sulting charcoal diminishes steadily, indicating progressive over-activation, *i. e.*, removal of activation centers on which the dye is presumably adsorbed. Simultaneously, there is an increase in the adsorption of caramel.

This difference in the types of adsorption of methylene blue and caramel on charcoal is also found in the charcoals prepared using neutral, acidulated and alkaline calcium chloride solutions for predigestion (Expts. 20, 21 and 22). No significant difference is observed in the adsorption of caramel but the adsorption of methylene blue is considerably higher when acidulated calcium chloride is employed. The above observations tend to indicate the development of different types of active centers during activation.

The authors wish to thank Dr. U. P. Basu, D.Sc., P.R.S., F.N.I., for his interest in the work.

Summary

Charcoal has been prepared from groundnut hull and coconut shell using zinc chloride, calcium chloride, sulfuric acid and caustic soda for predigestion of the raw material and subsequent carbonization at 600–800°, and studies have been made of the adsorptive powers of the resultant charcoals for methylene blue, caramel, iodine and acetic acid and of their ash contents and bulk density.

Predigestion with acidulated zinc chloride generally produces the most active charcoals. Increase in the proportion of zinc chloride is accompanied with lowering of ash content and of bulk density and increase of the absorption of methylene blue, iodine and caramel, but with groundnut shell charcoal there is a reduction in the adsorption of methylene blue.

Predigestion with calcium chloride, sulfuric acid and caustic soda generally fail to produce charcoals of high adsorptive power with the exception that charcoals prepared using calcium chloride show fairly high adsorption of caramel.

Zinc chloride is not effective as an activating agent unless it is present in the raw material during carbonization.

The mechanism of activation has been discussed in relation to the solvent power of the activating agent on the vegetable matter used for the preparation of charcoal.

BENGAL IMMUNITY RESEARCH LABORATORY
CALCUTTA, INDIA
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[CONTRIBUTION FROM THE UNIVERSITY OF MANITOBA, WINNIPEG, CANADA]

The System Iron–Tin: Liquidus Only

BY A. N. CAMPBELL, J. H. WOOD AND G. B. SKINNER

This work originated in an observation by the Consolidated Mining and Smelting Company of Canada, Trail, B. C., that the iron content of the tin metal recovered from their Sullivan ore was always much lower than the accepted value for the amount of iron in the iron–tin eutectic. This metal is filtered at about 353°; in experimental work it has been filtered at as low as 250°, but in no case did the filtrate contain more than 0.01% iron. Interpolation of existing data indicates a much higher iron content than this in the eutectic, although, since there has been no direct determination, it is difficult to quote a figure. Difference of opinion also exists as to whether the equilibrium diagram does or does not exhibit a miscibility gap in the liquid state. Unquestionably there is a long horizontal, or almost horizontal, portion, on the liquidus curve, which indicates the existence of such a gap, but the observation is only conclusive if the apparent horizontal portion is actually completely horizontal, *i. e.*, if there is no fall of temperature whatever over this region of concentration; a slight fall of temperature would defeat this argument. We therefore decided to investigate the liquidus curve over a range of concentration from pure tin to a point beyond the hypothetical gap, say 50% iron. The last portion of the liquidus, up to pure iron, presents little interest and is well known from the results of thermal analysis. We have succeeded in determining the iron content of the eutectic and in showing, beyond all reasonable doubt, that a miscibility gap exists.

Previous Work

It is only necessary to discuss the existing literature in so far as it refers to the liquidus. The most important literature references are given in Jänecke's "Kurzgefasstes Handbuch aller Legierungen,"[1] where, however, the liquidus is very incorrectly drawn. The only figures actually determining the form of the liquidus, and based on thermal analysis, are those of Isaac and Tammann.[2]

Our problem had three parts: the determination of the eutectic composition and temperature, the investigation of the liquidus curve from the eutectic temperature to the temperature of the gap, and the investigation of the limits of the gap.

The eutectic temperature and composition were determined by adding powdered iron to tin and observing the depression in the freezing point of tin.

Thermal analysis lacks sensitivity, at least in its crude form, as a method of determining a liquidus when the slope is steep. As a method of

(1) Spamer, Leipzig, 1937, pp. 217 and 220.

