Himmelstern[22] has found an increase of pressure from 1 to 968 atm. to increase the atomic ratio found on electrolysis by a negligible amount (from 0.7 to not more than 0.707).

Summary

Seven isotherms, from 200 to 313°, have been traced on the pressure–composition diagram for palladium and hydrogen, in most cases from zero pressure through the heterogeneous region and well into the second homogeneous solid phase. The diagram, including the previous results at lower temperatures of Gillespie and Hall, indicates that the compounds Pd_2H, Pd_3H, Pd_4H and Pd_8H have chemical individuality, even though in the second case, and possibly others, the tangent to the boundary curve is not vertical, the curve then resembling the analogous curve for FeO in the Fe–H–O system. In all cases the compound is to be regarded as a solid solution that has a stoichiometrical composition over a limited range of temperature. The finding of Brüning and Sieverts of a critical solution temperature for the solid phases near 300° is confirmed, and the critical constants are found to be: temperature, 295,3°; pressure, 19.87 atm. and atomic ratio H:Pd, 0.270.

In the discussion the validity is denied of (1) certain evidence against the existence of Pd_2H, and (2) certain evidence in favor of the existence of PdH.

Mention is made of palladium mercuride, probably Pd_4Hg_3, of very low decomposition pressure. The palladium investigated was found at the conclusion of the experiments to contain a presumably harmless amount of mercury, much less than 0.2%.

CAMBRIDGE, MASS. RECEIVED AUGUST 14, 1936

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[22] Von Samson-Himmelstern, *Z. anorg. Chem.*, **186**, 337 (1930).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 548]

The Extraction of Ferric Chloride from Hydrochloric Acid Solutions by Isopropyl Ether

BY RICHARD W. DODSON, GERARD J. FORNEY AND ERNEST H. SWIFT

Introduction

The extraction of ferric chloride from solutions approximately 6 formal in hydrochloric acid by ethyl ether has been studied repeatedly,[1-5] but, although such an extraction process offers obvious advantages over precipitation methods, this separation has not been used as widely in general qualitative and quantitative procedures as would seem justified. This has been due to several factors: the efficiency of the extraction process is critically dependent on the hydrochloric acid concentration; the solubility of ether in the acid is of such magnitude that the volume of the aqueous phase is increased by as much as 25%, making the concentration of the acid after an extraction uncertain or requiring the use of acid previously saturated with the ether; it has been feared that peroxide or alcohol which are frequently present in ether would reduce the iron to the ferrous state, in which form it is not extracted; finally, the volatility of ethyl ether makes the quantitative technique of the extraction somewhat difficult at room temperatures, and especially for student use, involves a serious fire hazard. Because of these facts, it has seemed worth while to investigate the use of other, less volatile ethers for this separation, and this paper presents the results of experiments with isopropyl ether. This ether is readily available, and the present cost of the best technical grade is somewhat less than that of ethyl ether of a comparable grade.

The Experimental Method

Materials.—Concentrated hydrochloric acid, C. P. grade, was standardized against sodium carbonate. Ferric chloride solutions were prepared and standardized, by permanganate, using the Zimmermann–Reinhardt method, or by thiosulfate, using the iodometric method.[6] In every case the ferric chloride used was shown to be free from ferrous salt by testing with ferricyanide. Except when testing the suitability of the technical product for routine analyses, the isopropyl ether used was prepared from a technical grade by fractional distillation, the fraction

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[1] Skey, *Chem. News*, **36**, 48 (1880).

[2] Rothe, *Mitt. könig‌. tech. Ver.*, **10**, 32 (1892); *Chem. News*, **66**, 182 (1892); *Stahl und Eisen*, **12**, 1052 (1892).

[3] Langmuir, THIS JOURNAL, **22**, 102 (1900).

[4] Kern, *ibid.*, **23**, 689 (1901).

[5] Speller, *Chem. News*, **83**, 124 (1901).

