come over first and stronger alcohol later. For the mixture boiling with constant composition the curve should be vertical showing that the composition did not change while for mixtures weaker in alcohol the slope would be to the right the mixture of constant composition tending to distil first and weaker mixtures later. The boiling point was read at the end of each fraction and corrected as related before. The vertical curve representing the low boiling mixture is plotted from the following gravities of the two fractions, D_4^{20} 0.81582 and 0.81586. On repeated distillation the value of 0.81583 was obtained. The observed constant boiling point was 79.6° at 756 mm. Adding 0.6° stem correction and 0.2° calibration correction gives 80.4° as the boiling point of the constant-boiling mixture. By interpolation between the original data for the specific gravity table a composition of 87.70% by weight and 91.09% by volume is obtained for the alcoholic content of this mixture. A number of samples taken from a run on a large rectifying column gave an average specific gravity of 0.81583, and ranging from 0.81570 to 0.81587.

The greatest accuracy is obtained for the low boiling mixture, being limited only by the accuracy of the specific gravity table of Part I.

Summary.

The specific gravity of *iso*propyl alcohol was found to be 0.7855 at 20/4°, its boiling point 82.4° at 760 mm. pressure. A table for specific gravity of alcohol—water mixtures is given.

The specific gravity of the mixture boiling with constant composition was found to be 0.8158 at 20/4°, its boiling point 80.4° and its composition 87.70% alcohol by weight and 91.09% by volume.

Curves showing the boiling points of alcohol—water solutions and the composition of the evolved vapor are given. These curves when compared with like curves for ethyl alcohol show that *iso*propyl alcohol is rectified more easily than is ethyl alcohol.

BAYWAY, N. J.

THE EFFECT OF FINELY DIVIDED MATERIAL ON THE FREEZING POINTS OF WATER, BENZENE AND NITROBENZENE.[1]

BY F. W. PARKER.

In a study of the salt content of the soil solution by different methods, including the freezing-point method of Bouyoucos and McCool,[2] results

[2] Bouyoucos and McCool, Mich. Agr. Exp. Sta., *Tech. Bull.* 24 (1915); 31 (1917).

were obtained which indicated that finely divided material of soils causes a considerable depression of the freezing point of the soil water at a certain range of moisture contents of the soil. These results did not agree in all respects with the conclusions of Bouyoucos and McCool, and hence a more extended study, the results of which are reported in this article, was made using known materials as well as soils.

The freezing points of colloidal solutions have been studied by several investigators, but in all cases the depression obtained has been negligible or extremely small. In a review of the literature the writer did not find any investigations in which a deliberate study was made of the effect of finely divided material on the freezing point when the amount of liquid was reduced until it was entirely in the film or capillary condition. Foote and Saxton,[1] however, in studying the forms of water in certain hydrogels by the dilatometer method, recognized that the hydrogels caused a depression of the freezing point of the capillary water. This has also been recognized by other investigators in studying the forms of water in gels and it is well known that the water in hydrogels has a low vapor pressure. Bouyoucos and McCool[2] were the first investigators to measure the magnitude of the depression by the freezing-point method, but they attributed the depresssion obtained by this method entirely to material in solution. The purpose of the present investigation was to study the depression due to finely divided material and to show that it is not due to material in solution.

Experimental.

Materials and Method.—For experiments of this nature the solid materials must be finely divided and insoluble in the liquids to be studied. The liquids used should be pure and freeze at a convenient working temperature.

The ferric hydroxide used was prepared by precipitation with ammonium hydroxide from a cold dilute solution of ferric chloride. It was washed free from chlorides, air-dried, and ground to pass a 200-mesh screen.

c. p. Aluminum oxide and silica, purchased in the open market, were used. Both contained a small amount of water-soluble material as indicated by the freezing-point determination at the highest moisture content, but there was not an appreciable amount of material soluble in benzene or nitrobenzene.

The soil was a Carrington silt loam containing 250 parts per million of soluble salts, determined by a 1:5 water extraction.

All solid materials except the ferric hydroxide were dried in an electric oven at 105° for 12 hours before using.

The benzene was twice distilled over metallic sodium to remove the water. The nitrobenzene was redistilled to remove dinitrobenzene. In both cases the first and last portions of the distillate were discarded.

The apparatus and procedure were essentially the same as those used by Bouyoucos and McCool. 15 to 25 g. of the moistened material was placed in a test-tube (25 × 175

[1] Foote and Saxton, THIS JOURNAL, **38,** 588 (1916); **39,** 1103 (1917).

[2] *Loc. cit.*

mm.) and the bulb of the Beckmann thermometer embedded in the material. This tube was then placed in a larger tube which served as an air jacket. The freezing mixture was 2° or 3° below the freezing point of the material under investigation.

