, fine dial units, with the hf-cell and 75 ml. acetone
29.8	0
28.2	36
26.5	138
24.3	181
20.5	228
19.5	270
18.0	320
16.1	360
15.1	400
13.8	440
11.6	500
7.0	600
4.7	650

EXPERIMENTAL DATA FOR FIGURE 12

Solvent	Temperature, °C.	Increase in CF-120 Titrimeter response, coarse dial units, with the hf-cell and 75 ml. solvent		
		Fundamental resonance	Harmonic resonance	
	57.6	0	0	
	42.9	.5	.3	
Water	34.6	.7	.6	
	13.1	1.6	1.2	
	2.3	1.7	1.5	
	18.7	0	0	0
	11.2	.5	.5	.8
Acetone	6.7	1.1	1.1	1.3
	4.8	1.3	1.2	1.6
	-.6	1.6	1.7	1.8

EXPERIMENTAL DATA FOR FIGURE 14

Titrant	Mmole of titrant per 100 ml. H_2O	Increase in response, Sargent Model V Chemical Oscillometer scale units	Titrant	Mmole of titrant per 100 ml. H_2O	Increase in response, Sargent Model V Chemical Oscillometer scale units
	.01	0		.20	324
	.02	-2		.40	383
	.04	3	HCl	.60	---
	.06	16		.08	421
	.08	30		1.00	432
KCl	.10	49			
	.20	122		.01	0
	.40	266		.20	0
	.60	327		.04	2
	.80	357		.06	5
	1.00	378		.08	9
			HOAc	.10	15
	.01	0		.20	20
	.02	5		.40	31
	.04	51		.60	45
HCl	.06	110		.80	57
	.08	165		1.00	73
	.10	208			

EXPERIMENTAL DATA FOR FIGURE 15

Ml. of .01M KOH per 100 ml. of .0005M HCl*	Increase in response, Sargent Model V Chemical Oscillometer Scale units
0	0
.5	8
1.0	1
1.5	-5
2.0	-14
2.5	-22
3.0	-25
3.5	-30
4.0	-30
4.5	-28
5.0	-29
5.5	-26
6.0	-23
6.5	-19
7.0	-13
8.0	-2
9.0	11
10.0	24

* End Point with Phenolphthalein   5.00 ml.

EXPERIMENTAL DATA FOR FIGURE 16

Mole fraction of CdI_2 in acetone, x 10^5	Increase in response, Sargent Model V Chemical Oscillometer scale units
.8	0
1.5	33
2.3	96
3.1	175
3.9	256
4.6	327
5.4	395
6.1	451
6.9	501
7.7	453
8.5	582
9.2	614
10.0	641
11.5	691
15.1	773

EXPERIMENTAL DATA FOR FIGURE 17

Ml. of water per 100 ml. of acetone	Increase in response, Sargent Model V Chemical Oscillometer scale units	
	No cell compensator	Cell Compensator
0	0	0
2	41	245
4	78	437
6	108	619
8	137	778
10	161	930
12	186	1060
14	207	1218
16	225	1332
18	243	1437
20	260	1541

EXPERIMENTAL DATA FOR FIGURE 18

Ml. of .19 M NH$_3$* added to 75 ml. of solution	Increase in response, Sargent Model V Chemical Oscillometer scale units	
	.0026 M CdI$_2$*	Pure acetone
0	0	0
.50	185	-2
1.00	267	-4
1.50	278	--
2.00	244	-3
2.50	200	--
3.00	168	--
3.25	157	--
3.50	156	--
3.75	157	--
4.00	155	-2
4.25	151	--
4.50	133	--
4.75	118	--
5.00	107	--
5.50	89	--
6.00	70	--
7.00	61	--
8.00	58	1
9.00	52	--
10.00	45	2

* All solutions used acetone as the solvent.

EXPERIMENTAL DATA FOR FIGURE 19

Solvent	Mole Fraction of solvent in liquid NH_3 at $-33^{\circ}C$.	Increase in response, Sargent Model V Chemical Oscillometer scale units
H_2O	.0083	6
	.014	28
	.027	68
	.040	110
	.050	138
	.077	220
	.100	307
CH_3OH	.0080	34
	.016	77
	.024	109
	.032	145
	.039	172
	.047	199
	.061	243
	.075	283

EXPERIMENTAL DATA FOR FIGURE 20

Mole fraction x 10^5 of salt in liquid ammonia at -33°C.					Increase in response, Sargent Model V Chemical Oscillometer scale units, using the hf-cell				
LiCl	NaCl	KCl*	RbCl	CsCl*	LiCl	NaCl	KCl	RbCl	CsCl
3.22	.79	.83	.70	.86	646	249	344	430	338
7.49	1.62	1.50	3.0	2.02	830	550	524	742	589
14.3	2.80	2.92	5.0	5.04	871	728	755	823	755
21.4	4.00	3.40	8.9	8.39	905	766	790	880	799
34.4	5.25	4.72	16.5	14.2	920	812	858	924	838
66.5	6.94	18.3	34.0	26.3	934	846	894	938	870
87.3	12.0	23.8	53.0		936	892		941	
	36.0					924			
	62.9					928			

*   Not all solute dissolved and estimates of corrected mole fractions have been made.