[6] E. H. Swift, THIS JOURNAL, **51**, 2682 (1929).

taken distilling over a temperature range of 0.1°. The ethyl ether used had been distilled over sodium, and before use was shaken with mercury to remove peroxide. Solutions of the chlorides of copper, cobalt, manganese, nickel, aluminum, chromium and zinc were prepared by dissolving appropriate amounts of these substances in distilled water, and adding such amounts of concentrated hydrochloric acid and water that the final acid concentration was 7.75 *f*, and the metal ion was present in the desired concentration. Hydrochloric acid solutions were prepared similarly of technical titanic sulfate solution, vanadol and vanadyl ions (from ammonium vanadate), sodium molybdate, sodium hydrogen sulfate and sodium dihydrogen phosphate.

Extraction Technique.—Twenty-five ml. of a solution of hydrochloric acid and ferric chloride in definite concentrations was introduced into a 50-ml., glass-stoppered, graduated cylinder, 25.0 ml. of ether added and the mixture shaken vigorously 500–1000 times. After a separation of the layers was obtained, the phase volumes were read and the mixture transferred to a dry separatory funnel. Portions for analysis were withdrawn from each phase. Except where otherwise stated, the extractions were performed at room temperatures. The same technique was used in the extractions of the other substances tested.

Analytical Procedure.—Small amounts of iron were determined colorimetrically with thiocyanate, larger amounts either by the Zimmermann–Reinhardt method or by the iodometric method. The peroxide content of the ethers used was estimated colorimetrically by means of titanium sulfate. In studying the reducing effect of peroxide and alcohol, ferrous iron was estimated by adding ferricyanide to the solution to be tested and comparing the precipitate so obtained with the precipitate obtained under similar conditions with known amounts of ferrous iron, also by the difference between thiocyanate determinations of ferric iron and, after permanganate oxidation, of total iron.

The Experimental Results

Effect of Varying the Acid Concentration.—Since the efficiency of the extraction with ethyl ether is known to be very dependent on the acid concentration, extractions using isopropyl ether were performed with 125 and 250 mg. of ferric iron over a wide range of acid concentrations. The results of these extractions are recorded in Table I. As noted, with these amounts of iron, three phases appear at hydrochloric acid concentrations above 7.5 formal. In these cases, the two upper layers are considered as ether phases, and the sum of their volumes is recorded. The volumes of these two phases at acid concentrations of 7.5–8.0 formal are approximately equal and the distribution ratio for iron between them varies from about 2.5 to 7.5, the ratio favoring the bottom layer of the two and increasing with increase in hydrochloric acid concentration.

For purposes of comparison there are recorded in Table II values obtained under similar conditions for the distribution of ferric iron between aqueous hydrochloric acid solutions and ethyl ether.

TABLE I

THE DISTRIBUTION OF FERRIC IRON BETWEEN ISOPROPYL ETHER AND AQUEOUS HYDROCHLORIC ACID SOLUTIONS

Initial HCl concn., moles per liter	Volume after shaking, ml. Ether layer	Volume after shaking, ml. Water layer	Iron found, mg. Ether layer	Iron found, mg. Water layer	% extracted	Distribution ratio $(Fe_{ether})/(Fe_{water})$
2.0	24.8	25.3	0	252.0	0	
3.0	24.5	25.4	1.1	250.9	0.44	0.0045
4.0	24.6	25.3	30.5	221.6	12.1	.142
5.0	24.8	24.9	203.9	48.1	80.9	4.25
5.5	24.7	24.9	235.2	16.8	93.3	14.1
6.0	24.7	25.0	247.3	4.7	98.1	53.3
6.5	23.9	25.9	124.7	1.1	99.1	123
6.6	24.5	25.2	250.4	1.6	99.4	161
7.0	24.2	25.5	251.1	0.92	99.6	287
7.0	23.7	26.0	123.7	0.65	99.5	208
7.5	23.7[a]	25.8	248.4	0.39	99.8	690
7.5	23.7	26.2	123.6	0.79	99.4	173
7.75	23.4[a]	26.2	248.6	0.24	99.9	1160
8.0	23.3[a]	26.2	251.9	0.16	99.9	1770
8.0	23.2[a]	26.6	124.2	0.19	99.8	750
8.25	22.5[a]	26.9	248.5	0.30	99.9	990
8.5	22.0[a]	27.4	247.9	0.88	99.6	351
8.5	22.4[a]	27.2	123.8	0.61	99.5	246
9.0	19.1[a]	30.1	238.5	13.5	94.6	27.8
9.0	18.5[a]	30.8	116.1	8.3	93.3	23.3