(2) Isaac and Tammann, *Z. anorg. Chem.*, 53, 281 (1907).

outlining the limits of the miscibility gap it apparently fails entirely, presumably because the heat of solution of the liquid metals is small. The method adopted by us was an isothermal one. Molten tin was kept at constant temperature in contact with excess of iron until equilibrium was attained, the melt then quenched and the top portion analyzed for iron. The obvious criticism that equilibrium, in this case saturation, should be approached from both sides could not be met here. Melts saturated at higher temperatures and kept for several hours and even days at a lower temperature before quenching invariably gave iron concentrations which were much too high; in other words, they reproduced fairly exactly the solubility of the higher temperature. This seems to be due to the fact that the solid phase separating has a density not greatly different from that of the mother liquor, or perhaps the phase is colloidally dispersed, but at all events, analysis shows but little gravitational segregation. The only resource, therefore, was to raise the temperature of the mixture from room temperature to the desired equilibrium temperature and keep it there a sufficient length of time to ensure saturation. This was ensured, as far as possible, by removing samples at successive intervals of time and analyzing. No attempt was made to filter; at these high temperatures diffusion rapidly homogenizes the melt. After quenching, drillings taken from various parts of the upper portion and well mixed will be representative of the composition of the liquidus although, of course, the structure will be quite different. Examination of vertical cross sections of the completely solidified melt showed that the iron, originally placed at the bottom of the crucible, had been completely converted to the equilibrium solid phase and had remained at the bottom of the crucible.

Occasionally samples were withdrawn from the melt at furnace temperatures, using alundum pipes. As, however, the melt solidifies in the pipe, no one portion of it represents the original composition of the liquidus, unless the whole of the test sample is analyzed. In any case, the operation is difficult to perform. This method was, however, occasionally used when investigating the miscibility gap, samples being withdrawn from both layers, in order to demonstrate the existence of two layers beyond the possibility of doubt.

For defining the limits of the gap the method of Alexejeff was found most suitable. This is the well known method in which mixtures of known composition are heated until they become homogeneous. As used by us, mixtures of known composition were heated (in glass to prevent oxidation) until equilibrium was attained, quenched and examined microscopically for heterogeneity.

Experimental

Purity of Materials.—For the study of the eutectic composition, spectroscopically pure tin, obtained from the Vulcan Detinning Works, Sewaren, N. J., was used. An analysis was supplied, but it is sufficient to say that all impurities were present in only spectroscopic amounts. For the general study of the liquidus "Commercial" tin from the same source was used. The analysis gave:

Fe	Pb	Sb	Cu	Sn
0.0020%	Trace	0.0023%	Trace	99.9957%

For the eutectic, Kahlbaum reduced iron was used. It had a total iron content of 95.4%. Direct determination of free iron by the method of Christensen[3] gave 90.4% metallic iron. For the study of the low temperature region of the liquidus, "Iron Wire for Standardization" was used. The Merck wire (fine wire in spools) was stated to contain at least 99.8% iron and the Cenco wire (thin 3″ rods) 99.7% iron. For the investigation of the miscibility gap, Wemco research iron, from the Westinghouse Electric Corporation, was used. The analysis accompanying the material showed it to be very pure, the carbon content being 0.005% and the iron content 99.95%. These different types of iron were used because of the effect of fineness of division on the rate of attainment of saturation. The purest iron, *viz.*, the Wemco product, could not be used for the low temperature work because it was supplied in relatively massive rods; the Merck iron, on the other hand, being in the form of fine wire, dissolved readily even at the lowest temperatures. It was essential to the success of our method that saturation should be obtained.

Methods of Analysis.—For concentration of iron less than one per cent., the iron was determined colorimetrically. For concentrations greater than one per cent., we used the method of Kolthoff and Sandell,[4] suitably modified.

Measurement of Temperature.—A Beckmann thermometer was used for the eutectic investigation, but for all other work a platinum-platinum rhodium (10%) was used. The thermocouple was calibrated in the usual way, the cold junction being thermostatically controlled at 32°. Using a Leeds and Northrup type K-1 potentiometer, temperatures could be read with an accuracy of ±1°.

Determination of Eutectic Temperature.—Attempts were made to determine this by melting spectrographically pure tin in a Pyrex container, in an atmosphere of pure nitrogen, and using a Beckmann thermometer to determine the freezing temperature. It was found to be impossible, however, to obtain a consistent reading of the thermometer in repeated trials. Over the period of a week of repeated trials there was a steady drift of the thermometer readings. Finally, after very approximate constancy had been obtained, 4 g. of Kahlbaum reduced iron was added to saturate the tin, the whole kept at 250° for several hours and the freezing temperature again determined. The same uncertainty in the results was observed. The most that can be said is that the eutectic temperature is not lower than the freezing point of pure tin by more than 0.1°.