In all cases the supercooling was about 0.5°. After supercooling, solidification was started by a slight movement of the thermometer or by inoculation with a small crystal.

The same sample was frozen only once, since Foote and Saxton using the dilatometer and Bouyoucos and McCool using the freezing-point method found that succes· sive freezings of the same sample gave different results in many cases. This was probably due to the partial destruction of the colloidal properties of the materials studied.

The method is very accurate at high moisture contents, duplicate determinations agreeing very closely. The accuracy decreases with decreasing moisture content and increasing freezing-point depression. When a depression of 1° to 1.5° is obtained duplicates may vary 0.1°. The results presented are in most cases the average of two or more determinations. The degree of supercooling affects the results to a marked extent at the lower moisture contents.

The Freezing-point Depression of Water in Finely Divided Material. —The results obtained using ferric hydroxide, silica, and the soil are given in Table I. Figs. 1 and 2 are the curves obtained by plotting the percentage of water as abscissas and the freezing-point depression as ordinates.
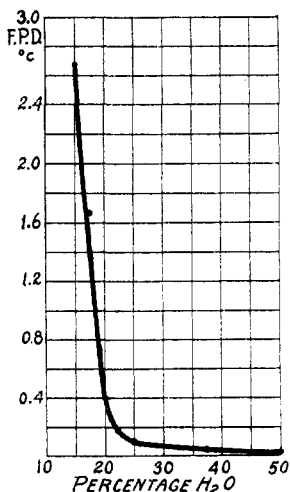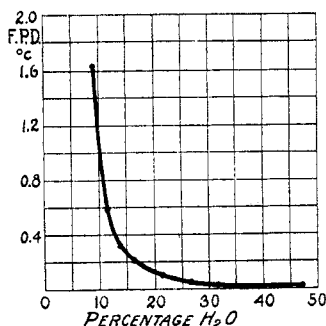

Fig. 1.—Freezing-point depression   Fig. 2.—Freezing·point depression
  of water in ferric hydroxide.   of water in a soil.

The results indicate a considerable depression of the freezing point due to the solid material. The effect due to soluble salts must have been very small, especially in the case of ferric hydroxide, since the material gave a depression of only 0.004° at a moisture content of 100%. If the depressions had been due entirely to material in solution, they should

be inversely proportional to the moisture contents. There is, however, no indication of this relation except at very high moisture contents.

TABLE I.

The Freezing-point Depression of Water in Fe(OH)₃, SiO₂, and a Soil at Different Moisture Contents.

Fe(OH)₃.		Carrington silt loam.		SiO₂.	
H₂O[a], %.	F. p. d., °C.	H₂O, %.	F. p. d., °C.	H₂O, %.	F. p. d., °C.
15.0	2.668	9.0	1.622	4.0	1.883
17.5	1.651	11.5	0.585	5.0	0.855
20.0	0.393	14.0	0.315	6.6	0.515
22.5	0.177	16.5	0.213	10.0	0.308
25.0	0.086	21.5	0.113	13.3	0.205
37.5	0.016	26.5	0.062	20.0	0.130
50.0	0.009	31.5	0.030	33.3	0.063
100.0	0.004	46.5	0.021	50.0	0.045

[a] Throughout this paper the liquid content is expressed on the dry basis.

Two factors, soluble material and finely divided insoluble material, cause a depression of the freezing point. In order to determine whether these factors are additive in their effect on the freezing point, a sample of aluminum oxide was moistened with water and another sample was moistened with an equal volume of a sugar solution which had a freezing-point depression of 0.126°. A sugar solution was used because there is no possibility of a reaction between the sugar and the aluminum oxide. If the two factors are additive the difference between the two freezing-point depressions at any moisture content should be 0.126°, the depression due to the sugar. The differences obtained are given in the last column of Table II.

TABLE II.

The Freezing-point Depression of Water and a Sugar Solution in Aluminum Oxide at Different Moisture Contents.

H₂O, %.	F. p. d. with water. °C.	F. p. d. with solution. °C.	F. p. d due to the sugar. °C.
25.0	2.118	2.290	0.172
30.0	1.227	1.312	0.075
35.0	0.650	0.740	0.090
40.0	0.370	0.500	0.130
50.0	0.220	0.344	0.123
75.0	0.075	0.195	0.120
100.0	0.053	0.173	0.120

The results undoubtedly prove that the two factors are very nearly additive in their effect on the freezing point. The differences found at the lowest three moisture contents are easily within experimental error, which is quite high at low moisture contents. The presence of the sugar did not affect the general order of results. Other determinations in which different solutions and solid materials were used confirmed these results in every case. It may therefore, be concluded that at the lower moisture

contents the depressions were due almost entirely to the solid material present. At the high moisture contents the depressions were probably due entirely to material in solution.

