ABSTRACT

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Thermodynamic Properties of Haloferric Acids, and of Hydrates and Solvates of Hydrogen Halides in Ethers.

Thermodynamic properties ΔG^{o}, ΔH^{o}, and ΔS^{o} at 25°C were evaluated from dielectric-constant measurements, for the reaction

$$HX + R_2O = R_2O.HX$$

in carbon tetrachloride; R_2O was di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran, and X was chloride or bromide. These properties were also evaluated by spectrophotometry, for the reaction

$$R_2O + HX + FeX_3.R_2O = (R_2O)_2H^+ FeX_4^-$$

in each of the three ethers, and for the two halides.

Standard enthalpies of solution of $FeCl_3$ and $FeBr_3$ in each of the three ethers, and of $(R_2O)_2HFeCl_4$ and $(R_2O)_2HFeBr_4$ in their corresponding ethers (R_2O), di-isopropyl ether and di-n-butyl ether, were measured.

Standard enthalpies for the gas-phase reaction

$$2 R_2O + H^+ = (R_2O)_2H^+$$

were deduced from a thermochemical cycle, and also independently estimated from literature data.

The values of ΔG^{o} at 25°C were obtained from vapour pressure measurements, for the reaction

$$HX + H_2O = H_2O.HX$$

in di-isopropyl ether; HX was HCl and HBr.

$HX + R_2O = R_2O.HX$ at 25° C

ETHER	X=Cl			X=Br		
	ΔG^o	ΔH^o	ΔS^o, e.u.	ΔG^o	ΔH^o	ΔS^o, e.u.
di-iso-propyl	1.6	5.3	13	0.67	4.5	14
di-n-butyl	1.2	4.4	12	0.92	4.2	12
tetrahy-furan	2.8	6.0	12	2.57	5.9	11
$HX + R_2O + FeX_3.R_2O = H(R_2O)_2^+ FeX_4^-$ at 25° C						
di-iso-propyl	4.1	16.0	40	4.4	15.2	36
di-n-butyl	3.7	13.8	34	5.2	13.6	28
tetrahy-furan	5.0	12.5	25	4.5	13.3	30

ΔG^o and ΔH^o are in kcal/mole.

CHEUNG, Miranda Mo-Tsing

Thermodynamic Properties of Haloferric Acids

THERMODYNAMIC PROPERTIES OF HALOFERRIC ACIDS, AND OF HYDRATES AND SOLVATES OF HYDROGEN HALIDES IN ETHERS

by

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LIST OF PRINCIPAL SYMBOLS

k_9	solvation constant for the reaction, $HX + S + FeX_3.S = HS_2FeX_4$
K_1	solvation constant for the reaction, $HX + R_2O = HX.R_2O$
k_1	solvation constant for the reaction, $HX + H_2O = HX.H_2O$
ΔG^o	standard free energy change
ΔH^o	standard enthalpy change
ΔS^o	standard entropy change
A	absorbance
M	molar concentration (moles/litre)
N	normality
m	molal concentration (moles/1000 gms of solvent)
kcal	kilocalorie
μ	micron
$m\mu$	millimicron
a	apparent absorptivity
a_1	molar absorptivity of ferric halides
a_2	molar absorptivity of tetrahaloferric acids
c_T	total(stoichiometric) concentration of iron
p_{HX}	partial pressure of hydrogen halide
V	volume
S	solvent
u_i	chemical potential of the ith component

μ^*	reduced dipole moment
D	dielectric constant
Δz	difference in capacitance readings between solution and solvent
x_a	dielectric proportionality constant of species a in solution
W.E.	water-equivalent of calorimeter
U	lattice energy
e	electronic charge
r	interionic distance
τ_c	Goldschmidt radii of cation
N	Avagadro's number
A_M	structural coefficient (Madelung constant)
n	ionic charge
Å	Angstrom

GENERAL INTRODUCTION

A principal purpose of the present investigation was the evaluation of the thermodynamic properties ΔG^o, ΔH^o, and ΔS^o for the reaction

$$FeX_3.S + HX + S = HS_2^+FeX_4^- \qquad [1]$$

in three ethers, namely, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran; X was halide (chloride and bromide), and S was the ether solvent. Complementary equilibrium studies included the formation of the etherates, and hydrates of hydrogen chloride and hydrogen bromide.

The solvent extraction of halometallic acids into oxygenated solvents is an important technique in analytical chemistry. For example, the extraction of ferric ion from solutions approximately 6N in hydrochloric acid into di-ethyl ether has been practised for a century (1). Other transition metals similarly extracted include cobalt (2), gold (3,4), molybdenum(5,6,7), nickel (2), platinum (8), tin (4,5), vanadium (6), mercury (9), niobium (10), and tellurium (4).

The solvent extraction of ferric chloride as tetrachloroferric acid into ethers has been widely studied in order to identify the extracted species. Thus, when the concentration of hydrochloric acid in the aqueous phase was below 8M, the extracted species have been characterized (11,12, 13) as being highly solvated $HFeCl_4$, with water playing an important role ; at a concentration of hydrochloric acid 10 M, $HFeCl_4$, H_2FeCl_5, and H_3F_eCl6 were found to be extracted (14). Moreover, polymeric species have been found (12,13) in the ether extracts at very high concentrations of acid and metal.

Axelrod and Swift (15) found that four to five molecules of water were bound to one molecule of tetrachloroferric acid in the organic solvent. As indicated above, the acid was highly solvated (11,12,13). Moreover, Laurene (16), and Fomin and Morgunov (17) prepared anhydrous tetrachloroferric acids by precipitation from several ethers.Analysis of the products showed that one molecule of the acid was solvated with approximately two molecules of the ether. However, the exact composition of the cation in the ether of the solvent extraction system is still the subject of speculation. It has been suggested (16) that the proton is both etherated and hydrated, with various proportions of ether to water being possible. The tetrachloroferrate ion in di-isopropyl ether, on the other hand, has been shown (18) by its paramagnetic resonance behaviour to be $FeCl_4^-$ with a tetrahedral configuration.

The extraction of ferric bromide as tetrabromoferric acid into di-ethyl ether has also been studied (19), but less extensively.

A rigorous understanding of the system FeX_3-HX-H_2O-ether, where X is a halide, requires reasonably accurate values of the basic thermodynamic properties $\Delta G^o, \Delta H^o$, and ΔS^o for the particular reactions. These properties have not previously been investigated and evaluated. Their measurement was , as stated in the introductory paragraph, a principal purpose of this investigation.

The existing uncertainty in, and possible complexity of the hydration and solvation of the proton in an extracted halometallic acid made it advisable to limit the present work to only parts of the general system. Thus the required thermodynamic properties were evaluated under strictly anhydrous conditions for reactions [1] and [2] in intensively dried solvents:

$$FeX_3.S + HX + S = HS_2^+ FeX_4^- \qquad [1]$$

$$HX + nS = HX.nS \qquad [2]$$

However, the composition and stability of the hydrates of hydrogen chloride and of hydrogen bromide in di-isopropyl ether containing added water were also determined. The halometallic acid itself was not studied in solvents containing water. Therefore the composition and stability of the various possible mixed hydrates and etherates of the proton are not reported. Reaction [1] was studied by spectrophotometry, reaction [2] by vapour pressure and independently by dielectric-constant measurements, and the hydrates by vapour pressure.

Available information on reaction [1] in anhydrous solvents was very limited. Kennard and M^{c}Cusker (20) carried out spectrophotometric studies on anhydrous ferric chloride and tetrachloroferric acid in dioxane and in some alkyl ethers. They reported the order of magnitude of the formations of the complex acid in these ethers. Fomin and coworkers (21,22, 23) found that anhydrous ferric chloride formed a monosolvate in di-isopropyl ether, in di-n-butyl ether. The anhydrous system $FeBr_3$-HBr-ether has not been previously studied. Its inclusion in the present investigation provided an important and interesting comparison of its thermodynamic constants with those of the chloride system.

Fairly extensive exploratory studies in the present work showed that a study of the system FeX_3-HX-ether was likely to be fruitful.

Of the halides of Fe(III),Cu(II), Co(II), Ni(II), Cr(III),and Mn(II), only those of Fe(III) were sufficiently soluble in the ethers ($> 10^{-3}$ M) to be amenable to the methods chosen for the investigation. Gold chloride dissolved easily in these ethers; but the resulting solution decomposed rapidly with the deposition of metallic gold, although the presence of hydrogen chloride stabilized the solution to some extent. However, the ultraviolet absorption spectra of anhydrous gold chloride and tetrachloroauric acid in ether appeared to be identical in the ultraviolet region. Gallium, indium, and thallium (III) halides dissolved in ether, to form colourless solutions which did not give well-defined spectra in the accessible region of the ultraviolet.

The ferric halides, on the other hand, were reasonably soluble in ethers, and the resulting solutions were reasonably stable. Moreover, the solutions were known to exhibit charge-transfer spectra in the visible and ultraviolet regions.(24).

Other exploratory studies failed to detect by spectrophotometric means the formation in ethers of mixed halides such as $FeCl_2Br$ and $FeClBr_2$. Thus, there was no shift in the absorption peaks of $FeCl_3$ and $FeBr_3$ nor any change in their molar absorptivities when $FeCl_3$ and $FeBr_3$ were mixed in di-isopropyl ether. However, the addition of hydrogen chloride to ether solutions of ferric bromide, or hydrogen bromide to ferric chloride solutions showed spectrophotometrically that mixed acids did form ; but equilibrium was reached very slowly. Thus, spectra of these solutions, run at different interval of time over a four to five day period, were constantly changing. Characterization of the species involved was not pursued in the present work.

Chloride and bromide were chosen as the anions because they were of greater analytical importance than most other anions. Iodides could not be used, because hydrogen iodide splits ethers into alkyl iodides and alcohols at room temperature. An added advantage of choosing hydrogen chloride and hydrogen bromide was that both were gases at room temperature. This volatility permitted the use of a vapour pressure method for the determination of the solvation constants of these hydrogen halides in ethers. It is to be noted that hydrogen bromide is somewhat less stable than hydrogen chloride; it is easily oxidized to bromine.

Of the possible oxygenated solvents for study, ethers were chosen. The solvation of hydrogen chloride in anhydrous acetone at 25.0°C had already been studied by N. Begum (25), by a vapour pressure method.She had found that side reactions occurred; thus, hydrogen chloride catalyzed the condensation of acetone into mesityl oxide, phorone, isophorone, mesitylene, and water. Side reactions were expected not to happen with the ethers, and in fact, the ethers were found to be stable in dilute solutions of hydrogen chloride and hydrogen bromide. Alcohols were not used, because with them the vapour pressure of the hydrogen halides were too small to be measured by the present method.

In the present work, three ethers, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran were used. They were commercially available in high degree of purity. Their boiling points conveniently permitted further purification by fractional distillation.

Tetrahydrofuran was included in the present investigation for two reasons : (i) it is cyclic, and (ii) it has a higher dielectric constant than either di-n-butyl ether or di-isopropyl ether. Its inclusion made possible a comparison of the thermodynamic constants for the equilibria in the systems FeX_3-HX-ether, and HX-ether, with respect not only to the structure of the ether, but also to the dielectric constant of the solvent.

PLAN AND SCOPE OF THE PRESENT INVESTIGATION

The value of ΔG^o at each of three temperatures 25.0°C, 35.0°C, and 45.0°C was found from spectrophotometric measurements, for the reaction

$$FeX_3.S + HX + S = HS_2^+ \; FeX_4^- \qquad [1]$$

at equilibrium in three anhydrous ethers as solvents, namely di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran. In reaction [1], X is chloride or bromide, and S is the ether.The value of ΔH^o and ΔS^o for reaction [1] were found in the usual way from the measured temperature dependence of ΔG^o. Care was taken to ensure that reaction [1] was studied under strictly anhydrous conditions.

The etherates of hydrogen chloride and hydrogen bromide present in ether-carbon tetrachloride solutions were identified. The value of ΔG^o at 25.0°C, 35.0°C, and 45.0°C was found under strictly anhydrous conditions from dielectric-constant measurements, for the reaction

$$HX + S = HX.S \qquad [2]$$

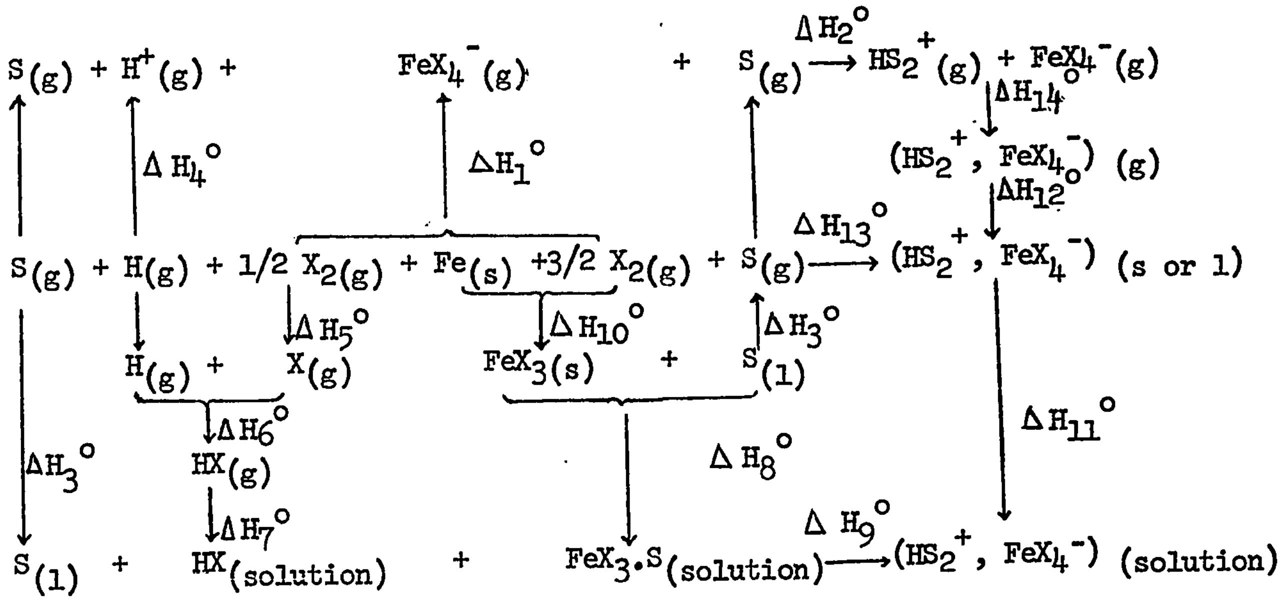
at equilibrium in each of the three anhydrous ethers. Therefrom, ΔH^o and ΔS^o were evaluated.

As confirmation of the validity of the dielectric constant method used here for the evaluation of ΔG^o for reaction [2] , a completely independent method was also used at 25.0°C.This was a vapour pressure method, which had been extensively used by N. Begum (25) for the system HCl-acetone.

Thus, two special cases of the general system, FeX_3-HX-H_2O-ether, were studied, namely : (i) FeX_3-HX-ether, and (ii) HX-ether-CCl_4. A third important special case was also studied: HX-H_2O-ether. The hydration constants of hydrogen chloride and hydrogen bromide in wet di-isopropyl ether at 25.0°C were evaluated by a vapour pressure method.

The usefulness, and a wider appreciation of the thermochemical data obtained for reactions [1] and [2] proved possible by including these reactons in conventional thermochemical cycles.

One such cycle, for enthalpy changes, was as follows:



where S= solvent ether

X= Cl or Br

s= solid state

l= liquid state

g= gaseous state

solution= solution of the species in the solvent ether S.

This cycle consists of fourteen steps. Some steps were evaluated experimentally in the present work, others were calculated theoretically in the present work, and the remainder were obtained from literature sources. The following table summarizes the methods used in order to evaluate ΔH^{o} for each step.

	Method for evaluation of ΔH^{o}
ΔH_1^{o}	Calculated theoretically from lattice energies
ΔH_2^{o}	Calculated from the cycle itself and estimated theoretically from literature data
ΔH_3^{o}	Literature data (26,27)
ΔH_4^{o}	Literature data (28,29)
ΔH_5^{o}	Literature data (31)
ΔH_6^{o}	Literature data (28,29)
ΔH_7^{o}	vapour pressure measurements and from literature data (30)
ΔH_8^{o}	Spectrophotometric measurements
ΔH_9^{o}	Calorimetry
ΔH_{10}^{o}	Literature data (32)
ΔH_{11}^{o}	Calorimetry
ΔH_{15}^{o}	$\Delta H_{12}^{o} + \Delta H_{14}^{o}$, calculated theoretically from lattice energies
ΔH_{14}^{o}	Calculated from Coulomb's law
ΔH_{12}^{o}	Calculated from the difference of ΔH_{15}^{o} and ΔH_{14}^{o}

In addition to the use of cycles , some of the thermochemical data permitted interesting comparisons to be made between the bromide systems and the chloride systems, as well as between the three ethers in the systems.

For intermediate data that have been calculated from initial measurements, two uncertain figures have been retained in all Tables. However, in the final data, such as the calculated values of the equilibrium constants, only one uncertain figure has been retained, and it was dictated by the value of the standard deviation.

REAGENTS AND SOLVENTS

Ethers (di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran)

Reagents grade ethers (Fisher, and Matheson, Coleman and Bell) were further purified and dried before use. Thus, calcium hydride was kept in the original bottles until bubbles of hydrogen were no longer being evolved. The dried ether was then passed through a twelve-inch column of activated alumina powder (chromatography grade, 80-200 mesh), and the eluate was passed through a second similar column; the purpose was to eliminate peroxide (33). With a 12-inch Vigreaux column it was then fractionally distilled in an atmosphere of dry nitrogen, and the centre third was collected in a dark bottle which was previously and continuously flushed with dry nitrogen, and which contained a few grams of calcium hydride. The product was stored in the bottle.

Just before use, the stoppered bottle was transferred to a dry box and the ether for use was passed through an alumina column. The eluate was collected directly into the volumetric flask to be used for the preparation of the standard solutions. This flask had previously been flushed with dry nitrogen.

Carbon tetrachloride - Fisher spectra-analyzed carbon tetrachloride was stored over phosphorus pentoxide. The stoppered bottle was transferred to a dry box just before use, and then the required solvent was decanted through an oven-dried glass wool plug into the receiver.

Benzene - Fisher reagent grade benzene was shaken in turn with concentrated sulphuric acid, distilled water, sodium hydroxide solution, and finally with distilled water. The product was fractionally distilled over silica gel in an atmosphere of dry nitrogen and using a three-foot Vigreaux column. The centre third was distilled directly into a dark bottle which had been previously flushed with dry nitrogen and which contained a few grams of calcium hydride. It was then stored.

Anhydrous ferric chloride and ferric bromide - analytical reagent grade (A. C. S. specification) was used without further purification.

The purity of each reagent was determined by a conventional gravimetric determination of the iron content (see Appendix 1 for the procedure) . Duplicate analyses were carried out and the results were calculated to % FeX_3 . The analyses were carried out on a sample of the ferric halide from the bottle and also on a sample which had been heated to sublimation temperature. The results of these analyses are in Table 1a .

TABLE 1a

Analyses of ferric halides for iron

Substance	% FeX_3
$FeCl_3$ (unheated)	100.15 , 100.06
$FeCl_3$ (heated)	100.02 , 100.20
$FeBr_3$ (unheated)	100.02 , 99.95
$FeBr_3$ (heated)	99.96 , 99.94

From the results of Table 1a , it was clear that further purification was not necessary for the present purpose. In particular, the water content of the reagent straight from the bottle must have been less than 0.1 %. Since the concentrations of ferric halides used in the present investigation were of the order of 10^{-3} M , the water content of the ferric halides was not significant for the present purposes.

Water - distilled water was used, unless otherwise specified.

Hydrogen chloride - the gas was generated by dropping reagent-grade concentrated sulphuric acid into anhydrous reagent-grade sodium chloride.

Hydrogen bromide - Matheson cylinder gas, 99.8 + % pure (highest purity available).

Stopcock grease - fluorosilicone stopcock grease (Dow Corning).

APPARATUS

All pipets and burets were calibrated to deliver solutions of carbon tetrachloride, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran. All volumetric flasks were calibrated to measure volumes of the three ethers and carbon tetrachloride, at 25.0°C.

All the glass apparatus was dried by flushing it with dry nitrogen immediately before use.

(i) Vapour pressure apparatus

The all glass apparatus used for the vapour pressure measurements has been described by N.Begum (25). It is a modified form of that used by Saylor (34) and it is illustrated in Fig. 1 . The bottom 200-ml bulb was connected to the middle 500-ml bulb through a 10-ml bore vacuum stopcock. The top 100-ml separatory funnel, which was connected through a 3-mm bore vacuum stopcock to the middle 500-ml bulb, was capped by a B-14 ground glass joint through which the apparatus was evacuated.

(ii) Hydrogen chloride gas generator

The all-glass apparatus is shown in Fig. 2 . It was flushed with dry nitrogen before use. Concentrated sulphuric acid was delivered from the 125-ml separatory funnel onto anhydrous reagent-grade sodium chloride contained in the 500-ml round-bottomed two-necked flask. The gas evolved was dried by passing it through a U-tube containing phosphorus pentoxide.It was then bubbled into the particular solvent being studied. Two types of receiver containing the solvent were used. One was the separatory funnel shown in the upper part of

Fig. 3 . After the solution had been prepared, the receiver was removed, quickly stoppered , and stored in the dry box.

(iii) Dispenser for anhydrous hydrogen halide solutions

The dispenser is shown in Fig. 3 . It was designed so as to permit the dispensing under anhydrous conditions of anhydrous ether or carbon tetrachloride solutions of hydrogen chloride or hydrogen bromide, from a buret into a volumetric flask. As a further precaution to ensure anhydrous conditions, the entire apparatus was used and stored in a dry box.

In use, the hydrogen halide solution was transferred in the dry box, from the 250-ml separatory funnel of Fig. 2 in which the solution had been prepared, into the 300-ml separatory funnel. With the latter funnel in place, and unstoppered, the solution was run slowly into the 50-ml buret until it overflowed into flask [A]. At this point, the tip of the delivery tube just cleared the surface of the liquid. The level of the liquid in the buret was adjusted to 0 ml, and the dispensing was then carried out into dry volumetric flasks.

(iv) Calorimeter

It is illustrated in Fig. 4 . A Dewar flask (28 cm height, and 12.5 cm inside diameter), fitted with 3-holed rubber cork wrapped in tin foil, was placed in a large copper container. The space between the copper container and the Dewar was packed with glass wool. A polyethylene stirrer driven by a motor was used for stirring. A thermometer (18^{o}-30^{o} C) graduated to read 0.01^{o} C was used to measure the temperature of the solutions. The thermometer* had been calibrated by the National Bureau Standards to one-hundredth of a degree over the range $18^{\circ} - 30^{\circ}$ C. A long glass tube of 30 mm diameter, and stoppered at the top, was fitted with a ₮ joint which in turn fitted into a conventional weighing bottle. This tube and bottle were suspended vertically through the rubber stopper in Dewar. The required substance for study was contained in the weighing bottle, in order to ensure temperature equilibration.

INSTRUMENTS

Unicam Spectrophotometer SP 500 - a single-beam spectrophotometer, used in the present work mainly for the colorimetric determination of iron by salicylic acid.

Beckman D. B. Spectrophotometer - a double-beam recording spectrophotometer, with the output being fed to a 10 mv potentiometric recorder (Sargent model SRL). The cell chamber of the spectrophotometer was fitted with a Beckman thermostat, through which constant-temperature water was circulated from a constant-temperature water bath (Sargent Liquid Circulator S-84880).

Beckman rectangular 1-cm silica cells with ground-glass stoppers were used. The path length was calibrated by using a conventional optical standard, namely a potassium chromate solution (35).

Dipolemeter - type DM01, manufactured by Wissenschaftlich-Technische Werkstatten GmbH Weilheim/OBY, Germany.

The cell was Model DFL1, a cylindrical, gold-coated cell with

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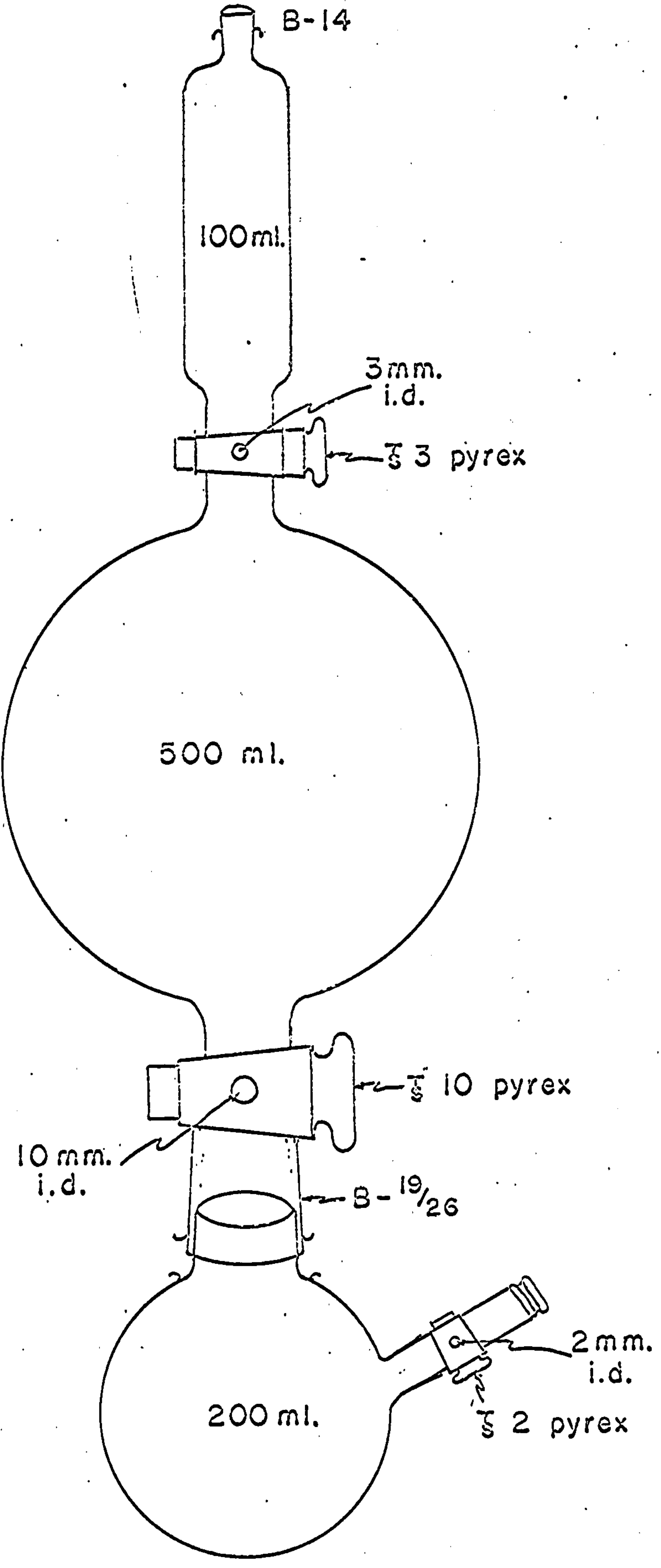
* Brooklyn Thermometer Company Inc., Cat. No. 22214, Springfield Gardens N.Y.C.



All-glass vapour pressure apparatus

Figure 1

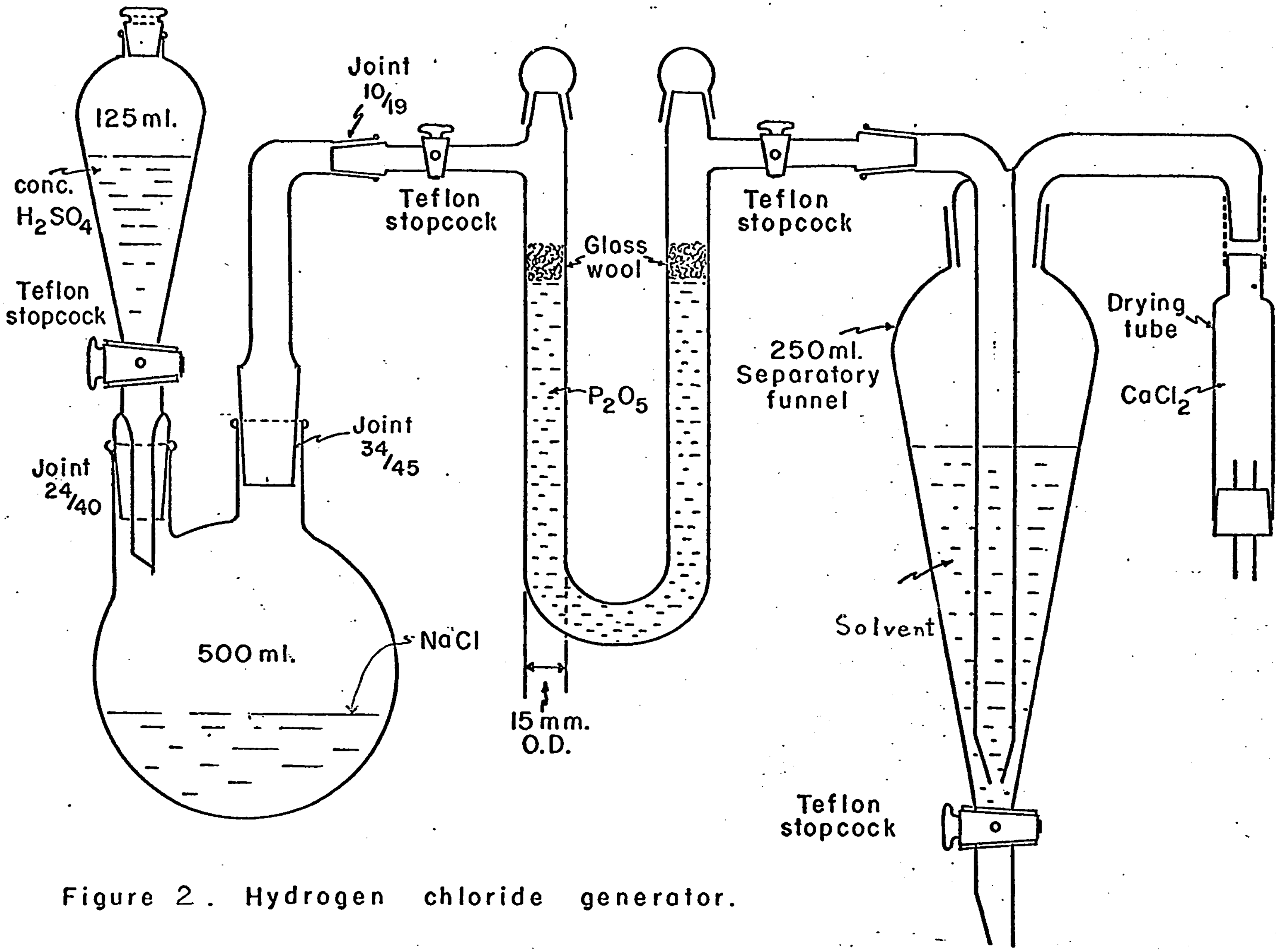


Figure 2. Hydrogen chloride generator.

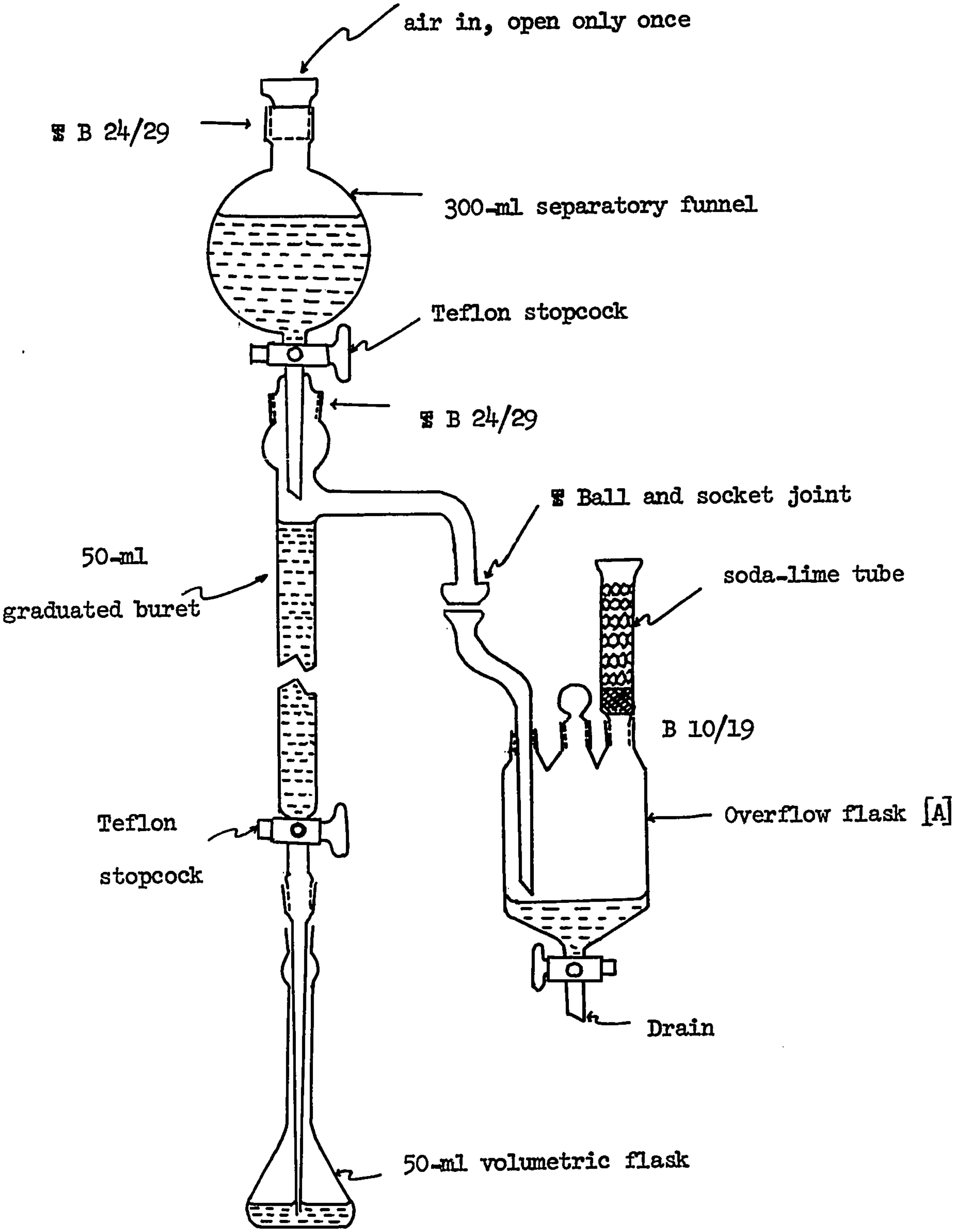


Fig. 3. Dispenser for anhydrous hydrogen halide solutions (not to scale).

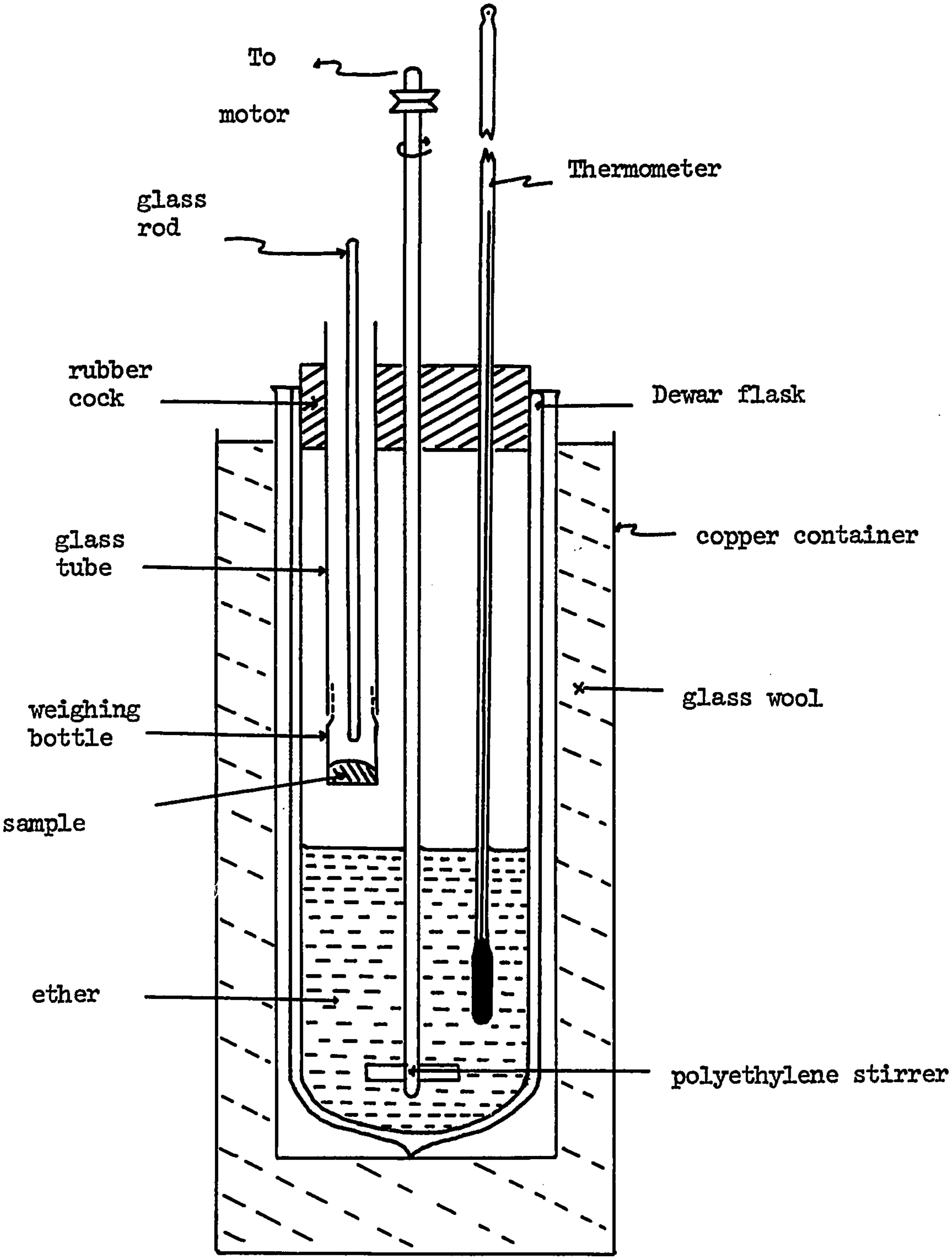


Fig. 4. Calorimeter

a volume of 20 ml. Its measuring sensitivity $\Delta D/D = 4 \times 10^{-5}$ (D is dielectric constant) at a measuring frequency of 2 megacycles/sec. The geometry of this cell was such that the instrument readings were strictly proportional to the dielectric constant of the liquid in the cell. The cell was maintained at constant temperature by circulation of constant-temperature water through its water jacket; the water was circulated from a Colora thermostat (Model NB 33655 Ultrathermostat) .

Automatic potentiometric titrator - a Radiometer pH meter type TTT1 , connected with a Radiometer Titrigraph, type SBR2. The titrator was assembled with a 5-ml buret (Radiometer type SBUI), a glass-calomel electrode pair, and a magnetic valve (Radiometer type MVVI) on the stand below the buret. There were three chart speeds. Full-scale deflection on the recorder chart indicated 5 ml with an accuracy of ± 0.001 ml.

EXPERIMENTAL AND RESULTS

I. Spectrophotometric method for the determination of the formation constants of tetrahaloferric acids in di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran.

(a) Synopsis

Ether solutions of ferric chloride and of tetrachloroferric acid exhibited quite different spectral transmission curves (Figs. 5 and 6) , and ether solutions of ferric bromide and of tetrabromoferric acid exhibited quite different spectral transmission curves (Figs. 7 and 8) . Moreover, the absorptivities of hydrogen chloride and of hydrogen bromide were found to be negligibly small at the three temperatures and over the visible and ultraviolet regions used in the present work. Consequently, absorbance measurements on ether solutions containing mixtures of the hydrogen halide and the corresponding ferric halide permitted the evaluation of the various equilibrium concentrations, and therefore of the equilibrium constant for reaction [1] .

$$HX + FeX_3 . S + S = HS_2^+ FeX_4^- \qquad [1]$$

First, the molar absorptivities of ferric chloride and of tetrachloroferric acid in each of the three ethers were determined at 25° C , 35° C , and 45° C . Then, ether solutions having a range of molar ratios of hydrogen chloride to ferric chloride were prepared, and the absorption spectra were recorded at the three temperatures. From these data ΔG^o, ΔH^o, and ΔS^o for reaction [1] with X = Cl, in the three ethers were calculated.

An identical procedure was used in order to evaluate ΔG^o, ΔH^o, and ΔS^o for reaction [1] with X = Br.

The $HX-FeX_3$-ether solutions were very hygroscopic ; absorption of water would have led to precipitation of hydrated ferric oxide. Moreover , even the anhydrous tetrahydrofuran solutions were not very stable ; they darkened after twenty-four hours. Therefore, both the stock solutions of ether-hydrogen chloride and those of iron-ether were prepared fresh daily, and the various determinations and measurements were made on the same day.

(b) Molar absorptivities of hydrogen halides and ferric halides

A cold stock solution of ferric halide in ether (approximately 10^{-3} M) was prepared by weighing the anhydrous solid, and dispensing it into pre-cooled dry ether. Six solutions with concentrations of ferric chloride ranging from 10^{-4} M to 10^{-5} M were made up in 50 ml volumetric flasks, by dilution of the stock solution dispensed from a buret. Beckman 1-cm silica cells with ground-glass stoppers were rinsed several times with the solution for measurement. They were then filled with the solution, capped, and removed to the thermostated cell chamber of the D. B. spectrophotometer. All the preparative operations in the present paragraph except the weighing of the solid were carried out in a dry box through which a continuous stream of dry nitrogen was passed. The dry box contained open beakers of indicating calcium sulphate. The solution was allowed to come to thermal equilibrium with the cell chamber (approximately 10 - 15 minutes). Then the spectrum of each ferric chloride solution was recorded from 400 - 250 mμ , using a hydrogen lamp source. The spectrophotometric blank was the pure solvent ether. The temperature of the solution in the cell chamber was measured with a thermocouple dipping into the sample solution and connected to a potentiometer .

The spectra of the ferric bromide solutions were similarly recorded from 600 - 320 mμ , using a tungsten lamp as the light source.

Stock solutions of hydrogen chloride and of hydrogen bromide in three ethers were prepared by using the apparatus shown in Fig. 2 . The separatory funnel containing the solution was removed to the dry box. An aliquot was taken for analysis of the hydrogen halide by using the procedure described in Appendix 6. A Beckman 1-cm silica cell was then rinsed, filled with solution, capped, and the absorption spectrum of the hydrogen halide in the ether was run against the pure solvent blank, in the D. B. spectrophotometer after the solution had come to thermal equilibrium.

(c) Molar absorptivities of tetrahaloferric (III) acids.

Solutions containing various ratios of hydrogen halide to ferric halide in each of the three ethers was prepared in the dry box. Thus a weighed amount of ferric halide was dissolved in the ether in the dry box and made up to volume. A stock solution of the hydrogen halide in the ether was prepared by using the apparatus in Fig. 2 and the separatory funnel was transferred to the dry box. The stock solution of the hydrogen halide was analyzed for its hydrogen halide content, by using the procedure given in Appendix 6 . The concentration of ferric halide of the stock solution was analyzed for iron by using the procedure given in Appendix 2 . Various known volumes of the hydrogen halide solution and of the ferric halide solution were then dispensed from burets in the dry box into a volumetric flask and the solution made up to volume with the particular ether . The absorbance of each of the solutions was then measured on the Beckman DB Spectrophotometer against a spectrophotometric blank consisting of the pure solvent ether.

The measurement showed that when the concentration of hydrogen halide exceeding 0.2 M for an iron concentration of 10^{-4} M - 10^{-5} M , the absorbance was no longer a measurable function of the hydrogen halide concentration. Therefore above 0.02 M of the hydrogen halide, essentially all the iron must have existed as the tetrahaloferric acid.

Therefore a 0.05 M hydrogen halide-ether solution was prepared. Aliquots of 2 to 12 ml of 10^{-3} M ferric halide stock solution in the same ether were delivered into 50-ml volumetric flasks which were then made up to the mark with the 0.5 M hydrogen halide solution in the same ether. The absorption spectra of these solutions were then recorded against the pure ether as the spectrophotometric blank, by using the same technique as described in Section (b) above.

(d) Results of the absorbance measurements

The absorbance measurements on the solutions described in the Subsections (b) and (c) are entered in Tables 1 and 12 and illustrated in Figs 5 to 8 inclusive. In each Table, the absorbances are given both as a function of wavelength and of the concentration of the hydrogen halide, ferric halide, or tetrahaloferric acid in the particular ether, against the pure ether as the spectrophotometric blank.

For each of the systems reported in Tables 1 to 12, and at each of the wavelengths, Beer's law was found to be obeyed over the entire concentration range used. Therefore the absorptivities for each system at each wavelength were averaged and the average molar absorptivity and its standard deviation are given in the last rows of Tables 1 to 12.

In the case of all systems reported in Tables 1 to 12, the molar absorptivities were found not to be a measurable function of temperature over the range 25.0°C to 45.0°C. For this reason, temperatures have not been reported in those Tables.

(e) Formation constants of tetrahaloferric acids

Stock solutions of ferric chloride, ferric bromide, hydrogen chloride, and hydrogen bromide were prepared separately in each ether. These twelve stock solutions were then analyzed by the methods described in Appendices 2 and 6. From these solutions, 10^{-3} M in ferric chloride or in ferric bromide, and standard working solutions 10^{-3} -10^{-4} M in hydrogen chloride or hydrogen bromide were prepared in each of the three ethers. Then, aliquots 2 - 12 ml of the 10^{-3} M ferric halide-ether stock solution were delivered into 50-ml volumetric flasks, and diluted to the mark with the standard 10^{-3} - 10^{-4} M hydrogen halide-ether stock solution.

With the solutions still in the dry box, the glass stoppered 1-cm silica cells were rinsed and filled in turn with the ferric halide-hydrogen halide-ether solutions, capped, and placed in the thermostated cell compartment of the DB Spectrophotometer. After temperature equilibrium had been reached, and the temperature of the solution recorded, its absorption spectrum was recorded against the pure solvent as the spectrophotometric blank.

(f) Analysis for iron and hydrogen halide

After the spectra had been recorded, each ether solution referred to in Subsection (b), (c), and (e) above was analyzed for its iron and hydrogen halide contents.

For iron, exactly 15 ml were pipetted into a 30-ml beaker,and the ether was evaporated on a steam bath in the fume-hood.The residue was dissolved in 3 ml of hydrochloric acid (1:1) and transferred quantitatively into a 50-ml volumetric flask. The iron was then determined colorimetrically with salicylic acid (36,37). Details of the determination are in Appendix 2 .

For hydrogen halide, exactly 25 ml of the ether solution were pip etted into a 250-ml beaker containing 100 ml of distilled water.

The total chloride was determined by potentiometric titration against standard 0.01 M sodium hydroxide, with an automatic titrator (Radiometer). It was found unnecessary to remove the ether phase; it did not interfere with the potentiometric titration. From the total chloride molarity determined this way, three times the molarity of iron (determined separately) was subtracted. The difference gave the total (stoichiometric) molarity of hydrogen chloride.

(g) Results of absorbance measurements

The absorbance measurements for all of the solutions refer to in Subsection (e) above are contained in Tables 13-30 inclusive. Absorbance measurement values are in all cases for a 1-cm path length. The concentrations of hydrogen halide and of ferric halide given in columns (1) and (2) respectively of each Table refer to the stoichiometric concentrations, not to the equilibrium concentrations.

In addition to the absorbance values, apparent absorptivities have been calculated. For the purpose of Tables 13- 30, apparent absorptivity, a , is defined as follows:-

$$a = A/(FeX_3)_T$$

(h) Treatment of the spectrophotometric data

The spectrophotometric data in Tables 13-30 inclusive were used to calculate the equilibrium constant for reaction [1] .

$$HX + FeX_3.S + S = HS_2^+FeX_4^- \qquad [1]$$

Table 1 Absorbance of $FeCl_3$-di-isopropyl ether solutions as a function of wavelength and concentration of $FeCl_3$, and mean absorptivity of $FeCl_3$.

Concentration $\times 10^4$ M	Absorbances of solutions at various wavelengths, 390–290 mμ.									
	390	380	370	360	350	340	330	310	300	290
1.609	0.300	0.417	0.591	0.810	1.001	1.045	0.942	0.729	0.640	0.537
1.351	0.250	0.348	0.496	0.680	0.840	0.880	0.789	0.605	0.532	0.450
1.132	0.210	0.210	0.291	0.415	0.570	0.706	0.738	0.661	0.510	0.447
0.908	0.170	0.230	0.355	0.456	0.570	0.591	0.530	0.409	0.360	0.300
0.680	0.128	0.175	0.250	0.342	0.425	0.441	0.400	0.310	0.270	0.250
0.420	0.080	0.108	0.156	0.212	0.263	0.272	0.245	0.191	0.168	0.142
Absorptivity	1860	2600	3680	5020	6220	6500	5830	4500	3950	3340
* s.d.	20	27	34	51	62	55	58	44	40	32

* s.d. = standard deviation

Table 2 Absorbance of $HFeCl_4$- di-isopropyl ether solutions as a function of wavelength and concentration of $HFeCl_4$, and mean absorptivity of $HFeCl_4$.

Molarity of HCl: 0.5 M.

Concentration $\times 10^4$ M	Absorbances of solutions at various wavelengths, 390-290 mμ									
	390	380	370	360	350	340	330	310	300	290
0.418	0.109	0.183	0.259	0.272	0.213	0.158	0.191	0.259	0.228	0.168
1.456	0.378	0.638	0.903	0.946	0.743	0.550	0.670	0.903	0.794	0.590
0.991	0.258	0.434	0.613	0.664	0.505	0.874	0.456	0.613	0.540	0.401
0.624	0.162	0.273	0.387	0.406	0.317	0.236	0.287	0.388	0.340	0.254
1.135	0.295	0.497	0.704	0.739	0.579	0.429	0.522	0.704	0.617	0.459
1.512	0.393	0.663	0.928	0.982	0.770	0.572	0.696	0.937	0.824	0.612
Absorptivity	2600	4380	6200	6500	5100	3780	4600	6200	5450	4074
* s.d.	24	44	60	62	52	38	45	60	57	42

* s. d. = standard deviation

Table 3 Absorbance of $FeBr_3$ - di-isopropyl ether solution as a function of wavelength and concentration of $FeBr_3$, and mean absorptivity of $FeBr_3$.

Concentration	Absorbances of solutions at various wavelengths, 510-410 mμ.									
x 10^4 M	510	500	490	480	470	460	440	430	420	410
2.335	0.397	0.472	0.560	0.635	0.723	0.907	1.331	1.471	1.460	1.331
2.148	0.365	0.434	0.516	0.584	0.666	0.836	1.224	1.353	1.343	1.224
1.562	0.264	0.316	0.376	0.425	0.484	0.607	0.890	0.984	0.976	0.890
1.133	0.193	0.228	0.272	0.308	0.351	0.441	0.646	0.714	0.708	0.647
0.840	0.143	0.170	0.202	0.228	0.260	0.327	0.479	0.529	0.525	0.479
0.778	0.132	0.157	0.187	0.211	0.241	0.303	0.442	0.490	0.486	0.443
Absorptivity	1700	2020	2400	2720	3100	3890	5700	6300	6250	5700
* s. d.	15	18	26	28	30	40	59	61	60	58

* s. d. = standard deviation

Table 4 Absorbance of $HFeBr_4$ - di-isopropyl ether solutions as a function of wavelength and concentration of $HFeBr_4$, and mean absorptivity of $HFeBr_4$.

Molarity of HBr : 0.5 M.

Concentration	Absorbances of solutions at various wavelengths, 510-410 mµ.									
x 10^4 M	510	500	490	480	470	460	440	430	420	410
2.122	0.525	0.807	0.983	1.215	1.290	1.192	0.998	1.045	1.086	1.121
1.840	0.455	0.700	0.852	1.055	1.119	1.035	0.864	0.915	0.942	0.972
1.380	0.342	0.535	0.639	0.790	0.839	0.775	0.648	0.686	0.706	0.729
1.179	0.291	0.448	0.546	0.675	0.717	0.662	0.554	0.586	0.604	0.623
0.920	0.228	0.350	0.422	0.525	0.559	0.517	0.432	0.457	0.471	0.486
0.632	0.156	0.240	0.292	0.361	0.384	0.355	0.297	0.314	0.323	0.334
Absorptivity	2474	3800	4627	5723	6080	5618	4696	4969	5120	5283
s. d.	22	41	37	58	61	55	47	51	54	50

s. d. = standard deviation

Table 5 Absorbance of $FeCl_3$ in di-n-butyl ether as a function of wavelength and concentration of $FeCl_3$, and mean absorptivity of $FeCl_3$.

Concentration	Absorbances of solutions at various wavelengths , 390-300 mμ.									
x 10^4 M	390	380	370	360	350	340	330	320	310	300
1.970	0.311	0.510	0.756	1.070	1.310	1.395	1.279	1.011	0.839	0.784
1.594	0.253	0.415	0.612	0.856	1.049	1.129	1.034	0.818	0.679	0.633
1.186	0.186	0.307	0.455	0.638	0.788	0.841	0.770	0.609	0.506	0.472
1.110	0.180	0.290	0.431	0.602	0.741	0.795	0.712	0.570	0.474	0.445
1.576	0.245	0.386	0.576	0.805	1.014	1.095	1.000	0.790	0.652	0.616
2.507	0.400	0.641	0.962	1.325	1.660	1.801	1.643	1.287	1.064	1.001
Absorptivity	1580	2588	3833	5382	6646	7089	6491	5134	4266	3981
s. d.	16	25	38	54	66	71	65	52	41	39

s. d. = standard deviation

Table 6 Absorbance of $HFeCl_4$ in di-n-butyl ether as a function of wavelength and concentration of $HFeCl_4$, and mean absorptivity of $HFeCl_4$.