[a] Two ether phases. The sum of the volumes is recorded.

TABLE II

THE DISTRIBUTION OF FERRIC IRON *BETWEEN* ETHYL ETHER AND AQUEOUS HYDROCHLORIC ACID SOLUTIONS

Initial HCl concn., moles per liter	Volume after shaking, ml. Ether layer	Volume after shaking, ml. Water layer	Iron found, mg. Ether layer	Iron found, mg. Water layer	% extracted	Distribution ratio $(Fe_{ether})/(Fe_{water})$
0.0	23.3	26.5	Trace	250	0.0	0.0
2.0	23.2	26.7	2.4	248	.96	.011
3.0	22.9	26.8	44.5	205	17.8	.25
4.0	22.7	26.7	204	46.4	81.5	5.18
5.25	21.2	28.0	246	4.4	98.2	74
6.2	19.6	29.4	247	2.6	99.0	143
7.0	17.3	31.7	244	5.5	97.8	81
7.1	17.1	31.8	244	5.9	97.6	72
8.0	11.8	36.6	218	32.4	87.0	20.9
8.6[a]	8.0	40.4	169	80.6	67.7	10.6
9.3[a]	5.3	43.2	35.0	215	14.0	1.33

[a] Separate ether phase metastable.

Values for the phase volumes and extraction percentages with ethyl ether at acid concentrations of 8.6 and 9.3 formal are recorded in Table II. In subsequent experiments it was found that at these concentrations the ether phase very slowly but completely dissolves in the other phase on continued shaking. The values given for these concentrations represent, therefore, extraction under metastable conditions.

In Fig. 1 are plotted the extraction percentages given in Tables I and II.

In order to determine the suitability of the technical grade of isopropyl ether for this extraction, experiments similar to those previously described were made using commercial isopropyl ether. The results of these experiments are given in Table III.

TABLE III

THE DISTRIBUTION OF FERRIC IRON BETWEEN TECHNICAL ISOPROPYL ETHER AND AQUEOUS HYDROCHLORIC ACID SOLUTIONS

Initial HCl concn., moles per liter	Volume after shaking, ml. Ether layer	Water layer	Iron found, mg. Ether layer	Water layer	% extracted	Distribution ratio $(Fe_{ether})/(Fe_{water})$
6.0	24.7	25.0	244.0	7.76	96.9	31.8
8.0	23.5	26.1	251.5	0.52	99.8	540

Effect of Varying the Iron Concentration.—In order to determine the effect on the distribution of varying the iron concentration, a series of extractions were made with isopropyl ether in which the acid concentration was kept constant and the amount of iron was varied. In these experiments the solutions were kept at 25° during the extraction process. A hydrochloric acid concentration (5.0 formal) below that for optimum extraction was selected in order that more accurate values for the distribution ratio might be obtained. The results of these experiments are given in Table IV. The isopropyl ether used in obtaining the data presented in Table IV was found to be 0.03 *N* in peroxide.

Because it was seen from the data recorded in Table IV that the distribution varies with the total amount of iron, extractions were performed with one milligram of iron with both ethyl and isopropyl ethers. The results are given in Table V.