The Freezing-point Depressions of Benzene and Nitrobenzene in Finely Divided Materials.—The use of organic liquids in which most inorganic salts are insoluble makes it possible to eliminate entirely the freezing-point depression due to substances in solution. Benzene and nitrobenzene were chosen because they are easily obtained and freeze at a convenient working temperature.
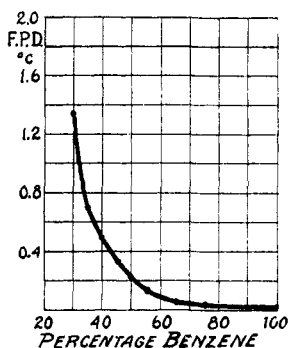

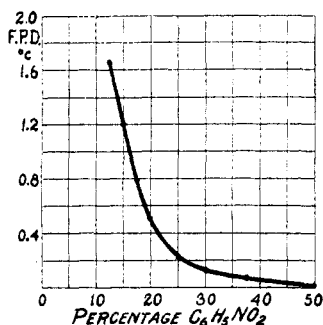Fig. 3.—Freezing-point depression of benzene in aluminum oxide.

Fig. 4.—Freezing-point depression of nitrobenzene in a soil.

The 3 materials studied, with the possible exception of silicon dioxide, contained nothing soluble in benzene, as is indicated by no depression of the freezing point at the high benzene content. The results obtained with benzene are shown in Table III and in all cases they are similar to those obtained with the same materials and water. Fig. 3 is the curve obtained for aluminum oxide by plotting the results.

TABLE III.

The Freezing-point Depression of Benzene in Aluminum Oxide, Silica and Carrington Silt Loam.

Carrington silt loam.		Al_2O_3.		SiO_2.	
Benzene. % .	F. p. d. °C.	Benzene. %.	F. p. d. °C.	Benzene. %.	F. p. d. °C.
5.0	0.660	30.0	1.337	3.3	0.670
7.5	0.355	35.0	0.682	5.0	0.490
10.0	0.150	40.0	0.492	6.6	0.360
12.5	0.060	45.0	0.326	10.0	0.225
15.0	0.033	50.0	0.212	13.3	0.190
20.0	0.025	55.0	0.115	16.6	0.150
25.0	0.010	65.0	0.052	20.0	0.110
37.5	0.000	75.0	0.030	33.3	0.050
..	...	100.0	0.000	50.0	0.015

Table IV gives the results obtained with nitrobenzene, using the same materials with the omission of silicon dioxide. The results are of the

same order as those obtained using water and benzene, and show a marked depression of the freezing point due to finely divided material. The results for the soil are plotted in Fig. 4. Nitrobenzene gives a more gradual curve with the soil than either water or benzene. This is probably specific for each solid and liquid studied. Further investigations should include a greater number of both solid and liquid materials.

TABLE IV.

The Freezing-point Depression of Nitrobenzene in Carrington Silt Loam and Aluminum Oxide.

Carrington silt loam.		Al_2O_3.	
Nitrobenzene. %.	F. p. d. °C.	Nitrobenzene. %.	F. p. d. °C.
12.5	1.630	50.0	1.720
15.0	1.200	60.0	1.175
17.5	0.780	70.0	0.810
20.0	0.510	80.0	0.580
25.0	0.230	90.0	0.340
30.0	0.130	100.0	0.200
37.5	0.075	110.0	0.130
50.0	0.000	150.0	0.020
..	...	200.0	0.000

Discussion.

The force holding water or other liquid films on solid particles and causing a freezing-point depression is adhesion. When the amount of liquid is increased a point is reached at which some of the liquid becomes so distant that this force no longer affects it sufficiently to cause a depression of its freezing point. At this point the depression becomes due entirely to material in solution. It should be noted that the effect is different than it would be if the force were similar to mechanical pressure, since this would cause an elevation of the freezing point,of those liquids which contract on solidification.

The depression obtained with the different liquids varies widely. Carrington silt loam at 15.0% liquid gave with water a depression of 0.250°, with benzene a depression of 0.033°, and with nitrobenzene a depression of 1.200. Aluminum oxide, at 50%, gave with water a depression of 0.220, with benzene 0.212°, and with nitrobenzene 1.720°.

The amount of depression caused by finely divided material in any case probably depends upon at least three factors; viz., (1) the ease with which the freezing point of the liquid can be lowered; (2) the amount of the surface of the solid, and (3) the affinity between the solid material and the liquid used. The first factor is probably expressed in the freezing-point constant of the different liquids. Further investigations are necessary before any generalizations can be made concerning the above factors. The heat of wetting of the materials with different liquids would probably give important results bearing on this problem.