Isothermal Investigation.—Resistance furnaces of the usual type, nichrome wound for the lower temperatures and platinum wound for the higher, were used. We are indebted to Mr. B. C. Lutz of the Physics Department of this University for the construction of a photoelectric control and circuit which gave constancy of temperature over the complete range of our work, with a variation of ±3°. The details of this circuit have been published elsewhere.[5]

Procedure.—For the low temperature work, up to 600°, graphite crucibles lined with alundum were used. The alundum lining effectually prevented contact of the metal with carbon. Iron was added in the form of fine wire and molten tin poured on top. The metal was then covered with a layer of finely powdered magnesia. The thermocouple case was inserted directly in the melt, the furnace brought to the desired temperature and kept, under control, for two days or longer; for example, at 270°, the

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[3] Christensen, *Z. anal. Chem.*, **44**, 535 (1905).

[4] "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., revised edition, 1946, p. 494.

[5] Lutz and Wood, *Can. J. Research*, **26A**, 145 (1948).

lowest temperature at which it was found possible to work in this way, the melt was maintained at constant temperature for three and one-half weeks. At the end of the heating period, the crucible was removed from the furnace and quenched, an operation which required about three minutes before the melt was solid. Since the gravitational fall of the separated solid phase takes place very slowly, there was no need for extremely rapid quenching. The solidified content of the crucible was cut down the center and drillings taken in a horizontal row as near the top as possible. Separate drillings were also taken from another row just below the first.

For temperatures above 600°, alundum crucibles were used. At these higher temperatures, it was found that the top layer contained less iron than the lower and this was found to be due to the preferential oxidation of the iron. To prevent, if possible, the increasing oxidation an atmosphere of purified nitrogen was resorted to without, however, obtaining the desired result. The problem was finally solved by sealing in Pyrex glass and supporting the capsule thus formed in packed alundum. It is surprising that this method is good up to 1300°, despite the fact that at this temperature the glass must be quite fluid. The mixtures used in investigating the miscibility gap were protected in this way and the solidified melts were always entirely free from any trace of oxidation. The method has the disadvantage that the thermocouple cannot be inserted in the melt, but this was of no importance here, since the furnace was kept at constant temperature. Another disadvantage is that a sample cannot be withdrawn for analysis while the alloy is in the furnace.

For work in the region of the gap, an Ajax–Northrup induction furnace was used to homogenize the melt before placing thermostatic control in the resistance furnace. The gravitational separation of the two liquid layers takes place quite readily, and for the application of the Alexejeff method it was necessary to be sure that all the iron added had entered the liquid state. Samples were sometimes withdrawn by suction at the furnace temperature, and for this purpose, of course, the alloy had to be uncovered, through a sillimannite or alundum tube and, in one case, samples were withdrawn from both layers. More usually, however, the two layer melt, scaled in glass, was quenched by removing from the furnace and inserting the whole crucible in a closely fitting copper mold, surrounded by cold water. Solidification required two or three minutes. In addition to chemical analysis, mixtures lying within the gap were polished and etched with alcoholic picric acid, and photomicrographs taken. For this latter service we are indebted to the advice and assistance of Professor George Russell of the Geology Department of this University. One of these photomicrographs is shown as Fig. 1. The relative hardnesses were also determined in a vertical line across the surface of separation of the solidified alloy, using a Rockwell hardness tester. The hardness changed abruptly on crossing the line of demarcation, becoming much greater for the lower (iron-rich) layer. In applying the Alexejeff method, the following procedure was adopted. Known weights of iron and tin were melted in the induction furnace, then maintained at constant temperature in the resistance furnace, to allow for the separation of two layers, if temperature and composition were such as to permit of the formation of two layers. The alloy was then quenched and examined microscopically for the presence of two liquids. In those mixtures near the iron-rich side of the gap, the division between the layers was easily seen by the naked eye, but with samples near the tin-rich end only microscopic examination could detect droplets of the bottom layer suspended in the top. Mixtures of such compositions were chosen that the sides of the gap were bracketed, one mixture showing two layers and the other of slightly different composition only one, at the same temperature. The accuracy of determination was about 0.5%.