Molarity of HCl: 0.5 M.

Concentration	Absorbances of solutions at various wavelengths, 390-300 mµ.									
x 10^4 M	390	380	370	360	350	340	330	320	310	300
2.990	0.851	1.369	1.834	1.945	1.548	1.285	1.482	1.831	1.791	1.481
1.800	0.512	0.824	1.104	1.170	0.931	0.774	0.891	1.102	1.077	0.891
1.021	0.291	0.467	0.626	0.663	0.528	0.438	0.505	0.625	0.611	0.505
2.095	0.597	0.960	1.286	1.363	1.085	0.901	1.038	1.283	1.255	1.038
1.522	0.433	0.696	0.933	0.987	0.787	0.650	0.754	0.932	0.910	0.755
1.117	0.318	0.511	0.685	0.726	0.578	0.481	0.553	0.684	0.670	0.554
Absorptivity	2864	4578	6134	6504	5177	4299	4956	6124	5989	4954
s. d.	29	46	61	66	52	43	50	62	61	50

s. d. = standard deviation

Table 7 Absorbance of $FeBr_3$ in di-n-butyl ether as a function of wavelength and concentration of $FeBr_3$, and mean absorptivity of $FeBr_3$.

Concentration	Absorbances of solutions at various wavelengths, 510-410 mμ.									
x 10^4 M	510	500	490	480	470	460	440	430	420	410
2.041	0.347	0.412	0.495	0.573	0.680	0.820	1.108	1.286	1.285	1.193
2.596	0.427	0.522	0.625	0.724	0.850	1.041	1.495	1.634	1.630	1.521
1.567	0.266	0.326	0.400	0.453	0.525	0.635	0.895	0.977	0.980	0.919
1.468	0.244	0.298	0.355	0.413	0.485	0.590	0.842	0.920	0.918	0.850
1.343	0.230	0.279	0.330	0.381	0.445	0.540	0.762	0.832	0.842	0.778
0.776	0.130	0.159	0.185	0.222	0.251	0.313	0.447	0.483	0.484	0.447
Absorptivity	1669	2027	2425	2815	3282	4041	5764	6272	6264	5811
s. d.	17	20	25	28	33	39	58	63	63	60

s. d. = standard deviation

Table 8 Absorbance of HFeBr$_4$ in di-n-butyl ether as a function of wavelength and concentration of HFeBr$_4$, and mean absorptivity of HFeBr$_4$.

Concentration	Absorbances of solutions at various wavelengths, 510-410 mμ.									
x 10^4 M	510	500	490	480	470	460	440	430	420	410
1.768	0.432	0.595	0.796	0.960	1.005	0.950	0.837	0.875	0.882	0.922
0.913	0.225	0.309	0.415	0.500	0.521	0.499	0.432	0.454	0.463	0.484
1.647	0.404	0.540	0.728	0.883	0.930	0.892	0.780	0.797	0.828	0.869
1.582	0.388	0.535	0.715	0.858	0.899	0.749	0.782	0.792	0.835	0.860
2.032	0.500	0.690	0.915	1.110	1.155	1.110	0.962	1.020	1.035	1.072
0.895	0.220	0.303	0.405	0.490	0.509	0.486	0.424	0.443	0.450	0.472
Absorptivity	2454	3382	4519	5424	5683	5438	4733	4944	5024	5278
s. d.	26	34	47	53	57	54	48	50	52	53

s. d. = standard deviation

Table 9 Absorbance of $FeCl_3$ in tetrahydrofuran as afunction of wavelength and concentration of $FeCl_3$, and mean absorptivity of $FeCl_3$.

Concentration	Absorbances of solutions at various wavelengths, 390-300 mμ.									
x 10^4 M	390	380	370	360	350	340	330	320	310	300
2.621	0.520	0.817	1.170	1.560	1.807	2.000	1.861	1.542	1.310	1.220
1.880	0.375	0.600	0.840	1.130	1.296	1.412	1.335	1.100	0.913	0.875
1.194	0.234	0.368	0.530	0.689	0.823	0.897	0.848	0.702	0.586	0.557
1.222	0.250	0.380	0.540	0.702	0.835	0.918	0.858	0.720	0.600	0.568
1.222	0.256	0.378	0.552	0.700	0.840	0.919	0.860	0.719	0.610	0.571
1.378	0.275	0.435	0.615	0.791	0.942	1.033	0.975	0.815	0.677	0.642
Absorptivity	2009	3124	4462	5768	6894	7511	7100	5881	4912	4650
s. d.	22	32	44	58	69	76	69	59	52	47

s. d. = standard deviation

Table 10 Absorbance of $HFeCl_4$ in tetrahydrofuran as a function of wavelength and concentration $HFeCl_4$, and mean absorptivity of $HFeCl_4$.

Molarity of HCl: 0.5 M.

Concentration x 10^4 M	Absorbances of solutions at various wavelengths, 390-300 mμ.									
	390	380	370	360	350	340	330	320	310	300
1.582	0.452	0.790	1.100	1.128	0.800	0.566	0.771	1.050	1.060	0.823
2.028	0.622	1.069	1.538	1.562	1.080	0.785	1.063	1.462	1.460	1.170
1.361	0.389	0.679	0.951	0.970	0.670	0.487	0.655	0.908	0.907	0.710
1.629	0.460	0.802	1.141	1.168	0.820	0.587	0.785	1.089	1.087	0.865
2.037	0.581	1.022	1.432	1.450	1.000	0.726	0.995	1.354	1.360	1.060
0.483	0.138	0.241	0.338	0.343	0.238	0.173	0.235	0.320	0.331	0.256
Absorptivity	2863	4991	6991	7111	4929	3584	4852	6650	6668	5291
s.d.	29	51	63	70	50	32	49	67	67	53

s. d. = standard deviation

Table 11 Absorbance of $FeBr_3$ in tetrahydrofuran as a function of wavelength and concentration of $FeBr_3$, and mean absorptivity of $FeBr_3$.

Concentration	Absorbances of solutions at various wavelengths, 520-380 mµ.									
x 10^4 M	520	510	500	490	480	470	410	400	390	380
2.901	0.241	0.348	0.496	0.678	0.865	0.985	1.188	1.105	1.015	0.942
1.755	0.144	0.210	0.297	0.410	0.528	0.615	0.705	0.684	0.626	0.595
2.095	0.171	0.248	0.352	0.485	0.626	0.730	0.859	0.803	0.737	0.687
2.835	0.237	0.340	0.479	0.660	0.837	0.960	10185	1.105	1.021	0.941
1.394	0.120	0.165	0.232	0.323	0.417	0.480	0.573	0.536	0.493	0.459
3.253	0.268	0.385	0.543	0.745	0.947	1.115	1.374	1.260	1.152	1.080
Absorptivity	827	1193	1690	2314	2936	3398	4100	3837	3527	3283
s. d.	10	12	12	22	27	35	40	39	34	33

s. d. = standard deviation

Table 12 Absorbance of $HFeBr_4$ in tetrahydrofuran as a function of wavelength and concentration of $HFeBr_4$, and mean absorptivity of $HFeBr_4$.

Molarity of HBr : 0.5 M.

Concentration	Absorbances of solutions at various wavelengths , 520-380 mμ.									
x 10^4 M	520	510	500	490	480	470	410	400	390	380
2.184	0.405	0.585	0.797	1.065	1.278	1.302	1.148	1.258	1.296	1.170
1.9100	0.350	0.500	0.689	0.922	1.110	1.140	0.966	1.094	1.138	1.022
1.421	0.260	0.370	0.515	0.691	0.833	0.842	0.741	0.828	0.845	0.758
2.029	0.371	0.530	0.730	0.975	1.178	1.198	1.062	1.159	1.193	1.082
1.880	0.342	0.487	0.672	0.902	1.078	1.091	0.962	1.070	1.102	0.990
1.238	0.228	0.325	0.447	0.600	0.721	0.736	0.647	0.714	0.736	0.661
Absorptivity	1844	2629	3610	4863	5824	5945	5255	5775	5931	5325
s.d.	18	25	37	49	58	53	58	59	52	57

s. d. = standard deviation

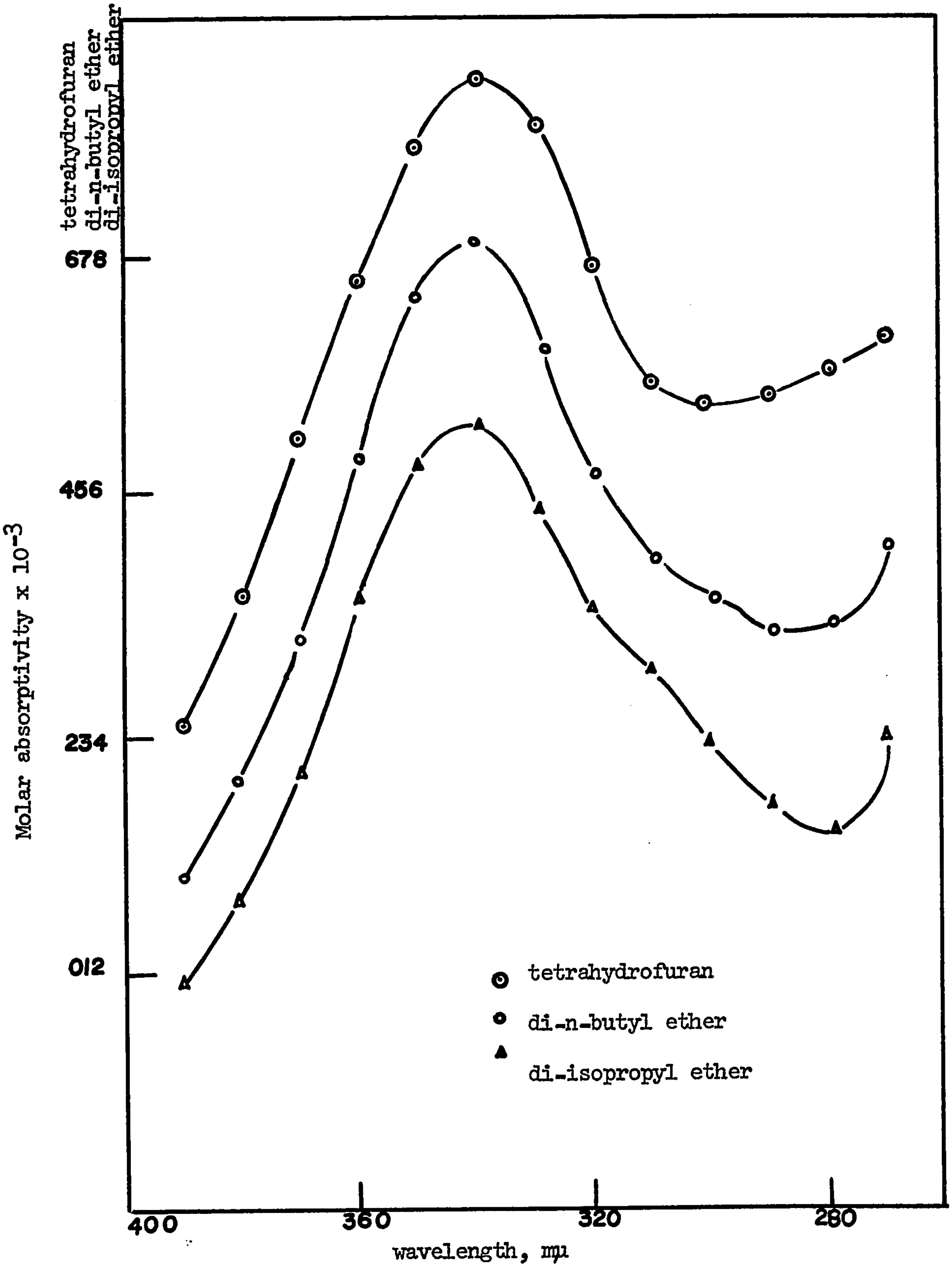


Fig. 5. Molar absorptivity of ferric chloride in three ethers

Data: Tables 1,5,9.

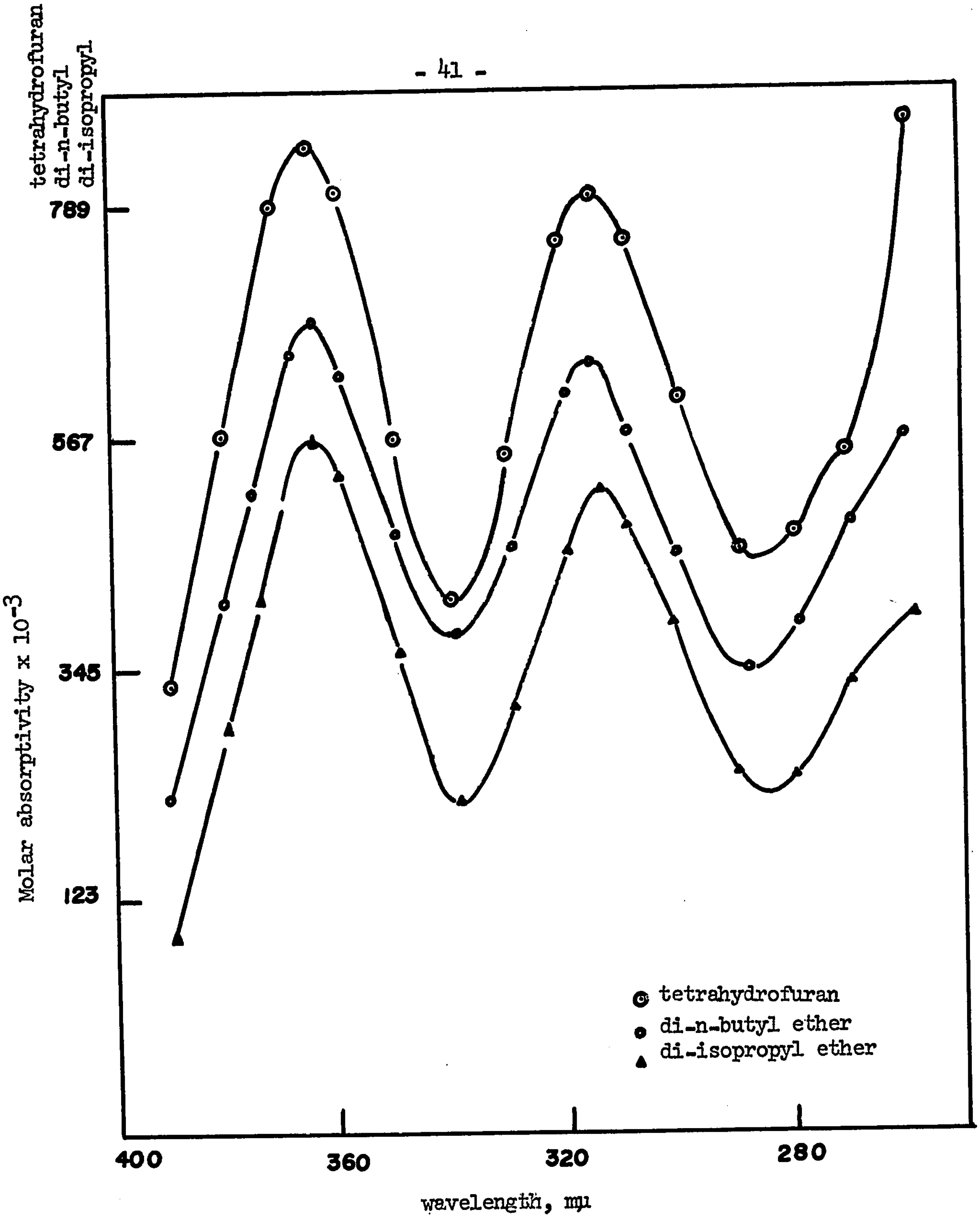


Fig. 6. Molar absorptivity of tetrachloroferric acid in three ethers

Data: Tables 2,6,10.

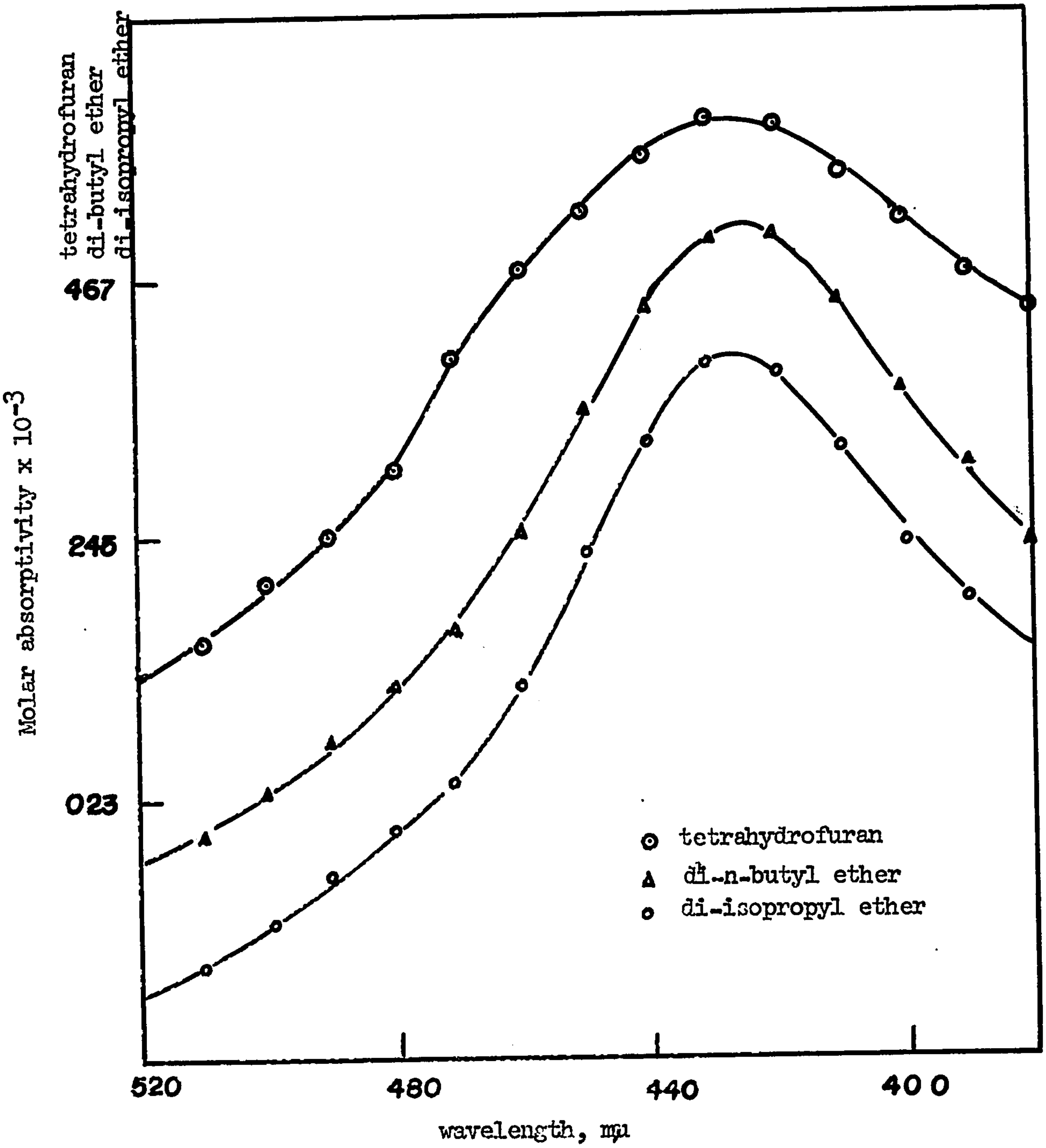


Fig. 7. Molar absorptivity of ferric bromide in three ethers

Data: Tables 3,7,11.

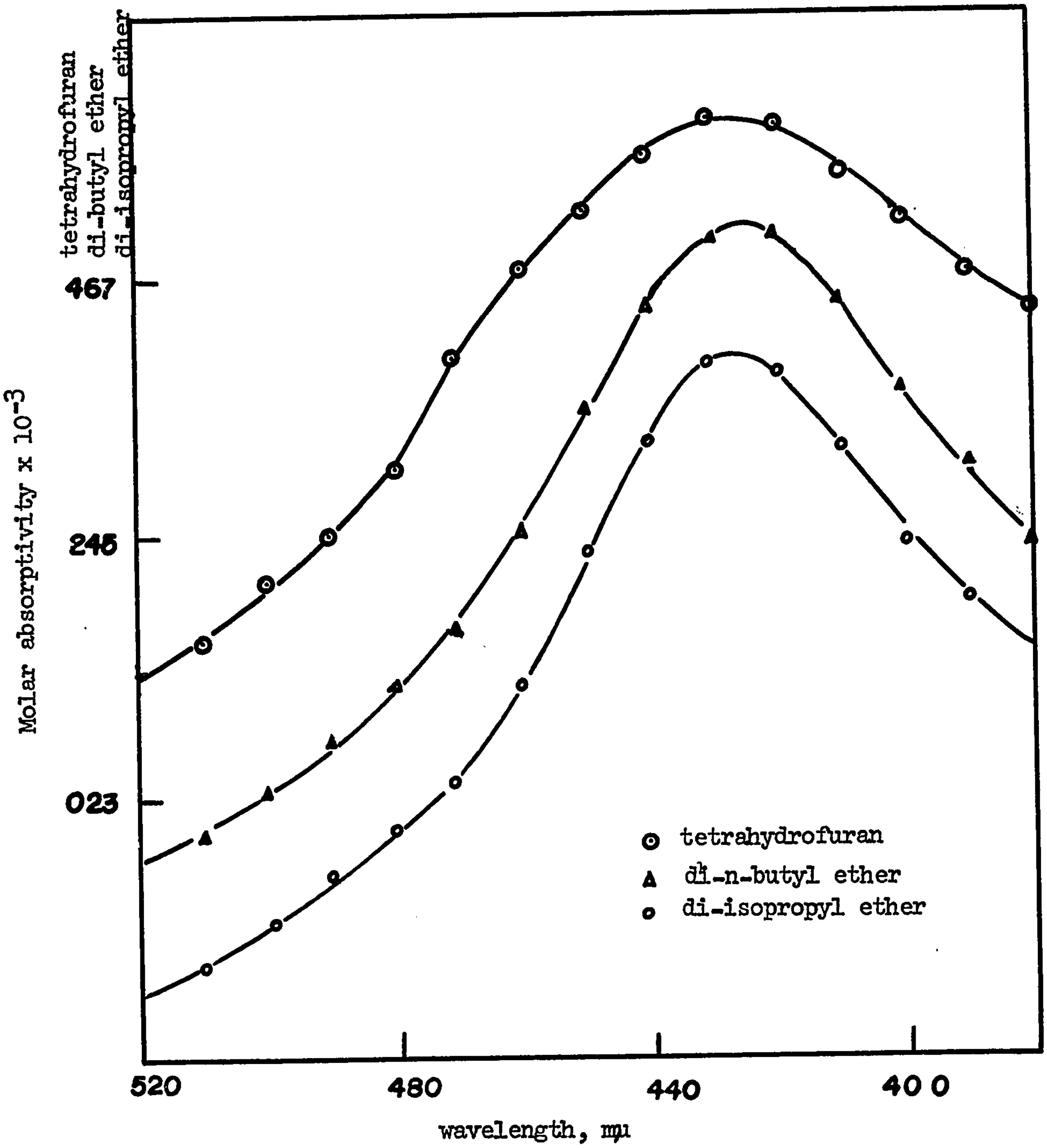


Fig. 7. Molar absorptivity of ferric bromide in three ethers

Data: Tables 3,7,11.

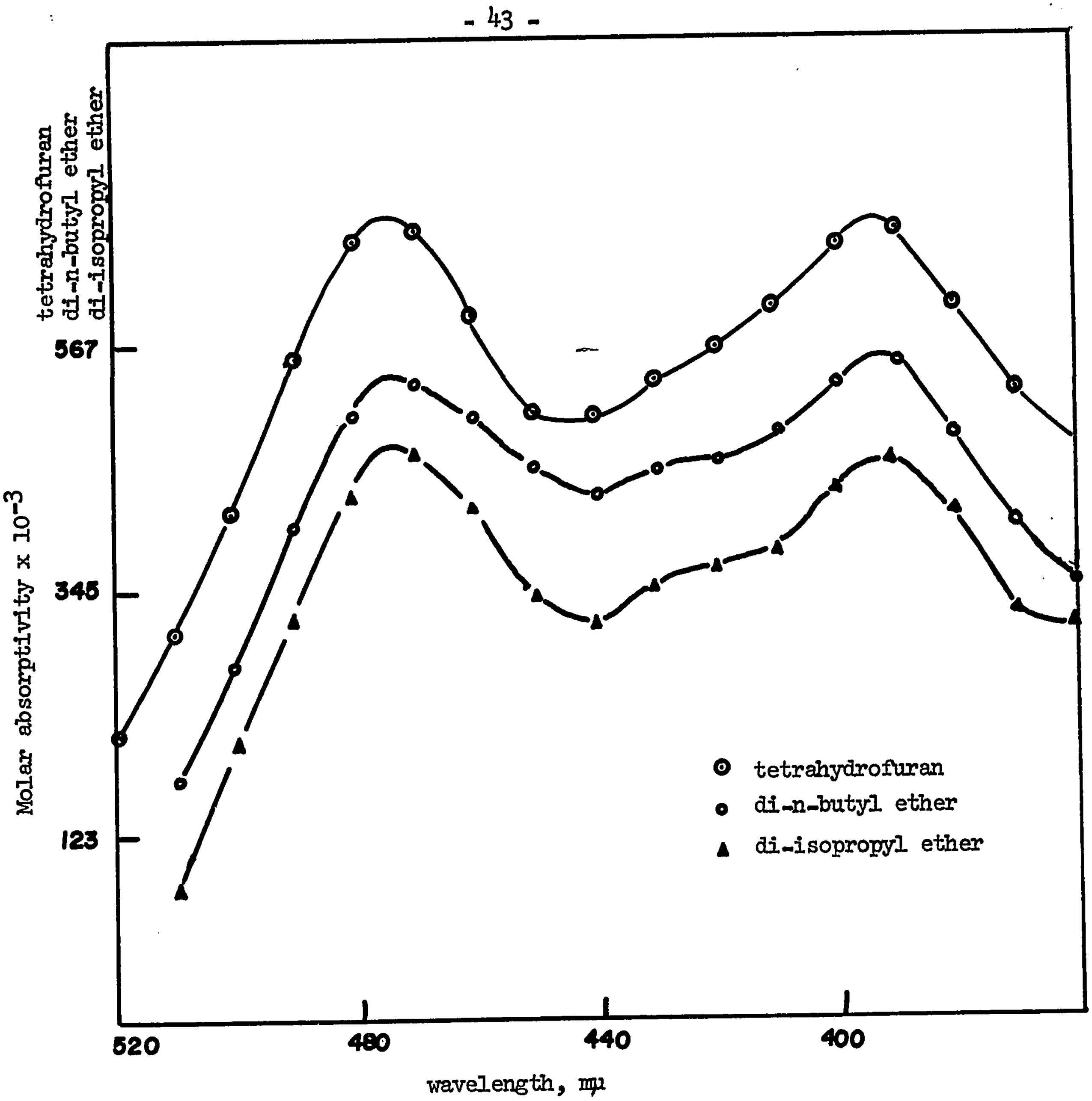


Fig. 8. Molar absorptivity of tetrabromoferric acid in three ethers

Data: Tables 4,8,12.

Table 13 Absorbance and apparent absorptivity of di-n-butyl ether solutions of $FeCl_3$-HCl at 25.0° C, for various wavelengths.

$(HCl)_T$** x 10^3M	$(FeCl_3)_T$ ** x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number) * wavelength, mμ ⟶ 390	380	370	360	350	340	330	320	310	300
9.640	2.555	0.684 2677	1.097 4294	1.481 5797	1.623 6351	1.378 5392	1.192 4666	1.324 5181	1.528 5982	1.468 5746	1.230 4816
1.754	2.465	0.550 2230	0.894 3628	1.235 5010	1.465 5943	1.448 5873	1.441 5682	1.401 5695	1.404 5635	1.389 5148	1.269 4484
1.040	2.043	0.420 2054	0.681 3335	0.960 4701	1.187 5810	1.242 6081	1.228 6010	1.208 5911	1.128 5523	1.005 4920	0.891 4364
1.380	1.972	0.428 2171	0.690 3498	0.967 4906	1.160 5882	1.179 3980	1.144 5801	1.142 5792	1.101 5581	0.990 5022	0.870 4419
1.042	1.322	0.272 2065	0.445 3368	0.626 4734	0.771 5823	0.802 6070	0.787 5965	0.776 5872	0.730 5525	0.654 4946	0.576 4356
8.334	1.443	0.381 2641	0.615 4261	0.834 5779	0.913 6328	0.782 5418	0.681 4717	0.750 5200	0.861 5969	0.826 5725	0.693 4802
4.049	1.506	0.375 2488	0.604 4013	0.829 5502	0.932 6185	0.842 5596	0.764 5075	0.809 5374	0.878 5832	0.828 5501	0.705 4683
1.636	1.345	0.299 2221	0.484 3598	0.670 4985	0.789 5930	0.792 5886	0.759 5646	0.772 5740	0.757 5629	0.694 5162	0.603 4480
1.405	1.569	0.338 2154	0.547 3489	0.768 4895	0.926 5899	0.933 5944	0.906 5773	0.906 5777	0.875 5578	0.790 5036	0.694 4424
14.29	2.328	0.634 2723	1.022 4389	1.376 5911	1.488 6391	1.238 5320	1.052 4517	1.188 5103	1.404 6032	1.354 5814	1.131 4857

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Table 13 continued

6.321	1.433	0.373 2600	0.600 4187	0.814 5681	0.901 6285	0.786 5484	0.691 4822	0.754 5263	0.849 5922	0.811 5656	0.684 4770
6.016	1.667	0.432 2592	0.693 4155	0.945 5666	1.045 6270	0.914 5482	0.802 4811	0.877 5262	0.988 5927	0.938 5627	0.792 4749
1.335	1.800	0.390 2164	0.623 3459	0.875 4863	1.058 5878	1.079 5997	1.044 5799	1.042 5991	1.002 5569	0.907 5039	0.797 4425
6.212	1.953	0.505 2585	0.814 4167	1.104 5654	1.225 6274	1.068 5466	0.942 4825	1.030 5275	1.157 5925	1.102 5641	0.930 4760

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* Apparent absorptivity, a = Absorbance / $(FeCl_3)_T$

** In Tables 13- 30 inclusive, $(HX)_T$ and $(FeCl_3)_T$ refer to total, ie. stoichiometric concentrations of HX and $FeCl_3$, respectively.

Table 14 Absorbance and apparent absorptivity of di-n-butyl ether solutions of $FeCl_3$-HCl at 35.0°C, for various wavelengths.

$(HCl)_T$**	$(FeCl_3)_T$**	Absorbance (upper number) Apparent absorptivity (lower number)*									
x 10^3M	x 10^4M	wavelength, mμ ⟶									
		390	380	370	360	350	340	330	320	310	300
9.640	2.555	0.644 2519	1.049 4104	1.425 5578	1.593 6235	1.412 5528	1.272 4977	1.857 5313	1.507 5898	1.416 5542	1.207 4722
1.754	2.465	0.496 2014	0.816 3311	1.141 4629	1.422 5769	1.517 6153	1.507 6112	1.463 5935	1.350 5479	1.200 4868	1.067 4329
1.040	2.043	0.387 1896	0.627 3068	0.892 4368	1.156 5658	1.288 6306	1.305 6388	1.252 6127	1.099 5378	0.960 4698	0.859 4207
1.380	1.972	0.387 1961	0.624 3165	0.889 4506	1.128 5721	1.225 6211	1.220 6186	1.185 6011	1.069 5420	0.945 4790	0.847 4294
1.042	1.321	0.249 1886	0.407 3079	0.585 4427	0.746 5646	0.830 6281	0.840 6352	0.809 6118	0.712 5384	0.619 4682	0.560 4232
8.334	1.443	0.359 2489	0.582 4036	0.797 5524	0.896 6210	0.805 5576	0.726 5032	0.772 5349	0.846 5863	0.801 5553	0.675 4677
4.049	1.506	0.342 2270	0.560 3717	0.776 5152	0.908 6027	0.877 5826	0.833 5534	0.847 5627	0.856 5685	0.787 5227	0.688 4568
1.636	1.345	0.270 2004	0.444 3299	0.620 4611	0.777 5774	0.829 6162	0.821 6102	0.803 5970	0.727 5481	0.655 4867	0.582 4328
1.405	1.569	0.309 1970	0.502 3197	0.712 4540	0.898 5726	0.971 6187	0.977 6225	0.944 6015	0.855 5448	0.755 4813	0.672 4281
14.29	2.328	0.609 2616	0.978 4200	1.335 5735	1.467 6303	1.266 5437	1.100 4724	1.220 5240	1.388 5962	1.323 5683	1.111 4771

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Table 14 continued.

6.321	1.433	0.348	0.559	0.774	0.880	0.809	0.745	0.784	0.829	0.783	0.668
		2431	3900	5404	6140	5648	5196	5471	5782	5462	4659
6.016	1.667	0.402	0.650	0.891	1.022	0.943	0.872	0.911	0.967	0.904	0.770
		2410	3899	5346	6163	5659	5234	5464	5800	5422	4621
1.335	1.800	0.350	0.571	0.810	1.031	1.117	1.126	1.089	0.975	0.857	0.767
		1947	3175	4501	5724	6204	6255	6048	5415	4753	4263
6.212	1.953	0.475	0.769	1.047	1.196	1.108	1.012	1.068	1.134	1.056	0.904
		2434	3937	5362	6122	5673	5182	5470	5807	5405	4628

* Apparent absorptivity = Absorbance / $(FeCl_3)_T$

Table 15 Absorbance and apparent absorptivity of di-n-butyl ether solutions of $FeCl_3$-HCl at 45.0°C for various wavelengths.

$(HCl)_T$ x 10^3M	$(FeCl_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)*									
		wavelength, mμ ⟶ 390	380	370	360	350	340	330	320	310	300
9.614	2.555	0.593 2320	0.962 3763	1.334 5220	1.548 6060	1.477 5781	1.361 5329	1.415 5539	1.464 5731	1.359 5317	1.165 4560
1.754	2.465	0.454 1840	0.744 3018	1.064 4316	1.391 5642	1.559 6326	1.601 6493	1.518 6159	1.317 5342	1.150 4664	1.033 4192
1.040	2.043	0.359 1759	0.585 2864	0.847 4143	1.133 5548	1.313 6427	1.364 6679	1.283 6278	1.076 5268	0.924 4521	0.843 4125
1.380	1.972	0.358 1816	0.581 2946	0.837 4242	1.099 5575	1.257 6376	1.295 6566	1.227 6221	1.047 5310	0.901 4568	0.820 4158
1.042	1.322	0.232 1752	0.378 2858	0.551 4169	0.732 5536	0.851 6434	0.886 6702	0.829 6274	0.698 5278	0.595 4501	0.545 4121
8.334	1.443	0.332 2304	0.536 3714	0.739 5124	0.870 6027	0.840 5829	0.778 53883	0.814 5639	0.821 5690	0.753 5219	0.653 4524
4.049	1.506	0.311 2086	0.513 3409	0.714 4740	0.875 5807	0.915 6076	0.905 6012	0.883 5860	0.832 5534	0.744 4942	0.656 4357
1.636	1.345	0.249 1852	0.405 3013	0.583 4333	0.755 5612	0.851 6327	0.872 6480	0.830 6171	0.719 5349	0.625 4644	0.564 4192
1.405	1.569	0.285 1819	0.462 2945	0.666 4244	0.878 5596	1.001 6381	1.027 6548	0.975 6217	0.833 5311	0.720 4588	0.652 4157
14.29	2.328	0.573 2459	0.922 3960	1.263 5425	1.436 6168	1.312 5638	1.202 5164	1.265 5433	1.355 5819	1.268 5446	1.082 4649

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Table 15 continued.

6.321	1.433	0.319	0.511	0.710	0.850	0.845	0.815	0.818	0.805	0.737	0.641
		2228	3564	4954	5929	4898	5687	5710	5618	5141	4475
6.016	1.667	0.370	0.595	0.830	0.990	0.982	0.948	0.952	0.937	0.849	0.746
		2221	3566	4982	5940	5894	5684	5714	5624	5092	4477
1.335	1.800	0.323	0.521	0.761	1.006	1.153	1.184	1.118	0.955	0.825	0.746
		1793	2894	4230	5589	6403	6579	6213	5307	4581	4143
6.212	1.953	0.435	0.699	0.972	1.157	1.152	1.099	1.119	1.099	0.994	0.874
		2227	3578	4975	5924	5900	5625	5732	5628	5091	4474

* Apparent absorptivity = Absorbance / $(FeCl_3)_T$

Table 16 Absorbance and apparent absorptivity of di-n-butyl ether solutions of $FeBr_3$- HBr at 25.0°C, for various wavelengths.

$(HBr)_T$ x 10^4M	$(FeBr_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mμ ⟶									
		510	500	490	480	470	460	440	430	420	410
14.38	1.354	0.324	0.444	0.589	0.707	0.743	0.722	0.652	0.684	0.694	0.720
		2390	3280	4351	5223	5485	5334	4815	5053	5122	5319
10.48	1.182	0.280	0.383	0.509	0.611	0.641	0.625	0.573	0.601	0.610	0.631
		2370	3239	4304	5165	5421	5290	4844	5081	5161	5336
3.910	1.770	0.394	0.528	0.691	0.820	0.882	0.886	0.891	0.945	0.954	0.962
		2223	2987	3902	4631	3983	5008	5032	5339	5389	5437
3.471	2.088	0.456	0.610	0.789	0.938	1.011	1.031	1.061	1.130	1.137	1.140
		2185	2920	3780	4491	4841	4939	5080	5410	5447	5458
5.874	1.622	0.374	0.504	0.669	0.798	0.848	0.835	0.800	0.844	0.855	0.873
		2306	3109	4125	4919	5228	5151	4934	5206	5269	5381
7.615	2.105	0.490	0.666	0.885	1.054	1.119	1.097	1.032	1.084	1.099	1.128
		2326	3165	4203	5007	5314	5212	4905	5151	5220	5360
3.540	1.520	0.335	0.448	0.585	0.704	0.750	0.762	0.769	0.813	0.821	0.827
		2203	2950	3850	4631	4932	5011	5059	5351	5398	5440
4.460	2.100	0.469	0.633	0.828	0.986	1.052	1.058	1.053	1.115	1.125	1.139
		2223	3016	3945	4696	5011	5039	5014	5308	5355	5424
5.370	1.250	0.287	0.390	0.513	0.611	0.650	0.643	0.617	0.653	0.660	0.674
		2297	3118	4107	4889	5202	5144	4935	5221	5277	5390
8.285	3.215	0.749	1.012	1.340	1.602	1.706	1.670	1.577	1.662	1.681	1.727
		2328	3149	4168	4984	5307	5194	4905	5169	5229	5370

* Apparent absorptivity = Absorbance / $(FeBr_3)_T$

Table 17 Absorbance and apparent absorptivity of di-n-butyl ether solutions of $FeBr_3$-HBr at 35.0°C, for various wavelengths.

$(HBr)_T$ x 10^4 M	$(FeBr_3)_T$ x 10^4 M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mμ ⟶									
		510	500	490	480	470	460	440	430	420	410
14.38	1.354	0.316 2337	0.432 3191	0.571 4218	0.681 5032	0.724 5350	0.710 5240	0.662 4886	0.697 5146	0.706 5213	0.725 5357
10.48	1.182	0.272 2298	0.371 3137	0.489 4137	0.582 4922	0.617 5222	0.610 5163	0.582 4921	0.613 5186	0.620 5250	0.636 5383
3.910	1.770	0.376 2122	0.496 2804	0.643 3634	0.761 4301	0.816 4612	0.850 4800	0.919 5194	0.976 5514	0.983 5551	0.976 5514
3.471	2.088	0.435 2082	0.569 2725	0.727 3481	0.872 4176	0.941 4509	0.991 4744	1.090 5219	1.165 5580	1.172 5613	1.154 5529
5.874	1.622	0.358 2206	0.477 2940	0.622 3838	0.749 4618	0.795 4900	0.811 4998	0.819 5051	0.872 5376	0.877 5407	0.883 5446
7.615	2.105	0.472 2244	0.637 3024	0.831 3949	0.997 4734	1.059 5029	1.061 5040	1.057 5022	1.117 5306	1.129 5364	1.140 5416
3.540	1.520	0.318 2094	0.423 2782	0.544 3581	0.649 4271	0.830 5458	0.727 4782	0.791 5203	0.845 5556	0.850 5593	0.840 5523
4.460	2.100	0.450 2141	0.595 2832	0.772 3674	0.909 4327	0.982 4676	1.019 4851	1.085 5168	1.153 5488	1.161 5530	1.154 5497
5.370	1.250	0.274 2192	0.368 2946	0.476 3810	0.572 4576	0.613 4901	0.622 4976	0.633 5063	0.674 5393	0.678 5421	0.631 5446
8.285	3.215	0.718	0.971	1.265	1.523	1.623	1.619	1.613	1.704	1.725	1.743

* Apparent absorptivity : Absorbance / $(FeBr_3)_T$

Table 18 Absorbance and apparent absorptivity of di-n-butyl ether solutions of $FeBr_3$-HBr at 45.0°C for various wavelengths.

$(HBr)_T$ x 10^4M	$(FeBr_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mµ ⟶									
		510	500	490	480	470	460	440	430	420	410
14.38	1.354	0.305	0.411	0.540	0.650	0.685	0.690	0.676	0.713	0.721	0.732
		2250	3034	3992	4799	5059	5094	4992	5269	5325	5407
10.48	1.182	0.262	0.350	0.453	0.546	0.581	0.591	0.597	0.635	0.641	0.644
		2214	2959	3835	4615	4916	4997	5049	5370	5424	5450
3.910	1.770	0.353	0.460	0.580	0.685	0.757	0.812	0.943	1.012	1.016	0.989
		1995	2598	3277	3870	4279	4590	5327	5716	5740	5586
3.471	2.088	0.409	0.527	0.676	0.793	0.878	0.949	1.123	1.203	1.212	1.172
		1960	2524	3235	3797	4207	4544	5379	5779	5802	5611
5.874	1.622	0.337	0.448	0.572	0.682	0.740	0.770	0.847	0.901	0.908	0.897
		2078	2760	3525	4205	4563	4747	5223	5558	5599	5532
7.615	2.105	0.450	0.595	0.773	0.914	0.985	1.018	1.086	1.152	1.165	1.156
		2139	2825	3672	4341	4678	4834	5154	5471	5536	5492
3.540	1.520	0.302	0.388	0.496	0.590	0.644	0.698	0.815	0.875	0.876	0.850
		1984	2554	3264	3879	4239	4593	5363	5756	5763	5594
4.460	2.100	0.425	0.553	0.701	0.835	0.911	0.975	1.116	1.195	1.203	1.171
		2026	2034	3339	3975	4337	4645	5313	5689	5729	5577
5.370	1.250	0.258	0.341	0.440	0.524	0.567	0.595	0.653	0.698	0.702	0.692
		2065	2729	3524	4190	4533	4760	5227	5587	5619	5539
8.285	3.214	0.687	0.912	1.183	1.394	1.509	1.560	1.657	1.764	1.781	1.769
		2135	2837	3679	4335	4694	4853	5153	5486	5538	5501

* Apparent absorptivity = Absorbance/ $(FeBr_3)_T$

Table 19 Absorbance and apparent absorptivity of tetrahydrofuran solutions of $FeBr_3$-HBr at 25.0° C, for various wavelengths.

$(HBr)_T$ x 10^4 M	$(FeBr_3)_T$ x 10^4 M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mμ ⟶ 520	510	500	490	480	470	410	400	390	380
4.357	1.523	0.195	0.277	0.389	0.519	0.643	0.683	0.703	0.713	0.689	0.641
		1283	1819	2555	3405	4223	4481	4615	4679	4582	4208
5.697	2.261	0.297	0.429	0.600	0.806	0.990	1.051	1.057	1.088	1.067	0.973
		1313	1900	2653	3564	4381	4651	4676	4814	4721	4304
5.167	2.326	0.299	0.428	0.605	0.823	0.996	1.070	1.081	1.106	1.087	0.981
		1285	1893	2601	3541	4283	4602	4649	4756	4672	4217
2.418	1.570	0.176	0.254	0.354	0.478	0.598	0.652	0.695	0.689	0.662	0.606
		1121	1619	2257	3046	3811	4154	4426	4390	4214	3860
6.257	2.640	0.356	0.502	0.703	0.955	1.162	1.239	1.235	1.274	1.256	1.136
		1350	1901	2663	3618	4402	4693	4681	4826	4760	4305
1.301	2.823	0.279	0.402	0.560	0.759	0.955	1.074	1.209	1.167	1.100	1.019
		987	1425	1982	2688	3384	3803	4283	4134	3896	3610
8.021	2.041	0.292	0.419	0.571	0.783	0.952	0.997	0.976	1.010	1.008	0.917
		1431	2054	2798	3837	4666	4884	4781	4947	4939	4491
9.058	2.104	0.304	0.437	0.612	0.816	1.002	1.049	1.015	1.061	1.062	0.953
		1445	2079	2908	3878	4763	4985	4826	5042	5048	4531
14.74	1.493	0.235	0.338	0.462	0.632	0.755	0.784	0.742	0.791	0.795	0.720
		1573	2261	3094	4236	5055	5249	4970	5298	5327	4824
10.10	2.012	0.296	0.430	0.588	0.807	0.975	1.015	0.976	1.032	1.017	0.929

* Apparent absorptivity = a : Absorbance/$(FeBr_3)_T$

Table 20 Absorbance and apparent absorptivity of tetrahydrofuran solutions of $FeBr_3$-HBr at 35.0°C, for various wavelengths.

$(HBr)_T$ x 10^4M	$(FeBr_3)_T$ x 10^4M	Absorbance(upper number) Apparent absorptivity (lower number)* wavelength, mμ ⟶ 520	510	500	490	480	470	410	400	390	380
4.357	1.523	0.172	0.248	0.344	0.468	0.580	0.629	0.677	0.674	0.641	0.595
		1131	1627	2260	3037	3808	4128	4443	4426	4211	3094
5.697	2.261	0.264	0.383	0.531	0.728	0.885	0.971	1.014	1.020	0.988	0.909
		1167	1694	2350	3219	3916	4294	4487	4512	4370	4020
5.167	2.326	0.269	0.389	0.542	0.726	0.890	0.984	1.040	1.040	0.995	0.922
		1158	1672	2330	3120	3827	4231	4474	4470	4277	3964
2.418	1.570	0.160	0.230	0.320	0.440	0.545	0.608	0.678	0.660	0.628	0.577
		1020	1463	2039	2801	3473	3872	4321	4207	3999	3678
6.257	2.642	0.313	0.456	0.636	0.862	1.051	1.149	1.192	1.206	1.167	1.057
		1187	1729	2372	3264	3980	4353	4515	4570	4420	4006
1.301	2.823	0.262	0.376	0.532	0.723	0.914	1.032	1.189	1.139	1.063	0.989
		929	1333	1889	2560	3234	3657	4210	4033	3764	3502
8.021	2.041	0.256	0.371	0.516	0.706	0.851	0.924	0.940	0.953	0.937	0.846
		1256	1817	2528	3458	4172	4524	4606	4671	4590	4144
9.058	2.104	0.274	0.895	0.549	0.734	0.912	0.961	0.973	0.996	0.980	0.887
		1304	1879	2609	3489	4333	4567	4623	4733	4656	4217
14.74	1.493	0.215	0.306	0.425	0.573	0.695	0.737	0.715	0.747	0.738	0.668
		1442	2046	2897	3836	4652	4934	4788	5006	4944	4473
10.10	2.012	0.267	0.385	0.534	0.723	0.880	0.932	0.939	0.958	0.956	0.862
		1326	1913	2653	3595	4374	4635	4670	4763	4750	4285

* Apparent absorptivity, a= Absorbance / $(FeBr_3)_T$

Table 21 Absorbance and apparent absorptivity of tetrahydrofuran solutions of $FeBr_3$-HBr at 45.0°C, for various wavelengths,

$(HBr)_T$ x 10^4M	$(FeBr_3)_T$ x 10^4M	Absorbance(upper number) Apparent absorptivity (lower number)* wavelength,mμ →									
		520	510	500	490	480	470	410	400	390	380
4.357	1.523	0.153 1003	0.222 1458	0.308 2020	0.421 2763	0.523 3431	0.586 3844	0.658 4320	0.642 4215	0.605 3907	0.553 3630
5.697	2.261	0.237 1048	0.342 1529	0.477 2111	0.652 2889	0.805 3562	0.896 3962	0.983 4349	0.968 4281	0.916 4053	0.852 3768
5.167	2.326	0.240 1034	0.343 1477	0.487 2095	0.653 2807	0.829 3563	0.912 3920	1.007 4331	0.985 4233	0.942 4051	0.856 3718
2.418	1.570	0.148 946	0.210 1340	0.300 1910	0.409 2608	0.508 3237	0.589 3691	0.665 4235	0.638 4063	0.593 3789	0.552 3518
6.257	2.640	0.280 1060	0.410 1553	0.563 2132	0.775 2935	0.948 3592	1.054 3993	1.157 4382	1.132 4289	1.083 4102	0.988 3744
1.301	2.823	0.251 890	0.360 1275	0.507 1795	0.699 2474	0.877 3106	0.999 3538	1.177 4168	1.113 3943	1.035 3668	0.962 3406
8.021	2.041	0.228 1118	0.329 1612	0.465 2277	0.619 3030	0.766 3752	0.848 4155	0.907 4444	0.893 4377	0.895 4210	0.795 3897
9.058	2.104	0.237 1129	0.341 1621	0.480 2280	0.661 3141	0.809 3844	0.877 4167	0.937 4459	0.939 4465	0.905 4300	0.829 3939
14.74	1.493	0.191 1277	0.270 1806	0.378 2529	0.517 3463	0.632 4236	0.677 4533	0.691 4629	0.694 4646	0.677 4538	0.628 4207
10.10	2.012	0.240 1194	0.341 1693	0.469 2330	0.634 3150	0.759 3951	0.853 4242	0.905 4499	0.911 4528	0.878 4367	0.807 4013

*Apparent absorptivity,a = Absorbance /$(FeBr_3)_T$

Table 22 Absorbance and apparent absorptivity of di-iso-propyl ether solutions of $FeCl_3$-HCl at 25.0°C, for various wavelengths.

$(HCl)_T$ x 10^3M	$(FeCl_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength , mu ⟶									
		390	380	370	360	350	340	330	310	300	290
1.643	1.432	0.336	0.541	0.768	0.869	0.783	0.670	0.717	0.809	0.712	0.553
		2347	3778	5360	6068	5464	4679	5005	5651	4973	3858
0.920	0.967	0.217	0.343	0.487	0.567	0.545	0.488	0.501	0.522	0.461	0.363
		2246	3543	5032	5864	5633	5043	5178	5394	4769	3755
0.428	0.716	0.152	0.229	0.324	0.399	0.417	0.389	0.387	0.365	0.320	0.260
		2123	3199	4519	5565	5823	5558	5410	5097	4472	3633
0.445	0.788	0.167	0.256	0.360	0.439	0.459	0.435	0.424	0.401	0.352	0.287
		2117	3245	4572	5568	5832	5521	5388	5085	4468	3641
0.287	1.719	0.351	0.521	0.735	0.930	1.022	1.003	0.951	0.847	0.741	0.614
		2040	3033	4277	5412	5946	5834	5534	4929	4308	3570
0.394	1.397	0.292	0.440	0.629	0.772	0.820	0.790	0.760	0.705	0.616	0.504
		2091	3153	4504	5524	5869	5655	5443	5049	4408	3611
3.703	2.901	0.716	1.180	1.663	1.833	1.540	1.234	1.401	1.709	1,501	1.144
		2468	4070	5734	6320	5311	4256	4830	5894	5174	3945
1.779	1.320	0.313	0.503	0.715	0.803	0.718	0.607	0.659	0.748	0.660	0.510
		2374	3813	5417	6088	5439	4604	4991	5669	4998	3864
4.324	2.149	0.532	0.884	1.249	1.366	1.134	0.904	1.029	1.275	1.119	0.852
		2477	4115	5815	6357	5280	4205	4790	5934	5207	3963
2.375	1.748	0.421	0.687	0.937	1.081	0.941	0.779	0.858	1.009	0.886	0.683
		2407	3933	5568	6189	5383	4459	4910	5771	5072	3906
1.194	0.881	0.203	0.324	0.460	0.525	0.490	0.432	0.450	0.486	0.426	0.335
		2308	3674	5218	5959	5563	4901	5109	5515	4836	3801
3.777	0.853	0.211	0.348	0.492	0.541	0.451	0.362	0.410	0.503	0.444	0.338
		2475	4076	5768	6340	5285	4250	4810	5896	5205	3962

* Apparent absorptivity, a= Absorbance/$(FeCl_3)_T$

Table 23 Absorbance and apparent absorptivity of di-isopropyl ether solutions of $FeCl_3$-HCl at 35.0°C, for various wavelengths.

