

VAPOR PRESSURE RELATIONS OF CERTAIN  
TYPICAL SOIL COLLOIDS

BY

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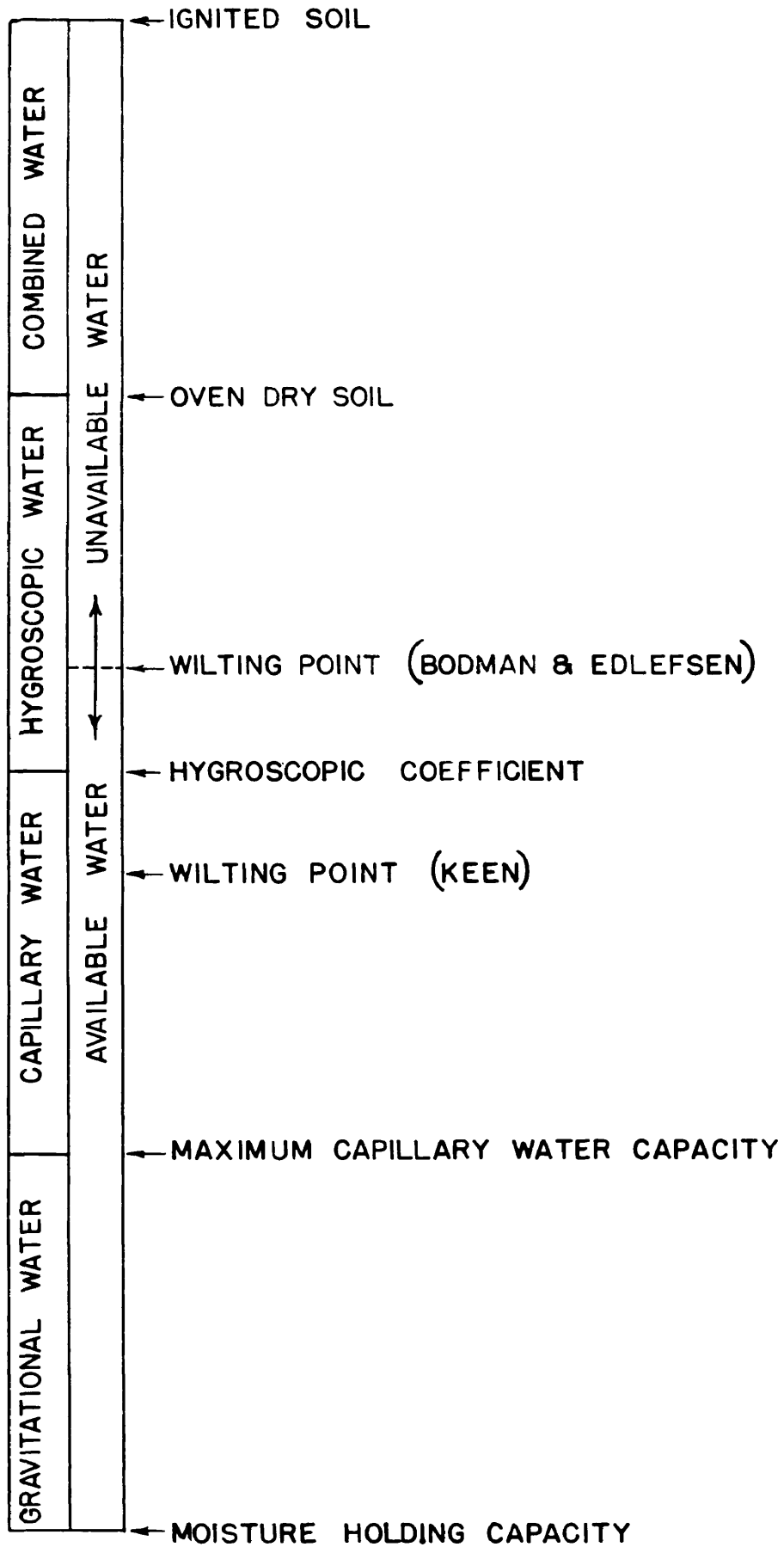
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## INTRODUCTION

The water present in soil is usually divided into three categories. The first of these, the water of constitution or combined water, is measured as the water lost on strong ignition after drying in an oven at 105°C. The second category, called hygroscopic water, is the water lost by the soil when it is dried in an oven at 105°C after it has been brought to equilibrium in an atmosphere saturated with water vapor. The third category includes all water present in the soil in excess of that held in a saturated atmosphere.

Keen (13) has used the diagram shown in Fig. 1 to represent the relations between the different categories of water and the moisture constants determined by soil physicists. To this diagram has been added the combined water or water of constitution. It may be said here that these divisions are entirely artificial and have no real existence. All the evidence available indicates that there are no "fixed points" or natural divisions of kinds of water in soils. These arbitrary divisions are useful, however, for orienting our conceptions of soil moisture.

The second category, hygroscopic moisture, has received less consideration than the others. The soil physicists have neglected this category because it is somewhat below the range of useful moisture. The chemists have neglected it because it is not con-



# SOIL MOISTURE RELATIONSHIPS

sidered chemically combined water. The investigations reported in this paper deal with this second category.

#### HISTORICAL

Several attempts have been made to utilize the information obtained by allowing air-dry soil to absorb moisture at various relative humidities. The water absorbed by soil colloids when allowed to come to equilibrium over a sulfuric acid - water mixture containing 3.3 percent sulfuric acid by weight has been made the basis for a method of estimating the quantity of colloid present in a soil (11). The water held under this condition (99 percent relative humidity) falls below the hygroscopic coefficient. The British soil workers (13) have also used a determination of the moisture held at 50 percent relative humidity as a criterion of soil properties. More recently, workers in the Bureau of Chemistry and Soils of the United States Department of Agriculture (7) have made determinations of the amounts of water held over sulfuric acid-water mixtures of various concentrations by different soil colloids. An attempt was made to correlate the ratios between some of the values so obtained with the chemical composition of the soil. The attempt was only partially successful.

With this work in view, it seemed that the most logical attack on the problem of the nature of this hygroscopic water was a determination of the vapor pressure-water content curves of the various types of soils.

The vapor pressure-water content curves of a number of soils have been studied by Thomas (21, 22) and by Puri, Crowther and Keen (19). They covered the entire range from oven-dry at 105° C to saturation. It was found in both investigations that an inflection point in the curves occurred near 50 percent of the vapor pressure of pure water. No breaks were found; this indicated no sudden change in the nature of the forces holding the water. Puri, Crowther and Keen reached the conclusion that the curves were all of the same type but that the general slopes of the curves were decreased with increases of clay and organic matter content. Thomas also reached the conclusion that the slope of the curve is influenced by the quantity of fine material present, but concluded that the organic matter played a minor role in water vapor absorption. Brown and Byers (7) and also Anderson and Mattson (3) have called attention to the correlation between the avidity of a soil colloid for water and its chemical constitution. Since it has been shown so many times that the coarser fractions of a soil only serve as a framework or as diluting material for the colloid, it seemed advisable to study the colloid extracted from the soil, rather than the soil itself. This would eliminate the variable factor mentioned by Puri, Keen and Crowther concerning the change in slope of the vapor pressure curve with clay content.