Results

The equilibrium concentrations in the liquid phase are given in Table I.

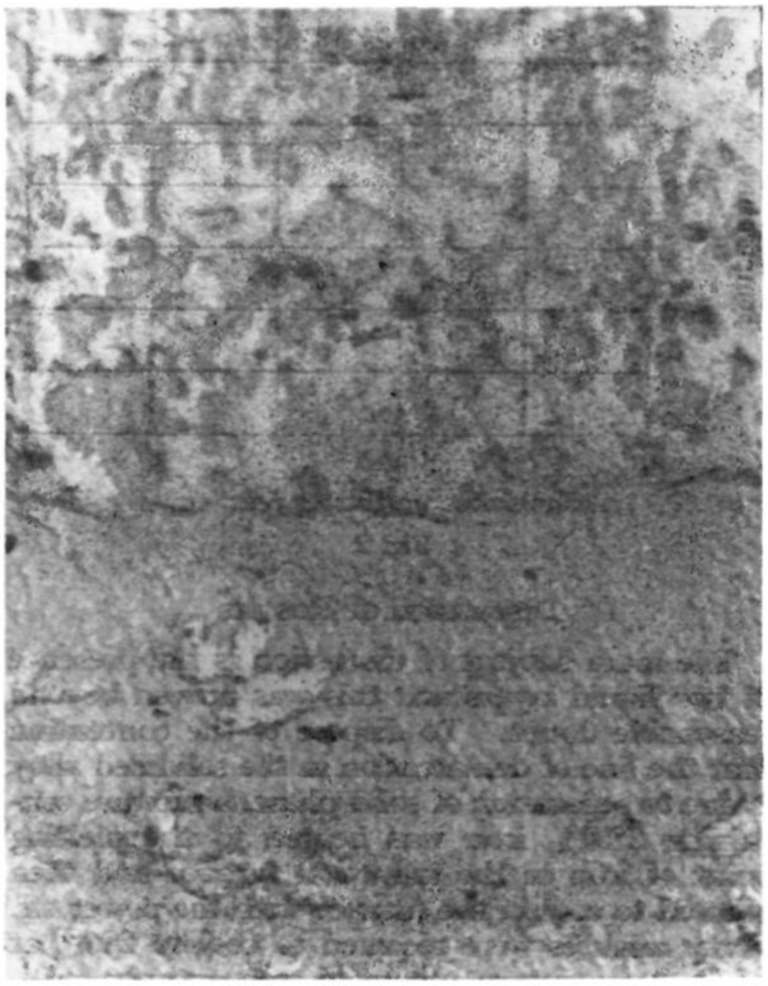

Fig. 1.

TABLE I

IRON CONTENT OF SOLUTIONS IN EQUILIBRIUM WITH SOLID PHASE

Temp., °C.	Iron, wt. %	Temp., °C.	Iron, wt. %
270	0.0047	773	1.24
329	.0073	775	1.31
382	.023	787	1.36
389	.029	795	1.56
394	.022	801	1.61
451	.046	826	1.72
454	.043	846	2.02
483	.070	857	2.11
502	.087	895	2.73
548	.141	916	2.88
576	.169	938	3.08
594	.222	962	3.60
606	.221	1008	4.31
637	.322	1045	5.19
654	.32	1065	6.27
700	.75	1125	11.10
746	.96	1128	12.00

Eutectic composition by extrapolation 0.003% ± 0.001.

The above results are plotted in Fig. 2 from which the solid diagram has been omitted entirely.

TABLE II

BOUNDARIES OF THE MISCIBILITY GAP

Temp., °C.	Composition in wt. % iron Iron-rich layer	Tin-rich layer	Mean
1150	40.1	17.4	28.8
1200	40.8	17.0	28.9
1300	41.2	16.8	29.0

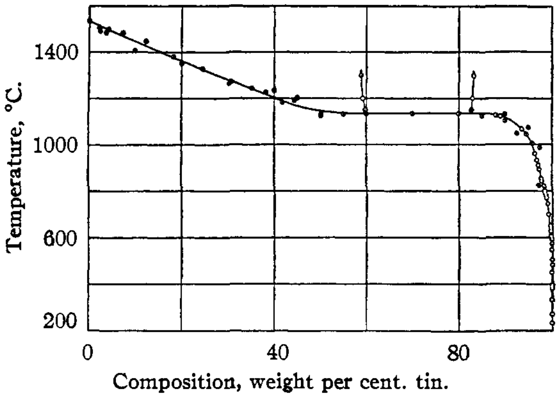

Fig. 2.