EXPERIMENTAL DATA FOR FIGURE 21

Mole fraction x 10^5 of salt in liquid ammonia at -33°C.				Increase in response, Sargent Model V Chemical Oscillometer scale units, using the hf-cell			
KF*	KCl*	KBr	KI	KF	KCl*	KBr	KI
	.83	1.87	.45		344	494	230
	1.50	2.57	.99		524	602	392
	2.92	3.72	1.37		702	668	474
	3.40	4.92	2.00		755	715	574
	4.72	8.21	2.80		790	755	631
	18.3	11.2	3.47		858	771	662
	23.8	21.8	4.78		894	792	697
		31.0	7.97			796	734
		40.8	14.0			800	750
		76.1				822	

* KF was so insoluble that no response was observed, and the KCl mole fraction 23.8 x 10^{-5}, was adjusted for the amount that failed to dissolve.

EXPERIMENTAL DATA FOR FIGURE 22

Mole fraction x 10^5 salt in Liquid ammonia at -33°C.						Increase in response, Sargent Model V Chemical Oscillometer scale units using the hf-cell					
LiF*	NaF*	NaBr	NaI	RbBr	CsI	LiF*	NaF*	NaBr	NaI	RbBr	CsI
1.06		.58	1.10	.36	.24	10		15	500	14	100
15.6		1.30	2.08	.92	.70	26		502	724	372	323
43.2		2.00	2.72	1.80	1.32	36		671	816	655	525
		3.40	5.80	3.28	4.50			826	892	771	782
		6.40	6.72	5.01	6.58			934	912	830	822
		13.1	11.8	9.10	9.92			997	945	875	850
		21.0	23.8	13.6	18.4			1023	967	897	875
		34.0	40.2	17.6	29.5			1040	976	904	888
		55.0	55.0	26.6	44.7			1047	978	916	894
		94.0		30.5	70.2			1055		902	

* NaF was so insoluble that no increased response was observed; and LiF was incompletely dissolved with the bulk of the apparent mole fraction being in suspension.

EXPERIMENTAL DATA FOR FIGURE 23

Mole fraction x 10^5 of substance* in liquid ammonia at $-33°C$.							Increase in response, Sargent Model V Chemical Oscillometer scale units, using the hf-cell						
Na	K*	NH_4F*	NH_4Cl	NH_4I	AgI	$CuBr_2$*	Na	K*	NH_4F*	NH_4Cl	NH_4I	AgI	$CuBr_2$*
.24	.39	2.00	5.60	.45	.10	.27	290	310	27	773	99	281	32
1.20	.80	5.0	11.6	.91	1.90	.72	835	750	67	828	349	365	190
2.50	.96	13.3	17.9	1.22	4.10	1.42	917	830	99	846	467	571	380
16.1	2.06	24.8	24.3	1.76	11.2	2.14	963	875	100	875	608	745	494
	2.57		30.9	2.26	16.4	3.81		900		866	706	782	668
			53.9	2.95	21.8	5.79				870	773	804	758
			81.0	5.65	49.1	8.02				878	884	844	811
				8.05		10.0					918		838
				12.3		14.0					944		866
				15.8		19.1					954		868
				37.0							972		
				55.6							983		

* $(NH_4)_2SO_4$ was so insoluble that no increased response was observed; NH_4F was incompletely dissolved with the bulk of the apparent mole fraction being in suspension; the K metal response curve was merely incomplete and does not represent limited solubility; and the $CuBr_2$ solution was turbid after the addition of the last pellet, suggesting that its solubility had been exceeded.

EXPERIMENTAL DATA FOR FIGURE 24

Reaction time, minutes	$\frac{1}{T}$, Reciprocal minutes *	Response increase, Sargent Model V Chemical Oscillometer Scale units with the hf-cell
0	----	0
80	.0125	68
95	.0105	93
135	.0074	140
180	.0057	211
225	.0044	275
270	.0038	358
330	.0030	414
375	.0027	450
405	.0025	467

* Calculated from the reaction time for the ammonolysis of 10 microliters of 1-iodopropane in 100 ml. of liquid ammonia at -33°C.

EXPERIMENTAL DATA FOR FIGURE 26

Mmoles of potassium per .19 mmole AgI in 90 ml. of liquid ammonia	Response increase, Sargent Model V Chemical Oscillometer scale units with the hf-cell
0	340*
.002	325
.008	270
.015	276
.035	294
.045	298
.059	321
.078	328
.158	353
.247	353

* This was the increased response due to the silver iodide and was in reference to zero for pure ammonia.

EXPERIMENTAL DATA FOR FIGURE 27

Mmole of NH_4I per .45 mmole KNH_2 in 90 ml. of liquid NH_3	Response increase of the Sargent Model V Chemical Oscillometer and the hf-cell
0	0
.02	280
.06	515
.13	640
.24	735
.52	850
1.09	875
1.92	895
3.10	905