$(HCl)_T$ x 10^3M	$(FeCl_3)_T$ x 10^4M	Absorbance(upper number) Apparent absorptivity (lower number)* wavelength, mμ →									
		390	380	370	360	350	340	330	310	300	290
1.643	1.432	0.318	0.492	0.701	0.826	0.813	0.744	0.749	0.766	0.668	0.534
		2218	3438	4896	5766	5675	5193	5225	5348	4665	3729
0.920	0.967	0.203	0.307	0.437	0.538	0.566	0.547	0.524	0.492	0.430	0.350
		2101	3170	4523	5566	5857	5654	5414	5089	4452	3623
0.4284	0.716	0.143	0.211	0.297	0.382	0.431	0.425	0.400	0.347	0.303	0.253
		2001	2945	4148	5333	6013	5938	5582	4851	4230	3536
0.445	0.788	0.159	0.232	0.331	0.420	0.473	0.469	0.439	0.382	0.333	0.278
		2015	2942	4205	5336	6004	5958	5571	4850	4230	3526
0.287	1.719	0.337	0.487	0.692	0.901	1.042	1.058	0.975	0.813	0.714	0.599
		1959	2833	4026	5243	6070	6153	5672	4731	4152	3486
0.394	1.397	0.279	0.407	0.575	0.739	0.842	0.840	0.784	0.667	0.591	0.490
		1995	2916	4119	5290	6032	6018	5613	4776	4233	3512
3.703	2.901	0.688	1.091	1.562	1.758	1.593	1.364	1.456	1.637	1.433	1.118
		2374	3762	5385	6062	5492	4706	5021	5642	4940	3855
1.779	1.320	0.293	0.462	0.653	0.770	0.745	0.678	0.689	0.703	0.621	0.495
		2219	3500	4947	5834	5642	5139	5219	5328	4705	3755
4.324	2.149	0.513	0.826	1.171	1.318	1.168	0.984	1.070	1.231	1.076	0.831
		2387	3845	5449	6123	5437	4580	4982	5731	5007	3868
2.375	1.748	0.401	0.632	0.896	1.038	0.974	0.858	0.893	0.951	0.837	0.659
		2293	3618	5125	5941	5572	4908	5112	5440	4790	3768
1.194	0.881	0.190	0.289	0.413	0.496	0.508	0.475	0.471	0.456	0.403	0.324
		2160	3286	4691	5635	5763	5394	5350	5175	4570	3675
3.777	0.853	0.201	0.324	0.462	0.521	0.467	0.398	0.425	0.483	0.425	0.329
		2353	3798	5421	6114	5479	4665	4987	3862	3724	4570

* Apparent absorptivity, a = Absorbance/$(FeCl_3)_T$

Table 24 Absorbance and apparent absorptivity of di-isopropyl ether solutions of $FeCl_3$-HCl at 45.0°C, for various wavelengths.

$(HCl)_T$ x 10^3M	$(FeCl_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mμ → 390	380	370	360	350	340	330	310	300	290
1.643	1.432	0.297 2070	0.445 3103	0.626 4372	0.787 5494	0.843 5885	0.817 5707	0.784 5476	0.719 5018	0.623 4352	0.514 3590
0.920	0.967	0.192 1983	0.285 2943	0.401 4142	0.514 5319	0.583 6062	0.578 5976	0.542 5605	0.464 4801	0.409 4233	0.342 3537
0.428	0.716	0.139 1936	0.198 2762	0.282 3935	0.371 5175	0.439 6126	0.444 6204	0.409 5705	0.334 4670	0.294 4130	0.248 3460
0.445	0.788	0.153 1938	0.219 2781	0.310 3941	0.408 5173	0.481 6109	0.491 6234	0.451 5722	0.369 4678	0.322 4092	0.273 3469
0.289	1.719	0.324 1904	0.468 2725	0.661 3847	0.883 5134	1.055 6137	1.085 6310	0.989 5750	0.792 4607	0.696 4049	0.591 3441
0.394	1.397	0.269 1926	0.383 2744	0.543 3887	0.718 5138	0.855 6125	0.874 6261	0.789 5716	0.547 4635	0.569 4072	0.482 3454
3.703	2.901	0.640 2208	0.999 3444	1.403 4838	1.667 5747	1.657 5721	1.500 5172	1.525 5258	1.542 5316	1.349 4651	1.083 3733
1.779	1.320	0.273 2072	0.412 3121	0.578 4378	0.726 5505	0.778 5899	0.747 5665	0.722 5471	0.665 5036	0.586 4439	0.476 3606
4.324	2.149	0.479 2230	0.757 3524	1.081 5032	1.257 5852	1.208 5621	1.085 5051	1.114 5187	1.161 5404	1.013 4715	0.807 3757
2.375	1.748	0.373 2132	0.575 3288	0.796 4555	0.978 5596	1.015 5806	0.981 5612	0.941 5381	0.895 5121	0.779 4458	0.638 3652
1.194	0.881	0.179 2034	0.265 3014	0.371 4214	0.472 5357	0.525 5957	0.517 5866	0.490 5557	0.430 4893	0.381 4322	0.314 3561
3.777	0.853	0.189 2212	0.298 3492	0.424 4970	0.494 5794	0.485 5684	0.447 5240	0.445 5220	0.452 5302	0.398 4671	0.316 3704

* Apparent absorptivity, a = Absorbance/$(FeCl_3)_T$

Table 25 Absorbance and apparent absorptivity of di-isopropyl ether solutions of $FeBr_3$-HBr at 25.0°C, for various wavelengths.

$(HBr)_T$ x 10^4M	$(FeBr_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mμ ⟶ 520	510	500	490	480	470	410	400	380	390
2.654	2.172	0.418 1924	0.556 2560	0.663 3055	0.795 3661	0.865 3982	0.958 4411	1.172 5396	1.281 5899	1.210 5570	1.287 5925
0.108	1.924	0.330 1713	0.394 2050	0.469 2437	0.533 2768	0.606 3149	0.754 3917	1.094 5684	1.208 6279	1.095 5693	1.199 6231
0.684	0.901	0.161 1787	0.200 2213	0.239 2649	0.277 3070	0.310 3438	0.367 4074	0.503 5586	0.555 6157	0.509 5665	0.552 6124
0.649	0.895	0.159 1781	0.198 2214	0.237 2647	0.272 3039	0.306 3419	0.364 4071	0.501 5593	0.551 6157	0.506 5655	0.549 6136
0.807	2.037	0.364 1789	0.451 2212	0.539 2645	0.624 3063	0.700 3436	0.832 4086	1.138 5587	1.252 6149	1.151 5653	1.247 6124
0.451	1.361	0.238 1752	0.292 2143	0.347 2552	0.398 2925	0.450 3308	0.546 4013	0.766 5627	0.845 6208	0.772 5670	0.839 6168
2.222	2.211	0.420 1901	0.545 2464	0.658 2975	0.780 3525	0.856 3872	0.962 4349	1.203 5443	1.313 5939	1.236 5591	1.319 5965
1.035	0.940	0.171 1812	0.218 2314	0.260 2763	0.299 3182	0.335 3563	0.391 4158	0.521 5547	0.572 6085	0.530 5633	0.570 6064
1.033	1.253	0.228 1818	0.287 2290	0.345 2752	0.401 3197	0.447 3567	0.520 4149	0.695 5541	0.764 6092	0.706 5633	0.762 6082
0.914	2.283	0.410 1794	0.513 2244	0.609 2668	0.704 3085	0.793 3473	0.937 4106	1.274 5579	1.402 6143	1.289 5648	1.396 6114
0.663	2.037	0.361 1774	0.445 2183	0.530 2602	0.611 3001	0.683 3354	0.824 4048	1.141 5604	1.259 6179	1.153 5663	1.253 6150
2.715	2.543	0.491 1933	0.643 2535	0.780 3066	0.920 3620	1.013 3984	1.114 4380	1.372 5397	1.501 5905	1.418 5577	1.504 5914

* Apparent absorptivity, a = Absorbance/$(FeBr_3)_T$

Table 26 Absorbance and apparent absorptivity of di-isopropyl ether solutions of $FeBr_3$-HBr at 35.0°C, for various wavelengths.

$(HBr)_T$ x 10^4M	$(FeBr_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mμ ⟶ 520	510	500	490	480	470	410	400	390	380
2.654	2.172	0.401 1845	0.511 2354	0.611 2812	0.710 3268	0.791 3644	0.916 4219	1.198 5517	1.313 6047	1.311 6036	1.221 5622
0.108	1.924	0.328 1707	0.392 2036	0.466 2420	0.528 2747	0.601 3126	0.751 3905	1.095 5691	1.210 6288	1.201 6240	1.096 5696
0.684	0.901	0.157 1745	0.192 2126	0.228 2529	0.261 2901	0.295 3277	0.360 3990	0.508 5639	0.560 6218	0.557 6184	0.511 5675
0.649	0.895	0.156 1745	0.190 2122	0.226 2525	0.259 2891	0.293 3277	0.358 3995	0.505 5642	0.557 6227	0.554 6185	0.508 5676
0.807	2.307	0.357 1751	0.433 2128	0.518 2545	0.593 2913	0.670 3291	0.815 4004	1.148 5638	1.266 6217	1.258 6176	1.156 5676
0.451	1.363	0.235 1730	0.285 2092	0.338 2487	0.387 2841	0.437 3212	0.528 3954	0.770 5661	0.851 6250	0.844 6205	0.773 5683
2.222	2.211	0.404 1828	0.507 2291	0.608 2751	0.708 3204	0.737 3561	0.922 4169	1.226 5545	1.342 6082	1.341 6066	1.246 5637
1.035	0.940	0.166 1767	0.205 2176	0.245 2603	0.281 2985	0.317 3364	0.380 4044	0.528 5615	0.581 6182	0.578 6152	0.532 5663
1.033	1.253	0.222 1769	0.272 2169	0.323 2581	0.373 2977	0.420 3351	0.505 4031	0.703 5611	0.776 6189	0.771 6149	0.710 5665
0.914	2.283	0.401 1755	0.490 2147	0.583 2554	0.668 2924	0.757 3318	0.917 4015	1.285 5627	1.417 6209	1.407 6171	1.294 5670
0.663	2.037	0.354 1740	0.430 2112	0.512 2514	0.587 2883	0.664 3258	0.812 3985	1.151 5650	1.268 6228	1.261 6191	1.157 5679
2.715	2.543	0.468 1842	0.596 2345	0.717 2821	0.837 3293	0.931 3661	1.068 4202	1.403 5516	1.541 6062	1.538 6048	1.430 5624

* Apparent absorptivity, a = Absorbance/$(FeBr_3)_T$

Table 27 Absorbance and apparent absorptivity of di-isopropyl ether solutions of $FeBr_3$-HBr at 45.0°C, for various wavelengths.

$(HBr)_T$ x $10^4 M$	$(FeBr_3)_T$ x $10^4 M$	Absorbance (upper number) Apparent absorptivity (lower number)*									
		wavelength, mμ → 520	510	500	490	480	470	410	400	390	380
2.654	2.172	0.386 1779	0.479 2206	0.571 2629	0.653 3003	0.740 3406	0.883 4066	1.217 5605	1.342 6179	1.333 6138	1.230 5661
0.108	1.924	0.328 1703	0.390 2028	0.464 2410	0.526 2734	0.599 3112	0.750 3898	1.096 5695	1.211 6294	1.202 6245	1.096 5698
0.684	0.901	0.155 1724	0.186 2069	0.222 2463	0.253 2805	0.287 3186	0.355 3941	0.511 5673	0.564 6261	0.560 6215	0.512 5688
0.649	0.895	0.154 1720	0.185 2069	0.220 2459	0.251 2800	0.285 3188	0.352 3936	0.508 5672	0.561 6263	0.557 6218	0.509 5689
0.807	2.037	0.351 1726	0.422 2072	0.504 2474	0.573 2813	0.650 3191	0.803 3944	1.154 5665	1.274 6254	1.265 6213	1.158 5687
0.451	1.361	0.233 1714	0.279 2053	0.333 2444	0.377 2772	0.430 3157	0.534 3924	0.773 5681	0.854 6276	0.848 6229	0.775 5693
2.222	2.211	0.391 1767	0.478 2162	0.574 2595	0.653 2954	0.745 3367	0.892 4035	1.242 5618	1.368 6187	1.360 6149	1.253 5667
1.035	0.940	0.163 1733	0.197 2100	0.235 2497	0.267 2844	0.303 3224	0.373 3968	0.532 5655	0.587 6242	0.583 6206	0.534 5683
1.033	1.253	0.217 1729	0.262 2091	0.312 2486	0.357 2849	0.404 3227	0.496 3957	0.709 5659	0.783 6246	0.778 6205	0.712 5682
0.914	2.283	0.394 1727	0.477 2089	0.567 2482	0.647 2833	0.731 3204	0.903 3954	1.293 5665	1.428 6253	1.418 6213	1.298 5684
0.663	2.037	0.350 1720	0.421 2068	0.501 2459	0.569 2796	0.649 3186	0.801 3935	1.155 5673	1.267 6219	1.276 6265	1.159 5690
2.715	2.543	0.453 1782	0.560 2202	0.668 2626	0.769 3203	0.862 3392	1.035 4069	1.424 5601	1.568 6168	1.559 6132	1.438 5657

* Apparent absorptivity, a=Absorbance/$(FeBr_3)_T$

Table 28 Absorbances and apparent absorptivity of tetrahydrofuran solutions of HCl-$FeCl_3$ at 25.0°C, for various wavelengths.

$(HCl)_T$ x 10^4M	$(FeCl_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mμ ⟶									
		390	380	370	360	350	340	330	320	310	300
5.803	1.018	0.266 2609	0.452 4435	0.632 6203	0.672 6600	0.548 5377	0.488 4749	0.567 5565	0.653 6414	0.617 6061	0.519 5094
2.756	1.426	0.347 2435	0.579 4059	0.822 5764	0.903 6336	0.804 5643	0.778 5460	0.845 5927	0.894 6270	0.817 5728	0.711 4988
3.292	1.629	0.406 2492	0.676 4146	0.954 5858	1.039 6379	0.908 5575	0.867 5230	0.956 5869	1.028 6311	0.948 5818	0.818 5020
2.993	1.833	0.450 2458	0.746 4070	1.053 5742	1.158 6319	1.033 5635	1.005 5481	1.094 5969	1.149 6271	1.054 5749	0.913 4983
1.765	2.037	0.468 2300	0.772 3788	1.089 5347	1.237 6073	1.197 5875	1.229 6035	1.289 6301	1.252 6148	1.100 5402	0.995 4888
2.263	2.444	0.573 2345	0.948 3878	1.339 5477	1.503 6150	1.418 5802	1.439 5890	1.518 6210	1.514 6193	1.348 5515	1.202 4919
1.222	0.611	0.141 2311	0.232 3798	0.327 5350	0.370 6055	0.361 5913	0.373 6100	0.387 6326	0.375 6135	0.332 5430	0.299 4885
1.365	0.815	0.189 2319	0.309 3788	0.439 5393	0.494 6067	0.478 5865	0.496 6089	0.513 6292	0.505 6161	0.443 5441	0.399 4892
1.742	1.222	0.287 2347	0.470 3846	0.665 5444	0.751 6144	0.712 5824	0.717 5865	0.761 6231	0.757 6192	0.674 5513	0.601 4914
5.163	0.847	0.220 2598	0.375 4430	0.528 6234	0.560 6609	0.453 5354	0.402 4748	0.466 5503	0.543 6411	0.516 6093	0.432 5103

To be continued on next page.

Table 28 continued.

6.766	1.018	0.270	0.463	0.649	0.684	0.539	0.460	0.549	0.658	0.632	0.524
		2647	4541	6374	6713	5288	4514	5395	6465	6202	5145
6.587	1.069	0.283	0.486	0.678	0.717	0.566	0.484	0.580	0.691	0.661	0.549
		2647	4545	6345	6705	5292	4522	5428	6461	6184	5132
4.982	1.222	0.317	0.535	0.753	0.806	0.657	0.585	0.680	0.786	0.742	0.622
		2596	4376	6159	6598	5379	4784	5562	6408	6074	5088
4.189	1.452	0.368	0.624	0.883	0.948	0.797	0.733	0.827	0.924	0.864	0.735
		2533	4295	6085	6529	5490	5049	5697	6366	5948	5060
6.600	1.426	0.378	0.642	0.901	0.952	0.759	0.653	0.772	0.920	0.878	0.732
		2651	4506	6317	6674	5321	4583	5418	6450	6160	5132

* Apparent absorptivity, a = Absorbance/$(FeCl_3)_T$

Table 29 Absorbance and apparent absorptivity of tetrahydrofuran solutions of HCl-$FeCl_3$ at 35.0°C, for various wavelengths.

$(HCl)_T$ x 10^4M	$(FeCl_3)_T$ x 10^4M	Absorbance (upper number) Apparent absorptivity (lower number)* wavelength, mμ ⟶									
		390	380	370	360	350	340	330	320	310	300
5.803	1.018	0.252 2474	0.422 4140	0.597 5860	0.650 6382	0.567 5571	0.541 5309	0.598 5870	0.642 6308	0.590 5797	0.510 5009
2.756	1.426	0.334 2342	0.548 3844	0.773 5425	0.869 6092	0.846 5863	0.849 5955	0.889 6234	0.879 6267	0.784 5497	0.699 4903
3.292	1.629	0.384 2359	0.633 3884	0.897 5504	1.009 6169	0.940 5766	0.945 5801	1.003 6156	1.011 6204	0.907 5568	0.803 4943
2.993	1.833	0.430 2384	0.707 3855	10000 5455	1.122 6123	1.071 5840	1.079 5884	1.140 6221	1.131 6167	1.004 5477	0.898 4901
1.765	2.037	0.454 2227	0.738 3625	1.037 5093	1.203 5909	1.226 6021	1.318 6469	1.329 6526	1.239 6084	1.071 5257	0.983 4828
2.263	2.444	0.555 2269	0.905 3705	1.278 5228	1.459 5969	1.455 5952	1.531 6265	1.573 6436	1.491 6101	1.304 5335	1.187 4856
1.222	0.611	0.135 2204	0.217 3556	0.310 5067	0.358 5850	0.370 6062	0.398 6517	0.403 6591	0.370 6049	0.316 5177	0.294 4812
1.365	0.815	0.181 2226	0.293 3592	0.415 5092	0.480 5886	0.489 6048	0.530 6508	0.535 6563	0.494 6063	0.426 5224	0.392 4814
1.742	1.222	0.275 2246	0.445 3642	0.630 5152	0.727 5950	0.734 6007	0.775 6343	0.788 6451	0.745 6094	0.645 5280	0.592 4842
5.163	0.847	0.210 2476	0.356 4198	0.497 5869	0.541 6384	0.470 5551	0.451 5325	0.495 5841	0.536 6327	0.491 5796	0.426 5025

To be continued on next page.

Table 29 continued.

6.766	1.018	0.514	0.604	0.648	0.581	0.510	0.559	0.664	0.615	0.436	0.260
		2558	4278	6035	6520	5489	5009	5707	6367	5928	5052
6.587	1.069	0.270	0.462	0.648	0.697	0.587	0.541	0.609	0.679	0.638	0.540
		2528	4319	6057	6514	5489	5063	5693	6365	5964	5049
4.982	1.222	0.303	0.505	0.713	0.777	0.683	0.648	0.715	0.770	0.710	0.612
		2478	4128	5832	6359	5592	5305	5851	6298	5809	5008
4.189	1.452	0.352	0.589	0.830	0.909	0.827	0.806	0.876	0.906	0.827	0.721
		2427	4054	5714	6261	5696	5548	6063	6243	5694	4967
6.600	1.426	0.360	0.610	0.855	0.922	0.784	0.717	0.819	0.905	0.843	0.720
		2526	4278	5997	6464	5498	5027	5744	6346	5916	5057

* Apparent absorptivity , a =Absorbance/$(FeCl_3)_T$

Table 30 Absorbance and apparent absorptivity of tetrahydrofuran solutions of $FeCl_3$-HCl at 45.0°C, for various wavelengths.

$(HCl)_T$ x 10^4 M	$(FeCl_3)_T$ x 10^4 M	Absorbance (upper number) Apparent absorptivity (lower number)*									
		wavelength, mμ ⟶									
		390	380	370	360	350	340	330	320	310	300
5.803	1.018	0.239 2345	0.389 3882	0.561 5505	0.621 6153	0.591 5806	0.598 5875	0.628 6162	0.631 6201	0.562 5518	0.500 4907
2.756	1.426	0.318 2228	0.513 3596	0.728 5106	0.841 5896	0.860 6030	0.914 6411	0.934 6553	0.865 6070	0.746 5231	0.689 4831
3.292	1.629	0.369 2267	0.602 3692	0.846 5192	0.971 5961	0.973 5970	1.028 6309	1.049 6435	0.996 6113	0.868 5330	0.788 4838
2.993	1.833	0.411 2245	0.660 3602	0.946 5159	1.088 5935	1.106 6034	1.167 6367	1.187 6473	1.115 6082	0.965 5251	0.885 4827
1.765	2.037	0.438 2152	0.705 3460	1.000 4908	1.175 5770	1.250 6139	1.377 6762	1.367 6713	1.223 6004	1.032 5066	0.972 4772
2.263	2.444	0.532 2177	0.857 3508	1.217 4978	1.419 5804	1.490 6097	1.618 6620	1.623 6640	1.476 6040	1.258 5147	1.173 4798
1.222	0.611	0.130 2127	0.209 3421	0.295 4824	0.350 5720	0.379 6197	0.422 6903	0.416 6802	0.366 5990	0.308 5037	0.290 4751
1.365	0.815	0.175 2143	0.278 3411	0.397 4875	0.469 5751	0.503 6169	0.556 6821	0.551 6768	0.489 5999	0.410 5035	0.389 4770
1.742	1.222	0.265 2171	0.425 3475	0.599 4899	0.707 5787	0.751 6145	0.819 6704	0.818 6694	0.735 6011	0.621 5079	0.583 4773
5.163	0.847	0.201 2376	0.330 3899	0.462 5459	0.519 6132	0.491 5794	0.500 5900	0.528 6300	0.526 6213	0.469 5536	0.417 4928

To be continued on next page.

Table 30 continued.

6.766	1.018	0.245	0.405	0.578	0.637	0.581	0.564	0.614	0.636	0.578	0.505
		2406	3976	5679	6251	5704	5536	6032	6245	5675	4955
6.587	1.069	0.257	0.432	0.605	0.672	0.609	0.608	0.645	0.666	0.608	0.531
		2399	4036	5656	6283	5692	5687	6063	6233	5686	4967
4.982	1.222	0.288	0.476	0.664	0.746	0.713	0.712	0.763	0.757	0.673	0.602
		2539	3891	5431	6100	5834	5825	6240	6193	5504	4924
4.189	1.452	0.336	0.549	0.777	0.880	0.854	0.888	0.915	0.891	0.785	0.708
		2314	3779	5352	6061	5885	6114	6299	6137	5405	4878
6.600	1.426	0.343	0.574	0.799	0.888	0.811	0.806	0.863	0.888	0.799	0.707
		2409	4027	5604	6227	5690	5656	6048	6230	5607	4957

* Apparent absorptivity, a =Absorbance/ $(FeCl_3)_T$

However, it was first necessary to be sure that the data used in the calculations,and the calculations themselves did in fact refer to the particular species written in reaction [1] .

For the concentration of hydrogen halide, the sum of the unsolvated HX and the solvated HX was used in the mass law, conformity with common practice. This choice was permissible, since the activity of the ether was essentially unity in all solutions. However, as described in a later section, the equilibrium constant for the solvation reaction

$$HX + S = HX.S \qquad [2]$$

where S is an ether, was also independently measured as a function of temperature . Therefore, the values of ΔG^o, ΔH^o ,ΔS^o calculated for reaction [1]can be corrected so a s to apply to the case where the concentration of unsolvated HX is used in the mass law , instead of the stoichiometric concentration of HX.

Ferric chloride has been shown by Fomin and co-workers to exist almost exclusively as the monosolvate $FeCl_3.S$ in di-n-butyl ether(21, 22, 23).It was considered reasonably true to assume that ferric bromide also existed as the monosolvate in ether. In the present work, Beer's law was obeyed for all the ether solutions of ferric halides reported in Tables 1, 3, 5, 7, 9 and 11. Moreover, the general shapes of the spectral transmission curves of ferric chloride in the three ethers were remarkably similar, as were those of ferric bromide in the three ethers. These facts suggested : (i) that one species of ferric halide was predominant in all the ether solutions, and (ii) that polymeric forms were absent in the solutions studied. Therefore it appeared proper to write $FeX_3.S$ as the one specie present in the solutions studied. However, as in the case of the hydrogen halide, it would be permissible to write for the concentration of FeX_3 in the mass law expression for reaction [1] , the sum of the unsolvated and the solvated FeX_3, provided that their molar absorptivities were the same.

The analysis of pure tetrachloroferric acid and tetrabromoferric acid, prepared from their solutions in di-isopropyl ether and in di-n-butyl ether, is reported in Section IV d. These analyses clearly established that the empirical formulae were $HFeCl_4.2S$ and $HFeBr_4.2S$, where S is the ether. Others (16, 17)have reported similar formulae. In the ether solutions used in the present study of reaction [1] , it was concluded that the tetrahaloferric acids existed in the ether solutions as $HS_2^+FeCl_4^-$ ion pairs. Tables 2, 4, 6, 8, 10 and 12 show that the absorbance of the ether solutions of the tetrahaloferric acid obeyed Beer's law in all cases. Moreover, the general shapes of the spectral curves of tetrachloroferric acid in the three ethers were remarkably similar, as were those of tetrabromoferric acid. Therefore it was concluded that : (i) a single specie of complex acid was present in all solutions (i.e. $HFeX_4.2S$), and (ii) polymeric species were absent. It is generally recognized that the anion is not solvated (11), and that the acid exists as an ion pair (11,16).

A mathematical expression was then derived as follows, to permit the equilibrium constant of reaction [1] to be calculated from the spectrophotometric data:

Let A = absorbance of solution

a_1 = molar absorptivity of ferric halide

a_2 = molar absorptivity of tetrahaloferric acid

C_T = total (stoichiometric) molar concentration of iron

C_1 = equilibrium molar concentration of ferric halides

C_2 = equilibrium concentration of tetrahaloferric acid

$(HX)_T$ = total (stoichiometric) molar concentration of hydrogen halide

(HX) = concentration of the unsolvated HX (i.e. $(HX)_f$),plus solvated HX (HX.S).

$(HX)_f$ = concentration of only the molecular species HX, exclusive of any definite solvates such as HX.S. Unless otherwise stated, this meaning will intended henceforth.

$$k_9 = \frac{(HS_2FeX_4)}{(HX)\ (FeX_3.S)} \quad ; \quad k_9{}^* = \frac{(HS_2FeX_4)}{(HX)\ (FeX_3.S)\ (S)}$$

Define apparent molar absorptivity of iron, $a = A/C_T$

Since the solutions were very dilute, the activity, (S) of the ether solvent was taken to be constant, so that

$$k_9 = k_9{}^* \ (S)$$

Now

$$C_T = C_1 + C_2 \qquad (1)$$

$$(HX)_T = (HX) + C_2 \qquad (2)$$

$$A = a\ C_T$$
$$= a_1\ C_1 + a_2\ C_2 \qquad (3)$$

It is then readily shown that

$$(HX) = (HX)_T - \frac{a - a_1}{a_2 - a_1} C_T \qquad (4)$$

$$\frac{a_1 - a}{a - a_2} = k_9 \left[(HX)_T - \left(\frac{a - a_1}{a_2 - a_1} \right) C_T \right]$$
$$= k_9\ (HX) \qquad (5)$$

$$\log \left(\frac{a_1 - a}{a - a_2} \right) = \log k_9 + \log \left[(HX)_T - \left(\frac{a - a_1}{a_2 - a_1} \right) C_T \right]$$
$$= \log k_9 + \log (HX) \qquad (6)$$

Equations (5) and (6) are modified forms of the conventional Benesi-Hildebrand equation .

Now a_1 and a_2 had been separately measured over a range of wavelengths (Tables 1-12). For each of a large number of solutions, $(HX)_T$, and C_T had been measured and the absorbance , hence " a ", of each solution had been measured for a series of wavelengths at 25.0°C, 35.0°C, and 45.0° C (Tables 13-30).

Therefore by means of least-squares fits, equations (5) and (6) were used to evaluate k_9 and log k_9, together with their standard deviations.* The values of log k_9 were used directly to evaluate ΔG^o.

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* The standard deviation of k_9 could not vigorously be used to evaluate the standard deviation of log k_9, for a given value of k_9.

The method of calculation of k_9 is now given in detail for one type of solution, at one temperature and for one wavelength. The solution is HCl-$FeCl_3$-di-n-butyl ether at 25.0°C. The wavelength is 390 mu. Then from Table 13 the values of $(HCl)_T$, $(FeCl_3)_T$ and the absorbance A were re- entered in Columns 1, 2, and 3 of Table 31. The values of $a = A / (FeCl_3)_T$ were calculated for each of the solutions , from Columns 3 and 2 of Table 31, and entered in Column 4 of that Table. The values of a_1 (ferric chloride) and a_2 (tetrachloroferric acid) were taken from Tables 5 and 6, respectively ; $a_1 = 1580$,and $a_2 = 2846$. The quotient $(a_1 - a)/ (a - a_2)$ and its logarithm were then calculated for each solution, and the results entered in Columns 5 and 6 of Table 31. By using equation (4), the concentration of the free hydrogen chloride (solvated and unsolvated) in each solution and its logarithm were calculated, and entered in Columns 7 and 8, respectively.

Least-squares fits of equations (5) and (6) to the relevant data in Table 31 gave

$k_9 = 660$; standard deviation = 53 ; degrees of freedom = 13

$\log k_9 = 2.84$; standard deviation =0.03; degrees of freedom = 13

The standard deviations were calculated according to the equations in Appendix 9 .

The least-squares lines, together with the experimental points used to compute them, are shown in Figs. 9 and 10.

Values of k_9 and $\log k_9$ were similarly calculated for all systems, wavelengths, and temperatures reported in Tables 13-30. The resulting

Table 31 Calculation of equilibrium constant k_9, for the system $HCl-FeCl_3-$ di-n-butyl ether at 25.0°C, for $= 390$ mμ

Basic data : Table 13

C_T $\times 10^4$M	$(HCl)_T$ $\times 10^3$M	A	a	$\frac{a_1-a}{a-a_2}$	$\log(\frac{a_1-a}{a-a_2})$	(HCl) $\times 10^3$M	log (HCl)
2.555	9.640	0.684	2677	6.489	0.8122	9.419	-2.0260
2.465	1.754	0.550	2230	1.056	0.0237	1.627	-2.789
2.043	1.040	0.420	2045	0.598	-0.2235	0.964	-3.016
1.972	1.380	0.428	2171	0.877	-0.0571	1.288	-2.890
1.322	1.042	0.273	2065	0.622	-0.2065	0.991	-3.004
1.443	8.334	0.381	2641	5.182	0.7145	8.213	-2.086
1.506	4.049	0.376	2488	2.534	0.4038	3.941	-2.404
1.345	1.636	0.299	2221	1.027	0.0115	1.568	-2.805
1.569	1.405	0.338	2154	0.831	-0.0806	1.333	-2.875
2.328	14.29	0.634	2723	9.261	0.9670	14.08	-1.852
1.433	6.321	0.373	2600	4.154	0.6182	6.205	-2.207
1.667	6.016	0.432	2592	3.983	0.6002	5.883	-2.230
1.800	1.335	0.390	2164	0.857	-0.0673	1.252	-2.902
1.953	6.212	0.505	2585	3.846	0.5850	6.057	-2.218

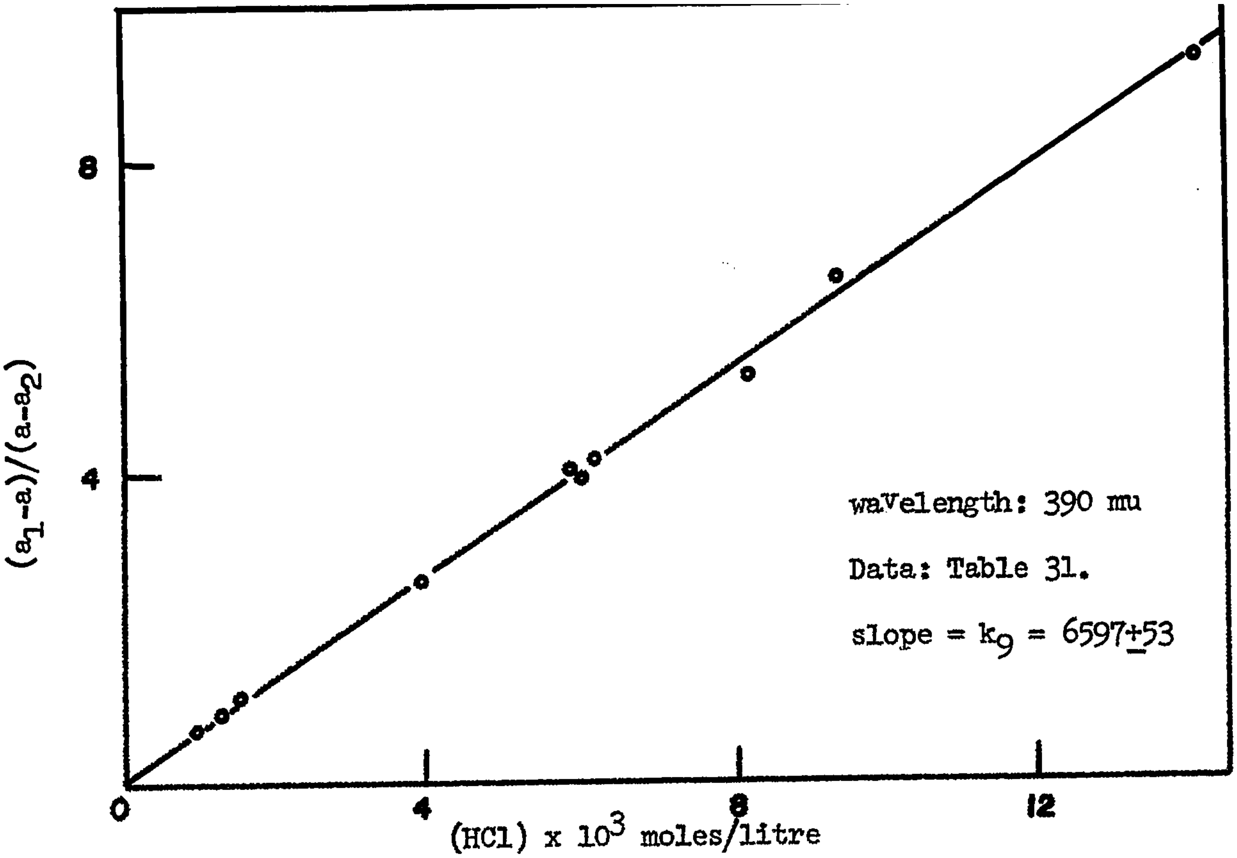

Fig. 9. Least-squares line and experimental points, for system $HCl-FeCl_3$-di-n-butyl ether at 25°C.

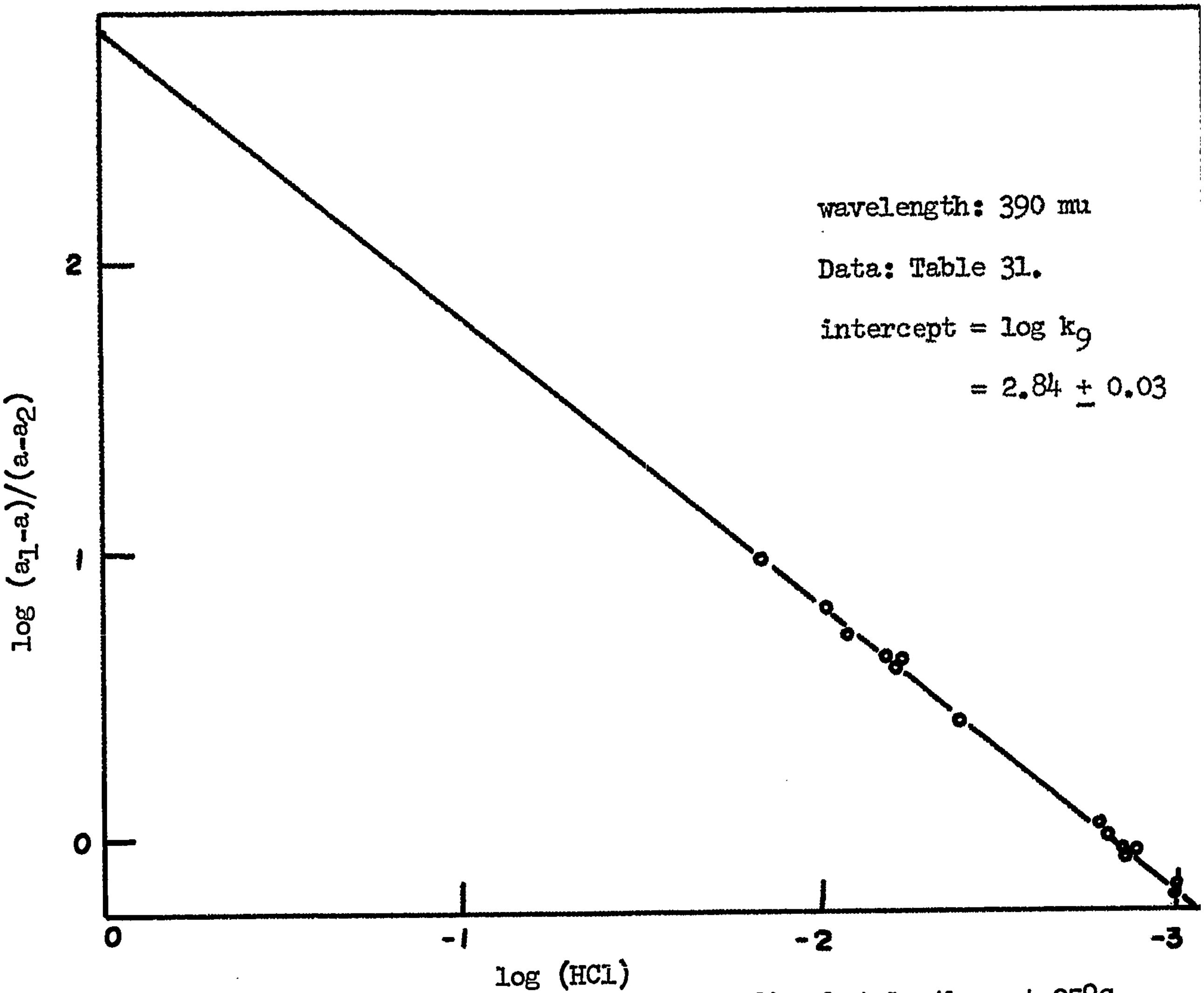

Fig. 10. Least-squares line for system $HCl-FeCl_3$-di-n-butyl ether at 25°C.

values are given in Tables 32-37 inclusive. For a given system at a given temperature, not only k_9 (and also log k_9), but also its standard deviations were estimated at each of the ten wavelengths used. In every case, for the set of ten wavelengths, the ten standard deviations proved to be homogeneous at the 99 $^o/_o$ level significance. Therefore the ten variances of a set were pooled to give a better estimate of the variance. It is the pooled values of the standard deviations that are reported in Tables 13-30.

Finally, the values of the equilibrium constant of each reaction in each solvent were averaged over all wavelengths used. The results are reported in Table 38.

For Tables 32-38 inclusive, the standard state for each of the solutes HS_2FeX_4, HX, and $FeX_3.S$ was chosen to be a hypothetical 1-molar solution of the reactant or product, at 25.0°C that obeyed Henry's law; for the solvent, the standard state was chosen to be the pure solvent at 25.0°C. For Tables 39 and 40, the thermodynamic properties are reported both for molar and molal concentrations. That is, on the molar basis, the standard state was a 1-molar solution, and on the molal basis it was a 1-molal solution which obeyed Henry's law. For Table 39a and 40a, the standard states of HX were chosen to be a 1-molar and a 1-molal solutions of unsolvated HX.

Table 32 Formation constants for the reaction

$HCl + FeCl_3.S + S = HS_2FeCl_4$

in di-n-butyl ether at 25.0°C, 35.0°C, and 45.0°C.

Basic data : Tables 13, 14, 15. All k_9 values are in litre/mole.

wavelength,	25.0°C		35.0°C		45.0°C	
mμ	k_9	log k_9	k_9	log k_9	k_9	log k_9
390	660	2.84	317	2.48	161	2.21
380	656	2.93	320	2.50	157	2.21
370	653	2.82	335	2.57	159	2.19
360	648	2.83	331	2.55	162	2.17
350	642	2.77	332	2.57	158	2.16
340	652	2.81	332	2.49	162	2.21
330	653	2.81	329	2.54	162	2.22
320	663	2.84	349	2.59	159	2.19
310	645	2.83	331	2.54	157	2.13
300	648	2.81	323	2.50	158	2.17
s.d.*	5.5	0.03	4	0.03	2	0.04

Table 33 Formation constants for the reaction

$HBr + FeBr_3.S + S = HS_2FeBr_4$

in di-n-butyl ether at 25.0°C, 35.0°C, and 45.0°C.

Basic data : Tables 16,17, 18. All k_9 values are in litre/mole.

wavelength,	25.0°C		35.0°C		45.0°C	
mμ	k_9	log k_9	k_9	log k_9	k_9	log k_9
510	8820	3.93	4360	3.49	2225	3.33
500	9113	3.98	4634	3.71	2234	3.37
490	9024	4.03	4509	3.67	2228	3.29
480	9165	4.09	4424	3.57	2310	3.42
470	8804	3.93	4415	3.52	2187	3.22
460	9252	4.06	4523	3.74	2282	3.42
440	8831	3.85	4457	3.65	2264	3.41
430	8811	3.93	4409	3.62	2280	3.44
420	8856	3.84	4431	3.57	2268	3.36
410	8986	3.91	4411	3.59	2269	3.34
s.d.*	99	0.07	56	0.08	24	0.08

* s.d. = standard deviation

Table 34 Formation constants for the reaction

$HCl + FeCl_3.S + S = HS_2FeCl_4$

in di-isopropyl ether at 25.0°C, 35.0°C, and 45.0°C.

Basic data : Tables 22, 23, 24. All k_9 values are in litre/mole.

wavelength,	25.0°C		35.0°C		45.0°C	
	k_9	log k_9	k_9	log k_9	k_9	log k_9
390	1285	3.09	591	2.77	243	2.35
380	1341	3.15	556	2.72	259	2.44
370	1312	3.13	586	2.77	258	2.39
360	1327	3.12	581	2.75	254	2.42
350	1298	3.11	554	2.75	254	2.42
340	1318	3.12	571	2.75	253	2.32
330	1299	3.11	564	2.72	254	2.41
310	1292	3.07	595	2.78	257	2.46
300	1310	3.15	576	2.75	246	2.37
290	1280	3.07	571	2.80	255	2.48
s.d.*	16	0.03	8	0.05	4	0.06

Table 35 Formation constants for the reaction

$HBr + FeBr_3.S + S = HS_2FeBr_4$

in di-isopropyl ether at 25.0°C, 35.0°C, and 45.0°C.

Basic data : Tables 25, 26, 27. All k_9 values are in litre/mole.

wavelength,	25.0°C		35.0°C		45.0°C	
mμ	k_9	log k_9	k_9	log k_9	k_9	log k_9
520	2119	3.26	1024	3.10	467	2.77
510	2108	3.26	996	2.96	457	2.68
500	2134	3.30	1014	3.01	462	2.69
490	2234	3.23	1021	3.03	438	2.59
480	2129	3.32	1007	3.06	460	2.75
470	2110	3.38	1016	3.06	460	2.69
410	2166	3.34	991	3.00	439	2.51
400	2184	3.41	1013	3.07	438	2.55
390	2077	3.20	1014	3.08	462	2.77
380	2193	3.36	994	2.95	441	2.58
s.d.*	22	0.06	9	0.05	6	0.08

* s.d. = standard deviation

Table 36 Formation constants for the reaction

$HCl + FeCl_3.S + S = HS_2FeCl_4$

in tetrahydrofuran at 25.0°C, 35.0°C, and 45.0°C.

Basic data : Tables 28, 29, 30. All k_9 values are in litre/mole.

wavelength,	25.0°C		35.0°C		45.0°C	
mµ	k_9	log k_9	k_9	log k_9	k_9	log k_9
390	5146	3.70	2732	3.35	1455	3.15
380	5139	3.74	2743	3.43	1451	3.18
370	5083	3.63	2749	3.39	1439	3.07
360	5085	3.59	2744	3.42	1441	3.10
350	5208	3.71	2762	3.48	1471	3.21
340	5134	3.69	2746	3.44	1441	3.15
330	5178	3.72	2725	3.40	1450	3.22
320	5181	3.71	2737	3.50	1446	3.23
310	5126	3.67	2731	3.37	1454	3.19
300	5175	3.68	2716	3.41	1436	3.18
s.d.*	49	0.06	30	0.06	20	0.08

Table 37 Formation constants for the reaction

$HBr + FeBr_3.S + S = HS_2FeBr_4$

in tetrahydrofuran at 25.0°C, 35.0°C, and 45.0°C.

Basic data : 19, 20, 21. All k_9 values are in litre/mole.

wavelength,	25.0°C		35.0°C		45.0°C	
mµ	k_9	log k_9	k_9	log k_9	k_9	log k_9
520	2026	3.22	1076	3.00	553	2.65
510	2125	3.26	1090	3.07	542	2.78
500	2065	3.28	1101	3.06	547	2.79
490	2201	3.50	1089	3.08	558	2.66
480	2125	3.31	1075	2.98	561	2.82
470	2036	3.20	1083	3.01	549	2.78
410	2186	3.36	1061	3.03	573	2.77
400	2191	3.42	1077	2.96	543	2.75
390	2142	3.37	1079	3.03	542	2.74
380	2169	3.33	1040	2.81	578	2.79
s.d.*	28	0.06	12	0.05	9	0.09

s.d. = standard deviation

Table 38 Summary of average values of equilibrium constants for the reactions

$$HX + FeX_3.S + S = HS_2FeX_4$$

at 25.0°C, 35.0°C, and 45.0°C for di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran.

Basic data : Tables 13-30.

solvent	halide	25.0°C				35.0°C				45.0°C			
	(X)	k_9	s.d.*	log k_9	s.d.*	k_9	s.d.*	log k_9	s.d.*	k_9	s.d.*	log k_9	s.d.*
di-n-butyl ether	chloride	652	6	2.82	0.03	330	4	2.53	0.03	160	2	2.19	0.04
	bromide	8966	99	3.96	0.07	4457	56	3.68	0.08	2255	24	3.36	0.08
di-iso-propyl ether	chloride	1307	14	3.12	0.04	599	8	2.76	0.05	254	4	2.41	0.07
	bromide	2145	22	3.33	0.06	1009	9	3.03	0.05	452	6	2.66	0.08
tetra-hydro-furan	chloride	5150	49	3.69	0.06	2744	30	3.43	0.07	1451	20	3.18	0.08
	bromide	2127	28	3.33	0.06	1077	12	3.00	0.05	555	9	2.75	0.09

degrees of freedom = 9 in each case.

* s.d. = standard deviation.

Standard free energy change, ΔG_9°

The values of log k_9 for the reaction

$$HX + S{+}FeX_3.S = HS_2FeX_4$$

were tabulated in Tables 36 and 37 for the various wavelengths used and the average of log k_9 together with its standard deviation was found. From this average, and standard deviation, the value of ΔG_9° was calculated by using the usual formula.

$$\Delta G_9^\circ = - RT \ln k_9$$

These values of ΔG°_9 and their standard deviations are tabulated in Tables 39 and 40, Column 3.

Enthalpy change ΔH_9°

The formation constant k_9 was evaluated at 25.0°C, 35.0°C, and 45.0°C. Ths standard enthalpy change was calculated by using the Van't Hoff equation on the assumption that over this limited temperature interval, ΔH_9° was constant :

$$\frac{d \log k_9}{d(1/T)} = \frac{-\Delta H_9^\circ}{2.303 R} \qquad (7)$$

where R = gas law constant, 1.987 calories / mole / degree

T = temperature in degree Kelvin

The values of k_9 listed in Table 38 are based on molar concentrations. In order to use equation (7), values of k_9 based on molal concentrations must be used. The relationship between the two values of k_9 is :

$$\log k_9 = \log k_9^{**} - \log d$$

where k_9 is on the molar basis, k_9^{**} is on the molal basis, and d is the density of the solution. The densities of the solutions were not known at the three temperatures. Therefore the reasonable assumption was made of using the densities of the pure ether at 25.0°C, 35.0°C, and 45.0°C. Then by using the above relationship, log k_9** was calculated from the known densities of the solvent and the values of log k_9 given in Table 38. The corresponding values of ΔG_9° were also calculated on the molal basis and are reported in Column 4 of Table 39 and 40.

Graphs of log k_9** versus 1/T proved essentially linear for both the hydrogen halides and for the three ethers. One graph is illustrated in Fig. 11. These graphs confirm the assumption that over the limited temperature interval used, ΔH_9° was constant within limits of experimental error.

A least-squares fit of equation (7) to the log k_9**, 1/T data for each of the hydrogen halides and each of the ethers gave at once the value of ΔH_9° for each of the systems, together with its standard deviation. These values of ΔH_9° are reported in Tables 39 and 40. Finally they were converted to a molar basis, which values are also reported in Tables 39 and 40. Then from the values of ΔG_9° and ΔH_9° on the molar basis, values were obtained for ΔS_9° by using the usual relationship:

$$\Delta G_9^{\circ} = \Delta H_9^{\circ} - T \Delta S_9^{\circ}$$

The equilibrium constants for the reaction

$$HX + R_2O = HX.R_2O$$

density of the solution. The densities of the solutions were not known at the three temperatures. Therefore the reasonable assumption was made of using the densities of the pure ether at 25.0°C, 35.0°C, and 45.0°C. Then by using the above relationship, log k_9** was calculated from the known densities of the solvent and the values of log k_9 given in Table 38. The corresponding values of ΔG_9^o were also calculated on the molal basis and are reported in Column 4 of Table 39 and 40.

Graphs of log k_9** versus 1/T proved essentially linear for both the hydrogen halides and for the three ethers. One graph is illustrated in Fig. 11. These graphs confirm the assumption that over the limited temperature interval used, ΔH_9^o was constant within limits of experimental error.

A least-squares fit of equation (7) to the log k9**,1/T data for each of the hydrogen halides and each of the ethers gave at once the value of ΔH_9^o for each of the systems, together with its standard deviation. These values of ΔH_9^o are reported in Tables 39 and 40. Finally they were converted to a molar basis, which values are also reported in Tables 39 and 40. Then from the values of ΔG_9^o and ΔH_9^o on the molar basis, values were obtained for ΔS_9^o by using the usual relationship:

$$\Delta G_9^o = \Delta H_9^o - T \Delta S_9^o$$

The equilibrium constants for the reaction

$$HX + R_2O = HX.R_2O$$

where X is the chloride or bromide, and R_2O is any one of the three ethers, were measured separately, and are reported in Tables 69 and 70 on page 143 . These values were used in conjunction with those reported in the present section, in order to calculate the equilibrium constants for reaction [1] where HX now represented only the unsolvated molecular species. Thus, the relevant mass-law used was

$$\frac{(\ HS_2FeX_4\ )}{(HX)_f\ (\ FeX_3.S\ )} = k_{9f}$$

The corresponding thermodynamic properties were also designated by a subscript f, namely ΔG^o_{9f}, ΔH^o_{9f}, ΔS^o_{9f} . All these values are given in Tables 39a and 40a.

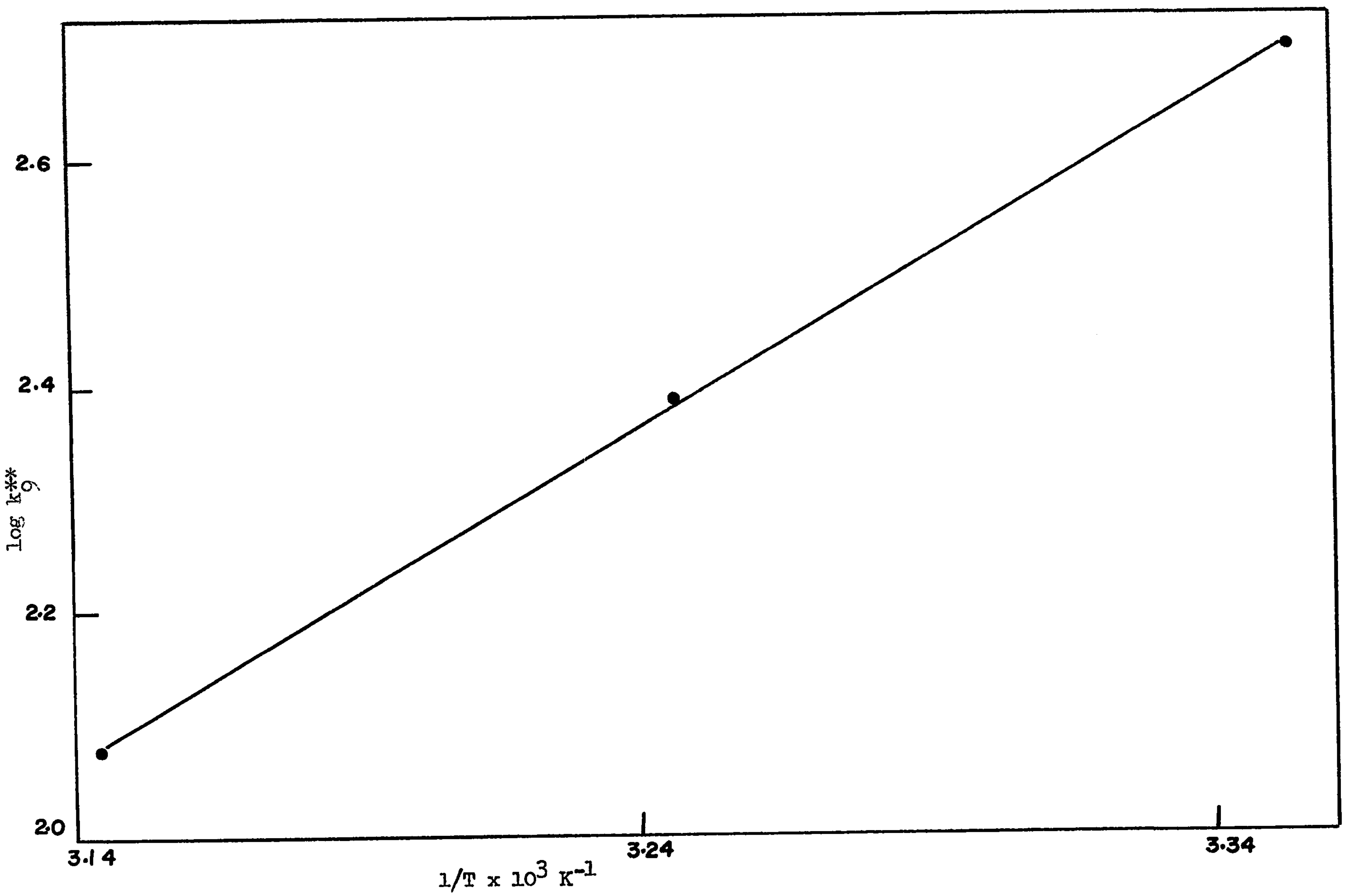

Fig. 11. Log k_9^{**} versus 1/T for the reaction $S + HCl + FeCl_3 = HS_2FeCl_4$ in di-n-butyl ether.