## MATERIALS USED

The soils selected for this study represent the widest range of progressive weathering found in the United States. The Barnes soil is a black dry land grass soil from North Dakota. It has been formed from calcareous glacial till. It has not been subjected to severe hydrolysis because of the low rainfall.

The Carrington soil is a fertile prairie soil of Iowa. Like the Barnes, it has been developed from calcareous glacial till but under conditions of more rainfall, and therefore its degree of weathering is greater.

The Miami, a gray-brown podzolic soil from Indiana, has been developed under somewhat higher rainfall than the Carrington. This is a timber soil and not a grassland one.

The fourth soil selected is the Cecil, a red soil from North Carolina, that has been developed from decomposed granites and gneisses under conditions of high rainfall and temperature, where the weathering has been severe.

The colloids were extracted from these soils by means of a Sharples super centrifuge. One kilogram of the soil, from which the colloid was to be extracted, was suspended in ten to fifteen liters of water by vigorous agitation. The coarser particles were allowed to settle for about two minutes and then the suspended portion was poured off. The settled portion of the sample was again suspended and the suspension poured off. When about twenty gallons of suspension had been obtained it was passed through a

centrifuge bowl of four inches in diameter turning at 17000 revolutions per minute. The dispersed colloidal particles passed through the centrifuge in suspension and the remainder adhered to the wall of the bowl. The material in the bowl was removed and rubbed in water to suspend it and again passed through the centrifuge. Sometimes as many as twenty extractions were necessary to remove the main portion of the colloid from a soil.

The rate at which the suspension was allowed to enter the centrifuge controlled the time during which the particles were subjected to the centrifugal force. The maximum size particles so obtained were calculated from Stokes law or estimated by observation in a dark field microscope. The two methods agree within reasonable limits. The suspended colloid passing through the centrifuge was concentrated by removing the water with clay suction filters.

The maximum diameter of particles in the colloid so extracted was about 0.5 micron. The samples were dried at room temperature to avoid any irreversible removal of water at elevated temperature.

Tables 1 - 4 show the chemical analysis of these samples.

Given also in these tables are the molecular ratio of silica to iron oxide plus alumina and of silica to alumina. These ratios are the ones customarily used to characterize the chemical composition of the soil colloid. These ratios will be used later in comparing the properties of these colloids.

Table 1. - Chemical Analysis of Barnes Loam Colloid

Sample No.	Depth	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO
	Inches	Percent	Percent	Percent	Percent	Percent
10305	0-9	45.90	9.96	19.12	2.28	1.81
10306	9-17	48.21	10.93	20.23	2.49	1.73
10307	17-33	49.21	9.76	19.44	2.68	5.03
10308	33-60	50.29	9.50	19.32	2.96	4.34

K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	Ignition loss
Percent	Percent	Percent	Percent	Percent	Percent
1.70	0.02	0.68	0.163	0.39	18.34
1.43	.13	.74	.147	.25	14.15
1.44	.06	.74	.096	.31	11.76
1.40	.20	.68	.133	.24	10.93

Total	Organic matter	CO <sub>2</sub> from carbonates	pH values (soil)	SiO <sub>2</sub>	
				Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
Percent	Percent	Percent			
100.36	10.12	0.0	6.4	3.05	4.07
100.44	5.77	.0	7.1	3.00	4.04
100.53	1.94	2.69	8.1	3.25	4.29
99.99	1.03	2.46	8.2	3.36	4.41

Table 2. - Chemical Analysis of Carrington Loam Colloid

Sample No.	Depth Inches	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO
		Percent	Percent	Percent	Percent	Percent
10082	0-3	41.12	10.36	20.90	1.52	1.31
10083	3-13	41.84	10.09	23.22	1.61	.97
10084	13-22	43.82	10.67	24.34	1.71	.94
10085	22-43	44.77	12.92	24.67	1.71	1.03
10086	43-70	45.42	13.69	24.30	1.81	1.14
10087	70-84	45.42	13.77	23.82	1.79	1.48

K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	Ignition loss
		Percent	Percent	Percent	
1.44	0.12	0.62	0.10	0.37	22.56
1.38	.04	.55	.14	.36	20.18
1.31	.06	.68	.09	.28	16.47
1.63	.01	.82	.08	.26	12.41
1.85	.05	.87	.07	.29	10.77
1.89	.13	.82	.08	.22	10.93

Total	Organic matter	CO <sub>2</sub> from carbonates	pH values (soil)	SiO <sub>2</sub>		SiO <sub>2</sub>
				Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	
Percent	Percent	Percent		Percent	Percent	Percent
100.42	12.92	0.0	5.5	2.53		3.33
100.38	9.94	.0	5.2	2.39		3.06
100.37	6.16	.0	4.9	2.38		3.05
100.30	2.53	.0	5.1	2.30		3.08
100.26	1.14	.0	6.4	2.33		3.17
100.35	1.07	.10	8.1	2.36		3.23

Table 3. - Chemical Analysis of Miami Silt Loam Colloid<sup>1</sup>

Sample No.	Depth	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO
	Inches	-Percent	Percent	Percent	Percent	Percent
10341	0-1½	44.86	7.40	22.04	1.67	1.71
10342	3½-9	47.46	7.94	22.98	1.39	1.20
10343	11-24	47.07	11.50	23.38	2.09	0.96
10344	28-48	46.13	10.66	22.97	2.14	2.65

K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	Ignition loss
Percent	Percent	Percent	Percent	Percent	Percent
2.98	0.29	1.05	0.22	0.51	17.78
2.90	0.22	0.70	.12	.40	14.90
4.37	0.24	0.67	.09	.33	9.45
4.25	0.22	0.60	.08	.37	9.53

Total	Organic matter	CO <sub>2</sub> from carbonates	pH values (soil)	SiO <sub>2</sub>	
				Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
Percent	Percent	Percent			
100.51	10.20	0.0	7.0	2.84	3.45
100.43	6.82	.0	6.4	2.87	3.50
100.27	1.68	.0	6.3	2.60	3.41
99.77	1.63	1.62	7.9	2.63	3.41

<sup>1</sup> Analyses by R. H. Holmes

Table 4. - Chemical Analysis of Cecil Sandy Clay Loam

Sample No.	Depth Inches	SiO <sub>2</sub> Percent	Fe <sub>2</sub> O <sub>3</sub> Percent	Al <sub>2</sub> O <sub>3</sub> Percent	MgO Percent	CuO Percent
9415	0-6	30.90	14.57	32.56	0.39	0.60
9416	6-32	33.88	17.11	32.30	0.22	.21
9417	32-60	34.27	17.10	33.03	.13	.21
9418	60-84	35.13	17.54	30.52	.22	.11

