

investigators do not find the effect. This can, however, be due to inadequate annealing.

An investigation of the resistance of these alloys at higher temperatures might then be expected to show the same characteristics as the investigation by Borelius, Johansson and Linde⁵ on Cu-Au and Cu-Pd, *viz.*, increase in resistance above the transition point but with a considerable hysteresis.

Figure 4 gives a tentative phase diagram of the system. Below is plotted the entropy and heat of transition (= difference between curves in Figs. 2 and 3 to the right). The left low entropy phase reaches very near the silver axis, but one might believe that the very lowest percentages are randomly distributed.

My thanks are due to Professor E. D. Eastman for suggesting to me the investigation of electrode potentials of alloys.

Summary

The potential of the cell Ag/AgCl, KCl/(Ag, Au) and its temperature coefficient have been measured between 400 and 625° for seventeen compositions of the alloy electrode and between 840 and 940° for two compositions.

At gold contents smaller than 18 atom per cent. there is a discontinuity and change of sign of the temperature coefficient at 800°.

The activity coefficient of silver has been plotted.

The temperature coefficient gives the difference in partial molal entropy of silver in the alloy from that of pure silver. By integration the total mixing entropy is found.

There exists a phase of low entropy below 800° from 0 to 18 atom per cent. of gold. Another less marked seems to exist above 50%.

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THE DENSITY AND SURFACE TENSION OF THE ISOMERS OF 2-PENTENE AND 2-METHYL-2-BUTENE

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RECEIVED MAY 27, 1931

PUBLISHED OCTOBER 5, 1931

Much interest has been aroused by the discovery of the two isomers of 2-pentene.¹ The exact nature of these isomers is still a matter of some dispute. With the object of obtaining further data that might be used in the solution of the problem Messrs. Clark and Hallonquist of these Laboratories prepared the two isomers and investigated some of their chemical and physical properties, the results of which are recorded in the *Proceedings of the Royal Society of Canada*.²

¹ Lucas and Moyses, *THIS JOURNAL*, **47**, 1459 (1925); Sherrill, Otto and Pickett, *ibid.*, **51**, 3023 (1929); Kharasch and Darkis, *Chemical Reviews*, **5**, 371 (1928).

² Clark and Hallonquist, *Proc. Roy. Soc. Canada*, **XXIV**, 115 (1930).

The idea of the parachor developed by Sugden and his co-workers has yielded us much information concerning the structure of chemical compounds. Consequently it was thought that a knowledge of the parachor of the two compounds concerned might be of value when compared with that of some other structural isomer of pentene. To make possible these measurements, Mr. Hallonquist kindly gave the writer 10 cc. of each of the isomers of 2-pentene which he had synthesized with a great deal of care. As a sample of Kahlbaum's trimethylethylene-2-methyl-2-butene was available it was used as a standard of comparison. Two values for the densities and surface tensions at different temperatures are given in the "International Critical Tables" but these were considered to be insufficient for an accurate calculation of the parachor. Therefore series of density and surface tension measurements over a range of temperature of 150° at 10° intervals were made on this hydrocarbon and the two isomers.

Purity of Materials.—The method of preparation of the two isomers of 2-pentene has been fully described by Mr. Hallonquist in the Journal previously mentioned.² The purity of the two compounds was indicated by their refractive indices, which were nearly the same as the values given by Sherrill and co-workers³ as shown below.

REFRACTIVE INDICES OF THE 2-PENTENES

| | Sherrill, Baldwin, Haas | Hallonquist |
|--|-------------------------|-------------|
| 2-Pentene from 2-bromopentane $n_D^{20} =$ | 1.37849 | 1.37845 |
| 2-Pentene from 3-bromopentane $n_D^{20} =$ | 1.37965 | 1.3796 |

The hydrocarbon obtained from 2-bromopentane (stable isomer) was found by Hallonquist to have a freezing point of -149° . This is the same as that found by the writer and Mr. A. F. Gill for a hydrocarbon prepared by the latter in the following manner.