Table 39 Thermodynamic constants for the reaction

$$HCl + FeCl_3.S + S = HS_2FeCl_4$$

in three ethers at 25.0°C, where HCl represents unsolvated species and solvated species.

solvent	k_9	k_9**	$-\Delta G_9^o$	$-\Delta G_9^{o}$**	$-\Delta H_9^o$ kcal/mole		$-\Delta S_9^o$
	litre/ mole	kg/ mole	molar	molal	molal scale	molar scale	e. u.
di-iso-propyl	1307±14	945±10	4.25± 0.09	4.06± 0.09	16.0± 0.9	16.0± 0.9	40 ± 4
di-n-butyl	652±6	499±5	3.84± 0.08	3.68± 0.08	13.8± 0.6	13.8± 0.6	34 ± 3
tetrahydro-furan	5150±49	4573±46	5.01± 0.10	4.99± 0.10	12.5± 0.5	12.5± 0.5	25 ± 3

Table 40 Thermodynamic constants for the reaction

$$HBr + FeBr_3.S + S = HS_2FeBr_4$$

in three ethers at 25.0°C, where HBr represents unsolvated species and solvated species.

Solvent	k_9	k_9**	$-\Delta G_9^o$	$-\Delta G_9^{o}$**	$-\Delta H_9^o$,kcal/mole		$-\Delta S_9^o$
	litre/ mole	kg/ mole	molar	molal	molal scale	molar scale	e. u.
di-iso-propyl	2145±22	1551±15	4.53± 0.09	4.35± 0.08	15.2± 0.7	15.2± 0.7	36 ± 3
di-n-butyl	8966±99	6855±76	5.38± 0.12	5.23± 0.10	13.6± 0.5	13.6± 0.5	28 ± 2.5
tetrahydro-furan	2127±28	1888±25	4.53± 0.09	4.47± 0.09	13.3± 0.8	13.3± 0.8	30 ± 3

Table 39a Thermodynamic constants for the reaction

$HCl + FeCl_3.S + S = HS_2FeCl_4$

in three ethers at 25.0°C, where HCl comprizes only the unsolvated species.

solvent	k_{9f}	k_{9f}	$-\Delta G^o_{9f}$	$-\Delta G^{o**}_{9f}$	$-\Delta H^o_{9f}$ kcal/mole		$-\Delta S^o_{9f}$
	litre/mole,x10^4	kg/mole,x10^4	molar	molal	molal	molar	e.u.
di-iso-propyl	8.83±0.09	6.39±0.07	6.75±0.07	6.55±0.07	21.0±1.3	21.0±1.3	48 ± 5
di-n-butyl ether	1.94±0.02	1.49±0.02	6.27±0.07	5.69±0.07	17.9±1.0	17.9±1.0	39 ± 4
tetrahydrofuran	429±5	380±4	9.05±0.10	8.99±0.1	18.4±1.1	18.4±1.1	31 ± 4

Table 40a Thermodynamic constants for the reaction

$HBr + FeBr_3.S + S = HS_2FeBr_4$

in three ethers at 25.0°C, where HBr comprizes only the unsolvated species.

solvent	k_{9f} x 10^4	k^{**}_{9f} x $1o^4$	$-\Delta G^o_{9f}$	$-\Delta G^{o**}_{9f}$	$-\Delta H^o_{9f}$ kcal/mole		$-\Delta S^o_{9f}$
	litre/mole	kg/mole	molar	molal	molal	molar	e.u.
di-iso-propyl	3.21±0.04	2.32±0.03	6.15±0.07	5.96±0.06	19.0±1.2	19.0±1.2	43 ± 4
di-n-butyl	16.7±0.20	12.8±0.15	7.12±0.08	6.97±0.08	17.7±1.0	17.7±1.0	36 ± 3
tetrahydrofuran	127±1.5	113±1.2	8.33±0.09	8.26±0.09	18.7±1.3	18.7±1.3	35 ± 4

II. Vapour pressure method

Two distinct systems were studied by a vapour pressure method in which the apparatus shown in Fig. 1 was used. First, the equilibrium constants were found for the reaction

$$HX + R_2O = HX.R_2O$$

where HX was HCl and HBr, and R_2O was di-isopropyl ether at 25.0°C. The studies on these reactions are described below, in Subsection A.

Secondly, the vapour pressure method was used to measure the equilibrium constants for the reaction

$$HX + H_2O = HX.H_2O$$

in di-isopropyl ether at 25.0°C. These studies are also reported below, in Subsection B.

A. Study of the reactions, $HX + R_2O = HX.R_2O$

(a) Synopsis

The partial vapour pressure of hydrogen chloride over a solution of hydrogen chloride and di-isopropyl ether in carbon tetrachloride as solvent was measured for several concentrations of hydrogen chloride and ether in the solvent at 25.0°C. Henry's law constant was evaluated from these data. Similar measurements were made with hydrogen bromide.

From the data, it proved possible to establish that each hydrogen halide formed with the ether a soluble monosolvate. It also proved possible to calculate the formation constants of these monosolvates in carbon tetrachloride at 25.0°C.

The hydrogen halide-carbon tetrachloride-ether solution was allowed to reach equilibrium with its vapour contained in a 500-ml bulb shown in Fig. 1. A period of seven hours was found to be sufficient to establish equilibrium (Table 41). The hydrogen halide vapour in the 500-ml bulb was then dissolved in water , and the acid concentration was determined by a potentiometric titration with standard alkali. The partial pressure of hydrogen chloride and bromide over the mixtures was calculated, after correcting for non-ideality of the vapour.

(b) Procedure

All operations were carried in a dry box. First, solutions of the hydrogen halides and the ethers in carbon tetrachloride were prepared. Thus, a concentrated stock solution of hydrogen halide in carbon tetrachloride was prepared with the apparatus shown in Fig. 2, by passing hydrogen halide gas into carbon tetrachloride for thirty minutes. The hydrogen halide content of the resulting solutions was determined by potentiometric titration of an aliquot, with 0.5M sodium hydroxide (previously standardized).

Aliquots of approximately 45, 40, 30, 20 and 10 ml of the above stock solution were delivered into separate, previously dried 50-ml volumetric flasks and made up to 50-ml with anhydrous carbon tetrachloride. The dispensing of these aliquots were carried out directly from the separatory funnel used in the generator of Fig. 2, and the volume dispensed was not accurately measured at this point.

A similar set of solutions of hydrogen halide was then prepared in a solvent which was 5% (V/V) ether in carbon tetrachloride . Thus 5 ml of the ether were pipetted into a 50-ml volumetric flask, the stock solution of hydrogen halide-carbon tetrachloride was added, and the contents were diluted to the mark with carbon tetrachloride. In this way, a set of solutions was obtained of the hydrogen halide in 5% ether in carbon tetrachloride. Similar set of solutions of the hydrogen halide were prepared in solvents that consisted of 10 % (V/V) ether, 50 % (V/V) ether in carbon tetrachloride, and pure ether. In practice, four of the above described solutions were prepared at one time, and vapour pressure measurements carried out on them. For this purpose, the 200-ml round bottomed flask shown in Fig 1 was cleaned , dried, and the stopcock greased as described in Appendix 4. The contents of the 50-ml flasks containing the hydrogen halide-ether-carbon tetrachloride were then poured carefully into the 200-ml round-bottom flask illustrated in Fig.1, in a dry box. The 2-mm side stopcock was closed. The filled flask was capped and removed for later use.

The entire vapour pressure apparatus is shown in Fig. 1. It was cleaned, and dried, and the stopcock greased, as described in Appendix 4. The 10-mm stopcock of the apparatus was closed, and the 200-ml flask containing the hydrogen halide- ether- carbon tetrachloride solution was then joined to the apparatus via § B- 19/26.

With the 10-mm stopcock closed, the 500-ml bulb was evaculated for ten to fifteen minutes by means of rubber tubing joined to a high vacuum pump through the quick-fit ground joint B 14 at the top of the

100-ml separatory funnel. The 3-mm stopcock of that separatory funnel was then closed, and the vacuum pump was disconnected. At this point, care was then taken to ensure that the solution in the 200-ml flask did not exceed 25.0°C. The 10-mm stopcock which led to the 200-ml flask that contained the HX-ether-carbon tetrachloride solution was then slowly opened. The whole apparatus was then immersed in a 25.0 ± 0.1°C constant-temperature bath, for equilibration. After seven hours, the 10-mm stopcock was closed before the apparatus was removed from the constant -temperature water bath. The 200-ml flask was removed, quickly capped, and reserved for analysis of its contents.

About 40 ml of water were placed in the 100-ml separatory funnel. Its 3-mm stopcock was then slowly and carefully opened, so that the water ran into the 500-ml bulb, but the stopcock was closed when 2-3 ml remained above it. The water was allowed to remain in the 500-ml bulb for 10 minutes, with occasionally shaking. Then the acid was transferred quantitatively to a 150-ml beaker, by using two 20-ml portions of water. The acid solution was titrated potentiometrically against 0.5 M or 0.05 M standard sodium hydroxide solution.

A 5-ml aliquot of the nonaqueous solution remaining in the 200-ml round-bottom flask was pipetted into a 150-ml beaker containing 100 ml water, so that to extract the acid from the ether-carbon tetrachloride solution. Without removing the organic phase, the aqueous extract was titrated potentiometrically with 0.5 M standard sodium hydroxide solution, by using the automatic titrator (Radiometer).

By using the above procedure, the vapour concentration of hydrogen halide (bromide and chloride) in each of the following anhydrous solutions was measured : (i) hydrogen halide in pure carbon tetrachloride, with the hydrogen halide concentration 0.003 M to 0.01 M; (ii) 5 % (V/V) di-isopropyl ether in carbon tetrachloride, with the hydrogen halide concentration 0.02 M to 0.08 M ; (iii) 10 % (V/V) di-isopropyl ether in carbon tetrachloride , with the hydrogen halide concentration 0.02 M to 0.1 M ; (iv) 50 % (V/V) di-isopropyl ether in carbon tetrachloride with the hydrogen halide concentration 0.03 M to 0.1 M ; and (v) in 100 % anhydrous di-isopropyl ether with the hydrogen halide concentration from 0.2 M to 1.0 M.

In order to calculate the equilibrium vapour pressure of the hydrogen halide gas, from the acid content of the aqueous extract of the 500-ml bulb, the exact volume of the 500-ml bulb was determined. Thus, with the 500-ml bulb inverted and the 3- mm stopcock closed, distilled water at 25.0°C was dispensed from a calibrated buret, through the 10-mm stopcock of the bulb, until the water level just reached the 10-mm stopcock. The volume of the water was then read directly from the buret.

The equilibrium vapour concentration of the hydrogen halide over the HX-ether-carbon tetrachloride solution was then calculated by using this measured volume of the 500-ml bulb, and the number of moles of hydrogen halide found by potentiometric titration of the water extract of the vapour in that bulb.

(c) Experimental results

Equilibrium studies were carried out in order to determine the period of time required for equilibration of HX-ether-carbon tetrachloride solution in the 200-ml bulb of the apparatus in Fig. 1, with the vapour in the 500-ml bulb. For these studies, two solutions were chosen, one was 0.0478 M HCl in carbon tetrachloride , and the other was 0.3528M HCl in di-isopropyl ether. The partial pressure of the hydrogen chloride above these solutions as a function of time is reported in Table 41. The pressures in Column 2 and 4 have not been corrected for non-ideality. It was clear that an equilibration period of seven hours was sufficient for these systems.

For convenience, the equilibrium vapour concentrations of the hydrogen halide obtained by using the procedure in the preceding Subsection were converted to the equivalent equilibrium vapour pressures of hydrogen halide, by using the ideal gas law:

$$p_{HX} = n\ R\ T/\ V$$

where p_{HX} = partial pressure of hydrogen halide , in atmospheres

n = number of moles of hydrogen halide vapour in the 500-ml bulb, above the HX-ether-CCl_4 solution. The value of n was found as already described, by direct analysis of the vapour in the bulb.

V = volume of the 500-ml bulb, in litres

R = gas law constant = 0.0821 litre-atmosphere per degree per mole

T = temperature in degree Kelvin

These calculated partial pressures are reported in Tables 42-45 inclusive and are illustrated in Figs. 12 and 13. It is to be noted that these partial pressures were used only for preliminary calculations. They are later corrected for non- ideality, prior to the final calculations.

Table 41 Vapour pressure of HCl in carbon tetrachloride and in di-isopropyl ether at 25.0°C, as a function of equilibration period.

Carbon tetrachloride (HCl) = 0.0478 M		di-isopropyl ether (HCl) = 0.3528 M	
Period, hours	Pressure, mm.	Period, hours	Pressure, mm.
1	160.1	1	21.3
2	176.0	2	22.4
3	189.9	3.5	23.8
4	197.2	5	24.8
4.5	199.0	6	25.4
5	200.0	6.5	25.6
6	199.7	7	25.7
7	200.6	8	25.7
8.5	200.0	9	25.7
10	201.0	11	25.7
11.5	200.0		

Table 42 Uncorrected vapour pressure of HCl over anhydrous HCl-di-isopropyl ether-carbon tetrachloride solutions at 25.0°C.

carbon tetrachloride		5%(V/V) di-isopropyl ether in CCl_4		50%(V/V) di-isopropyl ether in CCl_4	
(HCl),M	Pressure, mm.	(HCl), M	Pressure, mm.	(HCl), M	Pressure, mm.
0.0572	257.5	0.0573	71.4	0.0536	6.96
0.0332	169.6	0.0312	39.0	0.0692	9.06
0.0448	200.0	0.0198	25.9	0.0425	5.62
0.0221	97.0	0.0507	62.3	0.0981	12.9
0.0468	208.0	0.0829	110.9	0.0862	11.3
0.0480	215.6	0.0314	39.0	0.0328	4.27
0.0525	234.0				
0.0475	212.0				
0.0239	106.3				
0.0213	93.6				
0.0442	195.5				

Table 43 Uncorrected vapour pressure of HCl over anhydrous HCl-di-isopropyl ether-carbon tetrachloride solutions at 25.0°C.

10% di-isopropyl ether in carbon tetrachloride				di-isopropyl ether	
(HCl),M	Pressure, mm.	(HCl),M	Pressure, mm.	(HCl),M	Pressure, mm.
0.1038	76.8	0.1870	14.5	0.364	26.1
0.0821	60.1	0.0710	51.3	0.844	63.0
0.0835	61.3	0.0998	73.0	1.208	95.0
0.0953	69.7	0.1107	80.5	0.357	26.2
0.0619	44.2	0.0983	73.5	1.169	91.3
0.0479	34.1	0.1414	109.6	0.608	44.9
0.0279	18.9	0.1357	102.0	0.808	61.3
0.0284	18.9	0.0998	75.2	0.608	45.6
0.0917	68.3	0.0762	54.5	0.448	33.1
0.0622	44.7			0.191	12.4
0.0392	24.8			0.353	25.7
0.0267	18.4			0.334	24.7
0.0358	25.3			0.461	34.1
0.0175	10.9			0.601	45.3

Table 44 Uncorrected vapour pressure of HBr over anhydrous HBr-di-isopropyl ether-carbon tetrachloride solutions at 25.0°C.

carbon tetrachloride		5%(V/V) di-isopropyl ether in CCl_4		50% di-isopropyl ether in CCl_4	
(HBr), M	Pressure, mm.	(HBr),M	Pressure, mm.	(HBr),M	Pressure, mm.
0.0190	40.7	0.0545	60.2	0.0986	18.7
0.0140	27.6	0.0360	37.8	0.0787	16.0
0.0101	18.8	0.0320	33.0	0.0741	15.6
0.0101	19.3	0.0311	34.0	0.0926	18.8
0.0342	63.3	0.0245	26.3	0.0555	11.6
0.0243	51.0	0.0203	22.3	0.0331	6.4
0.0160	29.2				
0.0754	147.0				
0.0474	90.4				
0.0380	73.8				
0.0300	59.8				

Table 45 Uncorrected vapour pressure of HBr over anhydrous HBr-di-isopropyl ether-carbon tetrachloride solutions at 25.0°C.

10%(V/V) di-isopropyl ether in CCl_4		di-isopropyl ether			
(HBr),M	Pressure, mm.	(HBr),M	Pressure, mm.	(HBr),M	Pressure, mm.
0.0532	39.1	0.812	73.5	0.729	69.3
0.0477	33.7	0.883	76.6	0.465	41.8
0.0389	25.8	0.283	27.6	0.745	74.5
0.0392	26.3	0.233	20.8	0.401	37.2
0.0332	24.8	0.796	66.5	0.314	28.8
0.0270	22.6	0.326	25.8	0.250	22.0
		0.208	17.9	0.108	8.0

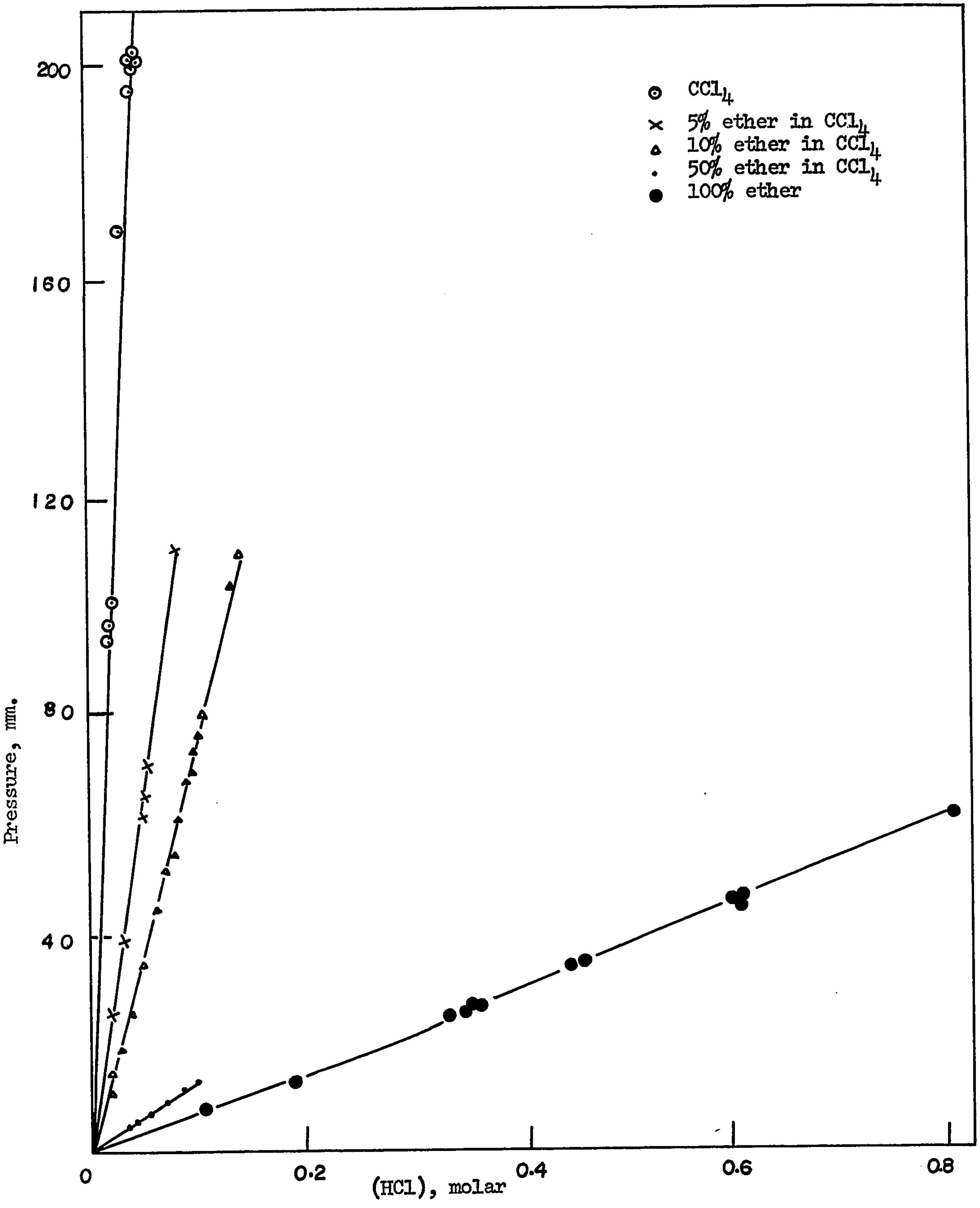

Fig. 12. Uncorrected vapour pressure of HCl over anhydrous HCl-di-isopropyl ether-carbon tetrachloride solutions at 25°C.

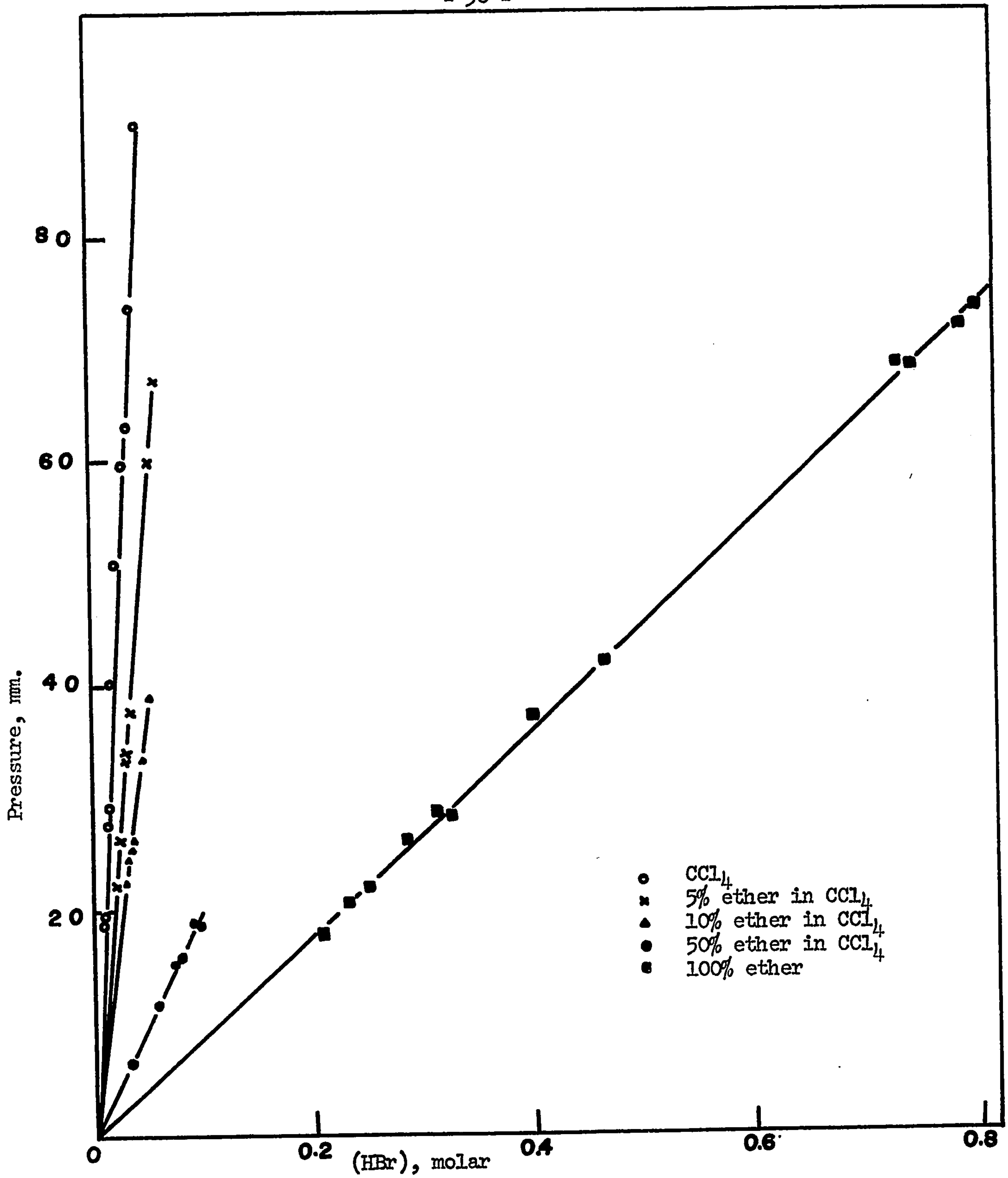

Fig. 13. Uncorrected vapour pressure of HBr over anhydrous HBr-di-isopropyl ether-carbon tetrachloride solutions at 25°C.

(d) Treatment of the data

(i) Synopsis

The measured vapour concentrations of both hydrogen chloride and hydrogen bromide in equilibrium with liquid mixtures of carbon tetrachloride and di-isopropyl ether at 25.0°C are reported in Tables 42-45. Etherates of the hydrogen halides in the solutions were postulated in order to explain the drop in the vapour concentration of the hydrogen halide as the ether content of the solution was increased. As a first approximation, the vapour was considered to be ideal; thereby uncorrected partial vapour pressures of the hydrogen halides were calculated. An algebraic equation was derived which related these vapour pressures to solution composition, and which contained the formation constants of the postulated etherates of the hydrogen halide. From a least-squares fit of this equation to the vapour pressure data, a monoetherate $HX.R_2O$ was found to be necessary and sufficient to explain the data, and its formation constant was simultaneously evaluated.

By using the formation constant found for $HX.R_2O$ in solution, it proved possible to correct the partial vapour pressure of the hydrogen halides for non-ideality due solely to hydrogen bonding in the vapour phase. These corrected partial vapour pressures were found to obey Henry's law over a wide range of concentration, which had not been the case with the uncorrected pressures.

The corrected partial pressures were then used to obtain a better and final estimate of the formation constants of $HX.R_2O$ in solution, by repeating the calculations described in the first paragraph. Use of these new values of the formation constant were found not to change the values of the non-ideality corrections to the partial vapour pressures.

Finally, the second virial coefficients for the vapours were calculated, and additional corrections to the already corrected partial vapour pressures of the hydrogen halides were calculated. They were found to be very much less than the experimental error in the measurement of the vapour concentrations and therefore they were ignored.

(ii) Derivation of the algebraic equation

In the ternary solution $HX\text{-}R_2O\text{-}CCl_4$ or the binary solution $HX\text{-}R_2O$, where HX is hydrogen chloride or bromide and R_2O is di-isopropyl ether, one or more etherates of the hydrogen halides may be postulated. Thus

$$HX + nR_2O = HX.nR_2O \qquad ,n= 1,\ 2,\ 3,\ \ldots\ldots$$

Assume that the solution is ideal.

$$K_n = \frac{(HX.nR_2O)}{(HX)_f\ (R_2O)^n} \qquad ,\ n = 1,\ 2,\ 3,\ \ldots\ldots \qquad (8)$$

where round brackets then denote molar concentrations.*

If $(HX)_b$ denotes the stoichiometric concentration of bound hydrogen halide, then it is readily shown that

$$\phi_1 = \frac{(HX)_b}{(HX)_f(R_2O)} = \sum_{n=1}^{n} K_n\ (R_2O)^{n-1} \qquad (9)$$

(iii) Initial estimation of the formation constant, K_n

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* The standard state for each reactant and product, including the ether, was chosen to be a hypothetical 1-molar solution of the reactant or product, at 25.0°C that obeyed Henry's law.

It was provisionally assumed that only the monoetherate, $HX.R_2O$, existed in the solutions. Then it is seen from equation (9) that the slope of a plot of ϕ_1 versus (R_2O) would give the value of K_1 directly; curvature would imply higher etherates. In practice, a least-square fit was made.

Only the total concentration of HX and of R_2O were measured; but the concentration of free HX and free R_2O were required. Figs 12 and 13 are plots of the data in Tables 42-45; they show the uncorrected partial vapour pressure of the hydrogen halide versus the total concentration of the hydrogen halide in a given ether-carbon tetrachloride solution. The hydrogen halide in this latter case was regarded as being " free ". Then for a given $HX-R_2O-CCl_4$ solution, by referring the uncorrected partial pressure of HX directly to the corresponding graph for pure carbon tetrachloride as solvent, the concentration of free HX in the particular $HX-R_2O-CCl_4$ solution was estimated. Since only a monosolvate was assumed, and the total concentrations of the hydrogen halide and of the ether were known, the concentrations of bound HX and of free ether could be deduced. These calculated values were then used to calculate the ϕ_1 of equation (9), which was then plotted against the corresponding value of the concentration of free ether. The data* are in Tables 46 and 47 for hydrogen chloride and hydrogen bromide, respectively.

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* In the case of hydrogen halide in pure ether, two sets of values are given in Tables 46 and 47. (Column 7) is one set which represents the initial estimates, by using the uncorrected vapour pressures. The second set (column 8) represents the final estimates, by using corrected vapour pressures found as described later.

Typical plots are shown in Fig. 14, with the least-squares lines drawn independently on the graphs.

That ϕ_1 was essentially constant over the entire range of ether concentrations indicates that (i) the monosolvate was the only important solvate, and (ii) the activity coefficients were not significantly different from unity, and (iii) it was unnecessary to apply Butler's correction (51) to the ternary systems, HX-R_2O-CCl_4, since the values of K_1 for them were not significantly different from the value found for the binary system HX-R_2O.

The values of ϕ_1, that is the formation constant K_1 of the monosolvate, in Tables 46 and 47 were averaged for each ether-carbon tetrachloride solution; and these averaged values with their standard deviations are entered in Table 48. In the case of hydrogen chloride in pure di-isopropyl ether, one value was found by using uncorrected vapour pressures, and the other by using vapour pressures corrected as described later, for non-ideality.

(iv) Non-ideality of the vapour phase due to hydrogen bonding

The initial estimates of the formation constants of the monosolvates of the hydrogen chloride and of the hydrogen bromide, obtained in the preceding section, were based on the assumption that the vapour phases were ideal for the system HX-ether-CCl_4. The demonstrated existence of a monosolvate $R_2O.HX$ in the solutions suggests its existence in the vapour, to produce non-ideality. MacFarlane and Wright (43) showed that when vapours of di-ethyl ether and hydrogen chloride were mixed, there was a contraction of pressure which indicated that hydrogen chloride and ether interacted in the vapour phase. In the present work, two types

Table 46 Values of ϕ_1 for various concentrations of free di-isopropyl ether, in the system HCl-ether-CCl_4 at 25.0°C.

ϕ_1 is defined by equation (9)

Basic data : Tables 42, 43.

5%(V/V)di-isopropyl ether in CCl_4		10%(V/V)di-isopropyl ether in CCl_4		50%(V/V)di-isopropyl ether in CCl_4		100% di-isopropyl ether		
						ϕ_1		
ϕ_1	Free (R_2O), M	ϕ_1	Free (R_2O), M	ϕ_1	Free (R_2O), M	From uncorrected partial pressures	From corr. partial pressures	Free (R_2O), M
8.09	0.312	9.15	0.618	8.58	3.48	9.10	9.50	6.70
7.46	0.331	7.80	0.638	8.70	3.46	9.40	9.80	6.23
9.63	0.239	7.96	0.636	8.46	3.47	9.41	9.80	5.87
8.08	0.317	8.04	0.627	8.58	3.43	8.37	8.60	6.71
7.87	0.295	7.73	0.654	8.62	3.44	9.49	9.90	5.91
7.45	0.331	7.72	0.666	8.58	3.49	9.16	9.60	6.46
		7.62	0.683			8.18	8.50	6.27
		8.01	0.682			9.02	9.40	6.46
		7.75	0.630			9.06	9.40	6.62
		7.79	0.654			9.79	10.2	6.87
		8.74	0.673			8.94	9.30	6.71
		7.63	0.684			8.53	8.90	6.73
		7.66	0.676			8.80	9.10	6.61
		7.96	0.691			8.77	9.10	6.47
		6.53	0.691					
		7.84	0.641					
		8.06	0.623					
		8.26	0.614					
		7.83	0.624					
		8.01	0.589					
		7.92	0.593					
		7.70	0.623					
		7.97	0.642					

Table 47 Values of ϕ_1 for various concentrations of free di-isopropyl ether, in the system HBr-ether-CCl_4 at 25.0°C.

ϕ_1 is defined by equation (9)

Basic data : Tables 44, 45.

5%(V/V) di-isopropyl ether in CCl_4		10%(V/V) di-isopropyl ether in CCl_4		50%(V/V) di-isopropyl ether in CCl_4		100% di-isopropyl ether		
ϕ_1	Free (R_2O), M	ϕ_1	Free (R_2O), M	ϕ_1	Free (R_2O), M	ϕ_1		Free (R_2O), M
						From uncorrected partial pressures	From corrected partial pressures	
2.25	0.330	2.40	0.673	2.67	3.44	3.22	3.35	6.29
2.46	0.337	2.55	0.676	2.45	3.46	3.41	3.56	6.22
2.55	0.338	2.79	0.681	2.35	3.46	2.76	2.84	6.79
2.24	0.340	2.74	0.681	2.45	3.45	3.02	3.10	6.84
2.31	0.332	2.33	0.676	2.37	3.48	3.45	3.58	6.40
2.20	0.344	1.91	0.681	2.56	3.50	3.45	3.58	6.75
						3.11	3.23	6.86
						3.03	3.10	6.37
						3.08	3.15	6.62
						2.86	2.94	6.35
						2.96	3.07	6.68
						2.95	3.06	6.76
						3.07	3.15	6.82
						3.56	3.64	6.96

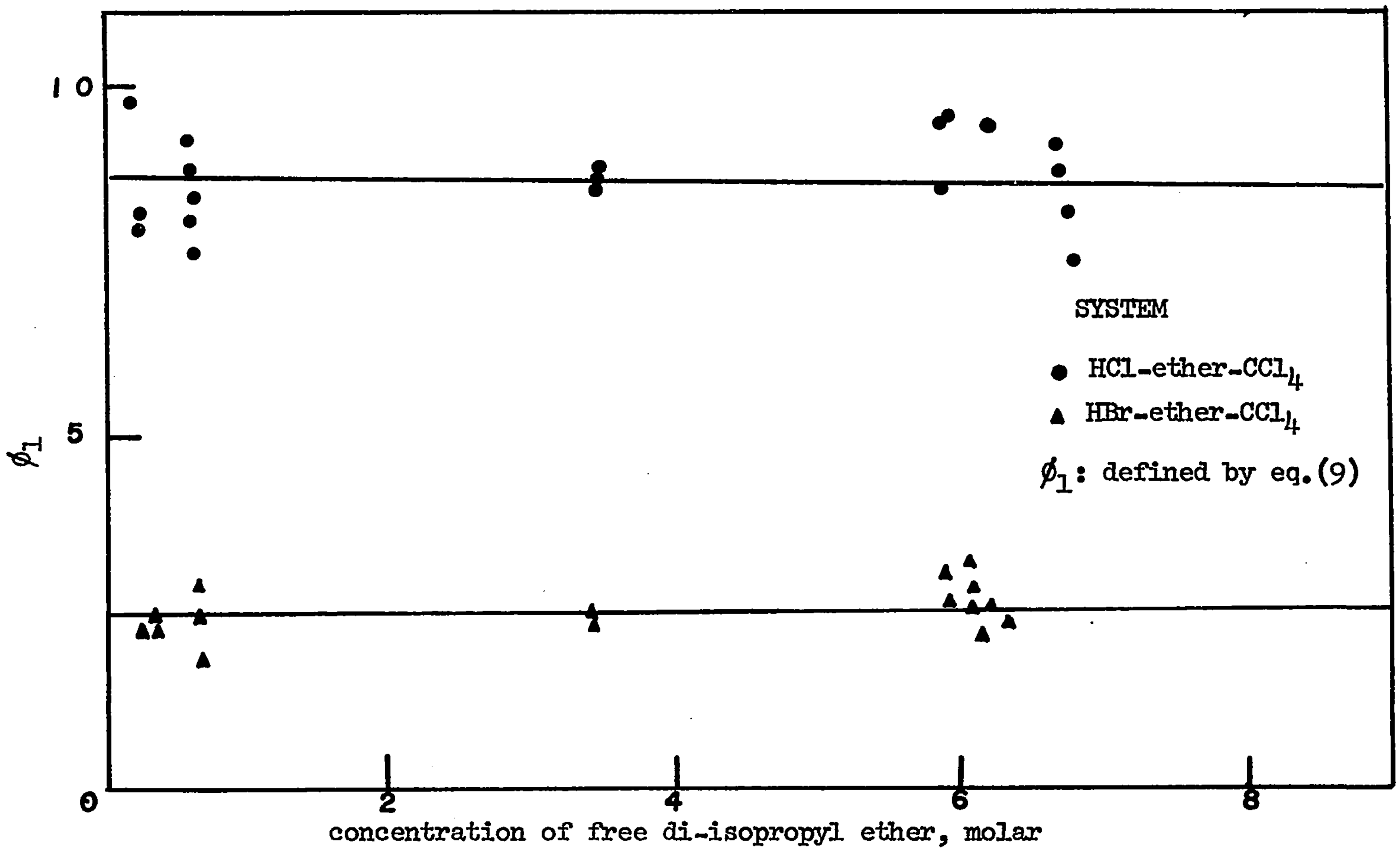

Fig. 14. ϕ_1 as a function of the molarity of free di-isopropyl ether in the systems HCl-di-isopropyl ether-carbon tetrachloride and HBr-di-isopropyl ether-carbon tetrachloride at 25°C.

Table 48 Equilibrium constant (K_1) for the reaction

$$HX + R_2O = R_2O.HX$$

in CCl_4 at 25.0°C.

HX is HCl or HBr; R_2O is di-isopropyl ether

HX	Ether % (V/V) in CCl_4	K_1 l./M	s.d.	d.f.
HCl	5	8.1	0.3	6
	10	7.9	0.3	23
	50	8.6	0.3	6
	100	9.1 (uncorr)	0.5	14
		9.3 (corr.)	0.6	14
HBr	5	2.3	0.3	6
	10	2.4	0.3	6
	50	2.5	0.2	6
	100	3.1 (uncorr)	0.3	14
		3.2 (corr.)	0.3	14

Table 48a Density of di-isopropyl ether and of HX-di-isopropyl ether solutions at 25.0°C

Solutions of HCl-di-isopropyl ether	density$^{25}_{4}$ gm/cc.	Solutions of HBr-di-isopropyl ether	density$^{25}_{4}$ gm/cc.
ether	0.7238	ether	0.7232(26)
0.0312	0.7247	0.0201	0.7253
0.0425	0.7249	0.0596	0.7281
0.0614	0.7252	0.0875	0.7307
0.1126	0.7252	0.1234	0.7336
0.2698	0.7296	0.2469	0.7435

of interaction were considered, Van der waals forces between like and unlike molecules, and chemical interaction due to hydrogen bonding.

A method was sought to correct the partial vapour pressures of hydrogen halide over the solutions $HX-R_2O-CCl_4$ for that part of the nonideality that was due to hydrogen bonding. The formation constants of $HCl.R_2O$ and of $HBr.R_2O$ in $HX-R_2O-CCl_4$ solutions were reasonably constant over a wide range of ether concentrations (see Table 48), and therefore over the range 2.2 to 3.9 of the dielectric constants of these solutions. Therefore as a reasonably approximation it was assumed that the formation constan was independently of dielectric constant of the solvent, so that the formation constant on a molar basis would then be the same in the vapour phase as it was in the ternary solutions.

Since for the vapour phase

$$(HX) = (HX)_f + (R_2O.HX) \qquad (10)$$

and $$(R_2O)_T = (R_2O) + (R_2O.HX) \qquad (11)$$

and $$\frac{(R_2O.HX)}{(R_2O)\ (HX)_f} = 9.0 \text{ for HCl, and } 2.6 \text{ for HBr} \qquad (12)$$

the values of $(HX)_f$ in the vapour could be evaluated, given (HX)and $(R_2O)_T$, which were the total vapour concentrations of the hydrogen halide and of di-isopropyl ether, respectively. The values of (HX) were known, but not those of $(R_2O)_T$.

The values of $(R_2O)_T$ were estimated by using the Gibbs-Duhem equation. Thus, from the uncorrected partial pressures of the hydrogen halide given in Tables 43, 45 (and repeated in Tables 52 and 53, column 2) and the mole-fractions of the hydrogen halide and the ether were calculated by a conventional graphical integration of the Gibbs-Duhem relationship, (see Appendix 11 for details), and listed in Tables 52 and 53, Column 4. The required mole-fractions in the solutions were found from the molarities given in Tables 43 and 45, and the measured densities of the solutions, given in Table 48a. These calculated values for the partial pressures of the ether for the binary system HX-ether are given in Tables 52 and 53, Column 5. It is to be noted that these values are approximate; but they were adequate for the purpose of correcting the vapour pressure values of the hydrogen halide. By using the ideal gas law, they were converted to vapour concentrations, and used for $(R_2O)_T$ in equation (11).

Then from the values of (HX) and $(R_2O)_T$ listed in Tables 52 and 53, and equations (10), (11), and (12), values were found for $(HX)_f$, the molarity of free hydrogen halide in the vapour. These values were converted to partial pressures, which are entered in Tables 52 and 53, Column 3. Comparison of Columns 2 and 3 of Tables 52 and 53 shows the deviation from ideality due to hydrogen bonding; and Figs 15 and 16 illustrate these deviations. Of special importance are two evident facts : (i) Henry's law is obeyed over the entire concentration range when the values of the corrected partial pressures are plotted; (ii) the deviations from ideality are only 2% to 5% for hydrogen chloride and 1% to 2% for hydrogen bromide.

(v) Correction of the partial pressures of hydrogen halides for non specific interaction in the vapour phase.

The corrections to the partial pressure of hydrogen halide over

Table 52 Uncorrected and corrected partial pressures of HCl and di-isopropyl ether solutions of HCl at 25.0°C.

(HCl), M	uncorrected partial pressure of HCl, mm	corrected partial pressure of HCl, mm	uncorrected partial pressure of di-isopropyl ether, mm	corrected partial pressure of di-isopropyl ether, mm
0.364	26.1	24.7	154.2	155.7
0.357	26.2	24.8	154.2	155.8
0.844	63.0	58.9	143.7	146.2
1.169	91.3	85.7	136.5	138.1
1.208	95.0	89.0	133.6	139.8
0.608	44.9	43.5	148.6	150.7
0.808	61.3	58.2	144.2	146.9
0.608	45.6	44.8	148.9	150.7
0.448	33.1	32.0	152.2	153.9
0.191	12.4	11.6	158.5	159.4
0.353	25.7	25.0	154.4	155.9
0.334	24.7	24.1	154.7	156.3
0.461	34.1	33.2	151.8	153.7
0.601	45.3	44.5	149.0	150.7

Table 53 Uncorrected and corrected partial pressures of HBr and di-isopropyl ether over di-isopropyl ether solutions of HBr at 25.0°C.

(HBr), M	uncorrected partial preesure of HBr, mm	corrected partial pressure of HBr, mm	uncorrected partial pressure of di-isopropyl ether, mm	corrected partial pressure of di-isopropyl ether, mm
0.812	73.5	71.8	145.2	146.8
0.883	80.1	79.0	143.5	145.5
0.283	27.6	26.9	156.0	157.4
0.796	72.2	71.3	145.1	147.1
0.233	20.8	20.7	157.7	158.5
0.326	28.4	28.0	156.3	156.5
0.208	17.9	17.8	158.3	159.0
0.729	69.2	67.7	146.2	148.4
0.465	41.8	41.2	152.7	153.4
0.745	68.0	66.7	145.0	148.1
0.401	37.2	36.5	153.7	154.9
0.314	28.8	28.3	155.6	156.7
0.250	22.0	21.9	157.6	158.1

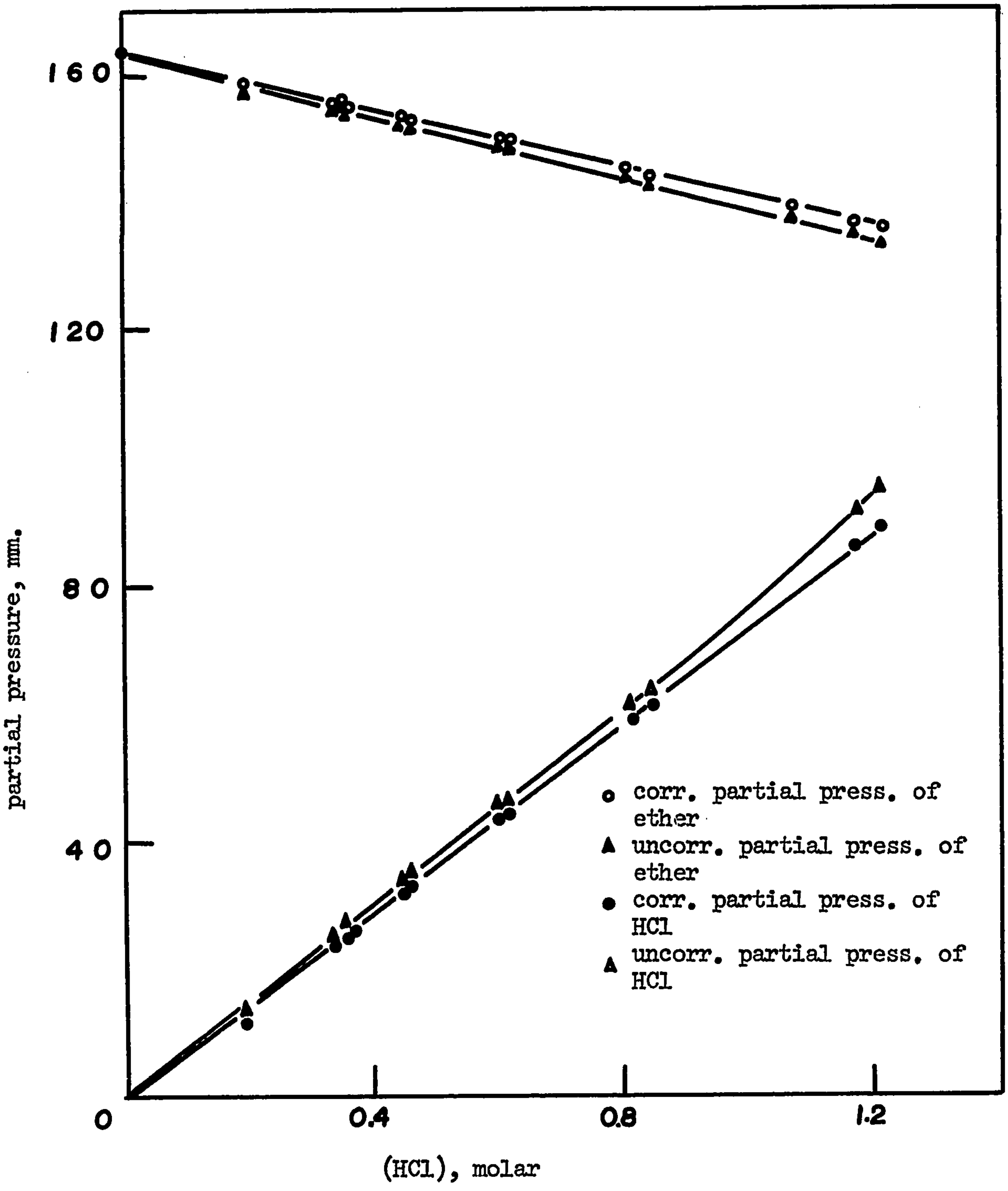

Fig. 15. Uncorrected and corrected partial pressures of HCl and di-isopropyl ether over di-isopropyl ether solutions of HCl at 25°C.

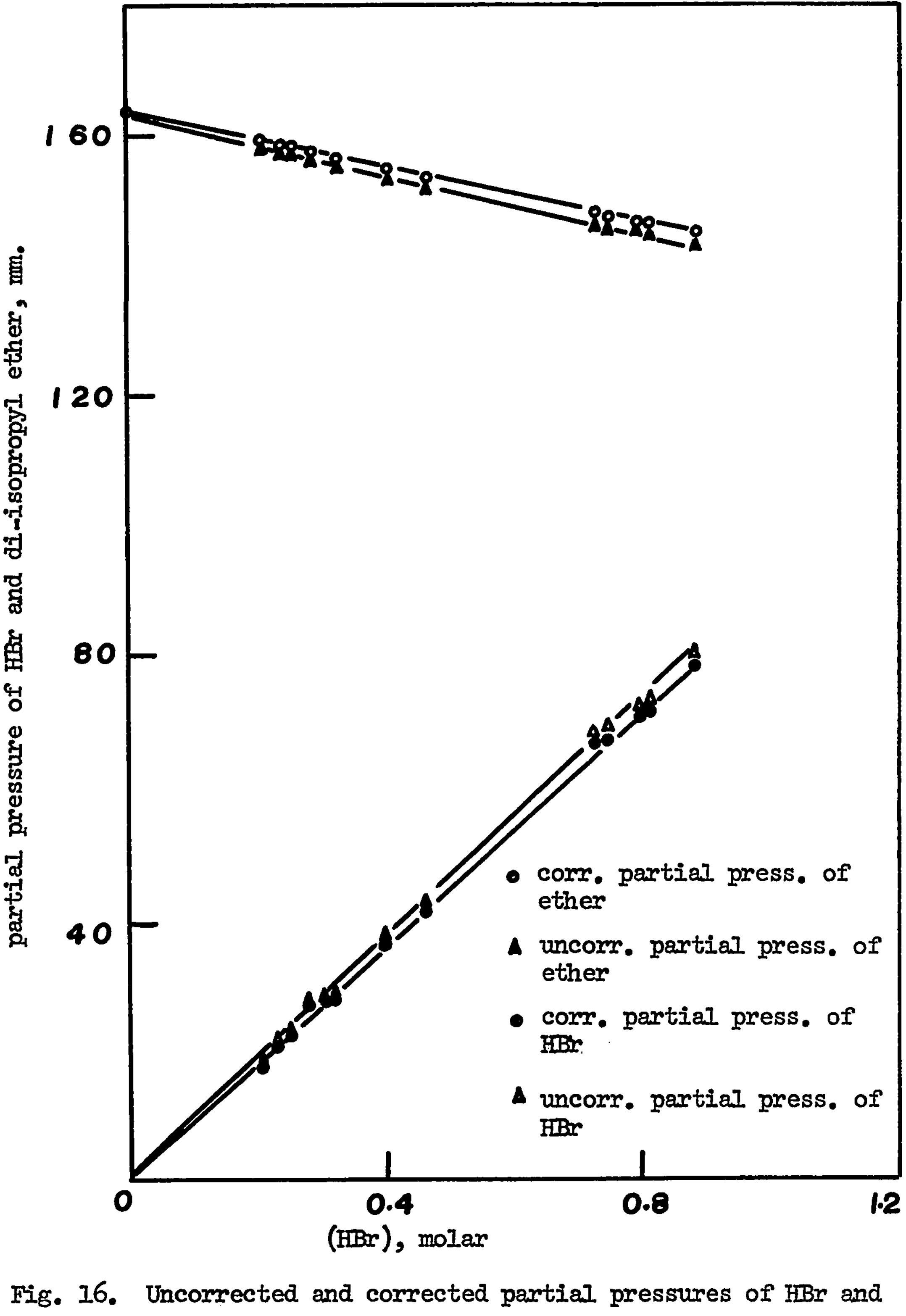

Fig. 16. Uncorrected and corrected partial pressures of HBr and di-isopropyl ether over di-isopropyl ether solutions of HBr at 25°C.

solutions of hydrogen halides in di-isopropyl, ether due to Van der Waals interactions were next calculated. For this purpose, only the second virial coefficients were used. The second virial coefficients for the pure gases HCl, HBr, and di-isopropyl ether alone were not available in the literature. Therefore they were calculated, together with the second virial coefficient in the vapour for each of the mixtures HCl-ether, and HBr-ether. All virial coefficients were calculated by using the Stockmayer potential (44) for polar gases. The Stockmayer method requires a knowledge of the dipole moment, the molecular diameter, and the force constant of the components (namely di-isopropyl ether, and the hydrogen halides). Even these data were not available for di-isopropyl ether, but they were available for di-ethyl ether. Therefore it was considered to be reasonable approximation to apply the values for di-ethyl ether to di-isopropyl ether. Monchick and Mason (45,46) measured the viscosities of HCl vapour, HBr vapour, and di-ethyl ether vapour; therefrom they computed the molecular diameters and the force constants for these species. These values, together with the dipole moments of the species were the parameters necessary for the Stockmayer potential. Therefore it proved possible to calculate the second virial coefficients for HCl alone, HBr alone, for di-isopropyl ether alone and for their vapour mixtures. By using the values of these virial coefficients, together with the calculated partial pressures of di-isopropyl ether in the HX-di-isopropyl ether vapour mixtures (see Tables 52 and 53), the corrections to the partial pressures of HCl, and HBr due to the presence of ether in the vapour phase were calculated by a method that has been described elsewhere (47). The corrections to the partial pressures of HCl and HBr proved in all cases to be less than 0.1% of the measured uncorrected pressures. Therefore this particular correction was not applied to the values tabulated fOr the partial pressures of HCl and HBr.