The Effects of Peroxide and Alcohol.—To determine the reducing effects of peroxide and alcohol, extractions were made with ethers containing known amounts of these impurities. A thirty-minute extraction of 250 mg. of ferric iron was performed with ethyl ether from hydrochloric

TABLE V

THE EXTRACTION OF ONE MILLIGRAM OF FERRIC IRON FROM AQUEOUS HYDROCHLORIC ACID SOLUTIONS BY ETHYL AND ISOPROPYL ETHERS

Ether used	Initial HCl concn., moles per liter	Volume after shaking, ml. Ether layer	Water layer	Iron found in water layer, mg.	% extracted
Ethyl	4.0	22.1	27.4	0.6	40
Ethyl	6.0	17.9	31.2	.2	80
Isopropyl	7.0	23.5	26.3	.1	90
Isopropyl	7.5	22.9	26.9	.04	96
Isopropyl	8.0	21.8	27.8	.04	96
Isopropyl	8.5	20.4	29.2	.1	90

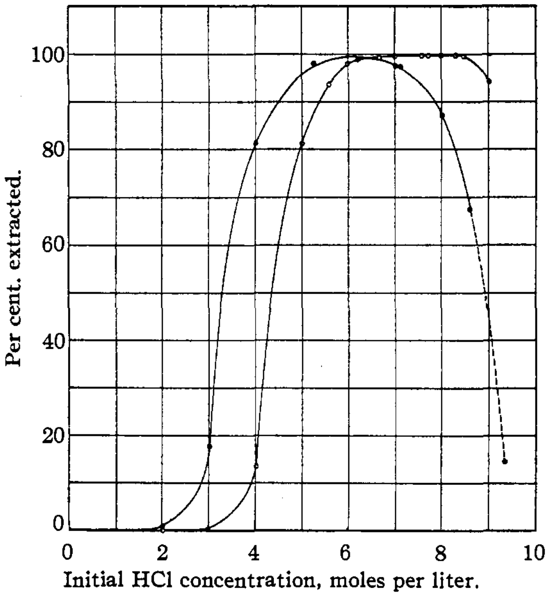

Fig. 1.—Extraction of ferric chloride from aqueous hydrochloric acid solutions by ethyl and isopropyl ethers: -●-, ethyl ether; -○-, isopropyl ether.

TABLE IV

THE DISTRIBUTION OF VARYING AMOUNTS OF FERRIC IRON BETWEEN ISOPROPYL ETHER AND 5.0 FORMAL HYDROCHLORIC ACID SOLUTIONS[a]

Initial HCl concn., moles per liter	Amount of iron taken, mg.	Volume after shaking, ml. Ether layer	Water layer	Iron found, mg. Ether layer	Water layer	% extracted	Distribution ratio $(Fe_{ether})/(Fe_{water})$
5.0	500	25.4	24.1	451	49	90.2	8.7
5.0	243	24.8	24.9	200	43	82.4	4.7
5.0	203	24.8	25.0	161	42	79.5	4.0
5.0	102	24.6	25.2	69	33	67.5	2.1
5.0	41	24.5	25.4	16	25	39	0.7
5.0	22	24.4	25.5	8	14	36	0.6

[a] It is to be emphasized that these data do not represent extraction under the most favorable conditions of acid concentration (see Table I).

acid 6.0 *f* and with isopropyl ether from hydrochloric acid 8.0 *f*. A small amount of ferrous iron was found in the aqueous layer after the ethyl ether extraction, less than 0.3 mg. when the ether was 0.003 *N* in peroxide and contained ethyl alcohol 4% by volume, and a like amount when no alcohol was present. With isopropyl ether, 0.1 *N* in peroxide, both with and without isopropyl alcohol present 4% by volume, no test for ferrous iron was obtained, or less than 0.0 mg. was formed.