Primary propyl alcohol purchased from Kahlbaum was converted to propylaldehyde by passing over copper turnings. Next the aldehyde was condensed with ethylmagnesium bromide and the product treated with water, which yielded the alcohol $(\text{CH}_3\text{CH}_2)_2 > \text{CHOH}$. This alcohol was transformed into the iodide by means of phosphorus triiodide. The hydrocarbon 2-pentene was then obtained by refluxing the iodide with a strong caustic potash solution. The freezing point of this hydrocarbon when determined with a standard resistance thermometer was found to be -149.3 ± 0.5 . The trimethylethylene, as stated before, was obtained from Kahlbaum. It was repeatedly distilled over sodium, shortly before use, until it no longer produced a red coloration when in contact with the hydrocarbon. It was found that coloration occurred whenever the trimethylethylene had been exposed to the air for more than a day, indicating probably the formation of peroxides. The freezing point of this hydrocarbon had been found by the writer and A. F. Gill to be -146.1 ± 0.5 .⁴ A density determination at 20° gave the value 0.6568 corrected to vacuum.

Density and Surface Tension Determinations.—Owing to the small amount available of the "electromeric" pentenes, the densities were de-

³ Sherrill, Baldwin and Haas, *THIS JOURNAL*, **51**, 3034 (1929).

⁴ Unpublished research on the solubilities of amylenes in sulfur dioxide.

terminated over the entire temperature range by means of three dilatometers. The volume of the bulbs and the diameter of the bore in the stems had previously been accurately calibrated with the help of mercury at 20°. At all other temperatures corrections were made allowing for the expansion of the dilatometers. As only about 2 cc. of the normal isomers remained for the density determinations, the values at 20°, recorded by Sherrill, Baldwin and Haas, were taken as correct and all others calculated therefrom by means of the known volume changes.⁵

The density of trimethylethylene at 20° was measured in a pycnometer having a volume of about 20 cc.

The differential rise method was chosen as the most suitable for the surface tension measurements.⁶

Two tubes were used, designated A and B. For the sake of accurate comparison of their surface tensions, the differential rise of the two isomers was observed in the same tube (B). Trimethylethylene was put in the tube (A). Carefully dried benzene which had been crystallized four times served as a standard liquid for determination of the constants for the two tubes. The values of the constants, the radii of the capillary tubes and the necessary corrections of the observed rise are given in the following table.

DIMENSIONS OF SURFACE TENSION TUBES

| | A | B |
|------------------------------------|---------|---------|
| Radius of large capillary, cm. | 0.8579 | 0.9630 |
| Radius of small capillary, cm. | 0.01256 | 0.01106 |
| Correction for rise, cm. | 0.028 | 0.028 |
| Value of constants over range used | 7.427 | 6.211 |

The Density and Surface Tension.—The density and surface tension observations were made simultaneously in the same bath. The bath itself was a large Dewar tube with an internal diameter of 9.5 cm. and a depth of 30 cm. Its optical properties were tested by measuring the length of an object immersed in the liquid of the bath and in the air at the same temperature. It was found that the error introduced in reading through the glass was not greater than the accuracy of reading on the cathetometer, *viz.*, 0.05 mm. Above 10° water was the liquid medium of the bath and below that a mixture of alcohol and ether. A Cenco turbine stirrer was used and stopped whenever the readings were taken. The temperature was controlled by hand and below room temperatures was maintained constant to within 0.1° by the addition of carbon dioxide snow, above by means of an immersion heater. A Leeds and Northrup resistance thermometer standardized at the Bureau of Standards was used throughout.

⁵ Ref. 3, p. 3038.

⁶ Richards, Speyers and Carver, *THIS JOURNAL*, **46**, 1196 (1924).

The density and surface tension tubes were all filled in the same manner. After having been thoroughly dried over fused calcium chloride, the hydrocarbons were placed in a reservoir and frozen by immersion in liquid air. This tube was then sealed to an apparatus which could be evacuated by a mercury diffusion pump and to which had already been sealed the desired density and surface tension tubes. The apparatus was next evacuated while the hydrocarbon was still in a frozen state. After the pump had been shut off, the hydrocarbon was allowed to liquefy. This procedure was repeated several times to insure the removal of any air which might have been absorbed by the pentenes. By cooling the measuring tubes, the desired amounts of the hydrocarbons could be condensed readily, whereupon the tubes were sealed off and removed from the rest of the apparatus.

The surface tension measurements were always made with a falling meniscus and continued until equilibrium was reached. This in the case of all three isomers was reached very quickly, which was otherwise with nicotine or sulfur dioxide.

The density determinations can be taken to be correct to 1 part in 1000, and the surface tensions to 1 part in 250, except for the values at -70° . Here the mist condensing on the bath was so great that the readings could only be made with great difficulty.