(vi) Henry's law constants

Henry's law constants for the hydrogen halides were found from the slope of vapour pressure-concentration curves, for different ether-carbon tetrachloride mixtures. The values were found by least-squares from the data in Tables 42 - 45 and Column 3 of Tables 52 and 53. The vapour pressure data used for the calculations had been corrected for non-ideality of the vapour. The Henry's law constants are reported in Tables 49 and 50.

Table 49 Henry's law constants for hydrogen shloride, at 25.0°C.

	5%(V/V)di-isopropyl ether	10%(V/V)di-isopropyl ether	50%(V/V)di-isopropyl ether	100%di-isopropyl ether	carbon tetrachloride
Henry's law constant	1246	732	108.7	73.1	4464

Table 50 Henry's law constants for hydrogen bromide, at 25.0°C.

	5%(V/V)di-isopropyl ether	10%(V/V)di-isopropyl ether	50%(V/V)di-isopropyl ether	100% di-isopropyl ether	carbon tetrachloride
Henry's law constant	1031	734.9	189.3	90.3	1993

B. Study of the reaction $HX + H_2O = HX.H_2O$

(a) Introduction

The formation constant for the reaction $HCl + H_2O = HCl.H_2O$ in acetone has been studied by N. Begum (25). She used both the method of vapour pressure used in the present investigation, and also near infrared spectroscopy. In the present work, the use of near infrared spectroscopy was not possible. Free water absorbs at 1.9 μ (48). Evidence for the existence of the hydronium ion in solution was found by Falk and Giguere (49) and also by Biermann and Gilmour (50), who assigned the absorption band at 1.7 μ to the hydronium ion. In the present work, the near infrared spectra of hydrogen chloride and water dissolved in di-isopropyl ether showed a broad peak at 1.8 μ. It overlapped extensively with the peak at 1.9 μ for free water. Therefore the use of the free water peak at 1.9μ could not be used in the present work for finding the free water content in the system.

(b) Synopsis

The vapour concentration of the hydrogen halide in the presence of various concentrations of water dissolved in di-isopropyl ether at 25.0°C was measured by using the vapour pressure method described in Subsection A above. After appropreiate corrections to the observed vapour concentrations, to be described later, the resulting values of the vapour concentration were converted to the corresponding partial vapour pressures. These vapour pressures were treated mathematically in order to identify the hydrates of the hydrogen halides present in the solutions, and to measure their formation constants there.

(c) Experimental and results

The reagents and the apparatus were those described in Part A. The procedure differs somewhat from that of Part A and is now separately described.

(i) Procedure

Solutions of water in di-isopropyl ether were prepared in two different ways. In one way, the di-isopropyl ether was saturated with water at 25.0°C by shaking the two phases together in a separatory funnel, followed by removal of the excess water. An aliquot of the resulting di-isopropyl ether solution was pipetted into the 200-ml round-bottom flask of the vapour pressure apparatus (Fig. 1). In all, five such aliquots were studied separately, namely, 5, 10, 20, 25, and 30 mls. A concentrated di-isopropyl ether solution of hydrogen halide was also prepared, as described in Part A. An aliquot of this solution was then added to the 200-ml flask containing the H_2O- di-isopropyl ether solution, so as to make a total volume of approximately 100ml. The partial pressure of the hydrogen halide above this solution was measured by using the same procedure as that described in Part A. After equilibration, which required a period of seven hours, the hydrogen halide content in the 500-ml bulb was determined as described in Part A. In addition, 10-20 ml aliquots of the solution in the 200-ml flask were titrated with standardized Karl Fischer reagent, in order to determine the water content (see Appendix 8 for procedure). In addition, a 5-ml aliquot of the solution in 200-ml flask was titrated potentiometrically with standard sodium hydroxide solution, in order to determine the hydrogen halide content after equilibration.

The second method of preparing the di-isopropyl ether solution of water was to weigh out accurately 0.1-0.3 gm of pure water into a 100-ml volumetric flask, and then to add the previously prepared di-isopropyl ether solution of hydrogen halide until after shaking, the water had dissolved. The resulting solution was then made up to 100 ml with di-isopropyl ether. The vapour pressure of the hydrogen halide above the resulting solution was then determined exactly as described above, and similar analyses were carried out on the equilibrium solution in the 200-ml flask.

(ii) Experimental results

The basic data are in Tables 51a and 51b. In those Tables, Column 1 and 2 give respectively the measured stoichiometric concentrations of the hydrogen halides and of water. Column 3 in each Table gives the uncorrected partial pressure of the hydrogen halide. Thus, the stoichiometric concentration of the hydrogen halide in the vapour was used in conjunction with the ideal gas law, to obtain a corresponding partial vapour pressure, and it is this partial vapour pressure that is reported. However, the existence of etherates and hydrates in gas phase required that this calculated partial pressure be corrected. This correction is described later; but the final, corrected partial pressures of HX are given in Column 4 of Tables 51a and 51b.

(d) Treatment of the data

(i) Butler's correction for a ternary system

In general, the addition of a third component to a two-component solution results in a change in the chemical potentials of the latter two components, even for ideal solution. The partial vapour pressures of the latter two components will then be changed, on addition of the third component.

The effect is expressed by the Gibbs-Duhem equation for a ternary system:

$$n_1 \, du_1 + n_2 \, du_2 + n_3 \, du_3 = 0 \qquad (13)$$

where n_1, n_2, and n_3 are the number of moles of each of the three components, and u_1, u_2, and u_3 are their chemical potentials.

Provided n_3, the added third component, is small, it is satisfactory to write

$$u_3 = u_3^{o} + R\,T \ln n_3 \qquad (14)$$

Butler(51) pointed out that for an ideal ternary solution, it would be expected that

$$\left(\frac{\partial u_1}{\partial n_3}\right)_{P,T,n_1,n_2} = \left(\frac{\partial u_2}{\partial n_3}\right)_{P,T,\, n_1,n_2} \qquad (15)$$

and that on combining equations (13, 14, and 15)

$$\left(\frac{\partial u_1}{\partial n_3}\right)_{P,T,n_1,n_2} = -\frac{R\,T}{n_1 + n_2} \qquad (16)$$

If partial pressure replaces fugacity for component 1, then for ideal ternary system equation (16) becomes*

$$\log \frac{p_1}{p_1^{\circ}} = - \frac{n_3}{2.303\ (\ n_1 + n_2\ )} \qquad (17)$$

where p_1 = partial vapour pressure of component 1 over the ternary solution containing n_1 moles of component 1, and n_2 moles of component 2, and n_3 moles of component 3.

p_1° = partial vapour pressure of component 1 over the binary solution containing n_1 moles of component 1, and n_2 moles of component 2 ($n_3 = 0$).

In the present work, the addition of water to the binary solution HX- di-isopropyl ether resulted in a reduction in the vapour pressure of the HX. A small part of this reduction must have been due to the effect Butler described, and expressed by equation (17). The remainder of the reduction was then attributed in the present work the formation of one or more hydrates of HX, viz:

$$HX + n\ H_2O = HX.nH_2O$$

The values of the vapour concentration of HX listed in Column 3 of Tables 51a and 51b were converted to partial pressures by using the ideal gas law. These values of the partial pressures of HX were then crrected by using equation (17),and the resulting values are in Column 3 of these Tables. These latter values are designated there as being "uncorrected"; this term

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* The difference in total pressure p for the binary and ternary solutions was too small in the present systems to produce a significant change in u_1.

indicates that the contributions of hydrates and etherates of HX in the vapour phase were yet to be corrected for.

(ii) Derivation of an algebraic equation for the vapour pressure data

It is proposed that the observed reduction in the values* of the partial vapour pressure of HX on the addition of water to the di-isopropyl ether solution of HX was due to the formation of hydrates:

$$HX + n\,H_2O = HX.nH_2O\ ; \qquad n = 1, 2, 3, \ldots\ldots$$

with the equilibrium constants

$$\frac{(\ HX.nH_2O\ )}{(\ HX\ )\ (\ H_2O\ )^n} = k_n$$

It is assumed that the solutions were ideal, so that molar concentration replaced activities. The standard state for each reactant and product was chosen to be a hypothetical 1-molar solution of the reactant or product, at 25.0°C that obeyed Henry's law.

Then (HX) = total molar concentration of unhydrated HX (unsolvated HX plus solvated $HX.R_2O$).

(H_2O) = molar concentration of free water

$(HX.nH_2O)$ = molar concentration of the n^{th} hydrate in the ternary solution

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* Corrected both by equation (17), and also for the presence of hydrates and etherates.

If $(HX)_b$= total molar concentration of HX combined as hydrates,

then $$\phi = \frac{(HX)_b}{(HX)\ (H_2O)} = \sum_{n=1}^{n} k_n\ (H_2O)^{n-1} \qquad (18)$$

A least-squares fit of equation (18) to the data, ϕ versus (H_2O), then provided for the intended values of k_n, and automatically identified the particular species of hydrates present.

(iii) Evaluation of ϕ_1 and application of equation (18)

Initially it was assumed that $HX.H_2O$ was the only hydrate present. Then a first estimate of k_1 in equation (18) was obtained via the following series of approximations:

(a) Fig. 15 is a graph of the partial pressure of HX versus its stoichiometric molarity in anhydrous di-isopropyl ether. Column 3 of Tables 51a and 51b contains the uncorrected partial pressures of HX above the ternary liquid solutions, the corresponding stoichiometric concentration of HX therein being in Column 1. By referring each of these partial pressures to Fig.15 the molarity of solvates and unsolvated HX in the particular ternary solution was read at once on the abscissa of Fig. 14. This value represented a first estimate of(HX) for use in equation (18). On subtracting this value from the corresponding one in Column 1 of Table 51a and Table 51b, the first value of $(HX)_b$ for that system was found. Moreover, if $HX.H_2O$ is the only hydrate present , then

$$(H_2O) =(H_2O)_T - (HX)_b$$

the first estimate of (H_2O) was found from the value of $(H_2O)_T$ in Column 2 of Table 51a and Table 51b together with the first estimate obtained for $(HX)_b$.

Thus for each ternary system listed in Tables 51a and 51b, an initial estimate of ϕ was found. This estimate was then obtained plotted against (H_2O). For both HCl and HBr ,the resulting graphs were straight lines with practically zero slope. Their intercepts gave the initial estimates of k_1. That their slopes were practically zero supported the original assumption that $K_n = 0$ for $n > 1$, that is a monohydrate existed in the ternary system.

(b) In the ternary solution, two equilibria existed:

$$HX + R_2O = HX.R_2O$$

$$HX + H_2O = HX.H_2O$$

The equilibrium constants of HCl and HBr in the former reaction were reported in Tables 48. Those for the latter reaction were estimated in the present Section. It was now assumed that these constants were the same for the reactions in the vapour phase, as for liquid solution phase. This assumption made it possible to estimate the fraction of HX in the vapour phase that existed as $HX.H_2O$, and $HX.R_2O$. Therefrom, the concentration of free HX, i.e. $(HX)_f$, in the vapour over each ternary solution was found. Then by using the ideal gas law, the partial pressure of HX (unhydrated) was found. It was called the "corrected" partial pressure, and is entered in Column 4 of Tables 51a and 51b.

By using these corrected partial pressures of HX, the calculations described in Subsection (a) above were repeated, to give second estimates of $(HX)_b$, (H_2O), ϕ, k_1. These second estimates were entered in Columns 5,6,7 of Tables 51a and 51b.

By using these corrected partial pressures of HX, the calculations described in Subsection (a) above were repeated, to give second estimates of $(HX)_b$, (H_2O), ∅, and k_1. These second estimates are entered in Columns 5, 6, and 7 respectively, of Tables 51a and 51b. In addition, the values of ∅ are plotted against those of (H_2O), in Figs 19 and 20.

(c) The second estimates obtained for k_1 in Subsection (a), the resulting values of k_1 did not differ significantly from those obtained in Subsection (b).

Inspection of the values of ∅ (i.e. k_1) in Tables 51a and 51b shows that ∅ was not a function of the composition of the ternary solution. Figs 17 and 18 illustrate this fact; the slopes of the lines drawn from the least-squares calculations are evidently zero, which supports the original assumption that only the monohydrate was present in significant amounts.

All the values of k_1 (∅) in Tables 51a were averaged to give the best estimate of k_1, and similarly for the values im Table 51b. These values and their standard deviations are entered in the bottom of Tables 51a and 51b.

These hydration constants were for the mass-law expression,

$$\frac{(HX.H_2O)}{(HX)\ (H_2O)} = k_1$$

From them, and the solvation constant K_1 for the reaction

$$HX + R_2O = HX.\ R_2O$$

it is possible to calculate the hydration constants for the mass-law expression

$$\frac{(HX.H_2O)}{(HX)_f\ (H_2O)} = k_1'$$

Thus equation (18) can be rewritten as

$$\phi = \frac{(HX)_b}{\left[(HX)_f + K_1(HX)_f\ (S)\right]\ (H_2O)}$$

$$= \frac{(HX)_b}{(HX)_f\left[1 + K_1\ (S)\right]\ (H_2O)}$$

and

$$k_1{*}= \phi\left[1 + K_1(S)\right] = \frac{(HX)_b}{(HX)_f\ (H_2O)}$$

where K_1 is the solvation constant of HX by di-isopropyl ether reported in Tables 48 ,(S)is the molar concentration of the solvent di-isopropyl ether, and $k_1{*}$ is the corrected hydration constant. The corrected hydration constants for both HCl and HBr are also reported in Tables 51a and 51b.

Table 51a Partial vapour pressure of HCl over the ternary solution HCl-H_2O-di-isopropyl ether at 25.0°C, and equilibrium constant k_1 for the reaction

$$HCl + H_2O = H_2O.HCl$$

in the ternary solution.

$(HCl)_T$, M	$(H_2O)_T$, M	Partial pressure of HCl, mm uncorr.	corrected	Second estimates $(HCl)_b$, M	(H_2O), M	$\phi(=k_1)$
1.195	0.172	83.3	79.1	0.121	0.051	2.19
0.902	0.116	62.4	60.8	0.076	0.040	2.32
1.384	0.270	91.7	85.9	0.209	0.061	2.90
1.083	0.210	71.3	68.6	0.148	0.062	2.56
1.431	0.256	97.1	91.2	0.194	0.062	2.52
1.504	0.267	100.0	95.2	0.227	0.040	2.26
1.236	0.225	82.8	78.4	0.164	0.061	2.50
1.102	0.200	73.4	70.2	0.142	0.058	2.50
0.758	0.109	51.7	50.1	0.066	0.043	2.21
1.380	0.178	99.7	94.2	0.130	0.048	2.15
1.002	0.174	66.8	64.8	0.121	0.063	2.17
1.220	0.114	88.2	83.5	0.081	0.030	2.44
1.229	0.231	81.8	78.4	0.168	0.063	2.51
1.182	0.240	77.5	73.2	0.174	0.066	2.64
0.982	0.142	66.9	65.0	0.099	0.043	2.61
0.926	0.105	64.8	63.1	0.069	0.036	2.24
1.384	0.270	91.7	85.7	0.214	0.056	3.20
1.073	0.194	71.3	68.3	0.139	0.055	2.71
1.626	0.171	117.8	109.4	1.490	0.141	3.10
0.091	0.084*	5.56	5.24	0.016	0.068	3.32
0.137	0.036*	9.11	8.80	0.013	0.023	4.71
0.093	0.108*	5.99	5.75	0.012	0.072	1.93
0.091	0.084*	5.50	5.31	0.017	0.127	1.74
0.065	0.072*	4.31	4.16	0.007	0.065	1.73

Average value of $k_1 = 2.55$ Standard deviation = 0.54 degree of freedom=23

$k_1{}^* = 156.0$ Standard deviation = 30 degrees of freedom=23

$\Delta G^\circ = - RT \ln k_1{}^* = 2.99$ kcal/mole

* These solutions were prepared by accurately weighing the water.

Table 51b Partial vapour pressure of HBr over the ternary solution $HBr-H_2O-$di-isopropyl ether at 25.0°C, and equilibrium constant k_1 for the reaction $HBr + H_2O = H_2O.HBr$ in the ternary solution.

$(HBr)_T$, M	$(H_2O)_T$, M	Partial pressure of HBr, mm		Second estimates		
		uncorr.	corr.	$(HBr)_b$, M	(H_2O), M	ϕ (= k_1)
0.048	0.036*	2.550	2.510	0.019	0.017	39.6
0.018	0.038	0.760	0.740	0.010	0.026	43.2
0.048	0.036*	2.380	2.340	0.021	0.017	45.8
0.011	0.104	0.181	0.180	0.003	0.105	34.3
0.004	0.108	0.072	0.071	0.012	0.029	46.1
0.020	0.040*	0.767	0.753	0.006	0.066	39.9
0.009	0.072	0.215	0.210	0.015	0.021	49.9
0.030	0.036	1.277	1.256	0.015	0.025	41.0
0.030	0.040	1.335	1.310	0.005	0.067	34.6
0.007	0.072	0.179	0.176	0.005	0.067	44.2
0.007	0.072	0.181	0.178	0.009	0.095	43.1
0.059	0.031*	2.990	2.930	0.019	0.013	35.8

Average value of k_1 = 41.4 Standard deviation= 5 degrees of freedom= 11

Corrected k_1^* = 730 Standard deviation = 89 degrees of freedom = 11

$\Delta G^o = - RT \ln k_1^* = - 3.9$ kcal/mole.

* These solutions were prepared by accurately weighing the water.

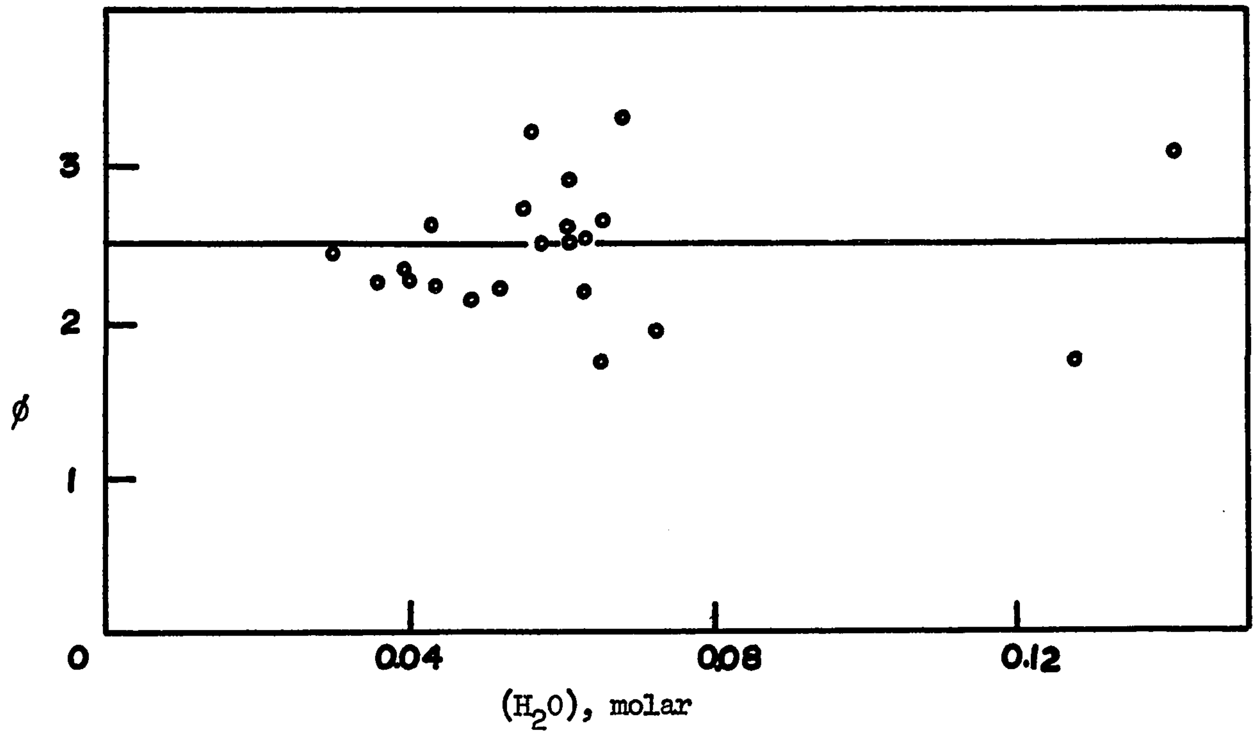

Fig. 17. Dependence of the hydration constant ($H_2O.HCl$) in di-isopropyl ether at 25°C on the concentration of free water.

Data: Table 51a.

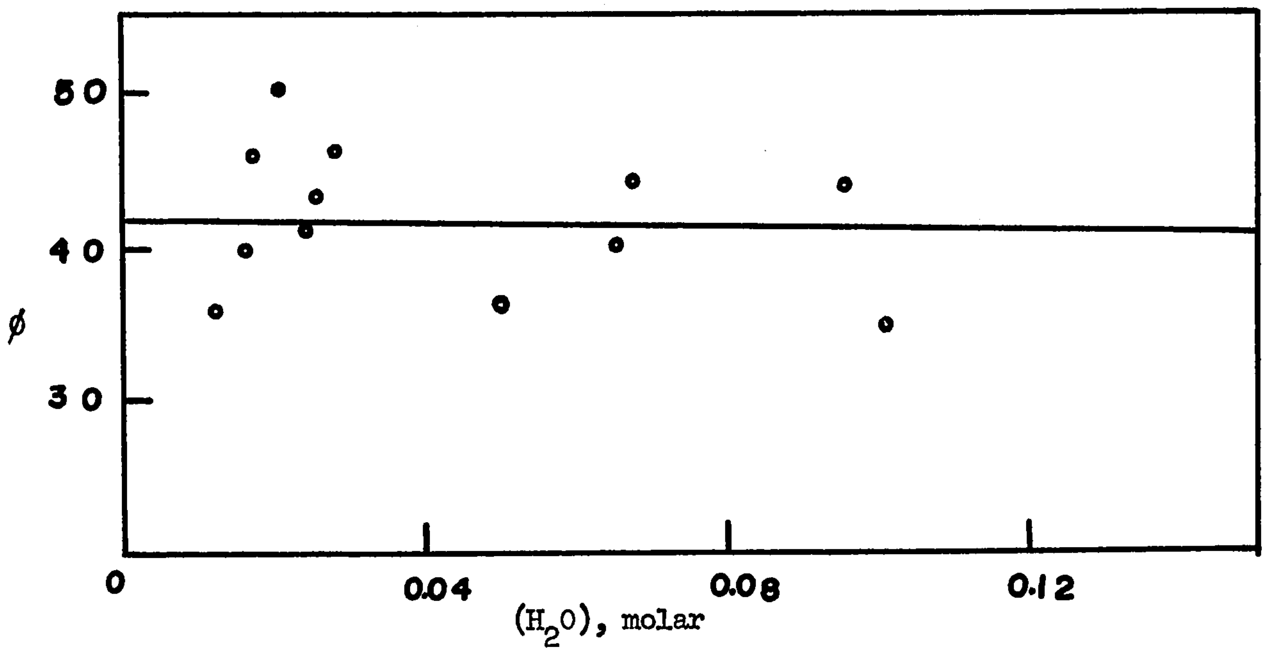

Fig. 18. Dependence of the hydration constant ($HBr.H_2O$) in di-isopropyl ether at 25°C on the concentration of free water.

Data: Table 51b.

III. Dielectric constant method

(a) Synopsis

The purpose of this experimental study was to evaluate the solvation constants for the reaction

$$HX + R_2O = R_2O.HX \qquad [2]$$

in carbon tetrachloride, at 25.2°C, 34.7°C, and 45.0°C. Two halides (HX) were used, hydrogen chloride and hydrogen bromide, and three solvents, ethers(R_2O), di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran.

The principle of the method was as follows : in the absence of interaction between HX and R_2O in carbon tetrachloride, the dielectric constant of a given ternary solution of HX-R_2O-CCl_4 should be given by the sum of the dielectric constants of the binary solutions HX-CCl_4, and R_2O-CCl_4, provided that the molar concentrations of HX and of R_2O respectively, are the same in the binary solutions as they are in the ternary solutions, and provided that the solutions are dilute. Interaction between HX and R_2O should result in a deviation from this additivity of the dielectric constants of the components.

The dielectric constants of various HCl-CCl_4 solutions and of various HBr-CCl_4 solutions were measured. Then the dielectric constant of an equimolar HX-R_2O mixture in carbon tetrachloride was also measured. The difference between the measured value for the ternary solution, and that expected on the basis of no HX-R_2O interaction was thereby found. From this difference the required solvation constants were calculated.

(b) Instrument

The instrument used for the dielectric constant measurements was a Dipolemeter, model DM01; the cell was a Dipolemeter cell, model DFL1, which was thermostatted.

(c) Calibration

The capacitance scale on the Dipolemeter was calibrated by using anhydrous solvents of known dielectric constants, at 25.2°C, 34.7°C, and 45.0°C. Anhydrous carbon tetrachloride, benzene, and cyclohexane, purified as described in the Section Reagent and Solvents on page 10, were used. The Dipolemeter cell was filled with the liquid, and above the liquid a stream of nitrogen prevented contact with moist air. The calibration data are reported in Table 54. The values used for dielectric constants of these pure solvents were those compiled by Maryott and Smith (38) and by Mecke and Klingenberg (39).

(d) Procedure

All solutions are prepared in the dry box. A concentrated hydrogen halide-carbon tetrachloride stock solution was prepared with the apparatus shown in Fig.2, by passing hydrogen chloride gas into carbon tetrachloride for 30 minutes. The hydrogen halide content of the resulting solution was determined by potentiometric titration of an aliquot with 0.5 M sodium hydroxide (previously standardized).

Aliquots of 45, 40, 30, 20, and 10 ml of the above stock solution were delivered into separate, previouly dried 50-ml volumetric flasks and made to 50ml with anhydrous carbon tetrachloride. The dispensing of these aliquots was carried out by using the apparatus shown in Fig.3 . The Dipolemeter cell was rinsed and filled with each solution in turn in an atmosphere of dry nitrogen. The capped cell was allowed to come to thermal equilibrium with constant-temperature water circulated through its jacket, from a Colora water thermostat. The capacitance of the solution was then read.

Into six 50-ml volumetric flasks that had priviously been dried and weighed, different portions (0.5-5.0 gms) of the ether was dispensed, and the capped flasks were removed and accurately reweighed. They were then returned to the dry box and filled to the mark with carbon tetrachloride. Capacitance of these solutions were then taken. Finally, a concentrated solution of hydrogen halide in carbon tetrachloride was prepared and its exact composition determined by titration. A solution of ether in carbon tetrachloride, of exactly the same concentration as that of the standardized hydrogen halide solution, was also prepared by weight. The volume of each of these stock solutions was 100 ml. Equimolar hydrogen halide and ether mixtures in carbon tetrachloride were then prepared by mixing equal aliquots of the two stock solutions together. Thus, 25, 20, 15, 10, 5 ml aliquots of both stock solutions were delivered into dry 50-ml volumetric flasks in the dry box, by using the dispensing apparatus shown in Fig. 3, the contents were then diluted to the mark with carbon tetrachloride. Capacitance readings of these solutions were then taken. The measurements were made at 25.2^{o}C on the solutions prepared with the two halides and three ethers in carbon tetrachloride as described above. After the measurements, the same solutions were brought into thermal equilibrium at each of the other two temperatures and the capacitances re-read.

The capacitance of the solutions were converted directly into dielectric constant values by using the calibration curve prepared as described in the above Subsection. Therefrom, values (ΔD) of the difference between the dielectric constant of the solutions and that of pure carbon tetrachloride.

(e) Experimental results

The capacitance readings and the literature values of the dielectric constants for the three anhydrous solvents used for calibration purposes are recorded in Table 54. It was found at each temperature that the capacitance reading was directly proportional to the dielectric constant over the range measured.

The capacitance readings for each of the solutions at each temperature, the difference (Δz) between the capacitance readings and that of the pure solvent, and also the difference (ΔD) between the dielectric constant of the solution and that of the pure solvent carbon tetrachloride are reported in Tables 55- 65 inclusive.

Table 54 Calibration of Dipolemeter

Temperature °C	Benzene		carbon tetrachloride		cyclohexane	
	cap. reading (z)*	dielectric constant**	cap. reading (z)*	dielectric constant **	cap. reading(z)*	dielectric constant**
25.2	1270.7	2.2721	1162.1	2.2259	671.3	2.0145
34.7	1227.7	2.2531	1120.3	2.2069	639.3	1.9993
45.0	1184.7	2.2325	1078.3	2.1863	605.2	1.9828

Table 55 Capacitance readings on carbon tetrachloride solutions of tetrahydrofuran, and values of Δz and ΔD, at 25.2°C, 34.7°C, and 45.0°C.

Temperature °C						
	(R_2O),M	0.2588	0.4970	0.7767	0.9618	1.2096
	z	1400.8	1589.6	1878.3	2048.4	2277.1
	Δz***	238.7	427.5	716.2	886.3	1115.0
25.2	ΔD	0.1015	0.1819	0.3047	0.3770	0.4743
	(R_2O),M	0.2557	0.4911	0.7674	0.9504	1.1952
	z	1344.2	1522.7	1795.0	1957.6	2173.3
34.7	Δz***	223.8	402.2	674.7	837.3	1053.0
	ΔD	0.0952	0.1711	0.2870	0.3562	0.4479
	(R_2O),M	0.2527	0.4852	0.7582	0.9390	1.1809
	z	1289.4	1458.3	1714.6	1869.8	2076.5
	Δz***	210.6	379.9	636.3	791.5	998.2
	ΔD	0.0896	0.1617	0.2707	0.3367	0.4247

* one unit of capacitance reading (z) is equilalent to14uF. With the Dipolemeter and the cells used, capacitance reading was directly proportional to uF.

** values are taken from references 38,and 39.

*** Δz is the difference in the capacitance reading between solution and pure CCl_4.

Table 56 Capacitance readings on carbon tetrachloride solutions of di-isopropyl ether, and values of Δz and ΔD, at 25.2°C, 34.7°C, and 45.0°C.

Temperature °C							
25.2	(R_2O)	0.1452	0.2755	0.4193	0.5574	0.6963	0.8356
	z	1228.5	1293.9	1363.9	1431.5	1499.8	1567.8
	Δz*	66.4	131.8	201.8	269.5	337.7	405.8
	ΔD	0.0282	0.0561	0.0859	0.1146	0.1437	0.1726
34.7	(R_2O)	0.1434	0.2722	0.4143	0.5508	0.6881	0.8257
	z	1188.0	1237.0	1305.0	1368.0	1432.3	1495.3
	Δz*	67.7	116.7	184.7	248.3	312.0	375.0
	ΔD	0.0288	0.0497	0.0786	0.1056	0.1327	0.1595
45.0°	(R_2O)	0.1417	0.2689	0.4093	0.5442	0.6798	0.8158
	z	1140.0	1185.6	1247.9	1308.2	1366.9	1425.7
	Δz*	61.7	107.3	169.6	229.9	288.6	347.4
	ΔD	0.0263	0.0457	0.0722	0.0978	0.1228	0.1478

Table 57 Capacitance readings on carbon tetrachloride solutions of di-n-butyl ether , and values of Δz and ΔD, at 25.2°C, 34.7°C, and 45.0°C.

Temperature °C							
25.2	(R_2O)	0.1176	0.2351	0.3543	0.4649	0.6008	0.7088
	z	1201.3	1240.7	1280.7	1317.3	1362.8	1400.8
	Δz	39.2	78.6	118.8	155.2	200.7	238.7
	ΔD	0.0167	0.0334	0.0505	0.0662	0.0854	0.1016
34.7	(R_2O)	0.1162	0.2323	0.3501	0.4594	0.5937	0.7001
	z	1156.7	1193.1	1230.6	1265.3	1308.2	1342.9
	Δz*	36.4	72.8	110.3	145.0	187.9	222.1
	ΔD	0.0155	0.0310	0.0469	0.0617	0.0799	0.0945
	(R_2O)	0.1148	0.2295	0.3458	0.4538	0.5865	0.6920
	z	1111.9	1145.9	1181.1	1213.3	1258.6	1287.5
	Δz*	34.1	67.6	102.8	134.9	180.3	208.9
	ΔD	0.0145	0.0288	0.0437	0.0574	0.0767	0.0889

*Δz is the difference in the capacitance reading between solution and pure carbon tetrachloride.

Table 58 Capacitance readings on carbon tetrachloride solutions of HCl, and values of Δz and ΔD, at 25.2°C, 34.7°C, and 45.0°C.

Temperature °C						
25.2	(HCl)	0.0344	0.0201	0.0502	0.0600	0.0700
	z	1170.9	1167.3	1175.0	1177.6	1180.2
	Δz*	8.8	5.2	12.9	15.5	18.1
	ΔD	0.0037	0.0022	0.0055	0.0066	0.0077
34.7	(HCl)	0.0340	0.0175	0.0475	0.0575	0.0700
	z	1128.0	1124.3	1131.1	1133.4	1136.3
	Δz*	7.7	4.0	10.8	13.1	16.0
	ΔD	0.0033	0.0017	0.0046	0.0056	0.0068
45.0	(HCl)	0.0336	0.0250	0.0501	0.0650	0.0757
	z	1085.4	1083.6	1088.8	1092.0	1094.3
	Δz*	7.1	5.8	10.5	13.7	16.0
	ΔD	0.0030	0.0023	0.0045	0.0058	0.0068

Table 59 Capacitance readings on carbon tetrachloride solutions of HBr, and values of Δz and ΔD, at 25.2°C, 34.7°C, and 45.0°C.

Temperature °C							
25.2	(HBr)	0.1001	0.0933	0.0820	0.0563	0.0539	0.0429
	z	1185.5	1183.9	1181.4	1175.4	1175.1	1172.1
	Δz*	23.4	21.8	19.3	13.3	13.0	10.0
	ΔD	0.0997	0.0929	0.0820	0.0057	0.0055	0.0043
34.7	(HBr)	0.0991	0.0922	0.0556	0.0533	0.0813	0.0420
	z	1142.2	1140.5	1133.0	1132.8	1138.2	1129.5
	Δz*	21.8	19.7	12.2	12.0	17.9	9.2
	ΔD	0.0093	0.0084	0.0052	0.0051	0.0076	0.0039
45.0	(HBr)	0.0979	0.0911	0.0801	0.0549	0.0526	0.0411
	z	1098.8	1097.1	1094.8	1090.0	1089.9	1086.8
	Δz*	20.5	18.8	16.5	11.4	11.3	8.5
	ΔD	0.0087	0.0080	0.0071	0.0049	0.0048	0.0036

*Δz is the difference in the capacitance reading between solution and pure solvent carbon tetrachloride.

Table 60 Capacitance readings on equimolar solutions of hydrogen chloride and di-n-butyl ether in carbon tetrachloride, and values of Δz and ΔD, at 25,2°C, 34.7°C, and 45.0°C.

Temperature °C							
25.2	(HCl)(R_2O)M	0.0350	0.315	0.0280	0.0232	0.0164	0.0118
	z	1212.5	1205.3	1198.7	1190.1	1179.3	1173.2
	Δ z*	50.4	43.2	36.6	28.0	17.2	11.1
	Δ D	0.0214	0.0184	0.0156	0.0119	0.0073	0.0047
34.7	(HCl)(R_2O)M	0.0383	0.0346	0.0311	0.0260	0.0211	0.0156
	z	1169.7	1163.1	1157.7	1149.0	1141.9	1134.7
	Δ z*	48.9	42.3	36.9	28.2	21.1	13.9
	Δ D	0.0208	0.0180	0.0157	0.0120	0.0090	0.0059
45.0	(HCl)(R_2O)M	0.0437	0.0389	0.0335	0.0297	0.0266	0.0159
	z	1130.6	1122.5	1113.9	1108.7	1104.1	1091.1
	Δ z*	52.0	43.9	35.3	30.1	25.5	12.5
	Δ D	0.0221	0.0187	0.0150	0.0128	0.0108	0.0053

Table 61 Capacitance readings on equimolar solutions of HBr and di-n-butyl ether in CCl_4, and values of Δz and ΔD , at 25.2°C, 34.7°C and 45.0°C.

Temperature °C							
25.2	(HBr)(R_2O)M	0.0865	0.0818	0.0755	0.0661	0.0600	0.0502
	z	1255.8	1249.1	1240.2	1227.7	1219.9	12.7.9
	Δ z*	93.7	87.0	78.1	65.6	57.8	45.8
	Δ D	0.0399	0.0370	0.0332	0.0279	0.0246	0.0195
34.7	(HBr)(R_2O)M	0.1164	0.1063	0.0907	0.0651	0.0533	0.0799
	z	1239.2	1225.7	1205.9	1175.9	1163.4	1192.7
	Δ z*	118.4	104.9	85.1	55.1	42.6	71.9
	Δ D	0.0504	0.0446	0.0362	0.0234	0.0181	0.0306
45.0	(HBr)(R_2O)M	0.1175	0.1077	0.0926	0.0789	0.0693	0.0503
	z	1191.6	1179.2	1160.8	1145.2	1134.8	1115.9
	Δ z*	113.0	100.6	82.2	66.6	56.2	37.3
	Δ D	0.0481	0.0428	0.0349	0.0283	0.0239	0.0159

*Δ z is the difference in the capacitance reading between solution and CCl_4.

Table 62 Capacitance readings on equimolar solutions of hydrogen chloride and di-isopropyl ether in CCl_4, and values of Δz and ΔD, at 25.0°C, 35.0°C, and 45.0°C.

Temperature °C							
25.2	$(HCl)(R_2O)M$	0.0507	0.0460	0.0365	0.0274	0.0147	0.0091
	z	122.1	1215.2	1201.8	1190.1	1175.6	1169.9
	Δz^*	59.3	53.1	39.7	28.0	13.5	7.8
	ΔD	0.0252	0.0226	0.0169	0.0119	0.0058	0.0033
34.7	$(HCl)(R_2O)M$	0.0746	0.0455	0.0361	0.0270	0.0148	0.0094
	z	1206.1	1167.2	1155.8	1145.5	1133.0	1128.2
	Δz^*	85.3	46.4	35.0	24.7	12.2	7.4
	ΔD	0.0363	0.197	0.0150	0.0105	0.0052	0.0032
45.0	$(HCl)(R_2O)M$	0.0542	0.0492	0.0465	0.0409	0.0367	0.0319
	z	1130.8	1124.9	1121.8	1115.5	1110.9	1105.9
	Δz^*	52.2	46.3	43.2	36.9	32.2	27.3
	ΔD	0.0222	0.0197	0.0184	0.0157	0.0138	0.0116

Table 63 Capacitance readings on equimolar solutions of HBr and di-isopropyl ether in CCl_4 and values of Δz and ΔD, at 25.2°C, 2 34.7°C, and 45.0°C

Temperature °C							
25.2	$(HBr)(R_2O)M$	0.0504	0.0476	0.0442	0.0412	0.0376	0.0321
	z	1236.3	1230.5	1223.6	1217.9	1211.2	1201.5
	Δz^*	74.2	68.4	61.5	55.8	49.1	39.4
	ΔD	0.0316	0.0291	0.0262	0.0237	0.0209	0.0168
34.7	$(HBr)(R_2O)M$	0.0524	0.0477	0.0438	0.0405	0.0363	0.0334
	z	70.0	61.1	54.3	48.5	41.7	37.2
	Δz^*	1190.8	1181.9	1175.1	1169.3	1162.5	1158.0
	ΔD	0.0298	0.0259	0.0231	0.0206	0.0178	0.0158
45.0	$(HBr)(R_2O)M$	0.0540	0.0494	0.0467	0.0430	0.0403	0.0359
	z	1146.7	1138.4	1134.0	1127.8	1123.4	1116.7
	Δz^*	68.1	59.8	55.4	49.2	44.8	38.1
	ΔD	0.0290	0.0254	0.0236	0.0209	0.0191	0.0162

* Difference in the a capacitance reading between solution and pure CCl_4

Table 64 Capacitance readings on equimolar solutions of HCl and tetrahydrofuran in CCl_4, and values of Δz and ΔD, at 25.2°C, 34.7°C, and 45.0°C.

Temperature °C							
	(HCl),(R_2O)M	0.0501	0.0481	0.0421	0.0361	0.0300	0.0240
	z	1295.6	1289.3	1271.1	1253.3	1235.3	1235.9
	Δz*	133.5	127.2	109.0	91.2	73.8	56.8
25.2	ΔD	0.0568	0.0541	0.0464	0.0388	0.0314	0.0242
	(HCl),(R_2O)M	0.0495	0.0475	0.0416	0.0356	0.0297	0.0238
	z	1245.5	1219.5	1205.6	1199.0	1185.2	1176.3
34.7	Δz*	124.7	98.7	84.8	78.4	64.4	55.5
	ΔD	0.0501	0.0477	0.0408	0.0340	0.0274	0.0210
	(HCl),(R_2O)M	0.0483	0.0464	0.0406	0.0348	0.0290	0.0232
	z	1181.0	1175.9	1162.0	1147.9	1134.5	1123.1
45.0	Δz*	102.4	97.3	83.4	69.3	55.9	44.5
	ΔD	0.0435	0.0414	0.0355	0.0295	0.0238	0.0189

Table 65 Capacitance readings on equimolar solutions of HBr and tetrahydrofuran in CCl_4, and values of Δz and ΔD, at 25.2°C, 34.7°C, and 45.0°C.

Temperature °C							
	(HBr)(R_2O)M	0.1258	0.1031	0.0762	0.0587	0.0467	0.0349
	z	1394.1	1349.3	1297.0	1263.6	1241.1	1219.4
	Δz*	232.0	187.2	134.9	101.5	79.0	57.3
25.2	ΔD	0.0987	0 0796	0.0574	0.0432	0.0336	0.0244
	(HBr)(R_2O)M	0.1345	0.0984	0.722	0.0575	0.0460	0.0342
	z	1346.8	1282.2	1235.8	1210.6	1190.9	1171.3
34.7	Δz*	226.0	161.4	115.0	89.8	70.1	50.5
	ΔD	0.0961	0.0687	0.0489	0.0382	0.0298	0.0215
	(HBr)(R_2O)M	0.1102	0.0889	0.0670	0.0559	0.0454	0.0394
	z	1255.7	1218.2	1181.0	1162.2	1144.9	1135.3
45.0	Δz*	177.1	139.6	102.4	83.6	66.3	56.7
	ΔD	0.0753	0.0594	0.0436	0.0356	0.0282	0.0241

* Difference in the capacitance reading between solution and pure CCl_4.

(f) Treatment of ths data

(i) Synopsis :

The values of ΔD in Tables 55-65 inclusive were used to calculate the values of the equilibrium constant for the reaction

$$HX + R_2O = R_2O.HX \qquad [2]$$

in carbon tetrachloride at 25.2°C, 34.7°C, anf 45.0°C. The method of calculation was essentially that proposed by Maryott (40, 41, 42).

From the temperature dependence of the equilibrium constants, the enthalpy change and the entropy change were calculated.

The principal symbols used in the present Section are:-

(HX) = total molar concentration of hydrogen halide

$(R_2O)_T$= total molar concentration of ether

$(HX)_b$ = total molar concentration of hydrogen halide bound to ether.

K = equilibrium constant for reaction [2] above

$(HX)_f$ = equilibrium concentration of free hydrogen halide (unsolvated)

(R_2O) = equilibrium concentration of free ether

ΔD = difference between the dielectric constant of a solution and that of pure CCl_4.

x_a = proportionality constant for hydrogen halide

x_b = proportionality constant for ether

x_{ab} = proportionality constant for the solvate $R_2O.HX$

(ii) Evaluation of the proportionality constants, x_a, x_b

For each of the solutes HCl, HBr, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran alone in carbon tetrachloride, the data in Tables 55-59 inclusive showed that over the concentration ranges studied, D was strictly a linear function of the molar concentration of the solute. That is, for the hydrogen halides alone in CCl_4

$$\Delta D = x_a \text{ (HX)}$$

and for the ethers alone in CCl_4

$$\Delta D = x_b \ (R_2O)_T$$

From the data, least-squares values were found for x_a (one for HCl, another for HBr), and for x_b(one for each of the three ethers). These five values are recorded in Tables 66 and 67, for each of the three temperatures.

(iii) Derivation of the necessary algebraic equation

In Section d(iii) on the vapour pressure method, only the monosolvate was found to exist in the solutions examined. In the dielectric constant measurements, the ratio $(HX)/(R_2O)_T$ in all cases lay within the ratio range of the vapour pressure studies. Therefore, in treating the dielectric constant data, only the monosolvate and the two reactants HX and R_2O were assumed present in the carbon tetrachloride solutions.

For Tables 69 and 70, the standard state for each reactant and product, including the ether, was chosen to be a hypothetical 1-molar solution of the reactant or product, at 25.0°C that obeyed Henry's law. For Tables 71 and 72, the thermodynamic properties are reported in molar and molal concentrations. That is, on the molar basis the standard state was a 1-molar solution, and on the molal basis it was a 1-molal solution which obeyed Henry's law.

It was shown in the preceding Subsection that x_a and x_b were independent of the concentration of the relevent solute. It was now assumed that the proportionality constant x_{ab} of the monosolvate $R_2O.HX$ in carbon tetrachloride was also independent of the concentration of the monosolvate.

Then for a carbon tetrachloride solution containing $HX.R_2O$, and HX, R_2O together in equilibrium at a given temperature, it become possible to write

$$\Delta D = x_a \ (HX)_f + x_b \ (R_2O) + x_{ab}(HX)_b \qquad (19)$$

where ΔD is the difference between the dielectric constant of the ternary mixture and that of pure carbon tetrachloride.
Moreover, the mass-balance equations are

$$(HX) = (HX)_f + (HX)_b \qquad (20)$$

$$(R_2O)_T = (R_2O) + (R_2O)_b \qquad (21)$$

and the mass law expression is

$$(HX)_b = K \ (HX)_f \ (R_2O) \qquad (22)$$

From equations (20),and (21), and by defining

$$x = x_{ab} - x_a - x_b \qquad (23)$$

equation (19) becomes

$$\Delta D = x_a\,(HX) + x_b\,(R_2O)_T + \Delta x\,(HX)_b \qquad (24)$$

In the actual solutions in carbon tetrachloride, the concentrations of hydrogen halide and of ether were always exactly equal; hence

$$(HX) = (R_2O)_T$$

and on the assumption of only a monosolvate,

$$(HX)_f = (R_2O)$$

Then it is readily shown that equation (24) together with equation(22) leads to

$$\left[\frac{\frac{\Delta D}{(HX)} - x_a - x_b}{(HX)}\right]^{\frac{1}{2}} = x_{ab}\left(\frac{K}{\Delta x}\right)^{\frac{1}{2}} - \frac{\Delta D}{(HX)}\left(\frac{K}{\Delta x}\right)^{\frac{1}{2}} \qquad (25)$$

(iv) Calculation of the solvation constants

The ΔD, (HX) data in Tables 60-65 inclusive were used in conjunction with equation (25), in order to evaluate K. Thus a plot of $\left[\frac{\frac{\Delta D}{(HX)} - x_a - x_b}{(HX)}\right]^{\frac{1}{2}}$ versus $\frac{\Delta D}{(HX)}$ gave an intercept of $x_{ab}\left(\frac{K}{\Delta x}\right)^{\frac{1}{2}}$, and a slope of $\left(\frac{K}{\Delta x}\right)^{\frac{1}{2}}$. These values yielded both K and x_{ab}.

In practice, equation (25) was fitted to the data in Tables 60-65 by least-squares, so that standard deviations were also evaluated.

To illustrate this use of equation (25) in order to evaluate K, the case of HCl-tetrahydrofuran at 25.2°C is given here in some detail.

Table 66 Values of x_b at three temperatures for three ethers in CCl_4

degrees of freedom = 5

Ether	Temperature, °C		
	25.2	34.7	45.0
di-iso-propyl	0.216±0.002	0.192±0.002	0.176±0.002
di-n-butyl	0.143±0.001	0.135±0.001	0.128±0.001
tetrahydrofuran	0.392±0.004	0.373±0.004	0.360±0.004

Table 67 Values of x_a for HCl and HBr in carbon tetrachloride at three temperatures. degrees of freedom = 5

HX	Temperature, °C		
	25.2	34.7	45.0
HCl	0.109±0.001	0.097±0.001	0.090±0.001
HBr	0.098±0.001	0.093±0.001	0.088±0.001

Table 68 Calculation of solvation constant K for HCl-tetrahydrofuran in CCl_4 at 25.2°C.

(HCl) or $(R_2O)_T$	ΔD	$\frac{\Delta D}{(HCl)}$	$\left[\frac{\Delta D}{(HCl)} - x_a - x_b\right] = \&$	$\frac{\&}{(HCl)}$	$\left[\frac{\&}{(HCl)}\right]^{\frac{1}{2}}$
0.0501	0.0568	1.134	0.633	12.64	3.56
0.0481	0.0541	1.126	0.625	13.01	3.61
0.0421	0.0464	1.102	0.602	14.31	3.78
0.0361	0.0388	1.076	0.575	15.96	3.99
0.0301	0.0314	1.042	0.542	18.04	4.25
0.0240	0.0242	1.004	0.504	20.96	4.58

$x_a + x_b = 0.501$

From Tables 66 and 67 ,

$$x_a = 0.1085$$

$$x_b = 0.3920$$

Then from the ΔD, (HCl) data in Table 64, the quantities necessary for equation (25) were calculated, and are entered in Columns 3-6 inclusive of Table 68.

In Fig.19 the values in Column 5 of Table 68 are plotted against the corresponding values in Column 3. The graph is linear. From a least-squares fit, it was found that

slope = $(K/\Delta x)^{\frac{1}{2}} = 7.89$; standard deviation = 0.14

intercept = $x_{ab}(K/\Delta x)^{\frac{1}{2}} = 12.49$; standard deviation = 0.13

$x_{ab} = 12.49/7.89 = 1.58$; standard deviation = 0.04

$\Delta x = x_{ab} - x_a - x_b = 1.08$; standard deviation = 0.04

Therefore, $K = 7.89^2 \times 1.08$

$= 67.4$; standard deviation = 3.5

(litre/mole)

Values of other solvation constants are reported in Tables 69-70.

(v) Thermodynamic constants for the reaction , $HX + R_2O = HX.R_2O$

Values of the equilibrium constants for the reaction

$$HX + R_2O = HX.R_2O$$

where X is Cl or Br and R_2O represents each of the three ethers, di-iso-propyl ether, di-n-butyl ether, and tetrahydrofuran have been listed in Table 69 for each of the three temperatures. From these values, the standard free energy shange, ΔG^o, on a molar concentration scale was calculated and is listed in Column 2 of Table 71.

For the calculation of the standard enthalpy change ΔH^{o}, these values of ΔG^{o} were evaluated to a molal basis, as described in Section I h on page 80, therefrom the standard enthalpy change on a molal basis was obtained from a conventional plot of log K versus 1/T. In practice, a least-squares fit was made. However, an example of the plot is given in Fig. 20, for the case of HCl-tetrahydrofuran. The graph is reasonably linear. This degree of linearity existed for other systems. The ΔH^{o} values obtained by the least-square fits were converted from molal to molar basis, and the resulting values are tabulated in Column 3 of Table 71. Finally, from the values of ΔG^{o}, and ΔH^{o}, the values of ΔS^{o} were calculated for the reaction, and are entered in the last column of Table 71.

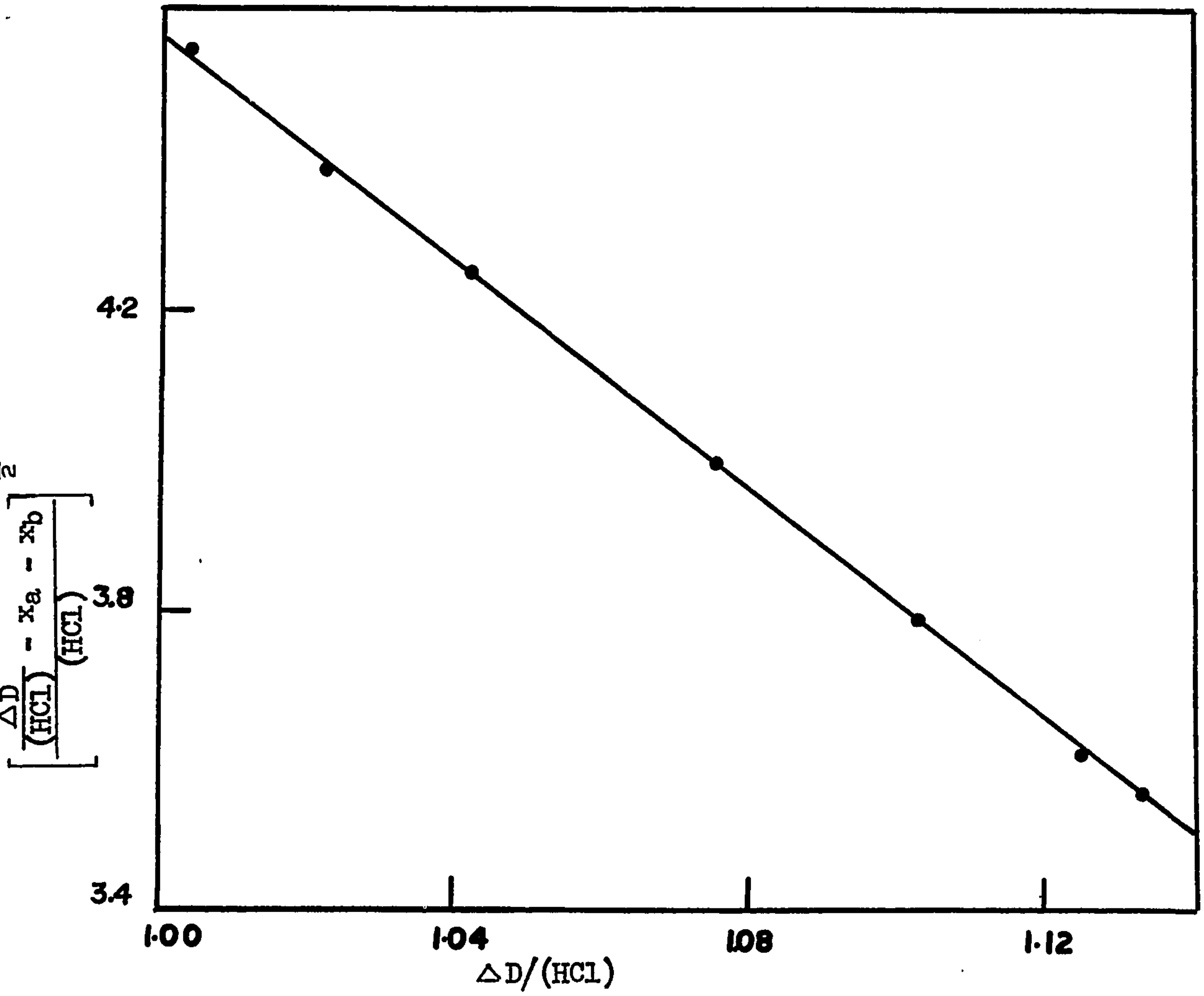

Fig. 19. Experimental plot of equation (25).