K <sub>2</sub> O Percent	Na <sub>2</sub> O Percent	TiO <sub>2</sub> Percent	MnO Percent	P <sub>2</sub> O <sub>5</sub> Percent	Ignition Loss Percent
0.32	0.05	1.13	0.35	0.36	17.85
.23	.08	.84	.07	.26	13.91
.26	.08	.83	.08	.27	12.97
.04	.07	1.65	-	-	12.85

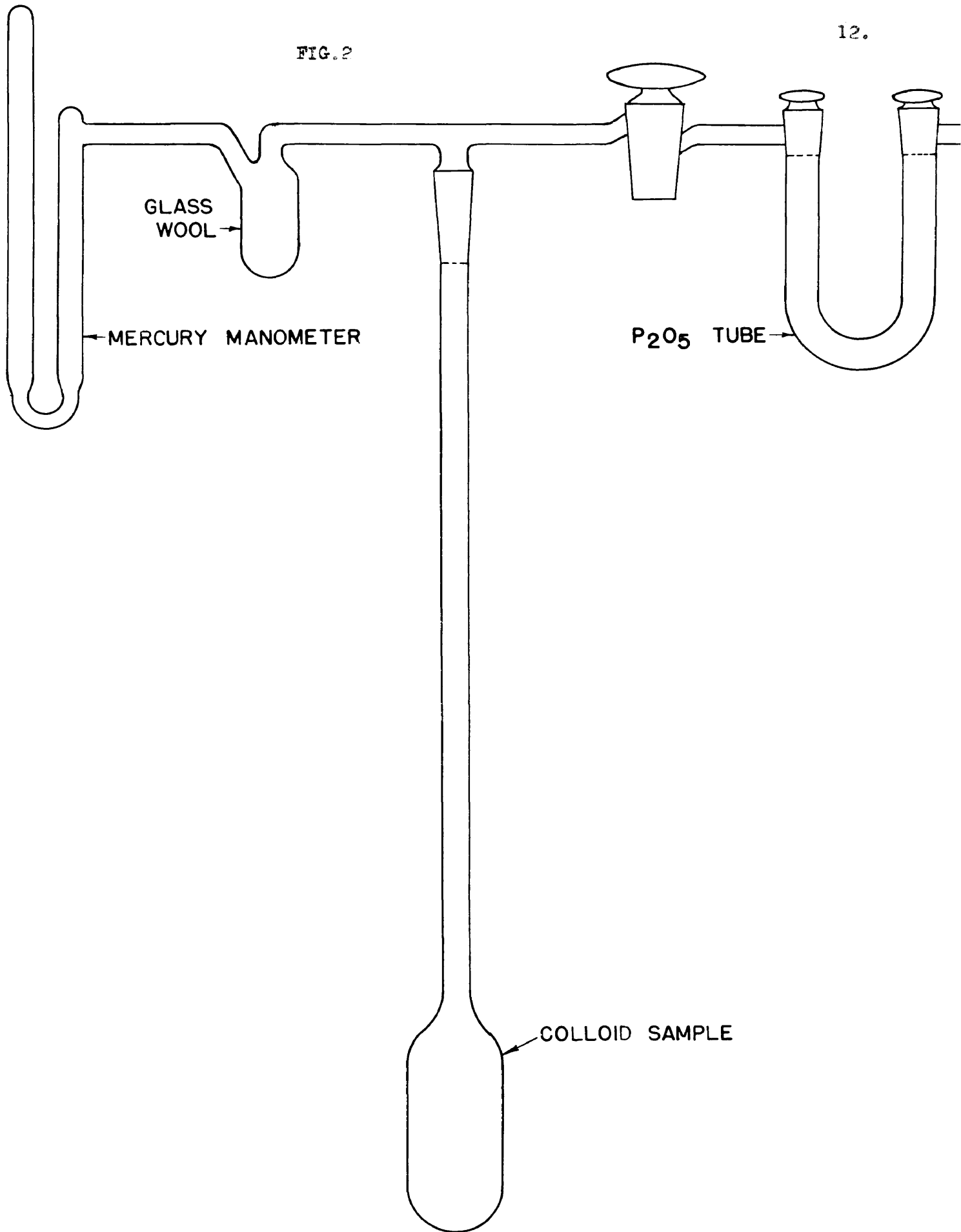
Total Percent	Organic matter Percent	CO <sub>2</sub> from carbonates Percent	pH values (soil)	SiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>
				Al <sub>2</sub> O <sub>3</sub>		
99.12	4.42	0.0	4.9	1.25	1.61	
99.11	.64	.0	4.8	1.33	1.78	
99.23	.55	.0	4.6	1.32	1.76	
-	.45	.0	4.6	1.43	1.95	

## EXPERIMENTAL WORK

The apparatus used for determining the detailed vapor pressure-water composition curves is essentially that used by Wales and Nelson (24). A diagrammatic representation of it is shown in Fig. 2.

After a 10-gram sample of air dry colloid ground to pass a 100-mesh sieve had been placed in an evacuated desiccator over 3.3 percent sulfuric acid for a period of five days, the sample was weighed and transferred to the bulb of the apparatus shown in Fig. 2. The apparatus was then evacuated through the phosphorus pentoxide tube until about 0.1 gram of water was collected. This amount of water was determined roughly by the heat developed. The stopcocks were closed and the whole apparatus allowed to stand until equilibrium was reached. The phosphorus pentoxide tube was then weighed and the difference in level of the two legs of the manometer read by means of a cathetometer. The apparatus was again evacuated and the process repeated. The experimental data obtained by this method are given in Tables 5 - 8. Also given in this table is the value for water held, at 25°C, by the colloid in an evacuated desiccator containing aqueous sulfuric acid, with a water vapor pressure of 23.3 mm Hg. Most of the values were taken after allowing twenty-four hours for equilibrium to be reached. Although this may not be a real equilibrium point no further change in pressure could be noted by allowing three or four days time.

FIG. 2



VAPOR PRESSURE APPARATUS



Table 5.