The freezing-point determinations as a means of studying the concentration of a solution in the presence of a large amount of finely divided material was first used by Bouyoucos and McCool.[1] These investigators introduced the method as a means of determining the concentration of the soil solution directly in the soil and obtained results similar to those for the soil in Table II. They attributed the depression of the freezing point entirely to material in solution, and advance an hypothesis to explain why the freezing-point depression of a soil is not inversely proportional to the moisture content.

"The hypothesis assumes that a portion of the water found in the soils is inactive and does not take part in dissolving the salts in the soil, and is removed from the field of action as far as the lowering of the freezing point is concerned. * * * * If a clay soil, for instance, causes 15% of water to become inactive, and this clay at 39% of moisture produces a lowering of the freezing point of 0.075° and at 22%, 0.987°, then at the former moisture content there is 24% of water free or available to dissolve the salts in the soil, while at the latter water content there is only 7% available for the same purpose. It would be natural, therefore, that the depressions of the freezing point would be many times greater at the low moisture content than at the high, as would be expected from the difference of the total moisture content, just as the experimental data really indicate.

"This hypothesis also assumes (and the assumption seems to have been proved) that the percentage of inactive water is greater at the low than at the high moisture content and tends to decrease from the former to the latter."

In the light of the present investigation the writer believes this hypothesis is untenable. It has been shown that finely divided material causes a depression of the freezing point when there is no soluble material present. It has also been shown that the depression due to soluble material and that due to the solid material are additive. If water had been rendered inactive, and no longer had a solvent effect, the depression due to the sugar in Table II would have increased many times at the lower moisture contents. It is not until relatively high moisture contents are reached that the depression is due entirely to the materials in solution.

The freezing-point method has been used by Bouyoucos and his associates[2] to determine the lime requirement of soils, the velocity of reactions between soils and chemical reagents, the solubility and absolute salt content of soils. In these investigations the moisture content was always very high, varying from 66% to several hundred per cent. At these high moisture contents the depression of the freezing point is due entirely to material in solution and the method gives a satisfactory measure of the soluble material present. Studies made in this manner have given interesting and valuable results.

The freezing-point lowering caused by finely divided material is also of

[1] *Loc. cit.*; *Bull.* **31**, p. 24.

[2] Bouyoucos, *et al.*, Mich. Agr. Exp. Sta., *Tech. Bull.* **27** (1916); **37** (1917); **44** (1919); *J. Agr. Research*, **15**, 331-6 (1918).

interest in biological studies. Living tissue is colloidal and undoubt-
edly has a great affinity for water. A portion of the water in the tissue
would not freeze at low temperatures and this factor might be of interest
in studying the behavior of living tissue at low temperatures.

Summary.

1. Finely divided material causes a depression of the freezing point of
a liquid when the liquid exists in the film or capillary condition in the solid
material.

2. The freezing-point depression due to solid material and that due to
material in solution are additive.

3. The concentration of the soil solution cannot be measured by the
freezing-point method except at very high moisture contents.

Further investigations on the freezing point and other methods of study-
ing the soil solution will be published later.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY.]

EQUILIBRIUM IN THE SYSTEM AMMONIA: AMMONIUM NITRATE: AMMONIUM THIOCYANATE.

BY H. W. FOOTE AND S. R. BRINKLEY.

The object in view in undertaking this work was to investigate the
vapor pressure and solubility relations in the ternary system ammonia:
ammonium nitrate:ammonium thiocyanate. In order to show the
limiting values of this system, the two binary systems ammonia:ammo-
nium nitrate, and ammonia:ammonium thiocyanate have been included.
At the working temperatures, ammonium nitrate and thiocyanate are
both solids with practically no vapor pressure, and hence the binary
system composed of these two salts falls out of consideration. We have
therefore determined (1), the vapor pressures up to two atmospheres and
(2), the solubility relations, of the ternary system at 0°, 10° and 20°;
and the corresponding values, so far as they have not been previously
determined, in the binary systems ammonia:ammonium nitrate and
ammonia: ammonium thiocyanate.

It is well known that when either of the two salts mentioned is treated
with dry ammonia at atmospheric pressure and room temperature or
below, deliquescence takes place and a clear solution of the salt and
ammonia results. Similar deliquescence occurs in the ternary system
composed of the two salts with ammonia. Either salt may serve, there-
fore, as an absorbent for free ammonia, particularly when it is desirable
to avoid the presence of water, and the ammonia can be recovered again
by warming or by reducing the pressure. It seemed not unlikely that