Data: Table 68.

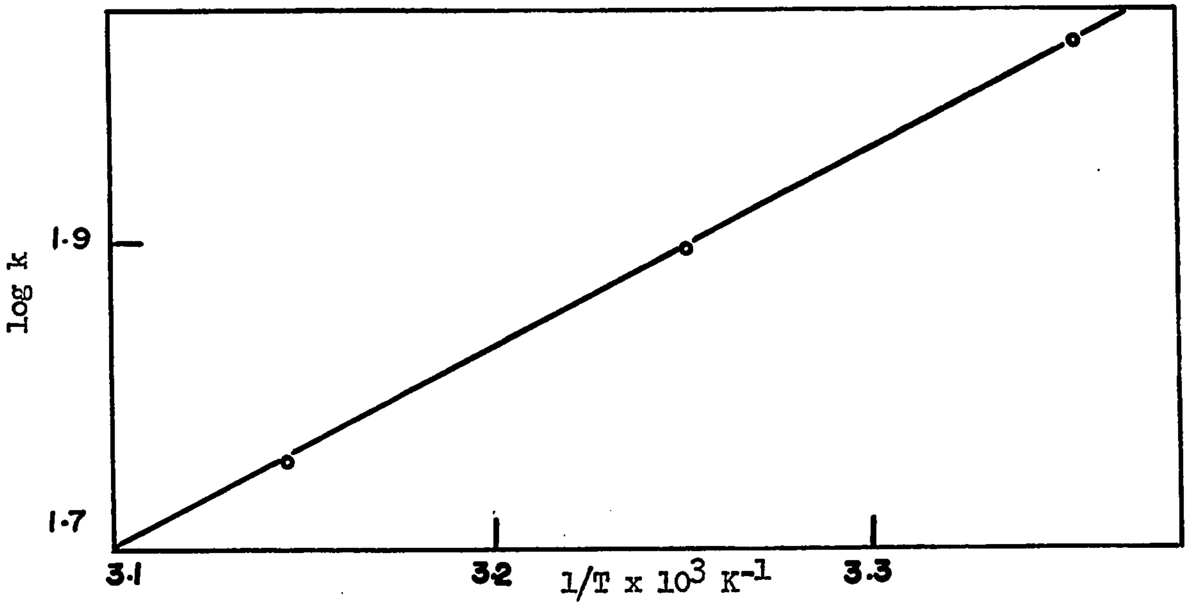

Fig. 20. Experimental plot of log K versus 1/T for the reaction

$HCl + R_2O = R_2O.HCl$, R_2O = tetrahydrofuran.

Table 69 Equilibrium constant for the reaction

$$HCl + R_2O = HCl.R_2O$$

in carbon tetrachloride at different temperatures.

R_2O	di-isopropyl ether		di-n-butyl ether		tetrahydrofuran	
Temperature, °C	K, litre/mole	log K	K, litre/mole	log K	K, litre/mole	log K
25.2	9.4±1.5	0.97±0.16	4.9±0.5	0.69±0.07	67.4± 3.5	1.83±0.09
34.7	7.3±0.6	0.86±0.08	4.0±1.3	0.60±0.20	50.2±2.4	1.70±0.09
45.0	5.6±0.2	0.75±0.03	3.2±1.5	0.51±0.30	37.0±9.0	1.57±0.39
d. f.*	5	5	5	5	5	5

Table 70 Formation constant for the reaction

$$HBr + R_2O = HBr.R_2O$$

in carbon tetrachloride at different temperatures.

R_2O	di-isopropyl ether		di-n-butyl ether		tetrahydrofuran	
Temperat- °C	K, litre/mo mole	log K	K, litre/mole	log K	K, litre/mole	log K
25.2	1.97± 0.1	0.29±0.01	3.0±0.05	0.48±0.01	48.5±1.6	1.69±0.55
34.7	1.57± 0.03	0.20±0.005	2.4±0.08	0.38±0.01	34.1±2.5	1.53±0.10
45.0	1.28±0.03	0.107±0.003	1.9±0.03	0.28±0.05	26.3±1.0	1.42±0.05
d. f.*	5	5	5	5	5	5

* d.f.= degrees of freedom.

Table 71 Thermodynamic constants for the reactions

$HCl + R_2O = HCl.R_2O$ and

$HBr + R_2O = HBr.R_2O$

for three ethers in anhydrous carbon tetrachloride at 25.2°C.

For $HCl + R_2O = HCl.R_2O$

Ether	$-\Delta G^o$, kcal/mole		$-\Delta H^o$, kcal/mole		$-\Delta S^o$
	molar	molal	molal	molar	e,u.
di-iso-propyl	1.33±0.2*	1.6±0.2	5.3±0.1	5.3±0.1	13.4±0.7
di-n-butyl	0.94±0.09	1.2±0.1	4.4±0.1	4.4±0.1	11.6±0.4
tetrahy-furan	2.5±0.1	2.8±0.1	6.0±0.1	6.0±0.1	11.6±0.8

degrees of freedom = 5

For $HBr + R_2O = HBr.R_2O$

Ether	$-\Delta G^o$, kcal/mole		$-\Delta H^o$, kcal/mole		$-\Delta S^o$
	molar	molal	molal	molar	e.u.
di-iso-propyl	0.40±0.02*	0.67±0.04	4.5±0.1	4.5±0.1	13.7±0.8
di-n-butyl	0.65±0.01	0.92±0.02	4.2±0.06	4.2±0.06	11.9±0.3
tetrahy-furan	2.30±0.07	2.57±0.08	5.9±0.20	5.9±0.20	11.2±1.0

degrees of freedom = 5

* the ± value after each number is the standard deviation.

IV Determination of heat of solution by calorimetry

(a) Synopsis

The heat of solutions of anhydrous ferric chloride and ferric bromide in each of the three ethers, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran were measured by simple calorimetry. By the same method, the heats of solution of tetrachloroferric acids and tetrabromoferric acids in di-isopropyl ether and in di-n-butyl ether were measured. Tetrahaloferric acid were too soluble in tetrahydrofuran to be isolated from that solvent by precipitation.

(b) Water equi-valent of the calorimeter*

The calorimeter is shown in Fig. 4. About 50 ml of di-isopropyl ether at approximately 20°C were introduced into the tared calorimeter; room temperature was 25°C. The calorimeter was then reweighed to give the weight of the ether introduced. The temperature was then read until it became constant (approximately fifteen minutes.) Readings were to 0.01°C.

Into a Dewar flask, another 50 ml of di-isopropyl ether at approximately 30°C, were introduced. The temperature was also read until it became constant. With continuous stirring, the ether at 30°C was quickly poured into the first calorimeter containing the ether at 20°C. The temperature of the resulting mixture was read at half-minute intervals, until five minutes after the temperature had reached its maximum. The calorimeter and the mixture were then reweighed.

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* The term"calorimeter" includes the suspended weighing bottle, as well as the stirrer and the thermometer.

A temperature-time curve was drawn, and the zero-time temperature was found by extrapolated of the cooling curve to zero-time. The water-equivalent of the calorimeter was then calculated from the weights of the liquids, the changes in temperature, and the specific heat of di-isopropyl ether. The data and water equivalent on five determinations are given in Table 73.

(c) Heats of solution of ferric chloride and bromide

About 100 ml Of the particular ether (di-isopropyl ether, di-n-butyl ether, tetrahydrofuran) were introduced into the tared calorimeter, and the calorimeter and contents were reweighed. Anhydrous ferric halide was then placed in the weighing bottle which was suspended inside the calorimeter. It was then suspended by a long glass tube to insure that the weighing bottle was close to the surface of the ether, thereby insuring that the temperature of the ferric halide was essentially that of the ether. The calorimeter and contents were then reweighed in order to be able to calculate exactly the weight of the ferric halide added to the weighing bottle. The temperature of the ether was then read until it became constant, this thermal equilibration requiring about fifteen minutes. A long, thin glass rod inside the hollow rod holding the weighing bottle was then used to push the weighing bottle down into the ether. With continuous stirring, the temperature of the solution was then read at halfminute intervals until five minutes after the temperature had reached its maximum. As before, extrapolation of the temperature-time curve to zero time gave the required corrected temperature. Solutions of the anhydrous ferric halides in the ether was almost instantaneous.

Five millilitres of the final solution in the calorimeter were pipetted into a 150-ml beaker. The ether was evaporated on a steam bath. The residue was dissolved in dilute hydrochloric acid. The amount of iron in the resulting solution was then determined by a conventional titration. Procedural details of the titration are in Appendix 3.

The data resulting from these measurements are in Table 74 and 75 ,for ferric chloride and ferric bromide respectively, in the three ethers.

From these data, by using the measured water equivalent of the calorimeter (Table 73), the integral heats of solution were calculated in the usual way, and are recorded in Tables 76 and 77, Column 2. From these values, the molal heat of solution was calculated, and entered in Column 3. Inspection of these values shows that for a particular ferric halide and a particular ether, the values in Column 3 are independent of the concentration of the ferric halide. Although the concentration range was of necessity very limited in each case, nevertheless it was considered that the average value of the molal heat of solution was a reasonable estimate of ΔH^o. These estimates of ΔH^o are entered in the last row of Tables 76 and 77. *

(d) Preparation of tetrahaloferric acids ($HF_eX_4.2R_2O$)

All preparations were carried in a dry box.

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* ΔH^o refers to the molal heat of solution for the change,

FeX_3(solid) $=$ FeX_3(solution, unit activity) with the standard state for the solution being the usual hypothetical 1 molal solution, and the reference state an infinitely dilute solution.

(i) Tetrachloroferric acid- di-isopropyl ether

A concentrated solution of hydrogen chloride in di-isopropyl ether was prepared in a separatory funnel by using the generator shown in Fig. 2, in the fume-hood. The stoppered separatory funnel containing the solution was transferred to the dry box and all subsequentoperations carried out therein.

A saturated solution of ferric chloride in di-isopropyl ether was filtered through a sintered glass filter to ensure that no residue of ferric chloride remained suspended in the solution, and was collected in a 250-ml erlenmeyer flask. The prepared hydrogen chloride solution was added slowly into this ferric chloride solution until there was no further precipitation of tetrachloroferric acid. The precipitate was a light -yellow gelatinous solid, extremely hygroscopic. Exposure to moisture was found to convert it immediately to a greenish liquid. The supernantant di-isopropyl ether solution was decanted off after the precipitate had settled. The precipitate was then washed with the pure ether, and filtered with suction onto a sintered glass filter, where it dried quickly. It was then scraped off into a weighing bottle, and stored in a desiccator containing anhydrous calcium sulphate.

(ii) Tetrachloroferric acid- di-n-butyl ether; tetrabromoferric acid - di-n-butyl ether; and tetrabromoferric acid - di-isopropyl ether.

These products, unlike the tetrachloroferric acid- di-isopropyl ether product, were liquids at room temperature. These liquids products were prepared by using the same procedure which differ somewhat from that used for the solid.

Thus, a saturated solution of the ferric bromide or chloride in the particular ether was prepared, and filtered through a fritted glass crucible into a 125-ml separatory funnel. A concentrated solution of the hydrogen halide in the same ether was prepared by using the generator shown in Fig. 2. This solution was then added slowly into the separatory funnel containing the ferric halide solution until no further precipitation of the heavy liquid product occured. This heavy liquid settled in the bottom of the separatory funnel; it was a yellowish-brown layer for chloroferric acid, and a dark red layer for bromoferric acid. After thirty minutes of settling, the lighter ether phase was decanted from the top, and the heavy liquid product was washed with two 20-ml portions of the dry ether. The wash solution was always decanted from the top of the separatory funnel. Finally the heavy layer was drained slowly into a 25-ml weighing bottle with a ground-glass lid; care was taken to ensure none of the light ether phase was allowed to leak through the Teflon stopcock into the weighing bottle. The products were stored in desiccators containing anhydrous calcium sulphate. Storage time before use did not exceed a few hours. The products were stable to light.

(e) Analysis of the tetrahaloferric acids

Analyses were in duplicate. Approximately one gram of the tetrahaloferric acid was transferred in a dry box, into a tared 50-ml volumetric flask, and the flask was accuately reweighed. The acid was

was then dissolved in a 1:2 (V/V) mixture of water and acetone. Aliquots were then taken for the determination of total halide, and of total iron. Total halide was determined by a conventional potentiometric titration with a standard solution of sodium hydroxide. Total iron was determined by a conventional complexometric titration; the procedural details are in Appendix 3. The ether content of the sample was found by difference. The results are reported in Table 72. It was found that for every molecule of iron, there was two molecules of ether in all four tetrahaloferric acids. The finding confirmed the results of Laurene (16) and Fomin and Morgunov (17).

(f) Heat of solution of tetrahaloferric acids dietherates

Since the tetrahaloferric acids were extremely hygroscopic, their heats of solution were measured with the calorimeter and accessories in a dry box flushed with dry nitrogen. The procedure used was the same as that described in Section (IV c), except that a saturated solution was formed in the calorimeter, by the addition of a very slight excess of tetrahaloferric acid. This excess of solid or liquid did not exceed approximately 10 mg, so that a correction for its presence was not necessary. The relatively low solubility of these acids in the ethers made necessary the use of a saturated solution.

The calorimeter data, and the heats of solution calculated therefrom are in Table 78. The solutions were assumed to be ideal, so that ΔH per mole was taken to be a reasonable estimate of ΔH^o. Due to the low solubilities of these solids in the ethers, the measured values of ΔH were relatively small. Therefore the values reported for ΔH^o can be regarded as being only approximate.

Table 73 Determination of water equivalent of calorimeter at 25.0°C

wt. of di-isopropyl ether, gms		increase in temp. of ether initially in calorimeter, ΔT_1 °C	drop in temp. of ether subsequently added to calorimeter, ΔT_2 °C	water equivalent, gms
initially in calorimeter	subsequently added			
35.8437	35.9511	1.48	3.09	20.6
35.7593	35.9188	1.18	2.43	20.1
0.0	35.7593	2.59	2.77	20.1
35.8826	35.9184	1.01	2.06	19.7
35.9385	35.8993	0.93	1.92	20.1

Average water equivalent of calorimeter = 20.1 gms

Specific heat of di-isopropyl ether : o.526 cal/gm (26, 27)

Table 72 Analyses of tetrahaloferric acids

ether and halide	wt. of tetrahaloferric acid sample, gms	hydrogen found		Fe found		Cl or Br*		ether by difference	
		gms x 10^3	moles x 10^3	gm	moles x 10^3	gm	moles x 10^2	gm	moles x 10^3
di-n-butyl and chloride	1.0118	2.205	2.188	0.1231	2.204	0.3130	0.882	0.5735	4.412
	1.5633	3.511	3.483	0.1895	3.393	0.4850	1.366	0.8853	6.810
di-n-butyl and bromide	0.8325	1.275	1.265	0.0729	1.323	0.4182	0.5234	0.3401	2.616
	1.2634	1.280	1.270	0.1058	1.894	0.6354	0.7952	0.5209	4.007
di-isopropyl and chloride	1.2453	3.082	3.058	0.1730	3.098	0.4385	1.2352	0.6308	6.173
	1.3114	3.306	3.280	0.1817	3.253	0.4629	1.3039	0.6635	6.493
di-isopropyl and bromide	0.7171	1.334	1.323	0.0687	1.230	0.4005	0.5013	0.2466	2.413
	0.7069	1.210	1.200	0.0680	1.217	0.3877	0.4852	0.2500	2.447

* Calculated from the amount of hydrogen found, on the basis of a 1:4 atomic ratio of H:X, i.e. hydrogen to halide.

Table 74 Calorimetric data for the heat of solution of $FeCl_3$ in three ethers at 25°C.

di-isopropyl ether		di-n-butyl ether		tetrahydrofuran	
molality of $FeCl_3$ $\times 10^{-2}$	ΔT °C	molality of $FeCl_3$ $\times 10^{-2}$	ΔT °C	molality of $FeCl_3$ $\times 10^{-2}$	ΔT °C
1.884	0.42	3.997	0.60	2.298	1.08
4.445	0.95	5.184	0.74	3.314	1.53
6.329	1.37	9.181	1.34	4.206	1.92
				4.910	2.26
				2.786	1.31
				4.625	2.09
				6.086	2.70

Table 75 Calorimetric data for the heat of solution of $FeBr_3$ in three ethers at 25°C.

di-isopropyl ether		di-n-butyl ether		tetrahydrofuran	
molality of $FeBr_3$ $\times 10^{-2}$	ΔT °C	molality of $FeBr_3$ $\times 10^{-2}$	ΔT °C	molality of $FeBr_3$ $\times 10^{-2}$	ΔT °C
2.034	0.33	3.123	0.42	2.291	0.69
2.149	0.37	6.248	0.88	4.548	1.36
4.183	0.70	9.371	1.31	6.839	2.05

Note : ΔT°C was the rise in temperature of the ether due to solution of the solid ferric halide, at zero time, i.e. corrected for radiation loss.

Table 76 Heat of solution of anhydrous ferric chloride in three ethers at 25°C.

di-isopropyl ether		di-n-butyl ether		tetrahydrofuran	
molality of $FeCl_3$ x 10^{-2}	Q, calories	molality of $FeCl_3$ x 10^{-2}	Q, calories	molality of $FeCl_3$ x 10^{-2}	Q, calories
1.884	-24.14	3.997	-35.56	2.298	-57.63
4.445	-56.61	5.184	-43.90	3.314	-81.65
6.329	-78.76	9.181	-79.46	4.206	-102.5
				4.910	-139.5
				2.786	-70.20
				4.625	-111.5
				6.086	-144.1
average ΔH^o k cal/mole	-17.5		-11.4		-25.1
s.d.	0.4		0.2		0.5

Table 77 Heat of solution of anhydrous of ferric bromide in three ethers at 25°C.

di-isopropyl ether		di-n-butyl ether		tetrahydrofuran	
molality of $FeBr_3$ x 10^{-2}	Q, calories	molality of $FeBr_3$ x 10^{-2}	Q, calories	molality of $FeBr_3$ x 10^{-2}	Q, calories
2.034	-18.95	3.123	-24.89	2.291	-36.60
2.150	-21.27	6.248	-52.22	4.548	-72.96
4.183	-40.22	9.371	-77.12	6.840	-109.4
average ΔH^o k cal/mole	-13.4		-10.8		-16.0
s.d.	0.3		0.2		0.4

Q = total heat change for the specified system

ΔH^o = standard enthalpy change per mole of solute

Table 78 Standard heat of solution of tetrahaloferric acid ($HFeX_4.2R_2O$) in two ethers at 25°C.

X = Cl, Br

R_2O = di-isopropyl ether, di-n-butyl ether

solvent	$HFeCl_4.2R_2O$			$HFeBr_4.2R_2O$		
R_2O	molality x 10^{-3}	Q, calories	ΔH^o, kcal/mole	molality x10^{-3}	Q, calories	ΔH^o, kcal/mole
di-iso-propyl	6.92	8.3	1.2	1.89	8.7	4.6
di-n-butyl	2.78	12.5	4.5	3.24	21.1	6.5

Q and ΔH^o have the same meaning as in Tables 76 and 77.

V. Calculation of standard enthalpy changes for the reactions

(i) $HS_2FeCl_4(\text{solid}) = HS_2^+{}_{(\text{gas})} + FeCl_4^-{}_{(\text{gas})}$ $\quad -\Delta H^o_{15}$

(ii) $Fe_{(\text{solid})} + 2Cl_2\ (\text{gas}) + e = FeCl_4^-\ (\text{gas})$ $\quad \Delta H_1^o$

(iii) $H^+_{(\text{gas})} + 2\ S_{\ (\text{gas})} = HS_2^+{}_{(\text{gas})}$ $\quad \Delta H_2^o$

where S denotes an ether

(a) Introduction

The lattice energy of an ionic crystal at a given temperature is the energy required to dissociate one molecule of the solid into its gaseous ions at infinite dilution.

A relationship that permitted the calculation of lattice energy was first proposed by Max Born (52).

$$U = A_M \frac{N\ e^2 \eta_1\ \eta_2}{r} \left(1 - \frac{1}{m} \right)$$

Born and Mayer (53) later proposed an improved equation:

$$U = A_M \frac{N\ e^2 \eta_1\ \eta_2}{r} \left(1 - \frac{\rho}{r} \right)$$

In both equations

η_1, η_2 = ionic charges

e = electronic charge

N = Avagadro's number

r = interionic distance

A_M = structural coefficient (Madelung constant)

= characteristic constant = 0.345.

For some crystals the interionic distances have not been reported, from X-ray measurements. However, it is possible to obtain an estimate of the lattice energy of an ionic crystal by using an equation proposed by Kapustinskii and Yatsimirskii (54,55,69)

$$U = 287.2 \sum n \frac{n_1 n_2}{\tau_c + \tau_a} \left[1 - \frac{0.345}{\tau_c + \tau_a} + 0.00453 \, (\tau_c + \tau_a) \right] \quad (26)$$

where $\tau_c + \tau_a$ are the Goldschmidt ionic radii of the cation and the anion respectively, and n is the total number of ions in the crystal.

All the calculated lattice energies in the present work were based on equation (26), for crystals of the rock-salt type.

(b) Lattice energies of tetrahaloferric acids, HS_2FeX_4

The enthalpy changes for the reaction

$$HS_2FeX_4(s \text{ or } l) \;=\; HS_2{}^{+}{}_{(g)} \;+\; FeX_4{}^{-} \qquad [3]$$

where S denotes an ether, and X denotes Cl or Br, were calculated by using equation (26). These calculations were made for each of the three ethers, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran.

In the case of tetrachloroferric acid and di-isopropyl ether the acid was a solid at 25°C and equation (26) was applied without change. In the other cases, the acid was a liquid at 25°C. Therefore in these cases, the values obtained from equation(26) were corrected for the estimated heats of fusion of the solids at 25°C.

These heats of fusion were estimated as follows:-

The entropies of fusion for most of the alkali metal halides are in the order of 6 e.u.(56,57). If the entropy of fusion of the tetrahaloferric acids are assumed to be 6 e.u., their heats of fusion can be calculated by the following relationship,

$$\Delta H_m = T_m \Delta S_m$$

where ΔH_m = heat of fusion at melting point

ΔS_m = entropy of fusion at melting point

T_m = melting point of the compound

The melting points of these tetrahaloferric acids were estimated from the melting points of similar tetrahalometallic acid dietherates, given in Table 80 (58,59). These estimated values of heat of fusion and their melting points are reported in Table 82.

Values for the Goldschmidt ionic radii of $FeCl_4^-$ and $FeBr_4^-$ were taken directly from the literature (60). The Goldschmidt ionic radii of the cation HS_2^+ were measured directly from constructed molecular models. Values of the bond length for $O\text{-}H^+$ were needed in order to construct the models of HS_2^+. The bond length of the short-lived species OH^+ has been reported (60,61) to be 1.03 Å. From proton NMR studies of solid hydrates (e.g. $HClO_4.H_2O$, $HNO_3.H_2O$, $H_2SO_4.H_2O$, $H_2SeO_4.H_2O$, $H_2PtCl_6.2H_2O$, and $H_2SO_4.2H_2O$ at 90°K, and $HClO_4.H_2O$ at 105-296 °K), Richards and Smith (62,63,64) reported the existence of the hydronium ion H_3O^+, having a mean inter-proton distance of 1.72 ± 0.02 Å. From this value, they also calculated the $O\text{-}H^+$ bond length in H_3O^+ to be 1.02 Å; and this value was used in the models of HS_2^+. In the measurement of the ionic radii of HS_2^+, the ion was orientated so that the $O\text{-}H^+\text{-}O$ bond was linear, and the alkyl groups of the ether molecules were arranged to give a minimum radius. The alkyl groups are arranged to form almost a circle with the carbon atoms in staggered position to minimize repulsion. The values found for the ionic radii of HS_2^+ and of FeX_4^- are listed in Table 82 for the three ethers and the two halides.

The lattice energies of the six tetrahaloferric acids were calculated in by using equation (26) on the basis of them being ionic crystals. The values are entered in Column 7 of Table 82. On subtracting the corresponding estimated heats of fusion, the enthalpy changes ΔH^{o}_{15} for reaction [3] are entered in Column 8 of Table 82.

Table 80 Melting points of some tetrahalometallic acids

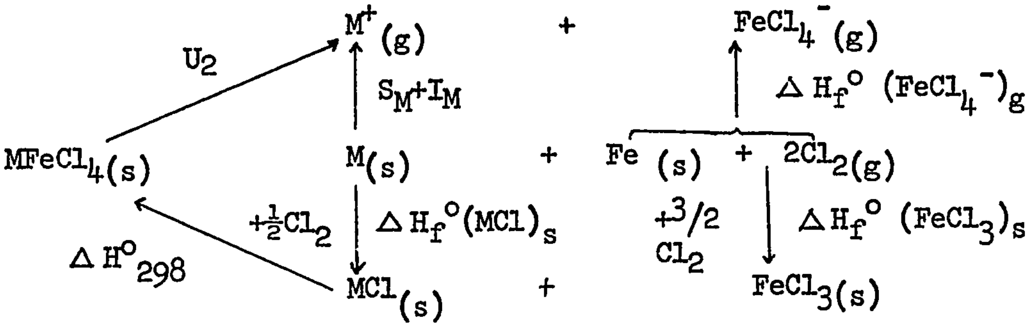
Compound	melting point, °C (59)	compound	melting point, °C (58)
$HFeCl_4.2(CH_3)_2O$	5	$HGaCl_4.2(C_2H_5)_2O$	25
$HFeCl_4.2(C_2H_5)_2O$	53	$HGaBr_4.2(C_2H_5)_2O$	-70
$HAlCl_4.2(CH_3)_2O$	-1	$HInCl_4.2(C_2H_5)_2O$	-35
$HAlCl_4.2(C_2H_5)_2O$	44	$HTlCl_4.2(C_2H_5)_2O$	-80
$HAlCl_4.2(C_3H_7)_2O$	69-71	$HAlCl_4.2(C_2H_5)_2O$	46
$HZnCl_3.2(CH_3)_2O$	-29	$HAlBr_4.2(C_2H_5)_2O$	-30
$HZnCl_3.2(C_2H_5)_2O$	25-26	$HInBr_4.2(C_2H_5)_2O$	-80

(c) Enthalpy of formation of $FeCl_4^-$ ion

The enthalpy of formation for the reaction

$$Fe_{(s)} + 2Cl_{2(g)} + e = FeCl_4^- \qquad [4]$$

with the gases at infinite dilution, was calculated by using the following double cycle:



where U_2 = lattice energy of metal chloroferrate, $MFeCl_4$

S_M = heat of sublimation of metal, M

I_M = ioniztion potential of metal, M

$\Delta H_f^o (FeCl_4^-)_g$ = enthalpy of formation of gaseous $FeCl_4^-$ ion, at infinite dilution

$\Delta H_f^o (MCl)$ = standard heat of formation of solid MCl

ΔH^o_{298} = standard enthalpy change for the reaction noted

$\Delta H_f^o (FeCl_3)_s$ = standard heat of formation of solid ferric chloride

From the cycles,

$$\Delta H_f^o (FeCl_4^-)_g = U_2 - S_M - I_M + \Delta H_f^o(MCl)_s + \Delta H_f^o(FeCl_3)_s + \Delta H^o_{298} \qquad (27)$$

The metals M used in the calculation were potassium and sodium because data on their tetrachloroferrates were available.

Table 81 Standard enthalpy change ΔH_f° $(FeCl_4^-)_g$ for the reaction

$$Fe_{(s)} + 2Cl_2(g) + e = FeCl_4^-(g)$$

at 25°C, from a thermochemical cycle.

Metal tetra-chloroferrate	ΔH°_{298} kcal/mole	U_2 kcal/mole	$\Delta H_f^{\circ}(FeCl_3)_s$ kcal/mole	$\Delta H_f^{\circ}(MCl)_s$ kcal/mole	S_M+I_M kcal/mole	$\Delta H_f^{\circ}(FeCl_4^-)_g$ kcal/mole
$NaFeCl_4$	-0.8 (68)	165.4	-95.7 (65)	-98.2 (65)	144 (66)	-173.3
$KFeCl_4$	-7.3 (68)	149.8	-95.7 (65)	-104.2 (65)	121.1 (66)	-178.3

Table 82 Lattice energies of tetrahaloferric acids

Ether	HS_2FeCl_4						
	state	estimated melting point, °C	heat of fusion ΔH_m°,kcal/mole	ionic radii,Å anion	cation	lattice energy U_3 kcal/mole	ΔH_{15}° kcal/mole
di-isopropyl	solid	79-80	2.1	2.19	4.34	86	-86
di-n-butyl	liquid	25-30	1.8	2.19	5.52	74	-72
tetrahydrofuran	-	-	-	2.19	4.12	89	-89
	HS_2FeBr_4						
di-isopropyl	liquid	0-5	1.7	2.21	4.34	86	-84
di-n-butyl	liquid	-51	1.3	2.21	5.52	74	-72
tetrahydrofuran	-	-	-	2.21	4.12	88	-88

The value of U_2 was found by using equation (26). The ionic crystal radii for Na^+, K^+, and $FeCl_4^-$ were taken to be 0.95 A (67), 1.33A (67), and 2.19 A (60) respectively.

The values of S_M and I_M were taken from the literature (29,40). The values of $\Delta H_f^o\ (FeCl_3)_s$, and of $\Delta H_f^o\ (MCl)_s$ for KCl and NaCl were also available (65).

Cook and Dunn (68) evaluated ΔH_{298}^o , both for $KFeCl_4$ and for $NaFeCl_4$.

All these data, together with the values found from equations(27) for $\Delta H_f^o\ (FeCl_4^-)_g$ are entered in Table 81.

(d) Enthalpy of formation of HS_2^+ ion

The values of the enthalpy change were required for the reaction

$$H_g^+ + 2S_g = HS_2{}^+{}_g$$

with the gases at infinite dilution, and where S denotes di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran. These values were not available in the literature. Therefore an attempt was made to estimate the proton affinities of these ethers from the available data on proton affinities of water, alcohols, aldehydes, and carboxylic acids. Then the energy involved on the addition of a second molecule of the ether was estimated, from the value obtained for the addition of a second molecule of water to H_3O^+.

(i) Proton affinity of ethers

Literature values for the proton affinities of water, alcohols, aldehydes, and carboxylic acids are recorded in Table 83.

Values for the proton affinities of the ethers in question have not been published. In order to estimate them, a published value of the proton affinity of water was used as a reference point. The value of 151 kcal/mole was used. It was obtained by Harrison and Van Raalt (70), using electron impact. Comparative information given by Munson (71) for other compounds was also used. Thus from the proton affinities of the homologous series of carboxylic acids (72), P(HCOOH) = 162 kcal/mole, P(CH_3COOH)= 184 kcal/mole, P(C_2H_5COOH)= 190kcal/mole; the replacement of one hydrogen by a methyl group gives a change of 22 kcal/mole, and the P(C_2H_5COOH) is larger than that of CH_3COOH by 6 kcal/mole. If the proton affinities of water, alcohols, and ethers are strictly comparable, then P(CH_3OH) would be equal to 173 kcal/mole i.e. some 22 kcal/mole more than the P(H_2O) which is 151 kcal/mole (70); and P(CH_3OCH_3) would be 44 kcal/mole more than that of water, namely 195 kcal/mole. These estimates both for CH_3OH and CH_3OCH_3 agree with the information found by Munson(71), who reported that P(CH_3OH) < P(CH_3CHO) which is 180 kcal/mole (72); and P(CH_3OCH_3) < P(NH_3) which is 202 kcal/mole (73). Moreover, the P($C_2H_5OC_2H_5$) might be expected to be larger than the P(CH_3OCH_3) by 12 kcal/mole, since the P(C_2H_5COOH) is 6 kcal/mole larger than P(CH_3COOH). Estimates of the proton affinities of di-isopropyl ether and di-n-butyl ether were obtained by using the same comparative process. The P(tetrahydrofuran) is assumed to be approximately to be the same as that of di-ethyl ether. These various estimated proton affinities are reported in Table 84.

(ii) The enthalpy change for the reaction, $R_2O_g + R_2OH_g^+ = (R_2O)_2H_g^+$

In the absence of literature values, it was necessary to estimate the enthalpy change on the addition of a second molecule of water to H_3O^+.

Consider the following thermochemical cycle:-

$$\begin{tikzcd}
H_g^+ \arrow[d] & + & 4H_2O_l \arrow[d, "\Delta H_c^o"] & \overset{\Delta H_b^o}{=} & H_9O_4^+ (aq) \arrow[d, "\Delta H_d^o"] \\
H_g^+ & + & 4H_2O_g & \underset{\Delta H_e^o}{=} & H_9O_4{}^+{}_g
\end{tikzcd}$$

From the cycle, $\Delta H_e^o = \Delta H_b^o - \Delta H_c^o + \Delta H_d^o$ (28)

where ΔH_b^o = standard enthalpy of hydration of gasous H^+

ΔH_c^o = standard enthalpy of vaporization of four moles of water

ΔH_d^o = negative enthalpy of solution of gaseous $H_9O_4{}^+$

ΔH_e^o = standard enthalpy of reaction of proton with four molecules of water in the gas phase to form gaseous $H_9O_4{}^+$.

Both ΔH_b^o and ΔH_c^o were available in the literature; and ΔH_d^o may be estimated from the enthalpies of hydration of other cations, as described in the next Section. The value of $\Delta H_e{}^o$, the enthalpy change for the addition of four molecules of water to a proton in the gas phase, could then be calculated by equation (28). The value of -287kcal/mole was used for ΔH_b^o. These enthalpy values are reported in Table 85. Now the enthalpy change, ΔH_a^o, for the reaction

$$H_g^+ + H_2O_g \overset{\Delta H_a^o}{=} H_3O_g^+$$

is reported to be -151 kcal/mole (70). Therefore, the enthalpy change ΔH_f^o, for the reaction,

$$H_3O^+_g + 3H_2O_g \overset{\Delta H_f^o}{=} H_9O_4{}^+{}_g$$

would be $\Delta H_f^o = \Delta H_e^o - \Delta H_a^o$

$= -281 + 151$

$= -130$ kcal/mole.

The enthalpy change for the addition in turn of each of these three molecules of water is assumed to be the same. Hence the enthalpy change for the addition of one molecule of water to H_3O^+ would be -130/3 = -43 kcal/mole. That is, the enthalpy change for the reaction

$$H_3O^+{}_g + H_2O_g \overset{\Delta H_g^o}{=} H_5O_2{}^+{}_g$$

would be -43 kcal/mole.

Kebarle (126) stated that the enthalpy change on the addition of a second molecule to the already monosolvated proton is larger for water than for ether, however, in the absence of quantitative data, it will be assumed that the enthalpy change for the reaction,

$$R_2OH^+_g + R_2O_g = (R_2O)_2H^+_g$$

is approximately the same as that for water (ΔH_g^o). Then the enthalpy change for the reaction,

$$2\,R_2O_g + H^+_g = H\,(R_2O)^+_2{}_g$$

would be as follows:-

$C_3H_7OC_3H_7 = -219 - 43 = -262$ kcal/mole

$C_4H_9OC_4H_9 = -231 - 43 = -274$ kcal/mole

$C_4H_8O = -207 - 43 = -250$ kcal/mole

These values are reported in Table 87 Column 4.

Table 83 Proton affinities of water, alcohols, aldehydes, carboxylic acids, and ammonia.

$$HX^+ \overset{P(X)}{=} H^+ + X$$

X	P(X),kcal/mole			
	proton transfer	ionic reactions(74)	electron impact	other
H_2O		$163 \leqslant P \leqslant 172$	151+3(70); 164 ± 4(75)	182(66); 173(76)
CH_3OH	$>H_2O$	$177 \leqslant P \leqslant 183$		
CH_3OCH_3	$>CH_3CHO>CH_3OH$			
$HCHO$			163+3(77); 161 ∓ 3(72)	
CH_3CHO	$>CH_3OH$		182 ∓ 3(77); 180 ∓ 3(72)	
C_2H_5CHO			$172\bar{?}$(72)	
$HCOOH$	$>H_2O$		166+2(77); 162 ∓ 3 (72)	
CH_3COOH			184 ∓ 3 (77,72)	
C_2H_5COOH			190 ± 3 (72)	
NH_3	$> CH_3OCH_3$			202(73); 239(76)

Table 84 Estimated values of proton affinities of ethers

X	P(X), kcal/mole
H_2O	151 (70)
CH_3OH	173
$CH_3CHO>CH_3OH$ (71)	180 (72)
$CH_3OCH_3>NH_3$ (71)	195
$C_2H_5OC_2H_5$	207
CH_3OCH_3	
$C_3H_7OC_3H_7$	219
$C_4H_9OC_4H_9$	231
C_4H_8O	207

Table 85 Enthalpy values for equation (28), all in kcal/mole

ΔH_a^o	ΔH_b^o	ΔH_c^o	ΔH_d^o	ΔH_e^o	ΔH_f^o	ΔH_g^o
-151(70)	-283(28,78) -287(79)*	44(61)	50	-281	-130	-43

* This is the value used in the present work.

(iii) Estimation of enthalpy of hydration of $H_9O_4{}^+{}_g$

By using the known(80) heats of hydration of different monovalent positive ions listed in Table 86, a graph was plotted of heat of hydration versus the reciprocal of the radii of the metal ion. A straight was obtained (Fig. 21). From the known radius of $H_9O_4{}^+$,4.14A, the enthalpy of hydration of this cation was read on Fig. 21 to be -50kcal/mole.

Table 86 Heats of hydration and ionic radii of selected cations

Ion	ionic radius (A)	$-\Delta H^o$ (hydration) k cal/mole
Na^+	0.95	115
K^+	1.33	95
Li^+	0.78	137
Rb^+	1.49	88
Cs^+	1.65	81
$H_9O_4{}^+$	4.14	50

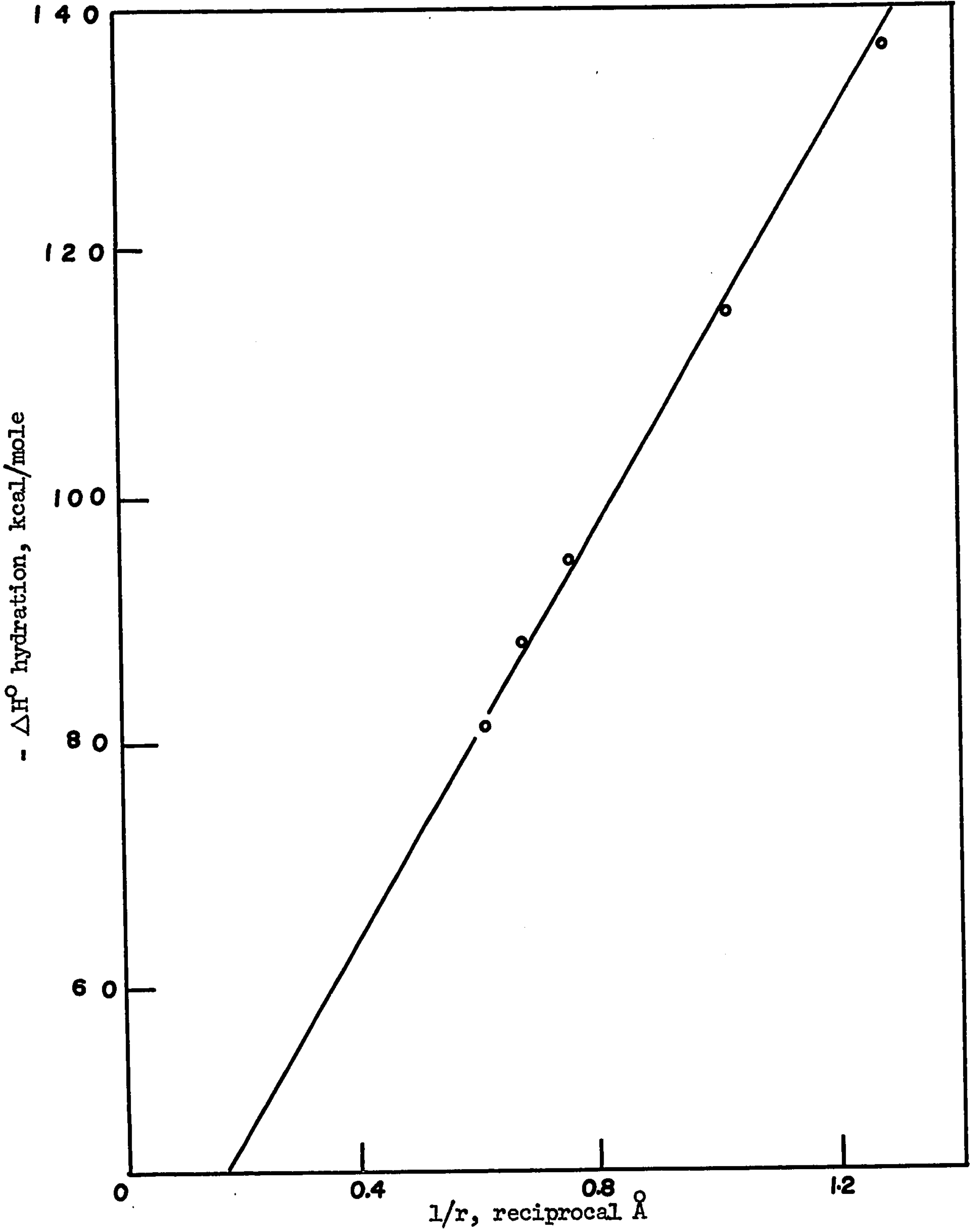
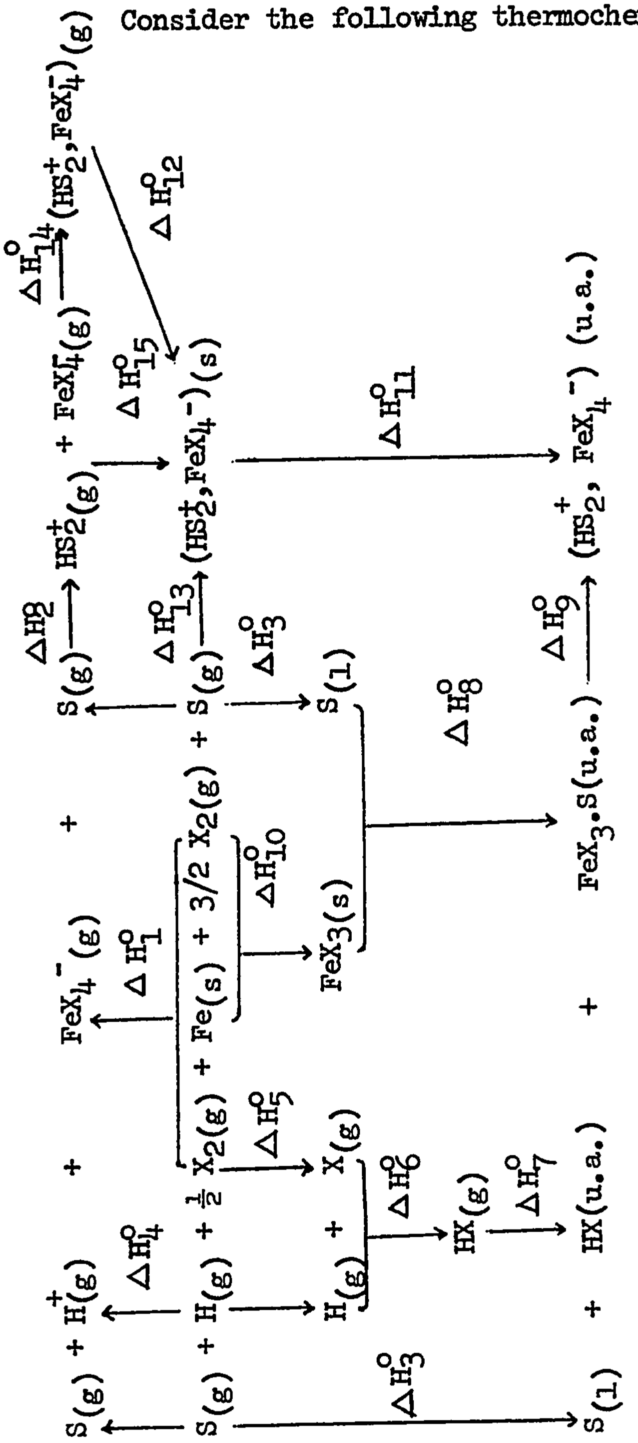


Fig. 21. Heat of hydration versus reciprocal of radius of metal ions.

VI Correlation of enthalpy changes for the system HX-FeX_3-R_2O, by a thermochemical cycle.

Consider the following thermochemical cycle, at 25°C



where X is Cl or Br, R_2O is di-isopropyl ether, di-n-butyl ether, or tetrahydrofuran, and where the reaction designated by ΔH^o_9 takes place in the ether (S) as solvent at 25.0°C.

$$\Delta H^o_2 = 2\Delta H^o_3 + \Delta H^o_5 + \Delta H^o_6 + \Delta H^o_7 + \Delta H^o_8 + \Delta H^o_9 + \Delta H^o_{10} - \Delta H^o_1 - \Delta H^o_4 - \Delta H^o_{11} - \Delta H_{15} \quad (29)$$

also $\Delta H^o_2 = \Delta H^o_{13} - \Delta H^o_1 - \Delta H^o_4 - \Delta H^o_{15}$ (30)

where ΔH^o_1 = standard enthalpy change for the formation of the tetrahaloferrate anion in the gas phase.

ΔH^o_2 = standard enthalpy of reaction of a proton with two molecules of ether in the gas phase.

ΔH^o_3 = standard heat of condensation of the ether

ΔH^o_4 = the ionization of the hydrogen atom

ΔH^o_5 = standard dissociation energy of halogen gas into atoms

ΔH^o_6 = negative value of dissociation energy of hydrogen halide gas in the solvent ether.

ΔH^o_7 = standard heat of solution of hydrogen halide gas in the solvent ether.

ΔH^o_8 = standard heat of solution of solid FeX_3 in the solvent ether

ΔH^o_9 = standard heat of formation of the tetrahaloferric acid in the solvent ether.

ΔH^o_{10} = standard heat of formation of solid FeX_3

ΔH^o_{11} = standard heat of solution of the tetrahaloferric acid in the solvent ether.

ΔH^o_{12} = negative standard heat of sublimation of solid tetrahaloferric acid

ΔH^o_{14} = standard enthalpy change of the ion-pair HS_2FeX_4 association.

ΔH^o_{15} = negative value of the lattice energy of the tetrahaloferric acid.

Methods have been described in the preceding Section (V) for the calculation of ΔH^o_1, and ΔH^o_{15}, and an attempt was made to estimate approximately the value of ΔH^o_2. Values for ΔH^o_3, ΔH^o_4, ΔH^o_5, ΔH^o_6, ΔH^o_7 and ΔH^o_{10} were available in the literature. Experimental values for the various heats of solution, ΔH^o_8, ΔH^o_9, and ΔH^o_{11} were obtained in the present work. All these values, with the literature sources, are entered in Table 87 for the six systems $HX\text{-}FeX_3\text{-}R_2O$, where X is chloride or bromide, and R_2O is di-isopropyl ether, di-n-butyl ether, or tetrahydrofuran.

By insertion of the relevant values from Tables 87 into equation (29), a value of ΔH^o_2 for the reaction

$$H^+_{(g)} + 2S_{(g)} = HS^+_{2(g)}$$

was obtained for each ether, and it has been entered in Column 3 of Table 87. Column 4 of Table 87 contains the rough values of ΔH^o_2 calculated as described in Section V(ii).

Table 87 Enthalpy values for the thermochemical cycle on page 169.

All values are in kcal/mole

ether	acid	ΔH_2^o calc.	ΔH_2^o est.	ΔH_1^o	ΔH_3^o	ΔH_4^o	ΔH_5^o	ΔH_6^o	ΔH_7^o (30)	ΔH_8^o	ΔH_9^o	ΔH_{10}^o	ΔH_{11}^o	ΔH_{15}^o
di-iso-propyl ether	HCl	-272	-261	-173.4 -178.4	-6.97 (26)	315 (29)	29.3 (82)	-103.2 (29)	-5.1	-17.5	-16	-93.6 (83) -95.7(65)	1.2	-86
	HBr	$\Delta H_2^o + \Delta H_1^o$ -411	-	-	-6.97	315	22.6 (82)	-87.5 (29)	-4.7	-13.4	-15.2	-63.5 (65)	4.6	-84
di-n-butyl ether	HCl	-290	-274	-173.4 -178.4	-8.96 (26)	315	29.3	-103.2	-4.6	-11.4	-13.8	-93.6 -95.7	4.5	-72
	HBr	$\Delta(H_2^o + H_1^o)$ -425	-	-	-8.96	315	22.6	-87.5	-4.5	-10.8	-13.6	-63.5	6.5	-72
tetrahydrofuran	HCl	-273	-250	-173.4 -178.4	-7.38 (27)	315	29.3	-103.2	-5.4	-25.0	-12.5	-93.6 -95.7	-	-89
	HBr	$\Delta H_2^o + \Delta H_1^o$	-	-	-7.38	315	22.6	-87.5	-5.5	-16.1	-13.3	-63.5	-	-88
Method used		calc. from the cycle	calc. from literature data	calculated from lit. data	literature data			literature data	vapour press. data	spectra measurements	calorimetry data	lit. value	calorimetry data	lattice energy

DISCUSSION

A. Introduction

In the present work, special cases of the solvent extraction system HX - FeX_3 - H_2O - R_2O where X is chloride or bromide, and R_2O is di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran respectively, have been investigated. In particular it was found that in the system HX - R_2O - CCl_4 , an unionized monoetherate $HX.R_2O$ existed ; and in the system HX - FeX_3 - R_2O , the ion-pair $(H_2O)_2H^+,FeX_4^-$ existed. Moreover, the thermodynamic properties, ΔG^o, ΔH^o, and ΔS^o were evaluated for two reactions, namely the formation of $HX.R_2O$, and the formation of the ion-pair ; and ΔG^o was found for the formation of $H_2O.HX$.

The present discussion will be concerned with : (i) justification of the assumptions inherent in the treatment of the data which led to the above results ; (ii) comparison of the thermodynamic constants for the formation of the monoetherate and the monohydrate of HCl and HBr, and for the corresponding haloferric acids, for the three ethers ; (iii) interpretation and use of the values found for the three thermodynamic properties ; (iv) the contribution of the present work to an understanding of the chemistry of solvent extraction systems of the type HX - MX_n - H_2O - S where M is a metal, X is a halide, and S is an oxygenated organic solvent.

It has been assumed in calculating all the equilibrium constants of the present work that all activity coefficients were unity.

Two pieces of evidence support this assumption : (i) in the case of hydrogen halide solutions in ethers and in carbon tetrachloride, Henry's law was obeyed, after correction had been made for imperfections in the gas phase ; and (ii) rather wide variations in the ratio of the concentrations of the reactants in the various systems did not produce a significant variation in the values of the equilibrium constants . However it is to be noted that the concentration of the ion-pair $HS_2^+FeX_4^-$ in no case exceeded 2×10^{-4} M. The assumption that its activity coefficient was unity is therefore intented to apply to concentrations of this magnitude or less. At much higher concentrations , dimers might be expected, although the solubilities that define the upper concentration limits are low.

B. The assumptions and their justification

1. The System HX - R_2O

The basic assumption in the treatment of the data was that there was only a 1:1 complex, $HX.R_2O$. However, the solvation constant varied only randomly throughout the range of hydrogen halide concentrations (0 - 1 M), and ether concentrations (5 - 100 %, i.e. 0.3 M - 6.7 M) . If significant concentrations of 1:2 or 2:1 complexes had also been existed, there would have been a statistically detectable trend in the variation of the equilibrium constant.

Gerrard and Macklen (91) also concluded from solubility and conductivity measurements of hydrogen chloride in di-ethyl ether that only the 1:1 complex $Et_2O.HCl$ existed. They concluded further that it was a hydrogen bonded complex rather than an oxonium salt of the kind (Et_2OH)$^+$$Cl^-$. Other conductivity measurements (97) also confirm that the 1:1 complex is not an ion-pair.