Relation between the Vapor Pressure and Water Content  
of the Barnes Colloid at 25°C

Sample No. 10307

Vapor pressure in mm Hg	Weight of water lost by sample in grams	Percent of water in sample
23.1	0.031	33.4
22.6	.156	32.0
22.6	.259	30.9
22.1	.352	29.8
21.8	.498	28.2
21.2	.623	26.9
21.0	.647	26.6
20.6	.722	25.8
19.9	.856	24.3
19.5	.934	23.4
19.0	1.020	22.5
18.5	1.072	21.9
18.1	1.134	21.2
17.3	1.200	20.5
16.6	1.280	19.6
15.7	1.368	18.7
15.4	1.459	17.7
14.1	1.560	16.6
13.2	1.619	15.9
12.8	1.641	15.7
11.8	1.702	15.0
10.9	1.760	14.4
9.9	1.825	13.6
9.3	1.869	13.2
8.7	1.902	12.8
8.0	1.961	12.1
7.0	2.027	11.4
5.9	2.112	10.5
5.3	2.143	10.1
4.0	2.283	8.6
2.8	2.363	7.7
1.8	2.478	6.5
1.0	2.583	5.3
0.0	3.069	0.0

Dry wt. of sample 9.101 gm.

Additional point by desiccator method  
23.3

35.4

Table 6.

Relation between the Vapor Pressure and Water Content  
of the Carrington Colloid at 25°C

Sample No. 10084

<u>Vapor pressure in mm.Hg</u>	<u>Weight of water lost by sample in grams</u>	<u>Percent of water in sample</u>
25.7	0.019	26.9
23.1	.137	25.6
22.4	.293	23.8
22.1	.499	21.6
20.7	.731	19.0
19.0	.974	16.6
16.4	1.233	13.4
15.8	1.343	12.2
12.2	1.492	10.5
10.1	1.621	9.0
6.5	1.819	6.8
5.3	1.898	6.0
1.4	2.130	3.4
1.2	2.158	3.1
0.0	2.432	0.0

Dry weight of sample 8.977 gm.

Additional point by desiccator method  
23.3

26.2

Table 7.

Relation between the Vapor Pressure and Water Content  
of the Miami Colloid at 25°C

Sample No. 10342

<u>Vapor pressure in mm.Hg</u>	<u>Weight of water lost by sample in grams</u>	<u>Percent of water in sample</u>
24.9	0.134	19.9
22.7	.212	19.1
22.7	.296	18.3
21.8	.346	17.6
21.7	.403	17.0
21.9	.523	15.8
21.5	.606	14.9
20.9	.692	14.0
20.3	.820	12.6
20.3	.895	11.8
19.6	.956	11.2
18.8	1.062	10.0
18.0	1.125	9.4
16.9	1.181	8.8
15.7	1.257	8.0
15.2	1.309	7.4
13.7	1.378	6.7
11.4	1.443	6.0
10.4	1.456	5.8
9.6	1.515	5.2
7.8	1.561	4.8
6.3	1.597	4.4
4.7	1.659	3.7
4.4	1.672	3.6
3.6	1.703	3.3
3.0	1.737	2.9
2.5	1.744	2.8
1.9	1.781	2.4
1.1	1.845	1.8
0.0	2.013	0.0

Dry wt. of sample 9.437 gm.

Additional point by desiccator method

23.3

25.0

Table 8.

Relation between the Vapor Pressure and Water Content  
of the Cecil Colloid at 25°C

Sample No. 9415

<u>Vapor pressure in mm.Hg</u>	<u>Weight of water lost by sample in grams</u>	<u>Percent of water in sample</u>
24.3	0.096	22.3
22.7	.274	20.5
22.7	.394	19.8
22.4	.529	17.9
22.1	.669	16.5
22.1	.794	15.3
22.1	.947	13.7
21.7	1.071	12.5
21.2	1.223	11.0
20.4	1.360	9.6
20.0	1.469	8.5
19.8	1.587	7.2
18.2	1.708	6.0
17.1	1.803	5.1
14.3	1.909	4.0
12.3	1.966	3.4
10.2	2.014	3.0
8.3	2.055	2.5
7.0	2.085	2.3
5.9	2.106	2.0
5.0	2.130	1.8
3.7	2.162	1.5
2.9	2.182	1.3
2.3	2.187	1.2
1.4	2.214	1.0
1.1	2.229	0.8
0.9	2.246	0.6
0.9	2.262	0.4
0.0	2.309	0.0

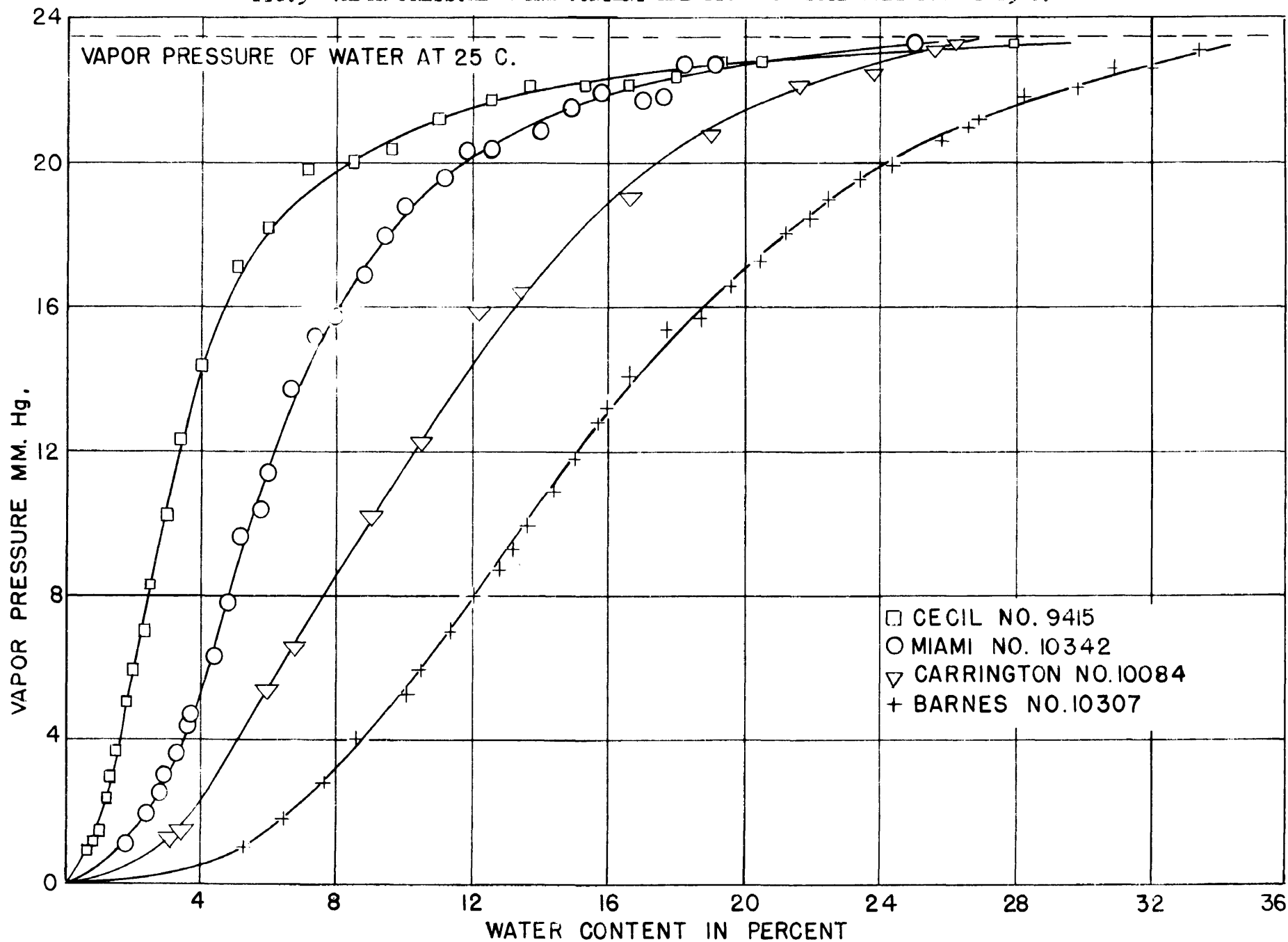
Dry wt. of sample 9.910 gm.