The Behavior of Elements Other than Iron.— In order to determine the behavior of other elements with isopropyl ether, extraction experiments were performed with copper, cobalt, nickel, manganese, aluminum, chromium, zinc, molybdenum, vanadium, titanium, sulfur and phosphorus. These extractions were performed at an initial hydrochloric acid concentration of 7.75 formal. The results are given in Table VI.

TABLE VI

THE EXTRACTION OF ELEMENTS OTHER THAN IRON FROM 7.75 *f* HYDROCHLORIC ACID SOLUTIONS BY AN EQUAL VOLUME OF ISOPROPYL ETHER

Element taken	Amount, mg.	Amount found in ether, mg.	% extracted
Cu^{II}	500	0.0	0.0
Co^{II}	500	.0	.0
Mn^{II}	500	.00	.00
Ni^{II}	500	.00	.00
Al^{III}	500	.00	.00
Cr^{III}	500	<.03	<.01
Zn^{II}	500	.0	.0
V^{V}	250	54	22
V^{V}	48.5	21	43
Fe^{III}	500		
V^{IV}	258	<0.2	<0.08
V^{IV}	51.5	.2	.4
Fe^{III}	500		
Mo^{VI}	250	53	21
Mo^{VI}	125	56	45
Fe^{III}	250		
Ti^{IV}	125	0.00	0.00
S (as H_2SO_4)	62.5	.2	.3
Fe^{III}	250		
P (as H_3PO_4)	125	.1	.1
P (as H_3PO_4)	62.5	39	62
Fe^{III}	250		

Discussion

It is to be seen from Tables I and II and from Fig. 1 that with 250 mg. of iron the extraction with ethyl ether reaches an efficiency of 99% or slightly greater at an initial hydrochloric acid concentration of 5.5–6.5 formal. Above 6.5 formal the efficiency of extraction falls off quite rapidly. With isopropyl ether the efficiency of extraction reaches 99% at an initial acid concentration of 6.5 formal, rises above the curve for ethyl ether, and does not fall off appreciably until an acid concentration of 8.5 formal is reached. Under optimum conditions (acid 7.75–8.0 formal) the extraction is 99.9% complete. From the standpoints both of maximum efficiency of extraction and of range of acid concentration over which a favorable extraction is obtained, isopropyl ether is seen to be markedly superior to ethyl ether.

Technical isopropyl ether was found to give an extraction almost as efficient as that obtained with the redistilled ether.

Tables IV and V show that, with both ethers, the percentage extraction decreases with decrease in total iron. However, as for the extraction of large quantities, isopropyl ether is also found to be superior for the extraction of small quantities of iron, the extraction of one milligram under optimum conditions being 96% with isopropyl ether as compared with 80% with ethyl ether. In view of the completeness of extraction of quantities of iron as small as one milligram it can be said that with isopropyl ether a very satisfactory separation of iron is possible. Shaking with three successive portions of isopropyl ether should give a separation that is practically quantitative.

Under conditions of maximum extraction the volume changes of the ether and aqueous layers are considerably less with isopropyl than with ethyl ether. This is an advantage in analytical separations in which it is desired to know the approximate acid concentration after an extraction. An optimum final acid concentration corresponding to an initial concentration of 8.0 *f* is calculated to be 7.4 *f*. (The assumption is made that the formula of the extracted complex is approximately $HFeCl_4$; the concentration of hydrochloric acid in isopropyl ether saturated from aqueous 7.5 *f* solution has been determined by us to be 0.0246 mole per liter at 25°.)

The reduction of ferric iron in the ether layer does not occur even when isopropyl alcohol and peroxide are both present in moderate amounts. With ethyl ether, reduction is slight.

The data recorded in Table VI indicate that a very satisfactory separation of iron from copper, cobalt, manganese, nickel, aluminum, chromium, zinc, quadrivalent vanadium, titanium and sulfur is to be obtained. Large amounts of pentavalent vanadium are extracted; phosphoric acid and molybdenum pass into the ether layer with ferric iron.