As no vapor measurements on these particular hydrocarbons were found in the literature, it was necessary to calculate them. By using the figure 314 joules for the latent heat of amylene, as given in the "International Critical Tables" and as the boiling point of each was accurately known, it was possible to obtain approximate values for the vapor pressure at various temperatures by means of the integrated form of the Clausius-Clapeyron equation. Thus, knowing the vapor pressure and assuming the molecular weight of 70.11, it was a simple matter to calculate the vapor densities.

The following tables contain the density surface tension and other derived values associated with surface tension measurements. The temperature coefficients of surface tension and molecular surface energy were taken from a smoothed curve.

Discussion of Results

It is at once obvious that there is a considerable difference in the physical properties of the three hydrocarbons. Figure 1 shows the densities plotted against temperature. The density of trimethylethylene when taken from curve 1 at 13° is 0.6700, which is slightly higher than the value given in the "International Critical Tables," 0.668. At the boiling point the density agrees very well with that found by Schiff.⁷ Schiff also measured the sur-

⁷ Schiff, *Ann.*, **223**, 47 (1885).

face tension of this hydrocarbon by the differential rise method, obtaining the value 15.41, against 15.14 calculated from the curve given in Fig. 2.

TABLE I
PHYSICAL PROPERTIES OF THE HYDROCARBON 2-METHYL-2-BUTENE (TRIMETHYL-ETHYLENE)

| Temp., °C. | Density | Density of liquid minus density of vapor | Corrected height in cm. | Surface tension, dynes per cm. | Molecular surface energy ergs per sq. cm. | Total surface energy in ergs per sq. cm. | Para- chor | Eötvös con- stant |
|---------------|---------|---|----------------------------------|---|--|---|---------------|-------------------------|
| -70 | 0.7384 | 0.7384 | 5.15 | 28.90 | 601.3 | 52.24 | 220 | |
| -60 | .7302 | .7302 | 4.99 | 27.06 | 567.2 | 52.62 | 218.9 | |
| -50 | .7216 | .7216 | 4.88 | 25.94 | 548.1 | 52.70 | 219.2 | |
| -40 | .7132 | .7132 | 4.67 | 24.73 | 526.6 | 52.69 | 219.1 | 2.20 |
| -30 | .7034 | .7038 | 4.49 | 23.57 | 506.5 | 52.73 | 219.4 | |
| -20 | .6948 | .6946 | 4.31 | 22.24 | 481.5 | 52.60 | 219.1 | |
| -10 | .6860 | .6854 | 4.12 | 20.97 | 454.3 | 52.53 | 218.3 | 2.20 |
| 0 | .6768 | .6758 | 3.93 | 19.75 | 435.5 | 52.41 | 218.6 | |
| 10 | .6672 | .6658 | 3.74 | 18.56 | 411.9 | 52.46 | 218.3 | |
| 20 | .6578 | .6559 | 3.56 | 17.34 | 389.7 | 52.50 | 218.0 | 2.23 |
| 30 | .6468 | .6442 | 3.37 | 16.13 | 366.6 | 52.49 | 218.0 | |
| 40 | .6352 | .6319 | 3.19 | 14.96 | 343.3 | 52.46 | 218.1 | |
| 50 | .6237 | .6195 | 3.01 | 13.85 | 322.5 | 52.61 | 218.2 | 2.25 |
| 60 | .6065 | .6009 | 2.82 | 12.67 | 299.0 | 52.63 | 218.3 | |
| 70 | .5950 | .5875 | 2.62 | 11.49 | 275.1 | 52.65 | 218.4 | |
| 80 | .5853 | .5766 | 2.42 | 10.36 | 251.7 | 52.72 | 218.1 | 2.23 |