Additional point by desiccator method  
23.3

27.9

The curves for the four soil colloids are shown in Figure 3. These are all of the same general form. They are similar to the curves for gelatine given by Freundlich (10) and to those for wood found by Stamm and Loughborough (20). They are also similar to that for aqueous sulfuric acid. Data are available in the International Critical Tables for the sulfuric acid. The first few values on each curve are undoubtedly too high because of removal of adsorbed air. The very low ones are a bit uncertain because the mercury manometer was not sensitive to small changes in pressure in the very low range.

FIG.3- VAPOR PRESSURE-WATER CONTENT RELATION FOR SOIL COLLOIDS AT 25°C.



MATHEMATICAL EXPRESSIONS FOR THE CURVES

Katz (10) expressed the vapor pressure-water content relation for an elastic gel by the equation

$$-\frac{RT}{V_0} \ln h = \frac{\alpha \beta}{(\beta - a)^2}$$

where  $\alpha$  and  $\beta$  are empirical constants

$h$  is the ratio of the vapor pressure of the gel to that of pure water at the same temperature.  $a$  is the water content in grams, per gram of dry colloid.

$V_0$  is the specific volume of water.

$R$  and  $T$  have their usual significance.

This equation was tested to see if it would fit the curves for the soil colloids studied. The results were not satisfactory. However, a satisfactory equation may be obtained as follows. Consider the reaction



where  $x$  is always less than  $y$ . The decrease in free energy for this reaction may be obtained from

$$(1) \Delta F = \frac{RT}{M} \ln \frac{P}{P_0}$$

where  $M$  is the molecular weight of water

$P$  is the equilibrium pressure of the system

$P_0$  is the vapor of water at the same temperature

$\Delta F$  is the free energy decrease at this temperature when 1 gram of water is added to an infinite amount of soil colloid ( $x \text{ H}_2\text{O}$ ).

These values have been calculated for vapor pressures taken from the curves of Fig. 3, and are presented in Tables 9 - 12. They are also represented graphically in Fig. 4.

As a rule such curves (Fig. 3) will be found to fit an equation of the type

$$(2) \quad y = ae^{-bx}$$

where  $a$  and  $b$  are constants and  $y$  and  $x$  represent the ordinates and abscissas, respectively, and  $e = 2.7183$ . Letting  $x =$  percentage water in sample and  $y = \Delta F$ , we have

$$(3) \quad \Delta F = ae^{-bx}$$

equating (1) and (3)

$$(4) \quad \frac{RT}{M} \ln \frac{P}{P_0} = ae^{-bx}$$

Since  $R$ ,  $T$ ,  $M$ , and  $a$  are constants, we may combine them with the conversion factor to Briggsian logarithms and obtain

$$(5) \quad \log \frac{P}{P_0} = a'e^{-bx}$$

$a'$  and  $b$  may be evaluated by throwing the equation into the logarithmic form

$$(6) \quad \log \log \frac{P}{P_0} = \log a' - bx \log e$$

$$(7) \quad \log \log \frac{P}{P_0} = \log a' - 0.4343 bx$$

$a'$  of course =  $\frac{Ma}{2.303 RT}$ .  $a'$  (and therefore  $a$ ) and  $b$  may then be evaluated by plotting  $\log \log \frac{P}{P_0}$  against  $x$  or by plotting  $\log \frac{P}{P_0}$  on semi-log paper against  $x$ .  $\log a'$  will be the intercept on the  $y$  axis and  $-0.4343 b$  the slope. Curves for the four soil colloids studied, plotted by the first method are given in Fig. 5. Straight portions are found for all the types especially at lower water percentages. Equations for the straight portions of each are



Table 9

Change in Free Energy per Gram of Water. Added at Various

Vapor Pressures for the Barnes Colloid at 25°C

Sample No. 10307

<u>Percent water in sample</u>	<u>Vapor pressure of sample mm Hg.</u>	<u>-<math>\Delta F</math> in cal. per gm H<sub>2</sub>O added</u>
1.0	0.1	161.7
2.0	0.2	155.0
3.0	0.4	134.1
4.0	0.6	120.1
5.0	1.0	103.5
6.0	1.6	88.4
7.0	2.3	75.5
8.0	3.2	65.6
9.0	4.2	56.6
10.0	5.4	48.3
11.0	6.6	41.8
12.0	8.0	36.5
14.0	10.6	26.2
16.0	13.2	18.9
18.0	15.3	14.1
20.0	17.1	10.4
22.0	18.6	8.1
24.0	19.9	5.5
26.0	20.9	3.9
28.0	21.7	2.6
30.0	22.2	1.9
32.0	22.7	1.1

Table 10

Change in Free Energy per Gram of Water Added at Various

Vapor Pressures for the Carrington

Colloid at 25°C

Sample No. 10084

<u>Percent water in sample</u>	<u>Vapor pressure of sample mm Hg</u>	<u>-ΔF in cal. per gm H<sub>2</sub>O added</u>
1.0	0.2	155.0
2.0	0.6	120.1
3.0	1.2	97.9
4.0	2.3	76.5
5.0	3.8	59.9
6.0	5.3	49.1
7.0	7.0	39.9
8.0	8.5	33.4
9.0	10.2	27.4
10.0	11.6	23.2
12.0	14.4	16.1
14.0	16.9	10.8
16.0	18.9	7.2
18.0	20.4	4.6
20.0	21.4	3.0
22.0	22.2	1.9
24.0	22.8	1.0