Experiments are in progress to determine the formula of the iron compound in the ether phase, and to study the factors affecting the distribution between phases and the formation of two ether phases under certain conditions. Experiments are planned to determine the efficiency of isopropyl ether in the separation of other elements, such as gallium and thallium.

Summary

It has been shown that isopropyl ether offers marked advantages over ethyl ether for the extraction of ferric iron from aqueous hydrochloric acid solutions, giving a more efficient extraction over a wider range of acid concentrations than does ethyl ether. Data are given which show the effect of varying the hydrochloric acid concentration, the amount of ferric iron, the effect of the presence of alcohol and peroxide and the behavior of other elements commonly occurring with or alloyed with iron.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY INSTITUTE OF THE UNIVERSITY OF COPENHAGEN]

The Strength of Acids in Formamide

BY FRANK H. VERHOEK

As a part of the study of the behavior of acids and bases in various solvents being carried on in this Institute, it was undertaken to investigate the strengths of acids in formamide. This substance is particularly interesting in that it is reported by Walden[1] to have a dielectric constant greater than that of water. It is a colorless, odorless, hygroscopic liquid, denser and more viscous than water, freezing at +2.55°, and it is a good solvent for both inorganic and organic salts. The study is concerned with the determination of the strength constants of representative groups of acids in formamide, from measurements of the conductivity of acid-base mixtures in that solvent, and from measurements of the potential differences set up between a standard buffer solution and buffer solutions made up with the different acids.

Purification of the Solvent.—Formamide obtained commercially is frequently acid and contains ammonium formate. The latter is volatile enough so that it is not readily removed by distillation at reduced pressure; further, it is so largely solvolyzed that the ammonia is pumped off in the distillation, leaving formic acid, which then appears in the acid distillate. Any water present in the solvent during the distillation reacts with the formamide to form ammonium formate. Formamide reacts with strong bases and with phosphorus pentoxide. The method adopted finally for the purification was to add solid brom thymol blue directly to the formamide, and neutralize with sodium hydroxide, avoiding an excess. The neutral liquid is heated at 80–90° under an oil pump vacuum until distillation is about to begin, ammonia and some of the water formed by the neutralization being pumped off. During this time the formamide has turned acid again, by loss of ammonia both from the ammonium formate originally present and from that formed by reaction with the water from the neutralization. The neutralization with sodium hydroxide is repeated, and the liquid heated in a vacuum to incipient distillation. This time less water is formed by the neutralization, and consequently less acid from the reaction *water* → *ammonium formate* → *formic acid*. With a repetition of the process four or five times, even quite impure samples will remain neutral when distillation begins. The whole of the formamide is now distilled from the sodium formate by evaporation from the surface at 80–90° in a vacuum, neutralized again with sodium hydroxide and redistilled in the same fashion, collecting the last four-fifths. This material is neutral, melts at about 2.2°, and has a specific conductance of about 5×10^{-5}. The neutral distillate is now further purified by fractional crystallization in a water- and carbon dioxide-free atmosphere. From 400–500 cc. five or six fractions are removed, giving a final 100 cc. with a specific conductance of 1 or 2×10^{-6}. The fractions removed, together with the first portion from the distillation, are returned again for treatment with sodium hydroxide, distillation, and recrystallization.

Residues were recovered by the same method as that for the purification of the original substance.

The pure material is not stable; the conductance increases by a factor of eight or ten in ten days or two weeks. It was found, however, that if a stream of air, purified by passing through a train containing soda lime, calcium chloride, phosphorus pentoxide and cotton, was bubbled rapidly through the liquid, the conductance would remain low for a longer period. With certain samples a decrease of conductance occurred at first on bubbling air through the formamide, followed by an increase. The solvent was considered still sufficiently pure for use when the specific conductance was less than 3.5×10^{-6}; the large majority of the experiments, however, were made on material having

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[1] Walden, *Z. physik. Chem.*, **46**, 175 (1903).