Moreover, form the dipole moment measurements of Smith (98), the dipole moment of hydrogen chloride in di-ethyl ether is just the summation of the individual moments of hydrogen chloride and diethyl ether. If this is the case, the dipole moments of the solvates in the present work would be in the range of 1.88 to 2.73 Debyes for various ethers and halides. The dipole moments of HCl and HBr are 1.10 Debyes and 0.79 Debyes respectively (87), and those for di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran are 1.26, 1.09, and 1.63 Debyes (87) respectively. Since these solvates of hydrogen halides in ethers have low dipole moments, it is then concluded that they existed as hydrogen bonded complex rather than oxonium salts of the kind ($R_2OH^+X^-$). The assumption was also made that the solvation constant of $HX.R_2O$, where R_2O is di-isopropyl ether, was independent of the dielectric constant of the solvent for the carbon tetrachloride- di-isopropyl ether mixtures. However, the solvation constant did not vary significantly for different mixtures of di-isopropyl ether and carbon tetrachloride as solvents (concentration of di-isopropyl ether varies from 0 % to 100%). Gordy and his co-workers (108 , 109 , 110 , 111) were among the first to explain the negative deviation from Raoult's law of hydrogen chloride in ether as being due to hydrogen bonding between hydrogen chloride and ether. They concluded from the infrared shift of the HCl band in different solvents that the extent of hydrogen bonding in a solvent is proportional only to the basicity of the solvent. The dielectric constant of solvents had little to do with the tendency of a solute to acquire protons for their systems. This, then, further supports the assumption that the solvation constant of $HX.R_2O$ does not depend on the dielectric constant of the solvents .

Furthermore, O'Brien and co-workers (112, 113, 114, 115, 116) measured the partial pressures of hydrogen chloride and hydrogen bromide in benzene , toluene, and nitrotoluenes . They found that in general hydrogen bromide was more soluble than hydrogen chloride in benzene and toluene, but the reverse was true in nitrotoluenes. They concluded that the relative strengths of the acids change considerably as the type of the solvent varies. From the present work, from the partial pressures of hydrogen halides (chloride and bromide) in carbon tetrachloride and di-isopropyl ether, the results agree with O'Brien's conclusion . Hydrogen bromide was more soluble is carbon tetrachloride than was hydrogen chloride (Henry's law constants for HCl and HBr are 4464 , and 1993 (Tables 49 and 50) respectively). However, the reverse is true in di-isopropyl ether (Henry's law constants for HCl and HBr are 73.1 and 90.3 respectively) . Hence care is clearly necessary when comparing two acids in two different solvents.

Additional strong evidence not only for the 1:1 complex but also for the correctness of the values reported for their formation constants is the fact that the values found by two completely different methods were in statistical agreement. Thus, the values for the formation constants found by the vapour pressure method are in Table 48 ; those found by the dielectric constant method are in Tables 69 and 70 . By using Student's t test and the standard deviations reported in those Tables, the values found by those methods for a given acid and a given ether were not statistically different at the 95 % confidence level.

The precision of the two methods was also compared, by using the standard deviations in conjunction with the conventional F test. It was found that the vapour pressure method was significantly more precise than the dielectric constant method for all ethers and for both halides, at the 95 % confidence level. In this connection, it is to be noted that the dielectric constant method was much quicker than the vapour pressure method.

Comparison of partial pressure of hydrogen choride in carbon tetrachloride with literature data .

Strohmeier and Echte (30) measured the vapour pressure of hydrogen chloride in mixtures of carbon tetrachoride (1 m. mole) and n-heptane (20 m. mole) from 200.8° K to 272.9° K. Using their data, partial pressures of hydrogen chloride in heptane, and carbon tetrachloride - heptane mixtures were plotted against temperatures for every mole fraction of hydrogen chloride and extrapolated to 25° C (298° K). Henry's law constants were found therefrom :-

HCl in heptane at 25° C = 33800 mm , HCl in 1 m. mole carbon tetrachloride and 20 m. moles heptane = 34418 mm per mole fraction.

The above two Henry's law constant were plotted against the mole fraction of carbon tetrachloride, and extrapolated to pure carbon tetrachloride, in order to get Henry's law constant for pure carbon tetrachloride. It was found to be 46000 mm . By using the present experimental data at 25° C , Henry's law constant was also found to be 46000 mm . The agreement between Strohmeier and Exhte's data and those of the present work serves to confirm the reliability of the present data.

2. The system $HX - H_2O - R_2O$

The basic assumption was that only a 1:1 complex, $HX.H_2O$, existed in the concentration range studied. The constancy of the values found for the formation constant over a wide concentration ratios of HX to H_2O (0.9 to 9) is justification for this assumption. The existence of a 2:1 and/or a 1:2 complex would have caused a statistically significant trend in the values found for the formation constant. However, it is realized that this is not unequivocal evidence; it has not been shown that the water obeyed Henry's law.

3. The system $HX - FeX_3 - R_2O$

The evidence for the existence of the monomer $HS_2^+FeX_4^-$ and of no other complex or dimer is as follows: when the ratio of the concentrations of total hydrogen halide to total ferric halide was varied from 1:70 , the formation constants calculated from the data did not show a statistical trend as the concentration ratio was varied. On the contrary, they remained constant within experimental error. This constancy could scarcely have existed if other complexes were present. Moreover, for those solutions used to evaluate the formation constants, the concentration of the tetrahaloferric acid was also obtained during the calculations. It was found that Beer's law was obeyed for this compound (see page 25 and Tables 2, 4, 6). Furthermore, the formation constant was evaluated from spectrophotometric data*separately at each of ten different wavelengths. The same value for this equilibrium constant was obtained at each wavelength. If an undisclosed complex had been present, there would have been a discrepancy in the values found at different wavelengths, except in the unlikely event that the undisclosed complex did not absorb in that region*.

It was inferred, but not experimentally proved in the present work, that the cation in the tetrahaloferric acid dissolved in the ether phase was $(R_2O)_2H^+$ rather than R_2OH^+ . This inference was drawn in the prepared solid, it was found by chemical analysis that the atomic ratio $H:Fe:X:R_2O$ was 1:1:4:2 . There seemed no good reason to suppose that in pure ether, the molecule did not also exist as

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* In the present work, three absorption bands for the tetrachloroferrate ion were found at 360 mμ , 319 mμ , and 242 mμ ; for the tetrabromoferrate ion, at 470 mμ , 425 mμ , and 393 mμ . Jorgensen (24) tentatively proposed that the tetrachlorferrate bands were due to electron transfer from filled molecular orbitals to half-filled subshells $\pi \rightarrow \gamma_3$ and $\pi \rightarrow \gamma_5$.

$H(R_2O)_2^+FeX_4^-$. Such dietherates are well known. Laurene (16) prepared the dietherate of tetrachloroferric acid for the case of di-isopropyl ether. Formin and Morgunov (17) prepared dietherates of tetrachloroferric acid for diethyl ether, di-isopropyl ether, and for di-n-butyl ether. Moreover, $HGaCl_4.2Et_2O$ (58), $HAlBr_4.2Et_2O$ (58) , $HBeCl_3.2Et_2O$, $HBeCl_2Br.2Et_2O$ (84, 85) ; $HAlClBr_3.2Et_2O$ (59) have been prepared** and these formulae have been confirmed by chemical analysis.

C. Discussion, and comparison of the thermodynamic properties of the special systems investigated .

1. The system HX - R_2O

The thermodynamic constants, found by the dielectric constant method, are listed in Table 71 for the reaction $HX + R_2O = HX.R_2O$ where Hx is hydrogen chloride or hydrogen bromide, and R_2O is di-isopropyl ether, di-n-butyl ether, or tetrahydrofuran (page 144) It is common practice to attribute differences in the equilibrium constants of two acids. with a given donor (e.g. ether) to differences in the "acidity" of the two acids. However, it is considered that by introducing the term "acidity", nothing fundamentally new is introduced ; rather, when the term "acidity" is used , it is

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** All of those etherates, together with those of iron, are either low-melting crystalline solids or viscous oily liquids, and most are intensely coloured. They are practically insoluble in non-polar solvents, such as benzene, and slightly soluble in solvents with low dipole moments,such as ether, and soluble in polar solvents, such as $CHCl_3$.

usually a restatement of the conventional thermodynamic property ΔG^o. Thus, a comparison of the "acidities" of HCl and HBr involves a comparison of ΔG^o for these two hydrogen halides. However, since $\Delta G^o = \Delta H^o - T\Delta S^o$, the fundamental quantities to be compared would seem to be ΔH^o and ΔS^o.

It is evident from Table 71 (page 144) that the values of ΔS^o for the reaction of HCl and HBr with any given ether are not significantly different. Therefore ΔH^o is the quantity which largely determined the solvation constants of these two acids. Inspection of Table 71 shows that for di-isopropyl ether, ΔH^o for HCl is 0.8 kcal/mole more negative than for HBr. This difference is explained as follows: according to Pauling (86), HCl has 17 % ionic character, and HBr has 12 % ionic character. Therefore the proton retains a larger positive charge in HCl than it does in HBr. This in turn should produce a stronger hydrogen bond between HCl and an ether than between HBr and the ether. Provided that the relevant partition functions are not different for the two acids, this means that ΔH^o will be more negative for HCl than for HBr.

For the reaction of di-n-butyl ether with HCl and HBr, it is seen from Table 71 that here also the values of ΔS^o are not significantly different : the difference in the enthalpy values is significant at the 60 % confidence level. Therefore, it can be said at least that the difference in the values of ΔH^o for the case of di-n-butyl ether does not contradict the interpretation given for the case of di-isopropyl ether. Exactly the same comments apply in the case of tetrahydrofuran. It is concluded that the evidence in Table 71 indicates that the values of the equilibrium constants for the solvation of HCl and HBr are determined largely by changes in ΔH^{o}, and that the differences in ΔH^{o} between the two acids with a given ether are determined largely by the electronegativities of the halides.

The variation in ΔG^{o} for the solvation of a given hydrogen halide with each of the three ethers will now be compared. It will be noted that in this sort of comparison, ΔG^{o} is often referred to as the basicity of the ether for a given acceptor. Here again, it is ΔH^{o} and ΔS^{o} that should be considered, in order to interpret any trends in basicity . Inspection of Table 71 shows that for a given hydrogen halide, the values of ΔS^{o} do not vary significantly among the three ethers. However , the values of ΔG^{o} do vary significantly. Therefore it is concluded that these variations in basicity are due to variations in ΔH^{o} . Thus, for the solvation of HCl with di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran respectively, the values given for ΔH^{o} are -5.3 , -4.4 , and -6.0 kcal/mole respectively. It seems clear that for a given hydrogen halide, these enthalpy differences among the ethers are due to differences in the hydrogen bond energy . This observation is supported by the fact that the dipole moments of di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran are 1.26 , 1.09 , and 1.63 Debyes (87, 88, 89) respectively, exactly the order of the values found for ΔH^{o} .

As for the order of basicity , cyclic ethers are in general more basic than are alkyl ethers. Arnett (90, 92) explained this higher basicity of cyclic ethers as being due to relief of the electron correlation repulsion in the free base upon co-ordination of the lone-pair electrons. For the alkyl ethers, basicity usually diminishes as the size of the alkyl groups increases (93) , due firstly to an inductive effect or electron correlation repulsion, and secondly to steric hindrance to solvation, by the longer alkyl groups. The following Table sums up the order of basicity of ethers found by different authors using different acids .

Table 88 Order of basicity of di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran.

Acid	Order of basicity of the three ethers, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran.
HCl,HBr(91,and the present work), phenol,O-cresol K,O-isopropyl phenol K,O-tert-butyl phenol K, 2,6 di-isopropyl phenol K(99), $CHCl_3$(96)	tetrahydrofuran> di-isopropyl>di-n-butyl
2,6-dimethyl phenol K(99)	tetrahydrofuran > di-n-butyl > di-isopropyl
O-cresol,phenol,O-isopropyl phenol, O-tert-butyl phenol,2,6-dimethyl phenol(99)	di-isopropyl > tetrahydrofuran>di-n-butyl

2. The system HX-H_2O-di-isopropyl ether

The values of ΔG^o for the reaction

$$HX + H_2O = H_2O.HX$$

were found to be -2.99,and -3.90 kcal/mole for HCl and HBr respectively. These values were calculated in Section IIB(d). In these particular mass-action expressions, it was free HX rather than total HX that was used in the calculation. The values of ΔH^o were not obtained.

These two values of ΔG^o were expectedly opposite in magnitude in to the corresponding values found for the two acids combing with a given ether. Since ΔH^o and ΔS^o were not evaluated, an explanation for this difference is not possible.

3. The system HX-FeX_3-R_2O

For the system HX-R_2O-FeX_3, the reaction of particular interest is

$$HX + FeX_3.S + S = HS_2^+ \ FeX_4^- \qquad [1]$$

where X is chloride or bromide, S is anyone of the three ethers, and HX is represented by the mass-law expression by (HX), which is the sum of the unsolvated HX plus the solvated HX, HX.S. Of the two thermodynamic properties ΔH^o, ΔS^o that determine the value of ΔG^o for reaction [1] , the values of ΔS^o are considered separately in a later Section; the standard enthalpy change is considered in the present one.

It is useful to treat the standard enthalpy change for reaction [1] as being the net result of the values of ΔH^o for several component reactions. These component reaction s are evident from an inspection of the thermochemical cycle shown on page 169 . The various component reactions shown in that cycle either are well known reations for which literature data are available, or are reactions for which thermochemical data have been obtained in the present work. The values of ΔH_7^o have been discussed on page 180. There remains to be discussed the values of ΔH_8^o . For a given ferric halide, the values of ΔH_8^o for the three ethers show the same trend as do the dipole moments of those ethers. In this connection, it was pointed out on page 182 that the values of ΔH^o for the formation of the species $HX.R_2O$ also showed the same trend as did the dipole moments of the three ethers.

For the thermochemical cycle, it is useful to know the value of $\Delta H_2^o + \Delta H_{14}^o$, i.e. the values of ΔH^o for the reaction

$$2S_g + H^+_g + FeX_4{}^-_g = HS_2{}^+\ FeX_4{}^-_g \qquad [7]$$

The complications of solvation effects are then elimated, to permit a more fundamental comparison of the values of ΔH^o among various ethers, and the halides.

Reaction [7] above consists of two steps, reaction [6] and reaction [8]

$$2S_g + H^+_g \overset{\Delta H_2^o}{=} HS_2^+ \qquad [6]$$

$$HS^+_{2g} + FeX_4{}^-_g = HS_2{}^+\ FeX_4{}^-_g \qquad [8]$$

The values of ΔH_2^o for reaction [6] have been tabulated in Table 87. The standard enthalpy change ΔH_{14}^o for reaction [8] is readily calculated from Coulomb's law for the three ethers, and is tabulated in Table 88. This makes available the value of ΔH^o for reaction [7] = $\Delta H_2^o + \Delta H_{14}^o$

in the gas phase. For HCl, ΔH° for reaction [7] is -323, -333, -326 kcal/mole for di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran respectively.

Moreover, since ΔH°_{14} for reaction [8] is known, it is evidently possible to calculate the heat of condensation ΔH°_{12} of the ion-pair $HS_2^+ FeX_4^-(s)$, from the lattice energy of the ion-pair $HS_2^+ FeX_4^-(s)$, $-\Delta H^\circ_{15}$ which has been reported in Table 87.

$$\begin{tikzcd}
HS_2^+(g) + FeX_4^-(g) \arrow[rr, "\Delta H^\circ_{14}"] \arrow[dr, "\Delta H^\circ_{15}"'] & & HS_2^+ FeX_4^-(g) \arrow[dl, "\Delta H^\circ_{12}"] \\
& HS_2^+ FeX_4^-(s) &
\end{tikzcd}$$

From the above cycle, $\Delta H^\circ_{12} = \Delta H^\circ_{15} - \Delta H^\circ_{14}$

All these enthalpy values are reported in Table 89.

Table 89 Standard enthalpy of sublimation ΔH°_1 for the reaction,

$HS_2^+ FeX_4^-(s) = HS_2^+ FeX_4^-(g)$

All enthalpy values are in kcal/mole.

ether	HCl			HBr		
	ΔH°_{15}	ΔH°_{14}	ΔH°_{12}	ΔH°_{15}	ΔH°_{14}	ΔH°_{12}
di-isopropyl	-86	-50.8	-35	-84	-50.7	-33
di-n-butyl	-72	-43.0	-29	-72	-42.9	-29
tetrahydrofuran	-89	-52.5	-36	-88	-52.4	-36

In examining the effect of the particular ether on the value for ΔH^o_9 for reaction [1]

$$HX + S + FeX_3.S = HS_2^+ FeX_4^- \qquad [1]$$

for the case where X is Cl, the thermochemical cycle on page 169 is again useful. However, in this case, the values of ΔH^o for two component reactions cannot be accurately evaluated. These reactions are:-

$$HS_2{}^+{}_g + FeX_4{}^-{}_g = HS_2{}^+ FeX_4{}^-{}_s \qquad [5]$$
$$H^+{}_g + 2S_g = HS_2^+ \qquad [6]$$

The values of ΔH^o_{12} for reaction [5] was estimated by a modification of the Born equation. This calculation required a knowledge of the ionic radii of $HS_2{}^+$ and $FeX_4{}^-$. Specifically, the estimates of the distance of closest approach is somewhat uncertain. This uncertainty as explained on page 158, is due to lack of precise knowledge of the geometry of the cation.

The values of ΔH^o_2 for reaction [6] can be regarded as being only rough estimates, because they were based in part on inference. The values of ΔH^o_9 for reaction [1] were, however, known with reasonable accuracy. Therefore it was useful to calculate the standard enthalpy change of reaction [6] by two methods : (i) using thermal data in Table 87, to give values shown in Column 3 of that Table; (ii) using literature values for the proton affinities of water, methanol, aldehydes, and carboxylic acids as described in Section V d . Comparison of the values shown in Columns 3 and 4 of Table 87 agree to within 20 kcal/

mole, which is reasonably good under the circumstances. In this connection, the proton affinity of water was taken to be 151 kcal/mole. Munson (71) regarded this as being the most reliable value. However, value as high as 182 kcal/mole has been reported, and they are tabulated in Table 83 on page 166. In view of the 30 kcal/mole discrepancy in published values for the proton affinity of water, it is not surprising that the values of ΔH_2^o for reaction[6] as tabulated in Columns 3 and 4 do not agree to better than 20 kcal/mole.

It is interesting to note that whether by calculation from the proton affinity of water or by calculation from the thermochemical cycle, the values for the formation of HS_2^+ in Columns 3 and 4 of Table 87 are in exactly the reverse order from the so-called basicity of these ethers. These basicities are in the order tetrahydrofuran , di-isopropyl ether, di-n-butyl ether. (91, 92,96,99).

D. Entropy changes and enthalpy changes

(1) Introduction

There is an extensive literature on the relationship between the energy and the entropy of solution of various compounds. Evans and Polanyi (117) and Bell (118) reported functional relationships between ΔH and ΔS of solution of solutes in various solvents. Bell(118) showed that molecular sizes and dispersion forces are very important, even compared to the effects of dipole moments; and he reported the empirical relationship $\alpha \Delta H + \beta = T\Delta S$ with $1 < \alpha < 0$. Butler (119) found a simple relationship for the heat of hydration and the entropy of hydration of some non polar organic molecules. Eley (120) related entropy of solution to energy of solution of some inert gases.

However, literature is very scarce on the relationship between ΔH^o and ΔS^o for a reaction in a non-aqueous solution, such as the reactions studied in the present work. Williams (121) concluded there was a relationship between the enthalpies and entropies of hydration of species that participated in the complex-ion formation in water. Further, equilibrium constant of reactions have been calculated by statistical mechanics (122, 123).

A simple, but very approximate treatment of ΔH^o and ΔS^o for reactions in solution has been presented by Prue (124), and his treatment is used in the present Discussion.

(2) Relationship between ΔH^o and ΔS^o

The observation of Bell(118) and others (117,119,121) led to a study of ΔH^o and ΔS^o for the reactions reported in the present work. Fig. 22 is a plot of ΔH^o versus $T\Delta S^o$, for the reactions,

$$R_2O + HX = R_2O.HX$$

$$HX + FeX_3.R_2O + R_2O = H(R_2O)_2^+ \; FeX_4^-$$

where X= Cl, or Br; and R_2O = the three ethers.

The standard deviation for ΔH^o and for $T\Delta S^o$ is $\pm$ 1-2 kcal/mole so that there is no justification for drawing more than one line for different solvents. Indeed, the use of a straight line is merely expedient, and can scarcely be defended except as a potentially useful empirical rule.

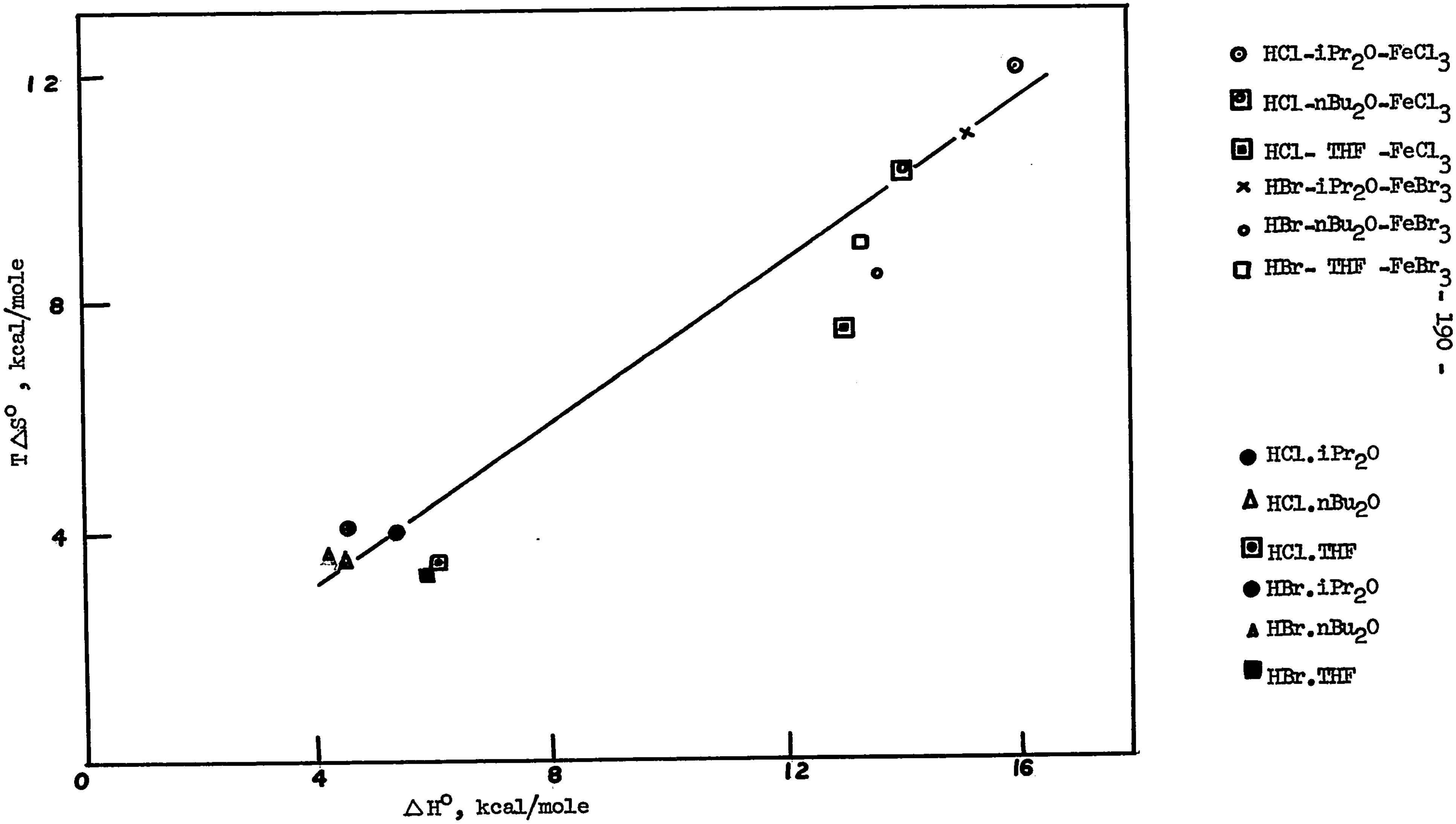

Fig. 22. A plot of $T\Delta S^o$ versus ΔH^o

3. Calculation of ΔS° for reactions investigated

It is useful to attempt the evaluation of ΔS° for the following reactions in solutions

$HX + R_2O = HX.R_2O$ (in CCl_4)

$HX + R_2O + FeX_3.R_2O = H(R_2O)_2^+FeX_4^-$ (in the ether)

It is possible, as Prue (124) has pointed out, to obtain only crude estimates. His treatment, which will be used, is described next.

The thermodynamic formation constant of the association reaction A + B = C in the ideal gas phase is given by the following expression :-

$$k_{ass} = \frac{(Q_c / NV)}{(Q_A/NV) (Q_B/NV)} e^{-\Delta E_0 /RT} \qquad (31)$$

where $\Delta E_o = N (E_{o_C} - E_{o_A} - E_{o_B})$

$$Q = \sum_i g_i \, e^{-(E_i - E_o)/kT}$$

= partition function

For a linear molecule,

$$Q = Q_t \times Q_r \times Q_v$$

$$= (\frac{2\pi mkT}{h^2})^{3/2} V \times (\frac{8\pi^2 IkT}{\sigma h^2}) \times \prod_v (1- e^{-h\nu/kT})^{-1}$$

and $Q_t = f_t^3$ for three degrees of freedom

The ratio of $f_t : f_r : f_v = 10^8 : 10^2 : 1 \text{ cm}^{-1}$. Therefore, the present calculations were made on the assumption that f_r and f_v were negligibly small compared with f_t, therefore only translational entropy was considered.

Then $$Q = Q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \qquad (32)$$

Now, $$\Delta G^o = - RT \ln k_{ass} \qquad (33)$$

$$\Delta H^o = RT^2 \, d\ln k_{ass} / \, dT \qquad (34)$$

and $$\Delta S^o = \frac{d}{dT} (RT \ln k_{ass}) \qquad (35)$$

By using equations (31) and (32), equations (33,34,35) become,

$$\Delta G^o = \Delta E_o - RT \ln \frac{(Q_c/NV)}{(Q_A/NV)\,(Q_B/NV)}$$

$$\Delta H^o = \Delta E_o + RT^2 \, d \ln \left(\frac{Q_c}{Q_A \, Q_B}\right) / \, dT$$

$$\Delta S^o = (\Delta H^o - \Delta G^o)/ \, T$$

$$= \frac{R \ln (Q_c/ NV)}{(Q_A/NV)\,(Q_B/NV)} + RT \, d \ln \frac{(Q_c/Q_A \, Q_B)}{dT}$$

An addition assumption was made for the present calculations, namely that the partition functions were independent of temperature, i. e. $\Delta H^o \doteq \Delta E_o$

Then $$\Delta S^o = R \ln \left(\frac{Q_c/NV}{Q_A/NV \times Q_B/NV}\right) \qquad (36)$$

In a similar way it may be shown that when three molecules associate to one linear molecule,

$$A + B + C = D$$

then, $$\Delta S^{o} = R \ln \frac{Q_D/NV}{(Q_A/NV)(Q_B/NV)(Q_C/NV)} \qquad (37)$$

In the above equations,

k_{ass} = association constant of a reaction

E_o = energy change at ground state

Q = partition function

Q_t = translational partition function

Q_r = rotational parition function

Q_v = vibrational partition function

m = reduced mass of compound

h = Planck's constant

k = Boltzman's constant

N = Avagadro's number

M = molecular weight of compound

Equation (36) was applied directly, to evaluate directly ΔS^{o} for the reaction $HX + R_2O = HX.R_2O$ in carbon tetrachloride. The assumption was made that in fact this formula for translational entropy applied equally well to a solution, as to the gas phase. The results are in Table 90.

For comparison with the calculated values of ΔS^{o}, the experimental values from Table 71 are entered in Column 5. The agreement is good; perhaps it is a degree fortuitous. However, the results do serve to suggest that there is little or no net solvation or desolvation for the reaction. In this connection, Earp and Glasstone(125) found from dielectric constant measurements that the equilibrium constant for the formation of a 1.:1 complex between di-isopropyl ether and carbon tetrachloride was only 0.07 (mole fraction basis).

Table 90 Evaluation of ΔS^o for the reaction

$HX + R_2O = HX.R_2O$

in CCl_4 solutions at 25°C.

acid	ether	$R\ln(\frac{m_c}{m_A\ m_B})^{3/2}$	$\Delta S^o_{calc.} = R\ln(\frac{m_c}{m_A\ m_B})^{3/2} + R\ln(\frac{h^2}{2\pi kT})^{3/2}N$ e.u.	$\Delta S^o_{expt.}$ e.u.
HCl	di-iso-propyl	153.3	-164 + 153.3 = -10.7	-13.4
	di-n-butyl	153.3	-164 + 153.3 = -10.9	-11.6
	tetrahy-furan	153.8	-164 + 153.8 = -10.4	-11.6
HBr	di-iso-propyl	151.8	-164 + 151.8 = -12.4	-13.7
	di-n-butyl	151.5	-164 + 151.5 = -12.7	-11.9
	tetrahy-	152.4	-164 + 152.4 = -11.8	-11.2

Equation (37) was applied directly, to estimate ΔS^o for the following reactions in ether.

$HX + FeX_3 = HFeX_4$ $\quad -\Delta S^o_a$

$HX + FeX_3.R_2O + R_2O = (R_2O)_2H^+FeX_4^-$ $\quad -\Delta S^o_b$

$HX + FeX_3.R_2O + 2R_2O = (R_2O)_3H^+FeX_4^-$ $\quad -\Delta S^o_c$

The results are listed in Columns 3,4,5 of Table 91. Column 6 contains the experimental value of ΔS^o taken from Tables 39 and 40. These values are for the case where the standard state of the hydrogen halide is a solution in which the concentration of the species HX.S is 1 molal. Column 7 contains the corresponding values (ΔS^o_f) where the standard state of the hydrogen halide is a solution of 1 molal in the unsolvated species HX only. (Tables 39a and 40a).

Table 91 Standard entropy change for the reaction

$$HX + xR_2O + FeX_3.R_2O = H(R_2O)^+_{x+1}\ FeX_4^-$$

in three ethers at 25°C.

acid	ether	x=0 $\Delta S^o_{a\,calc.}$ e.u.	x=1 $\Delta S^o_{b\,calc.}$ e.u.	x=2 $\Delta S^o_{c\,calc.}$ e.u.	$\Delta S^o_{expt.}$ e.u.	ΔS^o_{f} expt. e.u.
HCl	di-iso-propyl	-11.0	-25.3	-39.3	-40.1	-48
	di-n-butyl	-11.0	-25.9	-40.6	-34.2	-39
	tetrahy-furan	-11.0	-24.4	-37.4	-25.3	-31
HBr	di-iso-propyl	-13.3	-27.8	-42.0	-36.4	-43
	di-n-butyl	-13.3	-28.5	-43.3	-27.9	-36
	tetrahy-furan	-13.3	-26.9	-40.1	-29.5	-35

It has been supposed that throughout that the present work that the actual reaction was in fact for x=1. Comparison of x=1 ΔS^o_b with $\Delta S^o_{f\ expt}$ shows in all cases that the latter values are 7-15 e.u. more negative than the former ones. A reasonable explanation for this difference is as follows:-

HS_2FeX_4 is an ion pair with a large dipole moment, approximately 30 Debyes, for all the species studied. All the ethers studied have approximately the same dipole moments, 1.1-1.6 Debyes; and both hydrogen chloride and hydrogen bromide have low dipole moments (1.1 and 0.9 Debyes respectively). Therefore, it is reasonable to expect the species HS_2FeX_4 to be more solvated than the hydrogen halides. Such preferential solvation of the product HS_2FeX_4 over the reactants HX, R_2O, and

$FeX_3.S$ would contribute a negative term to the entropy change for reaction [1] , in the present systems approximately -7 to -15 e.u.

E. Summary - discussion of the chemistry of the general systems

The values of ΔH^o and ΔS^o found for reaction [2]

$$HX + R_2O = HX.R_2O$$

where X= Cl or Br; R_2O= di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran, enables estimates of these thermodynamic properties to be made in the case of other ethers and other acids. Thus, monosolvates would be expected to form for other monobasic acids in ethers, with ΔH^o in the order of -3 to -7 kcal/mole, and ΔS^o in the order of -10 to -13 e.u.

The values of ΔH^o and ΔS^o found for the reaction

$$HX + S + FeX_3.S = HS_2^+ \ FeX_4^- \qquad [1]$$

in three ethers permits at least rough estimates to be made of ΔH^o and ΔS^o for halometallic acids other than those of iron, as for example, those of the known complexes, $HGaX_4.2S$, $HInX_4.2S$, and $HAlX_4.2S$, and also for other ethers. The thermochemical cycle proposed in the present work illustrates the method and the data needed to make such predictions. A value of the proton affinity of the particular ether is required for the cycle. From the values estimated for the present work for three ethers, the proton affinities of other homogous ethers may be estimated. The standard heat of sublimation of the species $HS_2^+FeX_4^-{}_{(s)}$ can be estimated by using the method employed in the present work. The heats of solution of the metal chlorides in the ether would then require measurement, in order to complete the non-literature data necessary for the cycle, and therefrom to obtain estimates of ΔH^o and ΔS^o for reaction [1].

CLAIMS TO ORIGINAL RESEARCH

1. The thermodynamic properties , ΔG^o, ΔH^o, and ΔS^o at 25°C were evaluated by spectrophotometry for the reaction

$$HX + S + FeX_3.S = HS_2^+ FeX_4^- \qquad [1]$$

in three ethers, S, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran, with X = chloride or bromide.

2. The molar absorptivities of ferric chloride, ferric bromide, and their corresponding tetrahaloferric acids in each of the three ethers at 25°, 35°C, and 45°C were measured and tabulated for a range of wavelengths.

3. The thermodynamic properties ΔS^o, ΔH^o, and ΔG^o at 25°C were evaluated by a dielectric constant method , for the reaction

$$HX + R_2O = R_2O.HX \qquad [2]$$

in carbon tetrachloride. The ethers were di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran, and the halides X were chloride and bromide. It was also shown that over the range of concentration ratios HX:R_2O studied, the monoetherate was the only solvate present in significant amount.

4. The value of ΔG^o at 25 °C for reaction [2] was found not only from dielectric constant measurements, but also independently from vapour pressure measurements. Agreement was good. The precision of two methods was compared by a statistical analysis of the data, and the vapour pressure method found to be the more precise.

5. The constancy of the values of ΔS^o for reaction [2] in all three ethers permitted its use for the reaction in the gas phase. This

permitted the calculation of corrections of non-ideality of this gas phase , due to hydrogen bonding. When these corrections were applied to the vapour pressure data on the system $HX-R_2O-CCl_4$, the resulting partial pressure of HX obeyed Henry's law.

6. The hydration constant for the reaction

$$HX + H_2O = HX.H_2O$$

in carbon tetrachloride at 25°C was calculated from the vapour pressure data. It was also shown that over the range of concentration ratio $HX:H_2O$ studied, the monohydrate was the only solvate present in significant amount.

7. The standard enthalpies of solution of the two ferric halides in each of the three ethers, and of $(R_2O)_2FeCl_4$ and $(R_2O)_2HFBr_4$ in their corresponding ethers, di-isopropyl ether, and di-n-butyl ether were measured by calorimetry.

8. The standard enthalpies for the gas-phase reaction

$$2\ R_2O + H^+ = (R_2O)_2H^+$$

where R_2O is each of the three ethers, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran , were evaluated from a conventional thermochemical cycle. These values were compared with values estimated from the reported proton affinities of water, and other(71, 72)literature data.

9. The translational contribution to the entropy change in reaction [2] was calculated by using the conventional gas-phase formulae. The

values agreed well with the values for ΔS^o found experimentally.

10. The values of the standard enthalpy change for reaction [2] were satisfactorily accounted for in terms of the electronegativities of the halides, and the dipole moments of the ethers.

SUGGESTIONS FOR FURTHER INVESTIGATIONS

1. Evaluation of $\Delta G^o, \Delta H^o$, and ΔS^o for the formation of other tetrahalometallic acid dietherates, e.g. $HInX_4.2S$, $HGaX_4.2S$, $HAlX_4.2S$, $HZnCl_3.2S$, and $HAuCl_4.xS$ by the dielectric constant measurements.

2. The effect of water on the thermodynamic constants of trivalent halometallic acids. The reaction is:-

$$HX + xS + yH_2O + MX_3 = H(S)_x(H_2O)_y^+ \; MX_4^-$$

where S is the solvent. For the case of iron, spectrophotometry is a possible method; for other metals, such as Al, Ga, In, which do not absorb in the accessible region of the spectrum, dielectric constant measurements are practicable.

3. Determination of the thermodynamic properties for the reaction

$$HX + xS + MX_3 = HS_xMX_4$$

in solvents other than ethers, as for example, benzene and its homologs, halobenzenes, and other oxygenated solvents.

4. Determination of the vapour pressures of hydrogen halides at different temperatures in several other ethers, e.g. in di-n-butyl ether, di-n-propyl ether, and tetrahydrofuran, and in other oxygenated solvents such as ketones and esters.

5. Determination of the partial pressures of ethers over the binary solution $HX-R_2O$, and the ternary solution $HX-R_2O-CCl_4$, by gas chromo-

tographic analysis of the equilibrium vapour .

6. Evaluation of the thermodynamic properties for the reactions,

$$R_4NX + FeX_3 = R_4N^+FeX_4^-$$

$$HR_3NX + FeX_3 = HR_3N^+FeX_4^-$$

$$H_2R_2NX + FeX_3 = R_2H_2N^+FeX_4^-$$

$$H_3RNX + FeX_3 = RH_3N^+FeX_4^-$$

where R = an alkyl group

X = chloride, bromide, or iodide

in benzene and its homologs, or other solvents.

APPENDICES

Appendix 1

Gravimetric determination of the purity of solid anhydrous ferric chloride and ferric bromide.

A. Reagents :_

B.D.H. Analar grade anhydrous ferric chloride and ferric bromide
1.: 1 (V/V) hydrochloric acid.
concentrated nitric acid
1 : 1 (V/V) ammonium hydroxide
dilute acidified silver nitrate solution

B. Procedure:-

Weigh out 0.7-0.8 gm of the anhydrous ferric chloride or ferric bromide into a 400-ml beaker, and dissolve it in 40-50 ml water plus 10 ml 1:1 hydrochloric acid. Heat the solution to boiling. Dropwise , add with stirring 1 ml of nitric acid , and continue to boil the solution for three to five minutes. Dilute the solution to 200 ml, heat it nearly to boiling, and add 1:1 ammonium hydroxide slowly and with constant stirring until a slight excess of hydroxide is present. Remove it from the heat, and allow the ferric hydroxide precipitate to settle . Then filter it through a 9-cm ashless filter paper (Whatman number 41). Wash the precipitate by decantation three or four times with hot water, then transfer it to the filter. Wash the precipitate on the filter until the filtrate shows no reaction with acidified silver nitrate solution. Air-dry the precipitate in a tared porcelain crucible with a cover. Carbonize the filter and the precipitate, then ignite to constant weight. Weigh as Fe_2O_3. (100)

Appendix 2

Colorimetric Determination of iron by salicylic acid (36,37)

A. Instrument :-

Unicam spectrophotometer SP 500

Tungsten light source

B. Reagents :-

1% sodium salicylate solution

1 : 1 (V/V) ammonium hydroxide

1 : 1 (V/V) acetic acid

standard iron stock solution : dissolve 0.0859 gm of pure iron wire in 2 ml aqua regia. Add 1 ml of concentrated nitric acid, and evaporate the solution to moist dryness. Then add 100 ml 1:1 (V/V) hydrochloric acid, and heat the resulting solution to boiling. Cool the solution and dilute to one litre in a volumetric flask ; 1 ml of solution contains 0.0859 mg of iron.

C. Procedure:-

(i) Calibration curve- pipet 1,2,4,5,8, and 10 ml aliquots of the standard iron stock solution into 50-ml volumetric flasks. Add to each of them 5ml of 1% sodium salicylate solution . Then add ammonium hydroxide solution (1:1) dropwise until one drop changes the solution from purple to yellow. Then add two drops in excess. Add 1 : 1 (V/V) acetic acid dropwise until the solution turns pink, and then add an excess of 5 ml . Dilute each solution to 50 ml with water, and read its absorbance at 520 mµ. in a 1 cm cell (silica), with distilled water as the blank. It was found that the solutions of sodium salacylate, ammonium hydroxide, and acetic acid do not absorb at 520 mμ. A calibration curve is set up with absorbance versus mg of iron in 50 ml solution. Beer's law is obeyed. Table A1 gives the result.

(ii) Sample solution - pipet a 15 or 20 ml aliquot of the ether solution (containing a mixture of hydrogen halide and ferric chloride) into a 100-ml beaker. Evaporate the ether on a steam bath in a fume hood. Add 5 ml of 1:1 hydrochloric acid to dissolve the residue, and transfer the resulting solution quantitatively to a 50-ml volumetric flask. Sodium salicylate, ammonium hydroxide , and acetic acid are then added as in the calibration curve section.

The maximum absorbance of the standard solutions and the sample solution is reached almost immediately, and is constant for seventy-two hours. The method is useful for iron concentrations of 10^{-4} M to 10^{-5} M, for a 20-ml aliquot. Beer's law is obeyed.

Table A1 Calibration curve for colorimetric determination of iron at 520 mμ. (1 cm cell).

mg of iron in 50 ml solution	Absorbance
0.086	0.052
0.172	0.102
0.344	0.207
0.430	0.256
0.687	0.398
0.859	0.504

Appendix 3

Volumetric determination of iron with ethylendiaminetetraacetic acid (E.D.T.A.) (101)

A. Apparatus:-

50-ml buret

magnetic stirrer

150-ml beaker

B. Reagents:-

Standard E.D.T.A. solution,0.01 M- dissolve 372 gms of di-sodium ethylene-diaminetetraacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2.2H_2O$) in water, and dilute to one litre.

Pyridine acetate buffer- mixture of 77 ml of reagent grade and 63 ml glacial acetic acid.

Pyrocatechol violet indicator - 0.1% aqueous solution of pyrocatechol violet.

C. Procedure:-

(i) Standardization of E.D.T.A. solution- weigh out 0.25 gm of pure iron wire into a 150 ml beaker. Dissolve it with 2 ml of aqua regia. Add 1 ml of concentrated nitric acid, and evaporate to moist dryness. Add 50 ml of 1:1 hydrochloric acid , heat to dissolve the residue, cool, and make to 100 ml in a volumetric flask. Pipet a 5-ml aliquot of this iron stock solution into a 150-ml beaker, and dilute it to approximately 100 ml with water*. Add 2-5 ml pyridine acetate buffer, until an intense brownish-red colour appears. Then add 5-10 drops of pyrocatechol violet indicator, and titrate the blue or greenish - blue solution with E.D.T.A. solution to a bright yellow solution. When the concentration of iron is high , the end point is yellowish-green. Near the end point, the blue is transient and may return. However, when the end point is reached, the greenish-yellow coloration is stable. One ml of 0.01 M E.D.T.A. is equivalent to 0.5585 mg of iron.

(ii) Sample solution- pipet 5 ml or 10 ml of the ether solution of ferric halide into a 150-ml beaker. Evaporate the ether on a steam bath in the fume-hood. Dissolve the residue with 5 ml of 1:1 hydrochloric acid, and dilute it to 100 ml with water. Then follow the titration procedure given for the standardization , from the asterisk (*). Concentrations of iron 0.1 M to 0.001 M are satisfactorily determined by this procedure.

Appendix 4

Cleaning the vapour pressure apparatus

Fill the middle 500-ml bulb and the 200-ml round-bottom flask of the vapour pressure apparatus (shown in Fig. 1) with hot chromic acid, and let stand overnight. Then drain off the acid, and then wash the bulbs thoroughly with distilled water, and rinse them once with acetone , then leave them filled with acetone for an hour, to ensure that all the stopcock grease has been dissolved (Fluorosilicone stopcock grease is inert to acid , but dissolve easily in acetone). After all the grease had dissolved, vacuum-dry the whole apparatus at room temperature. (Do not use air-drying since compressed air contains impurities which might stick to the walls of the apparatus).

Further dry the whole apparatue for thirty minutes in a stream of dry nitrogen which has been passed through an indicating $CaSO_4$ tube containing a plug of glass wool. Then grease the stopcock with minimum amount of fluorosilicone grease. (Too much grease will readily contaminate the walls of the bulbs, due to creeping; too little grease will readily cause leakage). After the greasing, the dried nitrogen is again passed through the apparatus for an additional thirty minutes, just before use.

Appendix 5

Partial pressure of hydrogen chloride in benzene at 30°C.

A. Reagents :-

anhydrous hydrogen chloride

anhydrous benzene

B. Apparatus:-

vapour pressure apparatus (Fig.1)

C. Procedure :-

The method is that described in Section II b for the partial pressure of hydrogen chloride in di-isopropyl ether.

D. Results :-

moles of HCl/1000 gms of benzene	pressure of HCl, mm
0.207	373.7
0.185	352.0
0.072	135.7

Results obtained by J.H.Saylor(34)

moles of HCl /1000 gms of benzene	pressure of HCl, mm
0.0006	1.5
0.0022	6.2
0.0171	51.4
0.0391	78.0
0.1110	211.0
0.1720	321.0
0.1880	393.0
0.2750	510.0
0.2970	585.0
0.3020	570.0

Fig. 23 shows a plot of the partial vapour pressure of HCl versus molality of HCl in benzene . The values obtained in the present work lie on the same straight line as the literature values (34).

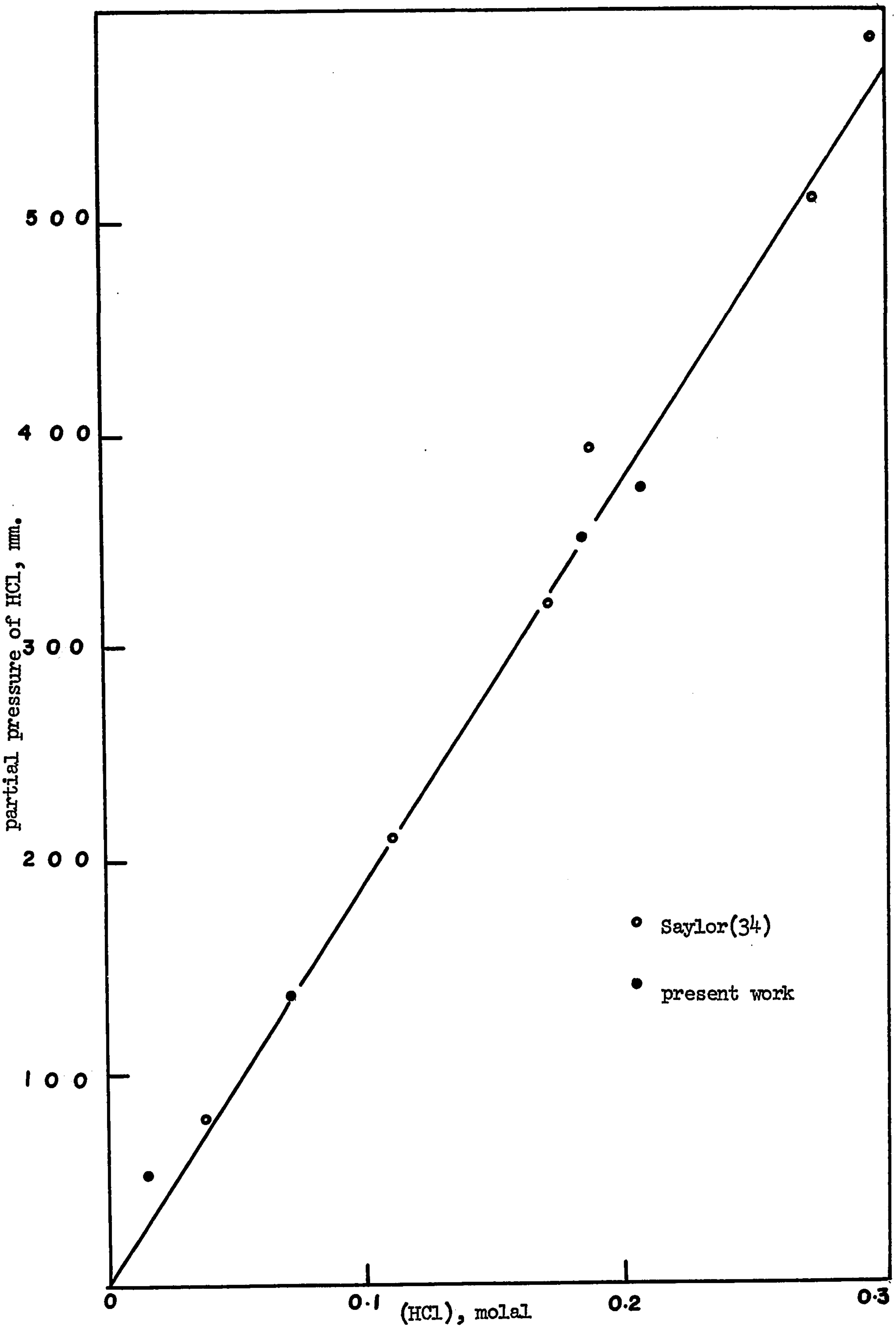

Fig. 23. Vapour pressure of HCl in benzene at 30°C.

Appendix 6

Potentiometric titration of total halides

A. Instrument :-

Automatic potentiometric titrator, Radiometer type TTT 1 , together with a Radiometer titrigraph, type SBR 2. Other parts of the titrator consist of a glass-calomel electrode pair, an SBUI-type 5-ml buret, and an MNV 1-type magnetic valve on the stand below the buret. The full width of the chart corresponds to 5 ml, which can be read with an accuracy of ± 0.001 ml. Use medium speed motor that drives the buret. Chart speed is 0.5 pH unit per cm.

B. Reagents :-

Sodium hydroxide , 0.5 M- prepare a 50% by weight solution of sodium hydroxide in a stoppered polyethylene bottle. Let it stand for a month so as to precipitate all the carbon dioxide as sodium carbonate. Then quickly filter the solution, through a Buchner-funnel with Whatman number 1 filter paper. Boil some conductivity water, then cool it in a polyethylene bottle fitted with a soda-lime guard-tube. Dilute the concentrated solution to 0.5 M with this water. Standardize the resulting solution against potassium acid phthalate (102).

Sodium hydroxide, 0.05 M- dilute the prepared 0.5 M sodium hydroxide solution with cold carbon dioxide-free conductivity water, and store the resulting solution in a polyethylene bottle fitted with a soda-lime guard-tube.

Sodium hydroxide , 0.01 M- dilute the 0.05 M sodium hydroxide solution with carbon dioxide-free conductivity water, and store in a polyethylene bottle with a soda-lime guard tube.

Both 0.05 M and 0.1M sodium hydroxide solution are standardized against potassium hydrogen phthalate.

C. Determination of total halide in solution

Pipet an aliquot of the HX- FeX_3- ether solution into a 150-ml beaker . Dilute the aliquot twenty times with distilled water, and titrate this solution with 0.05 M, 0.5 M, or 0.01 M sodium hydroxide, depending on the concentration of the halide. Calculate the end point by the method of second differences. The end point gives the total volume of sodium hydroxide required to neutralize all the hydrogen halide and to convert all the ferric halide to ferric hydroxide. The halide content is then calculated from that volume and the separately measured iron content.

Appendix 7

Dielectric constant method

A. Instrument:-

Dipolemeter*, type DM 01 with four switch positions, Korr., D1, D2, and M1 where D1, D2, and M1 cover different ranges of dielectric constant. The measuring frequency of the instrument is approximately 2.0 mega cycles/second, and the reading sensitivity of capacitance $\Delta C/C = 7 \times 10^{-6}$. The measuring condenser range is 50 picofarads. A built-in cathod-ray tube (DG7/32) of scanning frequency: 60 cycles/sec. serves as an indicator. Two cells are provided, gold-plated DFL 1 (20cc), and platinum-plated DFL 2 (5cc). In the present work, the DFL 1 cell was used with the D 2 position, which allows a dielectric constant range of 2-3.4, with a measuring sensitivity $\Delta D/D = 4 \times 10^{-5}$. The instrument operates on a superposition principle.

B. Procedure :-

Switch on the instrument before the internal thermostat is turned on . After 30 minutes, when the thermostat lamp goes on and off, the instrument is ready for use. Fill the clean cell with the solution. This stoppered cell is thermostated by using a Colora liquid circulator. Avoid air-bubbles inside the cell . When thermal equilibrium is reached (checked by a thermo-couple), and with the range switch at the Korr. position, bring the measuring oscillator into resonance with the refer-

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* manufactured by Wissenschaftlich- Technische Werkstatten GmbH Weilheim / OBY, Germany.

ence oscillator by means of the Korrection knob, i.e. Lissajous figures on the cathod-ray oscilloscope becomes a line, moving up and down with very small changes. Then turn the range switch to D2 position and adjust by means of the measuring condenser until resonance is again established. In order to obtain the highest accuracy, it is necessary to switch back and forth to the Korr. position and D2 position several times at each of the measurements for correction.

The cell is cleaned by rinsing it with spectra-grade acetone, the acetone is then vacuum-evaporated, and then the cell is dried by passing into it dry nitrogen for fifteen minutes.

Appendix 8

Karl Fischer determination of water (back titration) (103,104)

A. Reagents:-

absolute methanol (spectra-analysed)

Karl Fischer reagent (Fisher Scientific Co., cat. number S_o-K-3) with detection limit of 5 mg H_2O / ml is diluted 1:1 with diluent for stabilized Karl Fischer reagent (cat. number S_o-K-5).