TABLE II
PHYSICAL PROPERTIES OF HYDROCARBON FROM 2-BROMOPENTANE, 2-PENTENE (STABLE FORM)

| Temp., °C. | Density | Density of liquid minus density of vapor | Corrected height in cm. | Surface tension in dynes per cm. | Molecular surface energy in ergs per sq. cm. | Total surface energy in ergs per sq. cm. | Parachor | Eötvös con- stant |
|---------------|---------|---|----------------------------------|---|--|---|----------|-------------------------|
| -70 | 0.7314 | 0.7314 | 6.08 | 27.62 | 578.3 | 52.99 | 219.0 | |
| -60 | .7227 | .7227 | 5.87 | 26.35 | 556.2 | 52.87 | 219.8 | |
| -50 | .7140 | .7140 | 5.66 | 25.10 | 534.1 | 52.87 | 219.7 | |
| -40 | .7052 | .7052 | 5.44 | 23.83 | 511.3 | 52.67 | 219.6 | 2.23 |
| -30 | .6960 | .6959 | 5.23 | 22.61 | 490.2 | 52.25 | 219.6 | |
| -20 | .6866 | .6864 | 5.03 | 21.45 | 468.6 | 52.30 | 219.7 | |
| -10 | .6770 | .6764 | 4.32 | 20.35 | 448.8 | 51.81 | 220.0 | 2.20 |
| 0 | .6675 | .6665 | 4.62 | 19.12 | 425.5 | 51.88 | 219.9 | |
| 10 | .6580 | .6566 | 4.40 | 17.95 | 403.3 | 51.34 | 219.7 | |
| 20 | .6481 | .6462 | 4.17 | 16.74 | 380.0 | 50.43 | 219.4 | 2.20 |
| 30 | .6381 | .6355 | 3.95 | 15.59 | 357.5 | 50.40 | 219.1 | |
| 40 | .6275 | .6242 | 3.73 | 14.43 | 334.6 | 49.48 | 218.8 | |
| 50 | .6163 | .6121 | 3.51 | 13.34 | 313.1 | 49.97 | 218.8 | 2.21 |
| 60 | .6053 | .5997 | 3.29 | 12.24 | 290.7 | 48.87 | 218.6 | |
| 70 | .5938 | .5863 | 3.14 | 11.33 | 272.6 | 48.06 | 219.3 | |
| 80 | .5814 | .5727 | 2.87 | 10.25 | 250.1 | 48.00 | 219.0 | 2.18 |

TABLE III
 PHYSICAL PROPERTIES OF THE HYDROCARBON FROM 3-BROMOPENTANE, 2-PENTENE
 (METASTABLE FORM)

| Temp., °C. | Density | Density of liquid minus density of vapor | Corrected height in cm. | Surface tension in dynes per cm. | Molecular surface energy in ergs per sq. cm. | Total surface energy in ergs per sq. cm. | Parachor | Eötvös con- stant |
|---------------|---------|--|----------------------------------|---|--|---|----------|-------------------------|
| -70 | 0.7350 | 0.7350 | 6.22 | 28.39 | 592.6 | 53.76 | 220.1 | |
| -60 | .7269 | .7269 | 5.99 | 27.04 | 568.6 | 53.66 | 219.8 | |
| -50 | .7172 | .7172 | 5.79 | 25.79 | 547.2 | 53.44 | 220.2 | |
| -40 | .7085 | .7085 | 5.58 | 24.55 | 525.2 | 53.67 | 220.2 | 2.23 |
| -30 | .6995 | .6994 | 5.34 | 23.23 | 500.4 | 53.60 | 219.9 | |
| -20 | .6903 | .6901 | 5.11 | 21.94 | 477.0 | 53.56 | 219.7 | |
| -10 | .6811 | .6805 | 4.89 | 20.67 | 403.8 | 53.54 | 219.6 | 2.33 |
| 0 | .6710 | .6700 | 4.67 | 19.45 | 430.9 | 52.97 | 219.6 | |
| 10 | .6608 | .6584 | 4.46 | 18.12 | 406.9 | 52.64 | 219.6 | |
| 20 | .6503 | .6484 | 4.205 | 16.93 | 383.5 | 52.09 | 219.2 | 2.33 |
| 30 | .6392 | .6366 | 3.97 | 15.70 | 361.2 | 51.41 | 219.1 | |
| 40 | .6288 | .6255 | 3.76 | 14.61 | 338.3 | 50.71 | 219.0 | |
| 50 | .6181 | .6139 | 3.55 | 13.54 | 317.1 | 49.71 | 218.9 | 2.20 |
| 60 | .6112 | .6056 | 3.33 | 12.43 | 293.3 | 48.72 | 217.3 | |
| 70 | .5982 | .5907 | 3.11 | 11.35 | 271.7 | 47.35 | 217.8 | |
| 80 | .5824 | .5737 | 2.89 | 10.30 | 251.0 | 46.86 | 218.8 | 2.20 |