Table 11  
 Change in Free Energy per Gram of Water Added at Various  
 Vapor Pressures for the Miami Colloid

at 25°C

Sample No. 10342

<u>Percent water in sample</u>	<u>Vapor pressure of sample mm Hg</u>	<u>-<math>\Delta F</math> in cal. per gm H<sub>2</sub>O added</u>
1.0	0.5	127.2
2.0	1.5	90.5
3.0	3.0	67.7
4.0	5.2	49.7
5.0	8.6	33.1
6.0	11.5	23.6
7.0	13.9	17.3
8.0	15.8	13.0
10.0	18.6	7.7
13.0	20.2	4.8
14.0	21.2	3.4
16.0	21.9	2.3
18.0	22.4	1.6

Table 12

Change in Free Energy per Gram of Water Added at Various

Vapor Pressures for the Cecili Colloid

at 25°C

Sample No. 9415

<u>Percent water in sample</u>	<u>Vapor pressure of sample mm Hg</u>	<u>-<math>\Delta F</math> in cal. per gm H<sub>2</sub>O added</u>
1.0	1.8	84.4
2.0	6.0	44.9
3.0	10.2	27.4
4.0	14.4	16.1
5.0	16.6	11.4
6.0	18.1	8.6
7.0	19.0	6.6
8.0	19.8	5.7
10.0	20.8	4.0
12.0	21.6	2.7
14.0	22.0	2.2

FUNCTION OF WATER CONTENT AT 25°C.

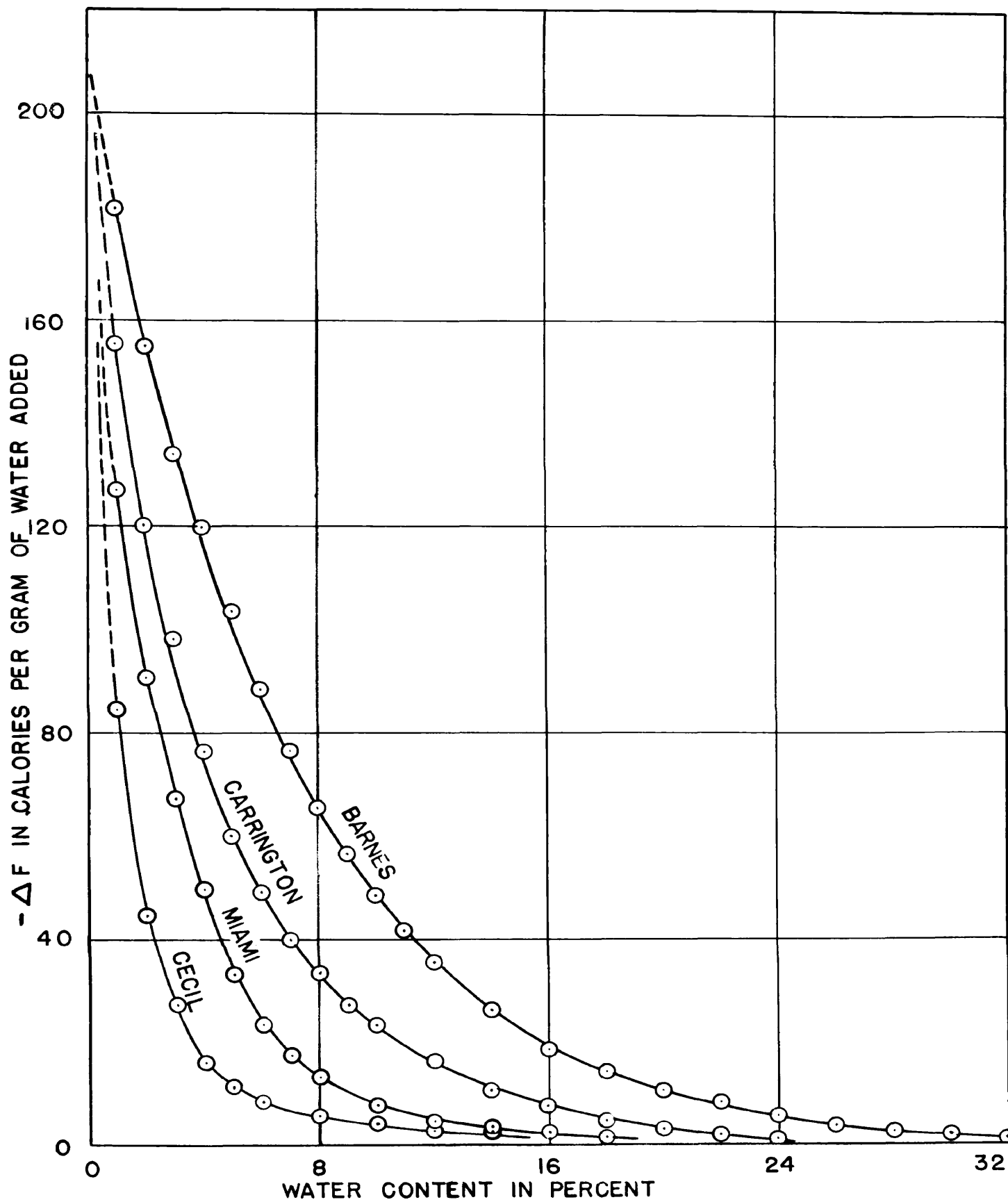
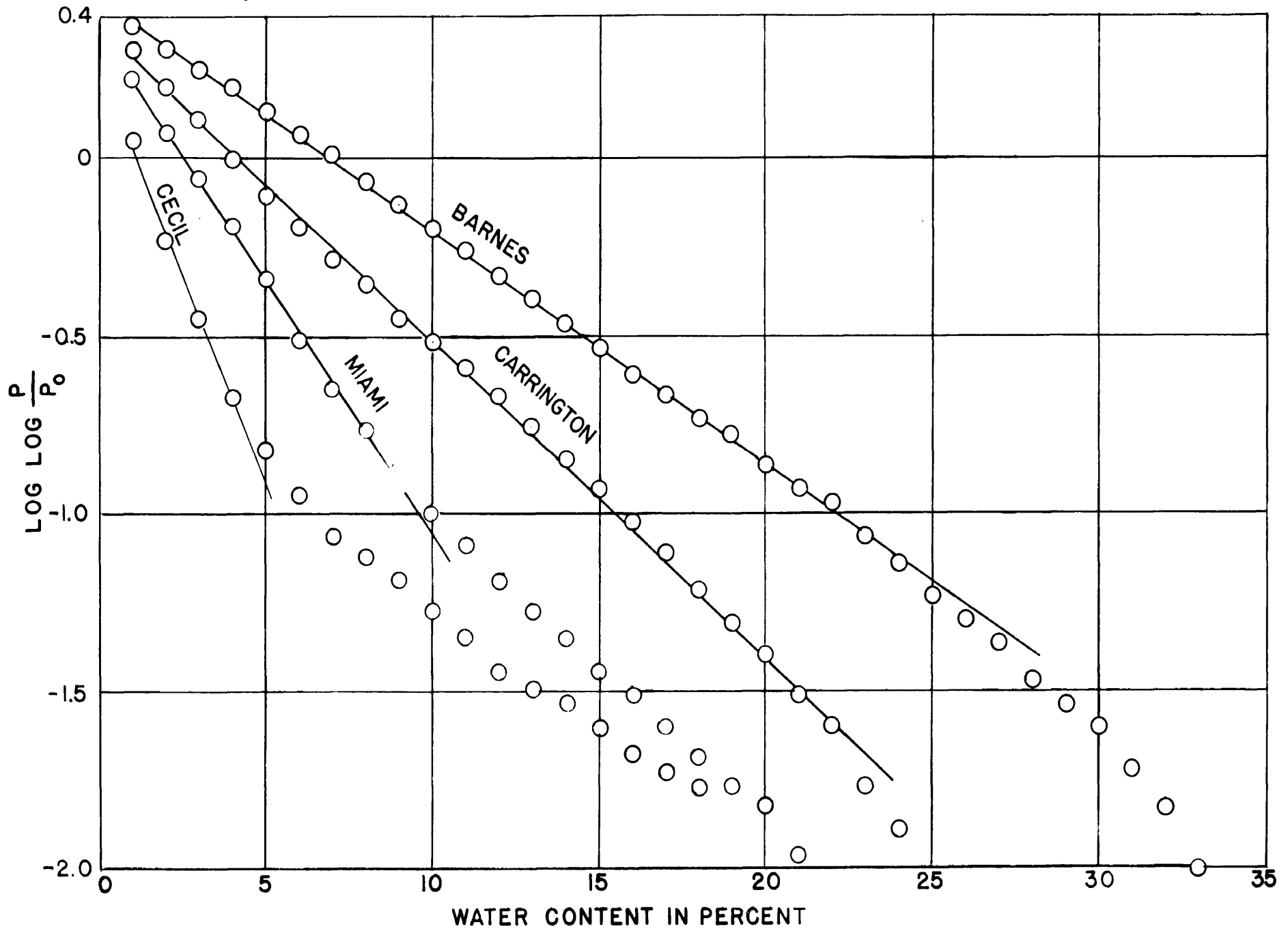