Pyridine (reagent grade).

B. Procedure :-

(i) Standardization of Karl Fischer reagent -two methods were used. For the first method, accurately weigh out approximately 1.0 gm of water into a dry 250-ml volumetric flask and make up to 250 ml with absolute methanol in a dry box. Perform the following titrations using this standard water-methanol solution as titrant.

a. 20 ml Karl Fischer reagent + 20 ml absolute methanol

b. 20 ml Karl Fischer reagent

c. 20 ml Karl Fischer reagent + 10 ml pyridine

Suppose a. requires a ml of water-methanol standard

b. requires b ml of water-methanol standard

c. requires c ml of water-methanol standard

Let w = actual weight of water in mg per ml of water-methanol standard

A = mg of water per ml of water-methanol standard weighed out

The following relationship holds,

$$w = A + \frac{b-a}{20} \times w$$

and $$w = \frac{A}{1 - (b-a)/20} = \frac{20\,A}{20 - b + a}$$

In this case, the actual weight of water in methanol-water standard and also pyridine is found, and mg of water equivalent to 1 ml of Fischer reagent can be calculated.

The second method involves the use of sodium monotartrate dihydrate with known water of crystallization as the standard. Accurately weigh out 0.05 - 0.07 gm of sodium monotatrate dihydrate into a 250-ml Erlenmeyer flask . Add 40 ml of Karl Fischer reagent , and titrate with the water-methanol standard solution. The difference in the volume of the standard solution for the two titrations is equivalent to the weight of the tartrate.

Let weight of tartrate = x gm $\equiv$(36/ 230.1)·x gms of water

40 ml K.F. + x gm tartrate requires y ml standard

40 ml K.F. requires z ml standard

therefore, (36/230.1)x gms of water is equilvalent to(z-y) ml standard, and hence, 1 ml of standard wter-methanol solution will be equivalent to 36x/ 230.1(z-y) gms of water.

Results of the above two methods agree to within 1% error.

(ii) Determination of water content in an unknown solution - pipet 10 ml of hydrogen halide-ether solution into a titration flask, add 10 ml of pyridine to neutralize all the hydrogen halide in solution, then pipet 20 ml of the Karl Fischer reagent into the flask. Back titrate this solution with the water-methanol solution. The amount of moisture in pyridine must be corrected for . The end point is from brown to yellow. All the glass apparatus must be dried before use.

and $$w = \frac{A}{1- (b-a)/20} = \frac{20\ A}{20 - b + a}$$

In this case, the actual weight of water in methanol-water standard and also pyridine is found, and mg of water equivalent to 1 ml of Fischer reagent can be calculated.

The second method involves the use of sodium monotartrate dihydrate with known water of crystallization as the standard. Accurately weigh out 0.05 - 0.07 gm of sodium monotatrate dihydrate into a 250-ml Erlenmeyer flask . Add 40 ml of Karl Fischer reagent , and titrate with the water-methanol standard solution. The difference in the volume of the standard solution for the two titrations is equivalent to the weight of the tartrate.

Let weight of tartrate = x gm $\equiv (36/ 230.1) \cdot x$ gms of water

40 ml K.F. + x gm tartrate requires y ml standard

40 ml K.F. requires z ml standard

therefore, $(36/230.1)x$ gms of water is equilvalent to$(z-y)$ ml standard, and hence, 1 ml of standard wter-methanol solution will be equivalent to $36x/ 230.1(z-y)$ gms of water.

Results of the above two methods agree to within 1% error.

(ii) Determination of water content in an unknown solution - pipet 10 ml of hydrogen halide-ether solution into a titration flask, add 10 ml of pyridine to neutralize all the hydrogen halide in solution, then pipet 20 ml of the Karl Fischer reagent into the flask. Back titrate this solution with the water-methanol solution. The amount of moisture in pyridine must be corrected for . The end point is from brown to yellow. All the glass apparatus must be dried before use.

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In this case, the actual weight of water in methanol-water standard and also pyridine is found, and mg of water equivalent to 1 ml of Fischer reagent can be calculated.

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Appendix 9

Statistical treatment of the data

The experimental results of the present investigation have been analysed statistically. The fundamental formulae and methods used for statistical calculations are as follows:-

s.d. = estimate of the standard deviation

$$= \sqrt{\frac{\sum(\bar{x} - x_i)^2}{n - 1}}$$

where $\bar{x}$ = sample mean

n = number of samples

A. Propagation of precision indices (105)

Consider that $\bar{x}$ and $\bar{y}$ are independent of each other, where $\bar{x}$, $\bar{y}$ are the means of two separate sets of samples with propable errors $p\bar{x}$ and $p\bar{y}$, $s\bar{x}$ and $s\bar{y}$ their standard deviations

Let $\bar{u} = f(\bar{x}, \bar{y})$

$s\bar{u}^2 = (\partial u/\partial x)^2_{\bar{u}}\, s\bar{x}^2 + (\partial u/\partial y)^2_{\bar{u}}\, s\bar{y}^2$ = standard deviation of $\bar{u}^2$

$p\bar{u}^2 = (\partial u/\partial x)^2_{\bar{u}}\, p\bar{x}^2 + (\partial u/\partial y)^2_{\bar{u}}\, p\bar{y}^2$ = propable error of $\bar{u}^2$

B. Least-squares fit of a straight line (106.107)

for $y = a + bx$,

the intercept a , and slope b are found from the following expressions:-

$$a = \frac{\sum y_i \sum x_i^2 - \sum x_i \sum x_i y_i}{n\sum x_i^2 - (\sum x_i)^2} \qquad (i)$$

$$b = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{n\sum x_i^2 - (\sum x_i)^2} \qquad (ii)$$

Let $\sigma^2 y$ = variance of the dispersion of the values y_i with respect to the straight line

The variance of x_i was taken as zero.

$$\sigma^2 y = \frac{\sum_{i=1}^{n} y_i^2 - \bar{y}\sum y_i - b\,(\sum x_i y_i - \bar{x}\sum y_i)}{n - 2}$$

and

$$\sigma_a^2 = \frac{\sigma^2 y \sum x_i^2}{n\sum x_i^2 - (\sum x_i)^2} \qquad \text{(iii)}$$

$$\sigma_b^2 = \frac{\sigma^2 y\, n}{n\sum x_i^2 - (\sum x_i)^2} \qquad \text{(iv)}$$

where σ_a^2 and σ_b^2 are the variances of intercept and slope respectively.

C. Precision of a product or quotient when x and y are not independent.

$\bar{u} = x/y$

$$\sigma \bar{u}^2 = (\bar{u}^2/x^2)\,\sigma x^2 + (\bar{u}^2/y^2)\,\sigma y^2 - (2\,\bar{u}^2/xy)\,\sigma xy \qquad \text{(v)}$$

where σxy is the covariance

special case :- a least-squares fit gives an intercept a and a slope b which are not independent. The variance of the quantity, $z=a/b$, is found as follows:-

$$a = \frac{\sum y_i - b\sum x_i}{n}$$

$$= \frac{\sum y_i}{n} - b\frac{\sum x_i}{n}$$

Since $\sum y_i/n = \bar{y}$, $\sum x_i/n = \bar{x}$

therefore, $a = \bar{y} - b\,\bar{x}$ (vi)

and since $z=a/b$, from equation (v),

$$\sigma^2_z = \frac{z^2}{a^2}\,\sigma^2_a + \frac{z^2}{b^2}\,\sigma^2_b - \frac{2\,z^2}{ab}\,\sigma_{ab}$$

where σ_z^2 = variance of z

σ_{ab} = covariance of ab, and it can be found as follows:-

Since $a = \bar{y} - b\,\bar{x}$ from equation (vi)

therefore, $ab = \bar{y}b - b^2\bar{x}$ x b

Then $\sigma_{ab} = \sigma_{\bar{y}b} - \sigma^2_b\,\bar{x}$

But $\bar{y}$ is independent of b , i.e. $\sigma_{\bar{y}b}$ which is the covariance of $\bar{y}b = 0$.

Therefore, $\sigma_{ab} = \sigma^2_b\,\bar{x}$

$$\text{Hence, } \sigma^2_z = \frac{z^2}{a^2}\sigma^2_a + \frac{z^2\sigma^2_b}{b^2} - \frac{2\,z^2}{ab}\sigma^2_b\,\bar{x} \qquad \text{(vii)}$$

Since, z, a, b, σ^2_a (from equation i) , σ^2_b (from equation ii), and $\bar{x}$ are known either experimentally or from calculations, σ^2_z can be calculated.

Appendix 10

Measurement of the second virial coefficient (44)

Use is made of the Stockmayer potential method, since all the components are polar. The virial coefficients of HCl, HBr, and di-isopropyl ether, and their vapour mixtures had not been measured. The use of the Stockmayer potential required the following parameters for each of the components in the vapour: dipole moment, the reduced dipole moment(see equation 3 below), the molecular diameter, and the force constant. These parameters were not known for di-isopropyl ether, but they were known for di-ethyl ether. As a reasonable approximation, di-ethyl ether values were used for di-isopropyl ether.

The values of the parameters were obtained for these measurements by Monchick and Mason (45,46) from their measurements of viscosity. They are reproduced in Tablr 50a. In order to evaluate these force constants for binary mixtures, namely HCl-di-isopropyl ether and HBr-di-isopropyl ether, equations (1,2,and 3) were used.

$$\sigma_{12} = \tfrac{1}{2}(\sigma_1 + \sigma_2) \qquad (1)$$

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{\frac{1}{2}} \qquad (2)$$

$$t^*_{12} = \mu_1\mu_2/(\sqrt{8}\,\epsilon_{12}\,\sigma^3_{12})$$

$$\doteq \sqrt{t_1^* t_2^*} \qquad (3)$$

Table 50 a Stockmayer potential parameters

gas	μ(Debyes)	$\sqrt{2}t^*$	σ (Å)	ϵ/k (°K)
HCl	1.08	0.34	3.36	328
HBr	0.80	0.14	3.41	417
$(C_2H_5)_2O$	1.15	0.08	5.49	362

The relevant Stockmayer potential formulae are as follows:-

$$B = 2/3 \pi N \sigma^3 = b_o \tag{4}$$

$$T^* = kT/\epsilon \tag{5}$$

$$B^*(T^*,\mu^*) = \left(\frac{4}{T^*}\right)^{\frac{1}{4}} \left[\Gamma\left(\frac{3}{4}\right) - \frac{\frac{1}{4} \sum_{n=1}^{\infty} \sum_{k=1}^{k \leq n/2} 2^{n-2k} G_k}{n!} \times \binom{n}{2k} \Gamma\left(\frac{2n-2k-1}{4}\right) \mu^{*4k} T^{*-(n+k)/2} \right] \tag{6}$$

$$\mu^* = \mu / \sqrt{\epsilon \sigma^3} \tag{7}$$

$$t^* = 8^{-\frac{1}{2}} \mu^{*2} \tag{8}$$

$$B'(T) = b_o \; B^*(T^*,\mu^*) \tag{9}$$

where μ = dipole moment in Debyes

σ, ϵ = parameters in intermolecular potential functions,

σ = molecular diameter, A (collision diameter)

ϵ = maximum energy of attraction(or depth of potential well)

k = Boltzmann's constant

t^* = measure of polarity of a molecule

$\Gamma(x)$= the gamma function

b_o = secondvirial coefficient of rigid spheres of diameter σ

$*$ = complex conjugate of a quantity which reduced by means of the simplest combinations of molecular parameters σ and ϵ.

T^* = reduced temperature

μ^* = reduced dipole moment

The method of calculation was the same for the pure gases as for the component in the mixtures, thus, B, T^*, μ^*, and t^* were calculated from equations (4,5,7,8), therefrom $B^*(T^*,\mu^*)$ was calculated by using equation (6). In practice, the values of $B^*(T^*, \mu^*)$ was obtained by tabulation in Hirschfelder (44). Then from the values of b_o and $B^*(T^*,u^*)$, $B'(T)$ was calculated from equation (9). This value was the sought-for virial coefficient.

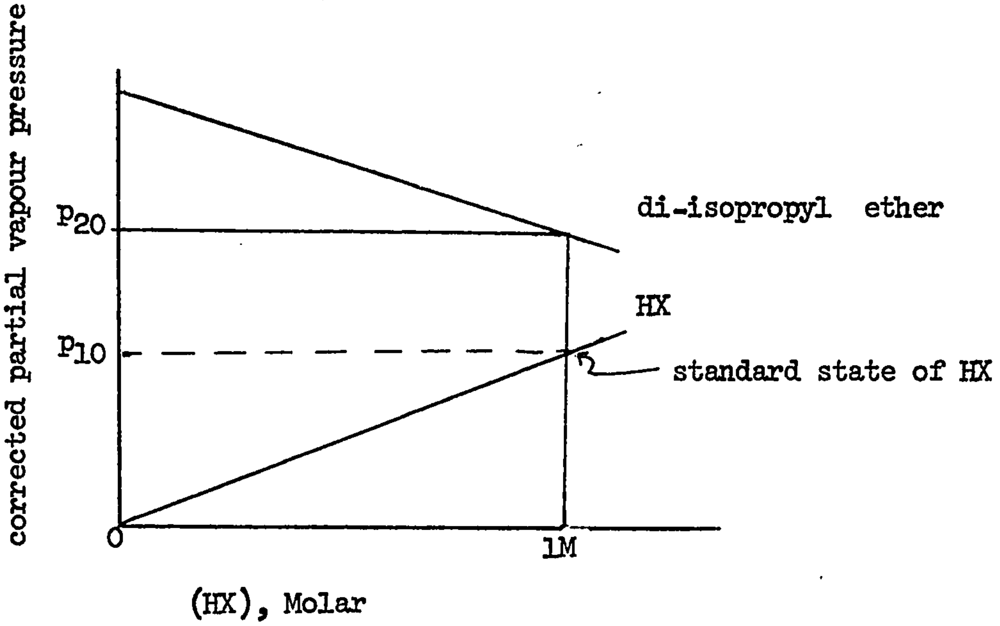
The calculated values of the second virial coefficients are reported in Table 51. It has been shown that (47)

$$u^M = RT \ln \frac{c}{c_{10}} + 2\,B_{11}\,(c_1 - c_{10}) + 2B_{12}\,(c_2 - c_{2o}) \qquad (10)$$

Use of the virial coefficients of Table 51 in equation(lo) enabled u^M to be calculated for the binary mixtures HCl-di-isopropyl ether, HBr-di-isopropyl ether. Before making these calculations of u^M, it was necessary to evaluate c_1, c_{10}, c_2, and c_{20} in equation (10). The values of c_1 and c_2 were obtained from Table 52 and 53 with conversion of the partial pressures via the ideal gas law to partial concentrations. Plots of these partial pressures versus the molarity of the hydrogen halide in the solutions produce two straight lines because Henry's law and Raoult's law were obeyed respectively. A sketch is shown in Fig. y. The standard states for the hydrogen halide solutions were chosen to be one-molar solution at 25°C as shown in the Fig. The partial pressure of the di-isopropyl ether above such a standard state solution was therefore immediately read from the Figure. By use of the ideal gas law, the partial pressure was converted to concentration . This value was the sought-for c_{20}.

On substitution of all these values into equations (10), it was found that the corrections to the partial pressures of HCl and HBr due to non-specific interactions as represented by the virial coefficients , amounted to less than 0.1% in every case. Therefore these corrections were not applied.

Fig. y Partial pressure of di-isopropyl ether and HX in HX-di-isopropyl ether solutions (not to scale).



Appendix 11

Calculation of the partial pressures of di-isopropyl ether over solutions of hydrogen chloride in the ether.

The vapour concentrations of HCl over solutions of HCl in di-isopropyl ether were measured directly, by using the apparatus shown in Fig. 1. In the 500-ml bulb only HCl and ether existed in equilibrium, since the bulb had been evaculated prior to the equilibration.

The vapour concentration of the ether over the HCl-ether solutions was not measured. However, it was calculated by using the Gibbs-Durham relationship:

$$x_1\, du_1 + x_2\, du_2 = 0 \qquad \text{(a)}$$

where x_1 and x_2 are the mole fractions of HCl and di-isopropyl ether, respectively, in the liquid phase; and u_1 and u_2 are the corresponding chemical potentials in the vapour phase.

From the conventional definition of fugacity, equation (a) may be written:-

$$\frac{x_1}{x_2}\, d \log f_1 = - d \log f_2 \qquad \text{(b)}$$

By using partial pressure as a reasonable approximation for fugacity, and integrating, equation (b) becomes

$$\log \frac{p_2''}{p_2'} = - \int_{x_1'}^{x_1''} \frac{x_1}{x_2}\, d \log p_1 \qquad \text{(c)}$$

where p_2' is the partial pressure of the ether over a solution of mole fraction x_2' in the ether, and similarly p_2'' corresponds to x_2''.

In practice, the value of x_1' was chosen to be the lowest HCl concentration for which a measurement of partial pressure was made, therefore it corresponded to an arbitrary reference point for the integration.

Let the integral on the right hand side of equation (c), i.e. the area under the curve , be denoted by log ϕ.

$$\text{Then } \phi = \frac{p_2''}{p_2'} \qquad \text{(d)}$$

In order to evaluate ϕ for selected values of x_1'', and with x_1' as the reference point, a conventional graphical integration was carried out for each chosen value of x_1''. In practice the graph of x_1/x_2 versus log p_1 was plotted on paper, and the appropr iate area was cut out and the paper weighed.

A plot of the values of ϕ so evaluated, against x_1 gave a straight line. On extrapolation of this line to $x_1=0$, the vapour pressure , p_2^o, of the pure ether was found. Then from equation(d) p_2' was found at once from the extrapolated value of ϕ, and the literature value(26) of p_2^o. Then on substituting into equation (d), the value found for p_2', and by using the already tabulated values of ϕ, the corresponding of p_2'' were found. These were the sought-for values of the partial pressures of the ether. They are tabulated in Tables 52 and 53.

Appendix 12

Sample calculation in the spectrophotometric determination of tetrahaloferric acids in three ethers (di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran) at three temperatures 25°C , 35°C, and 45°C.

Table A2-A13 principal symbols

The formation constant for the reaction

$$HX + S + FeX_3.S = HS_2^+ FeX_4^- \qquad [1]$$

where X = Cl or Br

S = ether

C_T = Total (stoichiometric) concentration of ferric halide

$(HX)_T$ = Total (stoichiometric) concentration of hydrogen halide

A = absorbance

a = apparent absorptivity = A/C_T

k_9 = formation constant for reaction [1]

a_1 = molar absorptivity of ferric halide in ether

a_2 = molar absorptivity of tetrahaloferric acid in ether

= wavelength

(HX) = concentration of solvated and unsolvated hydrogen halide

Table A2 Formation constant of HS_2FeCl_4 in di-n-butyl ether at 25.0° C, at λ = 380 mμ.

$C_T \times 10^4$ M	$(HCl)_T \times 10^3$ M	A	a	$(a_1-a)/(a-a_2)$	(HCl) $\times 10^3$ M	$\log(a_1-a)/(a-a_2)$	log(HCl)
2.555	9.640	1.097	4294	6.001	9.421	0.7782	-2.026
2.465	1.754	0.894	3628	1.094	1.625	0.0389	-2.789
2.043	1.040	0.681	3335	0.601	0.964	-0.2209	-3.016
1.972	1.380	0.690	3498	0.842	1.290	-0.0747	-2.890
1.322	1.042	0.445	3368	0.645	0.990	-0.1907	-3.004
1.443	8.334	0.615	4261	5.272	0.821	0.7220	-2.086
1.506	4.049	0.604	4013	2.522	3.941	0.4018	-2.404
1.345	1.636	0.484	3598	1.030	1.568	0.0128	-2.805
1.596	1.405	0.547	3489	0.828	1.333	-0.0819	-2.875
2.328	1.429	1.022	4389	9.557	14.07	0.9803	-1.852
1.433	6.321	0.600	4187	4.083	6.206	0.6110	-2.207
1.667	6.616	0.693	4155	3.702	5.885	0.5684	-2.901
1.800	1.335	0.623	3459	0.778	1.257	-0.1092	-2.218
1.953	6.212	0.814	4167	3.840	6.057	0.5843	-2.901

a_1= 2588 a_2= 4578

k_9=6.56 x 10^2 ± 0.056 x 10^2

log k_9 = 2.83 ± 0.022

Table A3 Formation constant of HS_2FeCl_4 in di-n-butyl ether at 35.0°C, λ = 380 mμ.

C_T x 10^4 M	$(HCl)_T$ x 10^3 M	A	a	$(a_1-a)/(a-a_2)$	(HCl) x 10^3 M	$\log(a_1-a)/(a-a_2)$	log (HCl)
2.555	9.640	1.049	4104	3.202	9.445	0.5054	-2.025
2.465	1.754	0.816	3311	0.571	1.664	-0.2435	-2.779
2.043	1.040	0.627	3068	0.318	0.991	-0.4974	-3.004
1.972	1.380	0.624	3165	0.408	1.322	-0.3887	-2.879
1.322	1.042	0.407	3078	0.327	1.010	-0.4853	-2.996
1.443	8.334	0.582	4036	2.674	8.229	0.4272	-2.085
1.506	4.049	0.560	3717	1.312	3.963	0.1180	-2.402
1.345	1.636	0.444	3299	0.556	1.588	-0.2551	-2.799
1.569	1.045	0.502	3179	0.441	1.357	-0.3557	-2.868
2.328	14.29	0.978	4200	4.271	14.10	0.6306	-1.851
1.433	6.321	0.559	3900	1.936	6.226	0.2870	-2.206
1.667	6.016	0.650	3899	1.931	5.906	0.2859	-2.229
1.800	1.335	0.571	3175	0.418	1.282	-0.3788	-2.892
1.592	6.212	0.769	3937	2.103	6.079	0.3230	-2.216

a_1= 2588 a_2= 4578

k_9= 3.20 x 10^2 ± 0.045 x 10^2

log k_9= 2.50 ± 0.03

Table A4 Formation constant of HS_2FeCl_4 in di-n-butyl ether at 45.0°C, λ = 380 mμ.

$C_T \times 10^4$ M	$(HCl)_T \times 10^3$ M	A	a	$(a_1-a)/(a-a_2)$	$(HCl) \times 10^3$ M	$\log (a_1-a/a-a_2)$	log (HCl)
2.555	9.640	0.962	3763	1.442	9.489	0.1591	-2.023
2.465	1.754	0.744	3018	0.276	1.701	-0.5599	-2.769
2.043	1.040	0.585	2864	0.161	1.012	-0.7934	-2.995
1.972	1.380	0.581	2946	0.219	1.344	-0.6594	-2.872
1.322	1.042	0.378	2856	0.157	1.024	-0.8049	-2.990
1.443	8.334	0.536	3714	1.304	8.252	0.1152	-2.083
1.506	4.049	0.513	3409	0.702	3.987	-0.1539	-2.399
1.345	1.636	0.405	3013	0.272	1.607	-0.5661	-2.794
1.569	1.405	0.462	2945	0.219	1.376	-0.6599	-2.861
2.328	14.29	0.922	3960	2.218	14.13	0.3459	-1.850
1.433	6.321	0.511	3564	0.963	6.251	-0.0170	-2.204
1.667	6.016	0.595	3566	0.967	5.934	-0.0144	-2.227
1.800	1.335	0.521	2894	0.182	1.308	-0.7405	-2.884
1.953	6.212	0.699	3578	0.991	6.115	-0.0041	-2.214

a_1 =2588 a_2 = 4578

$k_9 = 1.58 \times 10^2 \pm 0.013 \times 10^2$

$\log k_9 = 2.21 \pm 0.04$

Table A5 Formation constant of HS_2FeBr_4 in di-n-butyl ether at 25.0°C, λ =490mμ.

$C_T \times 10^4$	$(HBr)_T \times 10^4$ M	A	a	$(a_1-a)/(a-a_2)$	(HBr) $\times 10^4$ M	$\log(a_1-a)/(a-a_2)$	log (HBr)
1.354	14.38	0.589	4351	11.49	13.13	1.0602	-2.882
1.182	10.48	0.509	4304	8.731	9.424	0.9411	-3.026
1.770	3.910	0.691	3902	2.394	2.662	0.3791	-3.575
2.088	3.471	0.789	3780	1.833	2.120	0.2632	-3.674
1.622	5.874	0.669	4125	4.312	4.557	0.6350	-3.341
2.105	7.615	0.885	4203	5.633	5.827	0.7510	-3.235
1.520	3.540	0.585	3850	2.130	2.506	0.3284	-3.601
2.100	4.460	0.828	3945	2.648	2.934	0.4230	-3.532
1.250	5.370	0.513	4107	4.079	4.366	0.6106	-3.360
3.215	8.285	1.340	4168	4.966	5.609	0.6960	-3.251

a_1 =2425 a_2 = 4519

$k_9 = (9.02 \pm 0.11) \times 10^3$

$\log k_9 = 4.03 \pm 0.08$

Table A6 Formation constant of HS_2FeBr_4 in di-n-butyl ether at 35.0°C, λ=490mμ.

$C_T \times 10^4$ M	$(HBr)_T \times 10^4$M	A	a	$(a_1-a)/(a-a_2)$	(HBr) $\times 10^4$ M	$\log(a_1-a)/(a-a_2)$	log (HBr)
1.354	14.38	0.571	4218	5.951	13.22	0.7746	-2.879
1.182	10.84	0.489	4137	4.487	9.517	0.6519	-3.022
1.770	3.910	0.643	3634	1.367	2.888	0.1359	-3.540
2.088	3.471	0.727	3481	1.018	2.418	0.0079	-3.617
1.622	5.874	0.622	3838	2.074	4.780	0.3168	-3.321
2.105	7.615	0.831	3949	2.676	6.083	0.4274	-3.216
1.520	3.540	0.544	3581	1.233	2.701	0.0908	-3.569
2.100	4.460	0.772	3674	1.478	3.207	0.1698	-3.494
1.250	5.370	0.476	3810	1.953	4.543	0.2906	-3.343
3.215	8.285	1.265	3934	2.581	5.968	0.4118	-3.224

a_1= 2425 a_2= 4519

log $k9$= 3.67± 0.09

k_9= $4.51 \times 10^3 \pm 0.05 \times 10^3$

Table A7 Formation constant of HS_2FeBr_4 in di-n-butyl ether at 45.0°C, λ =490mμ.

$C_T \times 10^4$ M	$(HBr)_T \times 10^4$ M	A	a	$(a_1-a)/(a-a_2)$	$(HBr) \times 10^4$ M	$\log (a_1-a)/(a-a_2)$	log(HBr)
1.354	14.38	0.540	3992	2.970	13.37	0.4727	-2.874
1.182	10.48	0.453	3835	2.063	9.688	0.3144	-3.014
1.770	3.910	0.580	3277	0.686	3.910	-0.1640	-3.496
2.088	3.471	0.676	3235	0.631	2.663	-0.1999	-3.574
1.622	5.874	0.572	3525	1.107	5.022	0.0441	-3.299
2.105	7.615	0.773	3672	1.473	6.361	0.1681	-3.197
1.520	3.540	0.496	3264	0.668	2.931	-0.175	-3.533
2.100	4.460	0.701	3339	0.775	3.543	-0.1106	-3.451
1.250	5.370	0.440	3524	1.105	4.714	0.0432	-3.327
3.215	8.285	1.183	3679	1.492	6.360	0.1736	-3.197

a_1= 2425 a_2= 4519

$\log k_9 = 3.35 \pm 0.07$

$k_9 = 2.21 \times 10^3 \pm 0.03 \times 10^3$

Table A8 Formation constant of HS_2FeCl_4 in tetrahydrofuran at 25.0°C, λ =360 mμ.

$C_T \times 10^4$	$(HCl)_T x10^4$	A	a	$(a_1-a)/(a-a_2)$	(HCl) x 10^4 M	log $(a_1-a)/(a-a_2)$	log (HCl)
1.018	5.083	0.672	6600	2.173	4.385	0.3370	-3.358
1.426	2.576	0.903	6336	1.093	2.012	0.0385	-3.696
1.629	3.292	1.039	6379	1.215	2.398	0.0847	-3.620
1.833	2.993	1.158	6319	1.046	2.056	0.0194	-3.687
2.037	1.765	1.237	6073	0.561	1.033	-0.2510	-3.986
2.444	2.263	1.503	6150	0.687	1.268	-0.1631	-3.897
0.611	1.222	0.370	6055	0.535	1.009	-0.2715	-3.996
0.817	1.365	0.494	6067	0.553	1.075	-0.2571	-3.969
1.222	1.742	0.751	6144	0.676	1.249	-0.1701	-3.904
0.847	5.163	0.560	6609	2.229	4.578	0.3480	-3.339
1.018	6.766	0.684	6713	3.078	5.997	0.4882	-3.222
1.069	6.587	0.717	6705	2.992	5.786	0.4759	-3.238
1.222	4.982	0.806	6598	2.158	4.147	0.3340	-3.382
1.452	4.189	0.948	6529	1.784	3.259	0.2514	-3.487
1.426	6.599	0.951	6674	2.707	5.559	0.4324	-3.255

a_1= 5490 a_2= 7111

k_9= 5.09 $x10^3 \pm 0.05 \times 10^3$

log k_9= 3.59 ± 0.05

Table A9 Formation constant of HS_2FeCl_4 in tetrahydrofuran at 35.0°C, λ =360 mμ.

$C_T \times 10^4$ M	$(HCl)_T \times 10^4$ M	A	a	$(a_1-a)/(a-a_2)$	(HCl) $\times 10^4$ M	log $(a_1-a)/(a-a_2)$	log (HCl)
1.018	5.083	0.650	6382	1.223	4.523	0.0874	-3.345
1.426	2.756	0.869	6092	0.591	2.227	-0.2287	-3.652
1.629	3.292	1.009	6191	0.761	2.587	-0.1185	-3.587
1.833	2.993	1.122	6123	0.641	2.277	-0.1933	-3.643
2.037	1.765	1.203	5909	0.349	1.239	-0.4577	-3.907
2.444	2.263	1.459	5969	0.420	1.540	-0.3768	-3.813
0.611	1.222	0.385	5850	0.286	1.086	-0.5441	-3.964
0.815	1.365	0.480	5886	0.324	1.166	-0.4899	-3.934
1.222	1.742	0.727	5950	0.397	1.395	-0.4016	-3.856
0.847	5.163	0.541	6384	1.229	4.696	0.8960	-3.328
1.018	6.764	0.664	6520	1.741	6.119	0.2408	-3.213
1.069	6.587	0.697	6514	1.176	5.911	0.3345	-3.228
1.222	4.892	0.777	6359	1.155	4.327	0.0627	-3.364
1.450	4.189	0.909	6261	0.907	3.489	-0.0422	-3.456
1.426	6.600	0.922	6464	1.506	5.743	0.1779	-3.241

a_1= 5490 a_2=7111

k_9= 2.74 x 10^3 ± 0.03 x 10^3

log k_9= 3.42 ± 0.07

Table A10 Formation constant of HS_2FeCl_4 in tetrahydrofuran at 45.0°C, λ=360 mμ.

$C_T \times 10^4$ M	$(HCl)_T \times 10^4$ M	A	a	$(a_1-a)/(a-a_2)$	(HCl) x 10^4 M	$\log(a_1-a)/(a-a_2)$	log (HCl)
1.018	5.083	0.627	6153	0.692	4.666	-0.1602	-3.331
1.426	2.756	0.841	5897	0.336	2.398	-0.4743	-3.620
1.629	3.292	0.971	5961	0.409	2.819	-0.3883	-3.550
1.833	2.992	1.088	5935	0.378	2.490	-0.4225	-3.604
2.037	1.765	1.175	5770	0.209	1.413	-0.6801	-3.850
2.444	2.263	1.419	5804	0.241	1.789	-0.6187	-3.747
0.611	1.222	0.350	5730	0.165	1.136	-0.7826	-3.945
0.815	1.365	0.469	5751	0.192	1.234	-0.7171	-3.909
1.222	1.742	0.707	5787	0.225	1.518	-0.6486	-3.819
0.847	5.163	0.519	6132	0.656	4.827	-0.1828	-3.316
1.018	6.764	0.637	6251	0.884	6.288	-0.0532	-3.202
1.069	6.587	0.672	6283	0.957	6.064	-0.0191	-3.217
1.222	4.892	0.746	6100	0.604	4.522	-0.2192	-3.345
1.450	4.189	0.880	6061	0.544	3.678	-0.2647	-3.434
1.426	6.600	0.888	6227	0.833	5.952	-0.0792	-3.225

a_1= 5490 a_2= 7111

k_9= 1.46 x $10^3 \pm 0.02 \times 10^3$

log k_9= 3.20 ± 0.09

Table A11 Formation constant of HS_2FeBr_4 in tetrahydrofuran at 25.0°C, λ = 480mμ.

$C_T \times 10^4$ M	$(HBr)_T \times 10^4$ M	A	a	$(a_1-a)/(a-a_2)$	$(HBr) \times 10^4$ M	$\log(a_1-a)/(a-a_2)$	log(HBr)
1.523	4.537	0.643	4223	0.803	3.679	-0.0950	-3.434
2.261	5.697	0.990	4381	1.002	4.566	0.0008	-3.341
2.326	5.167	0.996	4283	0.874	4.082	-0.0583	-3.389
1.570	2.418	0.598	3811	0.4350	1.942	-0.3615	-3.712
2.640	6.257	1.162	4402	1.031	4.917	0.0133	-3.308
2.823	1.301	0.955	3384	0.184	0.863	-0.7361	-4.064
2.041	8.021	0.952	4666	1.494	6.798	0.1744	-3.168
2.104	9.058	1.002	4763	1.723	7.727	0.2363	-3.112
1.493	14.74	0.755	5055	2.754	13.64	0.440 0	-2.865
2.012	10.10	0.975	4845	1.951	8.772	0.2902	-3.057

a_1= 2936 a_2= 5824

k_9= 2.13 x 10^3 ± 0.03 x 10^3

log k_9= 3.31 ± 0.05

Table A12 Formation constant of HS_2FeBr_4 in tetrahydrofuran at 35.0°C, λ = 480mμ

$C_T \times 10^4$ M	$(HBr)_T \times 10^4$ M	A	a	$(a_1-a)/(a-a_2)$	$(HBr) \times 10^4$ M	$\log(a_1-a)/(a-a_2)$	log(HBr)
1.523	4.537	0.580	3808	0.433	3.897	-0.3639	-3.409
2.261	5.697	0.885	3916	0.513	4.931	-0.2897	-3.307
2.326	5.167	0.890	3827	0.446	4.450	-0.3508	-3.352
1.570	2.418	0.545	3473	0.229	2.126	-0.6411	-3.673
2.640	6.357	1.015	3980	0.566	5.303	-0.2469	-3.276
2.823	1.310	0.914	3236	0.116	1.008	-0.9364	-3.997
2.041	8.021	0.851	4172	0.748	7.148	-0.1213	-3.145
1.493	14.74	0.695	4652	1.464	1.385	0.1655	-2.859
2.104	9.058	0.912	4333	0.937	8.041	-0.0284	-3.095
2.012	10.01	0.880	4374	0.991	9.101	-0.0039	-3.041

$a_1 = 2936$ $a_2 = 5824$

$k_9 = 1.08 \times 10^3 \pm 0.01$

$\log k_9 = 2.98 \pm 0.07$

Table A13 Formation constant of HS_2FeBr_4 in tetrahydrofuran at 45.0°C, λ =480 mμ.

C_T x 10^4 M	$(HBr)_T$x10^4	A	a	$(a1-a)/(a-a_2)$	(HBr) x10^4 M	$\log(a_1-a)/(a-a_2)$	log(HBr)
1.523	4.357	0.523	3431	0.207	4.096	-0.6843	-3.388
2.261	5.697	0.805	3562	0.277	5.207	-0.5575	-3.283
2.326	5.167	0.829	3562	0.277	4.662	-0.5569	-3.332
1.570	2.418	0.508	3237	0.117	2.254	-0.9340	-3.647
2.640	6.257	0.948	3592	0.294	5.657	-0.5314	-3.247
2.823	1.301	0.877	3106	0.063	1.134	-1.2034	-3.945
2.041	8.021	0.766	3752	0.394	7.444	-0.4050	-3.128
2.104	9.058	0.809	3844	0.459	8.400	-0.3387	-3.076
1.493	14.74	0.632	4236	0.819	14.06	-0.0870	-2.852
2.012	10.10	0.795	3951	0.542	9.395	-0.2660	-3.027

a_1= 2936 a_2= 5824

k_9=5.61 x 10^2 ± 0.09

log k_9= 2.82 ± 0.08

BIBLIOGRAPHY

1. J.W. Rothe. Stahl u. Eisen. 12, 1052 (1892).
2. L. Garwin and A.M. Hixon. Ind. Eng. Chem. 41, 2303 (1949).
3. V. Lenher and C.H. Kao. J. Phys. Chem. 30, 126 (1926).
4. F. Mylius and C. Huttner. Ber. deut. Chem. Ges. 44, 1315 (1911).
5. E.H. Swift. J. Am. Chem. Soc. 46, 2378 (1924).
6. R. Dodson, G. Forney, and E. Swift. J. Am. Chem. Soc. 58, 2573 (1936).
7. R.P. Taylor. Thesis. Study of Solvent Extraction of Molybdenum. Rutzers University (1950).
8. W.W. Meinke. U.S. Atomic Energy Commission Report. AECD-2738.
9. E.R. Caley and H.D. Axilrod. Ind. Eng. Chem. Anal. Ed. 14, 242 (1942).
10. H.G. Hicks and R.S. Gilbert. U.S. Atomic Energy Commission Report. MTA-33.
11. H.L. Friedman. J. Am. Chem. Soc. 74, 5 (1952).
12. D.E. Metzler, D.E. Metzler, and E.H. Swift. J. Am. Chem. Soc. 72, 3767 (1950).
13. N.H. Nachtrieb and J.C. Conwey. J. Am. Chem. Soc. 70, 3547 (1948).
14. B.V. Nekrasor and V.V. Ovsyankina. Zhur. Neorg. Khim. 11, 573 (1941).
15. J. Axelrod and E.H. Swift. J. Am. Chem. Soc. 62, 33 (1940).
16. A.A. Laurene, D.E. Campbell, S.E. Wiberley, and H.M. Clark. J. Phys. Chem. 60, 901 (1956).
17. V.V. Fomin and A.F. Morgunov. Russ. J. Inorg. Chem. 5, 670 (1960).
18. G.S. Golden and H. Clark. J. Phys. Chem. 65, 1930 (1961).
19. G.S. Golden and H. Clark. J. Phys. Chem. 65, 1932 (1961).
20. P. McCusker and S.M. Scholastica Kennard, C.S.C. J. Am. Chem. Soc. 81, 2976 (1959).

21. V.V. Fomin, P.A. Zagorets, A.F. Morgunov, and I.I. Tertishnik. Russ. J. Inorg. Chem. 1038 (1959).

22. V.V. Fomin, P.A. Zagorets, and A.F. Morgunov. Russ. J. Inorg. Chem. 318 (1959).

23. V.V. Fomin and A. F. Morgunov. Russ. J. Inorg. Chem. 5, 670 (1960).

24. C.K. Jorgensen. Adsorption spectra and chemical bonding in complexes. Pergamon Press. N.Y. 1962, p 108.

25. N. Begum. PhD thesis, Department of Chemistry, McGill University (1966).

26. A. Weissberger and E. Proskauer. Organic Solvents. Interscience Publishers, New York, 1955, p 122.

27. C. Marsden and S. Mann. Solvent Guide. 2nd ed., Cleaver Hunt Press. Ltd., Interscience Publishers, London, 1954, p 514.

28. R.P. Bell. The proton in chemistry. Cornell University Press, New York, 1959, p 24, 91.

29. J. C. McCoubrey. Tran. Faraday Soc. 51, 743 (1955).

30. W. Strohmeier and A. Echte. Z. Fur Elehtrochim. 61, 549 (1957).

31. E.W. Washburn. International Critical Tables. McGraw Hill Book Co. Inc., New York, N.Y., Vol. III, 1930, p 228.

32. G.N. Lewis and M. Randall. Thermodynamics. McGraw Hill Book Co. Inc., New York, N.Y., 1961, p 674.

33. W. Dasler and C.D. Bauer. Ind. Eng. Chem. 18, 52 (1946).

34. J.H. Saylor. J. Am. Chem. Soc. 59, 1712 (1937).

35. G.H. Haupt. J. Research U.S. Nat. Bur. Stds. 48, 414 (1952).

36. J.P. Mehlig. Ind. Eng. Chem. Anal. Ed. 136 (1938).

37. R.O. Scott. Analyst 66, 142 (1941).

38. A.A. Maryott and E. Smith. Tables of dielectric constants of pure liquids. Nat. Bur. Stds., NBS Circular. 514, United States Department of Commerce, 1951.

39. V.R. Mecke and G. Klingenberg. Z. Elekrochem. <u>66</u>, 239 (1962).

40. A.A. Maryott. Nat. Bur. Stds. <u>41</u>, 1 (1948).

41. A.A. Maryott. Nat. Bur. Stds. <u>41</u>, 7 (1948).

42. F.J.C. Rossotti and H. Rossotti. The determination of stability constants. McGraw Hill Book Co.,Inc., New York , 1961, p 318.

43. W. Farlene and R. Wright. J. Chem. Soc. 207 (1934).

44. J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird. Molecular Theory of gases and liquids. With the assistance of the University of Wisconsin Naval Research Laboratory. N.Y.,1954, p 209.

45. L. Monchick and E.A. Mason. J. Chem. Phys. <u>35</u>, 1676 (1961).

46. L. Monchick and E.A. Mason. J. Chem. Phys. <u>36</u>, 1622 (1962).

47. P. Pollak and G.C.B. Cave. Can. J. Chem. <u>45</u>, 3089 (1967).

48. E. Greinacher, W. Luttke, and R. Mecke. Z. fur Elektrochem. <u>59</u>, 23 (1955).

49. M. Falk and P.A. Giguere. Can. J. Chem. <u>35</u>, 1195 (1957).

50. W.J. Biermann and J.B. Gilmour. Can. J. Chem. <u>37</u>, 1249 (1959).

51. J.A.V. Butler and D.W. Thomsen. Proc. Roy. Soc. London <u>A 141</u>, 86 (1933).

52. M. Born. Verhandl deut. phys. Ges. <u>20</u>, 202 (1918); <u>21</u>, 13 (1919).

53. M. Born and J. Mayer. Z. Physik. <u>75</u>, 1 (1932).

54. K.B. Yatsimirskii. J. Gen. Chem. <u>26</u>, 2655 (1956).

55. A.F. Kapustinskii. Quart. Revs. <u>10</u>, 283 (1956).

38. A.A. Maryott and E. Smith. Tables of dielectric constants of pure liquids. Nat. Bur. Stds., NBS Circular. 514, United States Department of Commerce, 1951.

39. V.R. Mecke and G. Klingenberg. Z. Elekrochem. 66, 239 (1962).

40. A.A. Maryott. Nat. Bur. Stds. 41, 1 (1948).

41. A.A. Maryott. Nat. Bur. Stds. 41, 7 (1948).

42. F.J.C. Rossotti and H. Rossotti. The determination of stability constants. McGraw Hill Book Co.,Inc., New York , 1961, p 318.

43. W. Farlene and R. Wright. J. Chem. Soc. 207 (1934).

44. J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird. Molecular Theory of gases and liquids. With the assistance of the University of Wisconsin Naval Research Laboratory. N.Y.,1954, p 209.

45. L. Monchick and E.A. Mason. J. Chem. Phys. 35, 1676 (1961).

46. L. Monchick and E.A. Mason. J. Chem. Phys. 36, 1622 (1962).

47. P. Pollak and G.C.B. Cave. Can. J. Chem. 45, 3089 (1967).

48. E. Greinacher, W. Luttke, and R. Mecke. Z. fur Elektrochem. 59, 23 (1955).

49. M. Falk and P.A. Giguere. Can. J. Chem. 35, 1195 (1957).

50. W.J. Biermann and J.B. Gilmour. Can. J. Chem. 37, 1249 (1959).

51. J.A.V. Butler and D.W. Thomsen. Proc. Roy. Soc. London A 141, 86 (1933).

52. M. Born. Verhandl deut. phys. Ges. 20, 202 (1918); 21, 13 (1919).

53. M. Born and J. Mayer. Z. Physik. 75, 1 (1932).

54. K.B. Yatsimirskii. J. Gen. Chem. 26, 2655 (1956).

55. A.F. Kapustinskii. Quart. Revs. 10, 283 (1956).

56. Janaf thermochemical data. Vol. 1 and 2, compiled and calculated by Dow Chem. Co., Thermal Lab., Midla, Michigan, U.S.A., 1960.

57. A. Bondi. Chem. Revs. 67, 565 (1967).

58. E. Wiberg, M. Schmidt, and A.G. Galinos. Angew. Chem. 66, 443 (1954).

59. F. Klages, H. Meuresch, and W. Steppich. Ann. der Chim. 592, 6 (1955).

60. H.J.M. Bowen, J. Donohue, and D.G. Jenkin. Tables of interatomic distances and configuration in molecules and ions. Special publications No. 11. Chem. Soc. London, Burlington House, W1 , 1958, p M67.

61. R.C. Weast, S.M. Selby, and C.D. Hodgman. Handbook of Physical Chemistry. 46th ed., The Chem. Rubber Co. Inc., Cleveland, Ohio, U.S.A., 1965.

62. R.E. Richards and J.A.S. Smith. Trans. Faraday Soc. 47, 1261 (1951).

63. R.E. Richards and J.A.S. Smith. Trans. Faraday Soc. 48, 307 (1952).

64. Y. Kakinchi, H.Shono, M. Matsu, and K. Kigoshi. J. Phys. Soc. Japan. 7, 108 (1952); J. Chem. Phys. 19, 1069 (1951).

65. G.N. Lewis and M. Randall. Thermodynamics. 2nd ed., McGraw Hill Book Co. Inc., New York , 1961. same reference as 32.

66. J. Sherman. Chem. Revs. 11, 93 (1932).

67. E. Cartmell and G.W.A. Fowles. Valency and molecular structure. Butterworths Scientific Publications, London, 1956, p 122.

68. C.M. Cook, Jr., and W.E. Dunn, Jr. J. Phys. Chem. 65, 1505 (1961).
R.R. Richards and N.W. Gregory. J. Phys. Chem. 68, 3089 (1964).

69. H. Reiss. Progress in solid state chemistry. vol. I, Pergamon Press, the Macmillan Co., New York, 1964, p 37.

70. D. Van Raalte and A. G. Harrison. Can. J. Chem. 41, 3128 (1963).

71. M.S.B. Munson. J. Am. Chem. Soc. 87, 2332 (1965).

72. A.G. Harrison, A. Ioko, and D. Van Raalte. Can. J. Chem.. 44, 1625 (1966).

73. A.P. Ahshuller. J. Am. Chem. Soc. 77, 3480 (1955).

74. V.L. Tal'roze and E.L. Frankevich. Dokl. Akad. Nauk SSSR 111, 376 (1956); E.L. Frankevich and V.L. Tal'roze. Zh. Fiz. Khim. 33, 1083(1959).

75. J.L. Beauchamp and S.E. Buttrill, Jr., J. Chem. Phys. 48, 1783 (1968).

76. F.W. Lampe and J.H. Futrell. Trans. Faraday Soc. 59, 1957 (1963).

77. M.S.B. Munson and J.L. Franklin. J. Phys. Chem. 68, 3191 (1964).
E.W. Godbole and P. Kebarle. Trans. Faraday Soc. 58, 1897 (1962).

78. W.J. Hamer. The structure of electrolyte solutions. John Wiley and Sons Inc., N.Y.,1959, p 64.

79. E.C. Baughan. J. Chem. Soc. 1403 (1940).

80. D.D. Eley and M.G. Evans. Trans. Faraday Soc. 34, 1093 (1938).

81. R.W. Gurney. Ionic processes in solution. Dover Publications, Inc., New York, 1953, p 48.

82. E.W. Washburn. International critical Tables. Vol. III, McGraw Hill Book Co.,Inc., New York, 1930, p 228. same reference as 31.

83. S.S. Todd and J.P. Coughlin. J. Am. Chem. Soc. 73, 4184 (1951).

84. J.A. Miliotis, A.G. Galinos, and J.M. Tsangeris. Bull. Soc. Chim. France 1413 (1961).

85. W. Hieker, J. Peterhans, and E. Winter. Chem. Ber. 94, 2572 (1961).

86. L.C. Pauling. The nature of chemical bond and the structure of molecules and crystals. 3rd ed., Ithaca, N.Y.,1960.
A.L. Companion. Chemical bonding. McGraw Hill Book Co., 1964, p 50.

87. A.L. McClellan. Tables of experiment l dipole moments. W.H. Freeman and Co. San Francisco and London, 1963, p 114, 221, 311, 512.

88. G.A. Barlay, and R.J.W. LeFevre. J. Chem. Soc. 1643 (1952).

89. (a.) J.S. Allen and H. Hibbert. J. Am. Chem. Soc. 56, 1398 (1934).

(b.) C.W.N. Cuper and A.I. Vogel. J. Chem. Soc. 3521 (1959).

(c.) C.P.Smyth and W.S. Walls. J. Am. Chem. Soc. 54, 3230 (1932).

90. E.M. Arnett and C.Y. Wu. J. Am. Chem. Soc. 84, 1684 (1962).

91. W. Gerrard and E.D. Macklen. Chem. Revs. 59, 1105 (1959).

92. E.M. Arnett. Progress in Physical Organic Chem. Vol. I. Quantitative comparison of weak organic bases. Interscience Publishers, John Wiley and Sons, Inc., 1963.

93. S. Searles, M. Tamres, and D.E. McLaughlin. J. Am. Chem. Soc. 82, 5618, 5621 (1960).

94. S. Searles, E.F. Lutz, and M. Tamres. J. Am. Chem. Soc. 82, 2932 (1960).

95. S. Searles, M. Tamres, and E.R. Lippincott. J. Am. Chem. Soc. 75, 2775 (1953).

96. S. Searles, and M. Tamres. J. Am. Chem. Soc. 73, 3704 (1951).

97. G.J. Janz and S.S. Danyluk. Chem. Revs. 60, 209 (1960).

98. J.W. Smith. Electric Dipole Moments. Butterworths Scientific Publications, London, 1955, p 86, 314.

99. L.J. Bellamy, G. Egleniton, and J.F. Morman. J. Chem. Soc. 47, 62 (1961).

100. I.M. Kolthoff and E.B. Sandall. Text book of quantitative inorganic analysis, 3rd. ed., The Macmillan Co., N.Y.,1959, p 310.

101. F.J. Welcher. The analytical uses of E.D.T.A. D. Van Nostrand Co., Inc., Princeton, 1957, p 227.

102. A.I. Vogel. Quantitative Inorganic Analysis. 2nd ed., Longman, Green, and Co.,New York and Toronto, 1951, p 407.

103. I.M. Kolthoff and R. Belcher. Volumetric analysis. Vol. 3, Interscience Publishers Inc., New York, 1957, p 409.

104. I.M. Kolthoff and P.J. Elving. Treatise on analytical chemistry. Part II, Vol I, Interscience Publishers, New York, 1962, p 82.

105. A.G. Worthing and J. Geffner. The treatment of experimental data. John Wiley and Sons Inc., N.Y.,1943, p 205.

106. V.V. Nalimov. The application of mathematical statistics to chemical analysis, translated by P. Basu. Addison- Wesley Publishing Co., Inc., Toronto, 1963, p 167.

107. C.A. Bennett and N.L. Franklin. Statistical analysis in chemistry and chemical industry. John Wiley and Sons, Inc., New York, London, Sydney, 1966.

108. W. Gordy. J. Chem. Phys. 7, 93 (1939).

109. W. Gordy, and P.C. Martin. J. Chem. Phys. 7, 99 (1939).

110. W. Gordy and S.C. Stanford. J. Chem. Phys. 8, 170 (1940).

111. W. Gordy . J. Chem. Phys. 9, 215 (1941).

112. S.J. O'Brien and J.B. Byrne. J. Am. Chem. Soc. 62, 2063 (1940).

113. S.J. O'Brien and C.L. Kenny. J. Am. Chem. Soc. 62, 1189 (1940).

114. S.J. O'Brien and E.G. Bokalek. J. Am. Chem. Soc. 62, 3227 (1940).

115. S.J. O'Brien. J. Am. Chem. Soc. 63, 2709 (1941).

116. S.J. O'Brien, C.L. Kenny, and R.A. Zuercher. J. Am. Chem. Soc. 61, 2504 (1939).

117. M.G. Evans and M. Polanyi. Trans. Faraday Soc. 32, 1333 (1936).

118. R.P. Bell. Trans. Faraday Soc. 33, 496 (1937).

119. J.A.V. Butler. Trans. Faraday Soc. 33, 229 (1937).

120. D. D. Eley. Trans. Faraday Soc. 35, 1281, 1421 (1939).

121. R.J.P. Williams. J. Phys. Chem. 58, 121 (1954).

122. T.L. Hill. An introduction to statistical thermodynamics. Addison-Wesley Publishing Co., Inc., London, 1960.

123. S. Glasstone. Theoretical chemistry, an introduction to quantum mechanics, statistical mechanics, and molecular spectra for chemists. D. Van Nostrand Co.,Inc., Princeton, New Jersey, New York, 1961.

124. J.E. Prue. The international encyclopedia of physical chemistry and chemical physics. Topic 15, Vol. III. Ionic equilibria, Pergamon Press, New York, 1966, p 82.

125. D.P. Earp and S. Glasstone. J. Chem. Soc. 1709 (1935).

126. P. Kebarle. Div. Fuel Chem. Preprints. Part I 11 (2), 66 (1967); C. A. 66 , 119705 m.