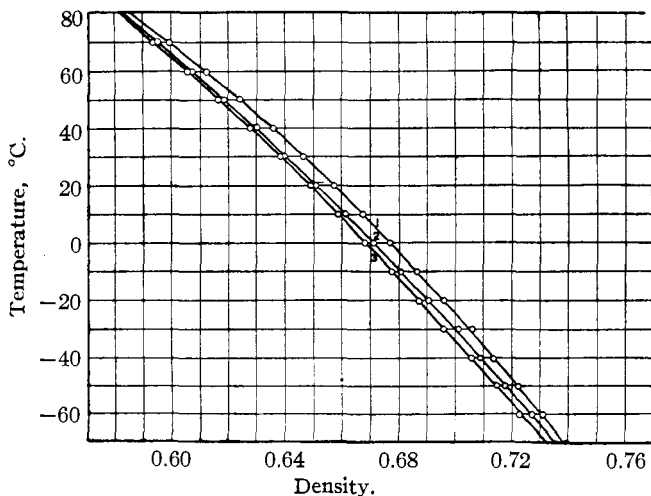


Fig. 1.—1, 2-Methyl-2-butene; 2, metastable pentene; 3, stable pentene.

Davis⁸ determined the surface tension of the same substance in air at 20° and got 17.26 ± 0.1 , which agrees, within the limits of experimental error, with that recorded in Table I, 17.34 ± 0.1 .

As one would expect from the densities, the surface tensions of the

⁸ Harkins, Brown and Davis, THIS JOURNAL, 39, 354 (1917).

metastable compound lie between those of the other two. The most outstanding differences between the three hydrocarbons, as is graphically

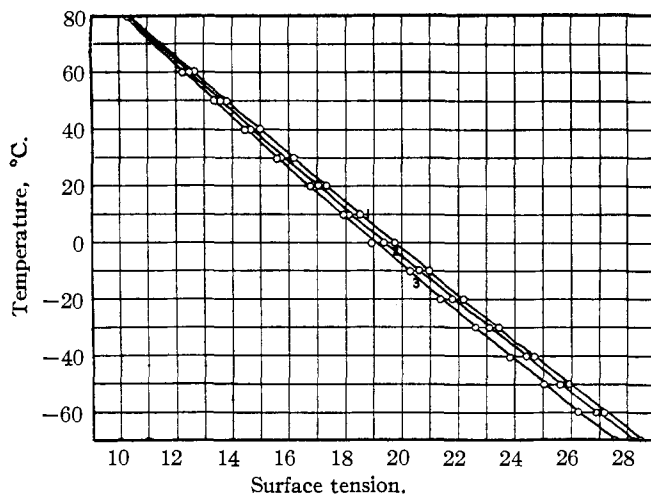


Fig. 2.—1, 2-Methyl-2-butene; 2, metastable pentene; 3, stable pentene.

illustrated in Fig. 3, is the change in total surface energy with change in temperature. The total surface energy for 2-methyl-2-butene is fairly

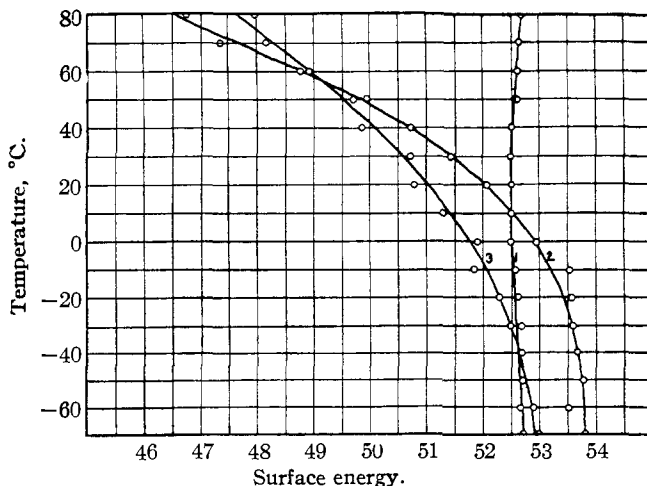


Fig. 3.—1, 2-Methyl-2-butene; 2, metastable pentene; 3, stable pentene.

constant, and the greatest change is found in the case of the metastable isomer. While the points do not lie as well on the curves as might be desired, it is nevertheless evident that there is a falling off in the property

under discussion. No explanation can be given at this time just why this should be so. It appears to be associated with the slight variation of the parachor, the values of which at the different temperatures are given in the eighth column of figures.