FIG.5- LOG LOG OF VAPOR PRESSURE RATIO AS A FUNCTION OF WATER CONTENT AT 25°C.



Given below. They are valid, naturally, only for colloids of water content lying on the straight portion.

$$\text{Barnes. } \log \frac{P}{P_0} = 2.82a - 0.148x$$

$$\text{Carrington. } \log \frac{P}{P_0} = 2.32a - 0.205x$$

$$\text{Miami. } \log \frac{P}{P_0} = 2.21a - 0.311x$$

$$\text{Cecil. } \log \frac{P}{P_0} = 1.15a - 0.491x$$

Possible explanations for the failure to obtain straight lines at higher water contents will be offered later.

It is interesting to note that, were  $\Delta F$  - water content curves available at various temperatures, the heat of hydration and entropy of hydration could both be obtained. The first of these quantities can be calculated from the Gibbs-Helmholtz equation:

$$(8) \quad Y = \Delta H + T \left( \frac{\partial \Delta F}{\partial T} \right)_P$$

and the second from:

$$(9) \quad \Delta F - \Delta H = -T\Delta S$$

It is to be observed that the  $\Delta F$  values we have obtained are really differential values, that is, the free energy change in hydration when the composition of the phase receiving water remains virtually unchanged. We may obtain the total free energy for an addition of an amount of water corresponding to 99 percent of saturation. These values are obtained by determining the area

under the curves shown in Fig. 4. The values obtained are given below:

	$\Delta F$ in Cal. per gram colloid
Barnes	14
Carrington	9
Miami	6
Cecil	3

Anderson and Mattson (3) measured the total heat of wetting of soil colloids and found a range from 17.6 to 4.5 cal. per gram of soil colloid. Although these values are of the same order of magnitude as those for  $\Delta F$  given above, they cannot be compared with each other because the measurements were made on different colloids.

#### SWELLING PRESSURE OF SOIL COLLOIDS

Katz (12) made the assumption that the change in free energy was equal to the total heat of wetting for swelling colloids. He derived the equation

$$P = - \frac{RT}{M V_0} \ln \frac{P}{P_0}$$

where  $V_0$  is the specific volume of water and from it calculated the swelling pressure ( $P$ ) of some colloids. The pressures so obtained are very high. According to his equation, at 99 percent humidity the swelling pressure of a sample of colloid would be 200 lb./sq. in. Recently Olstead (17) has



measured the water content of some soil colloids at very high centrifugal forces. For a particular sample of colloid he was able to reduce the water content to 31.1 percent by a centrifugal force of 332000 gravity. The highest pressure obtained, that is, at outside of layer of colloid was about 2000 pounds per square inch. The same colloid holds 29.4 percent water at 99 percent humidity. The average pressure obtained in the centrifuge was considerably more than that calculated necessary to reduce the water content to 29.4 percent, but the water content obtained was somewhat higher (31.1 percent). The reasons for this discrepancy may lie in the imperfect drainage of the centrifuge bowl and rigidity of the soil colloid. Given below are the moistures of two other samples of colloid together with this one, at 99° relative humidity, and at a centrifugal force of 333000 gravity. All were extracted from the same soil profile.

		Percent Moisture at -	
	Depth inches	332000 gravity	99 percent rela- tive humidity
Columbiana colloid	0-10	30.0	27.3
"	" 10-25	31.1	29.4
"	" 25-40	31.7	30.3

## VARIATIONS WITHIN THE PROFILES

It has been shown that the vapor pressure-water content curves show an orderly variation from the little hydrolyzed Barnes to the highly hydrolyzed Cecil. In order to determine what differences occur among the vapor pressure curves of the colloids extracted from the various horizons of the profiles, vapor pressure-water content data were obtained on the colloids of all the layers of the four soils profiles used in this investigation.

From the standpoint of time it was out of the question to determine the complete curves for each layer of the soil profiles considered here. Hence it was decided to use the vacuum desiccator method to determine a few points for each layer of the profile and to draw the curves from these points. Although it is recognized that this method is open to objections not found in the one previously used, it will serve, however, to compare the several layers of a soil profile with each other.