Discussion of Results

The main subject of discussion is the presence of two liquid layers and this was proved beyond reasonable doubt. To dispose of the contention that the line of demarcation in the solidified alloy is due to separation of solid phase, a mixture containing 28.0% iron was heated to the melting point of iron in the induction furnace and then allowed to cool in the furnace with the power off. Forty minutes were required to cool to 200°, at which temperature the mass was entirely solid. These conditions were very favorable to the gravitational separation of solid phase. Drillings were taken at four points spaced equally from top to bottom of the solidified mass. From top to bottom the results in per cent. of iron were 23.5, 27.2, 28.7 and 31.5. Hence gravitational separation is entirely inadequate to account for the appearance of two layers. The polished and etched sample exhibited no discontinuity to the eye. This and similar experiments show that the two layers observed when an alloy of appropriate composition is kept at constant temperature for a sufficient length of time are not due to the rapid settling out of a solid, as Wever and Reinecken suggested.[6] Figure 1 is a photomicrograph of an alloy containing 27.6% iron, maintained for two days at 1166° and quenched (magnification = 100 diameters.) The photograph shows part of the dividing line between the layers. Each of the layers has a typical structure. The upper has a light colored continuous component which is almost pure tin, with a small amount of the various intermetallic compounds, and a dark component scattered through it which is a solid solution, shown by Wever and Reinecken to contain about 82% iron. In the lower layer the solid solution appears to be continuous but in both layers the solid solution shows up too much on account of its hardness.

The Rockwell hardness test was carried out on a sample containing 29.8% iron and quenched from 1176°. This alloy was cut down the center, filed flat, and a series of hardness readings taken in a line from top to bottom. The readings on the "B" Rockwell scale were: 22, 19, 21, 45 (on surface of separation), 99, 100, 100, 100. This test shows that two nearly homogeneous layers are present, with a sharp difference between them.

Attempts to determine the compositions of the layers by withdrawing portions from the molten alloys were not entirely successful. Between 1140 and 1200°, values for the upper layer ranged from 19.0 to 31.2% iron and for the bottom layer from 30.0 to 48.8% iron. This, however, is sufficient to show that the melts were richer in iron at the bottom than the top and is therefore direct experimental evidence for the existence of two layers, since the system was entirely liquid, no solid phase existing at this temperature and composition. Microscopic examination of the two layers showed that there were always droplets of the bottom layer suspended in the upper, and this accounts for the erratic behavior of the analyses of the upper layer. It is not easy to see why the bottom layer analyses varied, unless this was due to segregation in the tube used for sampling.

The figures of Table II were obtained by examination of nineteen alloys by the method of Alexejeff. The values can be considered accurate to not more than ±0.5% since a certain amount of each layer had to be present before it could be recognized. Alloys containing less than 20% iron appeared homogeneous to the eye, but the limits could be established by microscopic examination for drops of the bottom layer. It would have been desirable to have traced the gap to higher temperatures, but this was impossible with the equipment available. A sample containing 29.0% iron was heated in the induction furnace to a temperature above the melting point of iron, probably about 1600°. On examination after quenching, large droplets of one layer in another were observed. Hence two liquid layers are present at a high temperature, probably about 1600°: the uncertainty is due to the inaccuracy of the optical pyrometer when examining a shining metallic surface protected by glass.

The figures in Table II, together with the last two points in Table I, show that the base of the gap (the horizontal on the liquidus) lies at a temperature higher than 1128° and lower than 1150°. Hence Edwards and Preece were in error in placing the horizontal at 1110°. Of the other workers, Wever and Reinecken[6] appear to have had the most refined technique and the purest materials. The average of their second set of thermal analyses —1134—is probably better than any of their first set, and we take this to be the most probable value for the temperature of the horizontal.

Previous workers have all assumed that the high iron liquidus met the horizontal about 1140° and at an iron content of 50%. Our work shows that the curve terminates about 1134° and certainly at 40.0% iron. In Fig. 2 are plotted some of the data of Isaac and Tammann, Wever and

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(6) Wever and Reinecken, *Z. anorg. allgem. Chem.*, **151**, 349 (1926).