Neglecting the first figure in Table I under the heading parachor, it is seen that the value is fairly constant. Indeed, the average value, 218.3, agrees very well with the calculated one of 218.2 as given by Sugden.⁹ In the other two cases the average value of the parachor is somewhat higher, as shown below.

PARACHOR VALUES OF THE THREE PENTENES

| Substance | <i>P</i> (calcd.) | <i>P</i> (obs.) | % Diff. |
|------------------------|-------------------|-----------------|---------|
| 2-Methyl-2-butene | 218.2 | 218.3 | 0.05 |
| 2-Pentene (stable) | 218.2 | 219.5 | .55 |
| 2-Pentene (metastable) | 218.2 | 219.5 | .55 |

In the case of the two pentenes the parachor shows a decrease with rise in temperature, and is therefore apparently a function of temperature. At the boiling point the difference between the calculated and observed parachors is less than 0.3%. The Eötvös, or Ramsay-Shields, constant is in all cases higher than the normal value, 2.12.

No evidence has been forthcoming to show that the hydrocarbon prepared from 3-bromopentane is more unstable than that from 2-bromopentane. At the time the hydrocarbons were received, Hallonquist was not sure but what some of the metastable might have changed over into the stable form. That complete change had not taken place is proved by the constant difference in heights obtained for the two hydrocarbons at all temperatures. Again, if a certain amount of transformation had occurred, then the density assumed, 0.6503 at 20°, for the metastable form would be too high. The value of the surface tension would not be affected very much, as the corresponding decrease in height would tend to nullify this. As will be seen, however, from the following data, no changes within the limits of experimental error could be detected in the differential capillary rise of the metastable hydrocarbon.

| Time in days after placing in tube | Observed difference in height |
|--|-------------------------------|
| 0 | 4.227 |
| 4 | 4.230 |
| 16 | 4.230 |
| 66 | 4.230 |
| 124 | 4.235 ^a |
| After cooling to -70° and heating to 80° | 4.235 ^a |

^a Observations taken by a student assistant.

As is evident, the results given are of little value toward settling the

⁹ Sugden, *J. Chem. Soc.*, 125, 1180 (1924).

controversy as to whether the isomers represent electromers according to the theory of Kharasch¹ or are merely *cis* and *trans* formations of 2-pentene.

As already pointed out, the total surface energies of the three isomers show appreciable differences. Part of this divergence may be attributed to experimental error, the lack of accurate vapor pressure data and impurity of compounds, but it is doubtful whether it would account for a gradual decrease of almost 5 ergs in the total surface energy. According to Traube the "*trans*" modification has usually the smallest density,¹⁰ which would indicate that the metastable form represented the "*cis*" compound.

Summary

1. The densities and surface tensions of the two 2-isomers of 2-pentene and 2-methyl-2-butene have been measured over a range of temperature of 150°.

2. The total surface energies of the three compounds differ considerably at different temperatures.

3. The observed parachor agrees tolerably well with the calculated value but shows a decrease with rise in temperature.

4. The Eötvös or Ramsay-Shields constant is higher than the normal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF RUTGERS UNIVERSITY]

COPPER, COBALT, NICKEL, ZINC AND CADMIUM TETRAPYRIDINE FLUOSILICATES¹

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RECEIVED JUNE 4, 1931

PUBLISHED OCTOBER 5, 1931

The salts of fluosilicic acid have come into extensive use, in recent years, as insecticides. As a result, a number of investigations of the properties of some of these salts have appeared. In a study of the solubility of certain of these salts, reference² was found in the literature to the effect that copper fluosilicate is insoluble in pyridine. When an experiment was performed to test the degree of solubility, it was found that whereas the compound does not dissolve appreciably, a reaction occurs which results in the formation of a new compound. Similar compounds were also formed with the fluosilicates of cobalt, nickel, zinc and cadmium. These new compounds are described in the present paper. Attempts to prepare

¹⁰ Traube, *Ann.*, **240**, 46 (1886).

¹ This paper is based on a thesis submitted by Walter T. L. Ten Broeck, Jr., to the Faculty of Rutgers University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1925, Vol. VI, p. 950.