Reinecken, and ourselves. In previous diagrams the horizontal was drawn extending to 50% iron because the liquidus is extremely flat in this region and it was assumed to be quite flat. Knowing from our work the actual composition of the iron-rich layer, it is apparent that the horizontal extends to only 40% iron and that from 40 to 50% iron there is an ascent in temperature. The curve as drawn by us does no great violence to the experimental points of other workers. We have drawn the limits of the two liquid region as if the mutual solubility decreased with rising temperature, since this is what our figures indicate. Since, however, the sides of the gap are certainly very straight and our accuracy not much better than one per cent., it is easily possible that the sides slope in the other direction, that is, that the (real or hypothetical) critical solution temperature is approached by raising, not lowering, the temperature.

Acknowledgment.—Two of us (J. H. W. and G. B. S.) are indebted to the Consolidated Mining and Smelting Company of Trail, B. C., for Fellowships which enabled them to pursue this work, and for funds for the purchase of apparatus and chemicals.

Summary

1. The eutectic temperature and composition of the system iron–tin have been determined.

2. The equilibrium curve for tin–iron solid phase in contact with tin–iron liquid phase, the liquidus curve, has been determined from the melting point of tin, 232°, up to 1134°, the temperature of the miscibility gap.

3. The existence of a miscibility gap has been proved and its limits determined from 1134 to 1300°.

WINNIPEG, MAN. RECEIVED NOVEMBER 29, 1948

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE CO.]

Colorless Crystalline Perchloric and Hexafluorophosphoric Acid Salts of Sterols. The Color Formation between Sterols and Perchloric Acid

BY WILLY LANGE, ROBERT G. FOLZENLOGEN AND DON G. KOLP

Introduction.—The general object of this paper is to show that common sterols form colorless crystalline salts when properly treated with stoichiometric quantities of perchloric or hexafluorophosphoric acids. In the presence of excess acid, the colorless salts are transformed to already well recognized halochromic compounds.

Formation of Colorless Sterolium Salts.—It has been found that colorless, well formed crystals of Sterol·$HClO_4$ are precipitated when sterols containing the 3(β)-hydroxy-Δ^5-ene groups are dissolved in chloroform and then treated with stoichiometric quantities of perchloric acid containing more than 55% $HClO_4$. The sterols capable of yielding colorless salts include cholesterol, stigmasterol, beta-sitosterol and ergosterol. Since the sterolium salts hydrolyze instantaneously on contact with excess water, it is possible to recover quantitatively the unchanged sterol by allowing hydrolysis to proceed in the presence of a water-insoluble solvent for the sterol.

The precipitation of the perchlorate may be carried out with anhydrous sterol as well as with the compound containing water of crystallization. Salt precipitation and hydrolysis may be written as an equilibrium reaction

$$\text{Sterol}\cdot H_2O + [H_3O]^+ + ClO_4^- \rightleftharpoons [\text{Sterol}\cdot H]^+ClO_4^- + 2H_2O.$$

In the absence of excess acid the crystals, which are hexagon-shaped microscopic plates, remain colorless for a day or so when suspended in the chloroform solution or even longer when stored in dry form in a desiccator. They appear to be stable against shock and friction, but burn fiercely when heated on a spatula. In the reaction between sterol and perchloric acid, chloroform may be replaced with other oxygen- and nitrogen-free solvents, such as carbon tetrachloride, bromoform, ethylene chloride, trichloropropane, 1,4-dichlorobutane, Skellysolve B, benzene, toluene, and monochlorobenzene.

Hexafluorophosphoric acid (60–70% HPF_6) is the only other mineral acid found which reacts in the same manner as perchloric acid. Its use is advantageous in certain respects because its salts are non-inflammable.

Alteration of one of the two essential groups in common sterols results in failure to observe the formation of crystallized salts, while color formation takes place, *i. e.*, a halochromic ion is formed when a conjugated double bond system could be formed under the dehydrating influence of the strong acid. The introduction of a second (conjugated) double bond into ring B makes the sterol molecule very sensitive toward an excess of acid but does not change its ability to form a colorless crystalline precipitate with perchloric acid. The precipitability is lost, however, when the iso-octyl chain in 17-position is replaced with a ketonic oxygen atom.

Information on crystallized salts or addition compounds of sterols with strong mineral acids from which the sterols may be recovered un-