Table 13 gives the data for these colloids obtained by allowing 2-gram samples of the colloids to stand for five days at a temperature of 25°C over sulfuric acid-water mixtures of known concentration. The air in the desiccator, and probably a part of the adsorbed air of the colloid, was removed by evacuation before placing in the thermostat. The procedure was to allow the colloid to take up water vapor first at 99 percent relative humidity and after weighing it to use the same sample for the next lower vapor

Table No. 13. - Water held by soil colloids in equilibrium  
with different vapor pressures

**Barnes profile colloids**

Sample No.	Depth	Water held at a vapor pressure of --				
		0.3 mm Hg	3.0 mm Hg	6.8 mm Hg	18.2 mm Hg	23.3 mm Hg
	inches	percent	percent	percent	percent	percent
10305	0-9	2.9	6.1	9.1	18.4	31.6
10306	9-17	3.0	6.4	9.8	19.6	33.8
10307	17-33	2.4	6.3	9.9	20.1	35.4
10308	33-60	2.0	6.0	9.4	20.2	36.5

**Carrington profile colloids**

10082	0-3	2.1	4.8	7.0	14.7	24.4
10083	3-13	2.0	4.8	7.1	15.5	25.6
10084	13-22	2.0	4.7	7.1	15.6	26.2
10085	22-43	1.7	4.6	7.2	16.6	29.3
10086	43-79	1.8	4.6	7.4	17.6	31.2
10087	70-84	1.9	5.1	8.0	18.2	33.2

**Cecil profile colloids**

9415	0-6	1.1	2.1	2.9	6.3	27.9
9416	6-32	.7	1.3	2.0	5.1	35.2
9417	32-60	.6	1.3	2.0	5.1	36.1
9418	60-84	.6	1.4	2.1	5.5	33.4

**Miami colloid profile**

Sample No.	Depth	Water held at a vapor pressure of --				
		0.3 mm Hg	2.9 mm Hg	10.3 mm Hg	18.2 mm Hg	23.2 mm Hg
	inches	percent	percent	percent	percent	percent
10341	0-1 $\frac{1}{2}$	1.6	3.6	6.2	9.8	24.2
10342	2 $\frac{1}{2}$ -9	1.6	3.6	6.2	10.0	25.0
10343	11-24	1.5	3.8	7.6	14.3	31.1
10344	28-48	1.3	3.1	6.2	11.3	30.8

pressure measurement. Thus one 2-gram sample served to furnish all the data for the curve.

It is to be noted that this procedure differs radically from the one used before in that air was allowed to saturate the sample at the end of each run when the weighing was made. The presence of this adsorbed air undoubtedly prevents the attainment of equilibrium. Since all the samples had the same treatment the data are good for comparative purposes.

The data shown in Table 13 are plotted in Figs. 6, 7, 8, and 9. It is noteworthy that in every case the surface colloid has a curve lying to the left of the subsurface layers. The difference between the curves of the individual layers of the profile is much less, however, than that between the curves of the groups.

An interesting feature of these curves is that at low vapor pressures in case of the Carrington and Barnes, the family of curves converge to a point and cross. Since the differences between the curves at low pressures is so small this reversal might be attributed to experimental error were they not so regular. The Cecil reversal takes place at much higher vapor pressure.

FIG. 6\_VAPOR PRESSURE-WATER CONTENT RELATION FOR THE COLLOIDS OF THE BARNES PROFILE

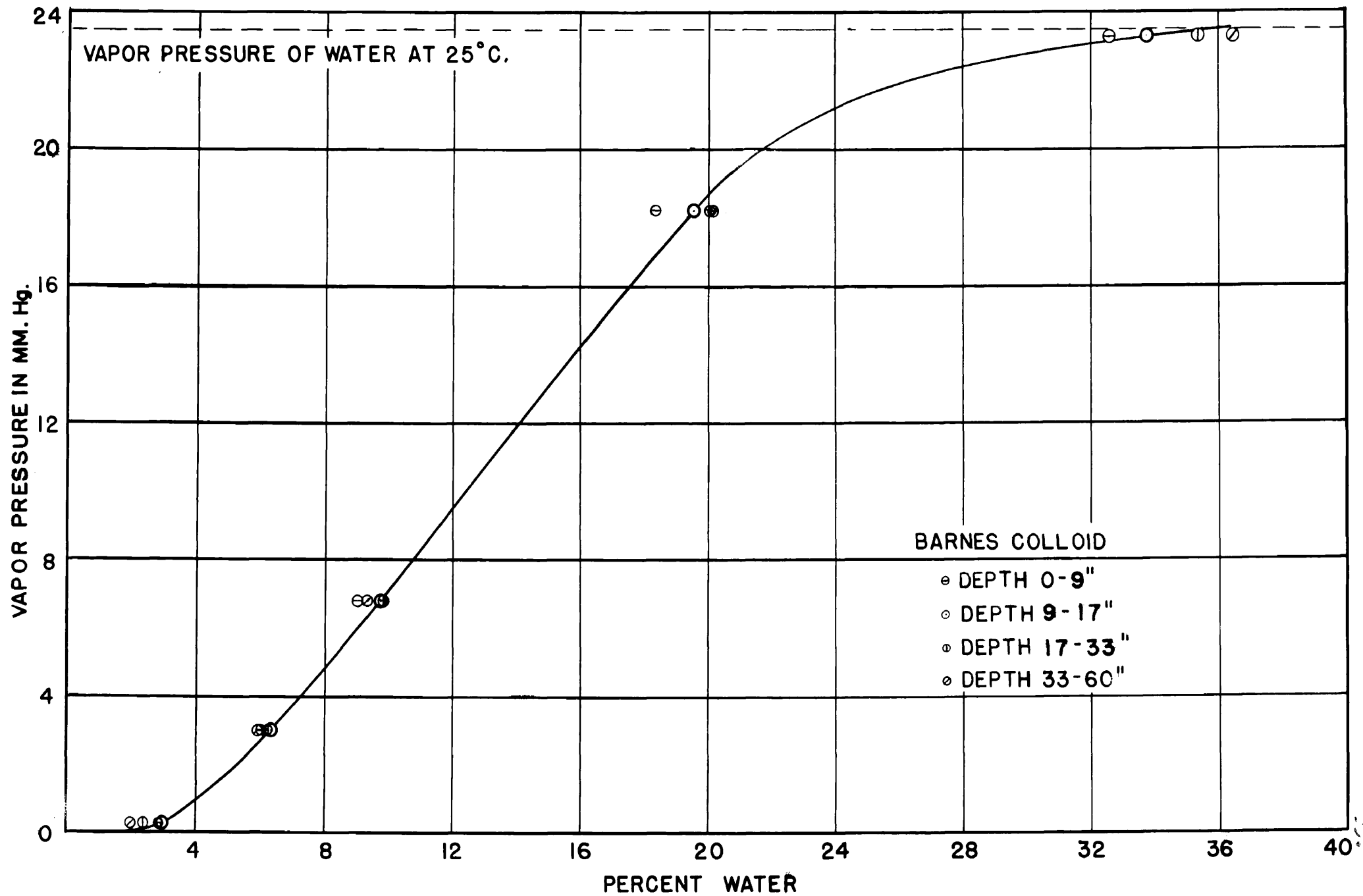


FIG. 7- VAPOR PRESSURE-WATER CONTENT RELATION FOR THE COLLOID OF THE CARRINGTON PROFILE

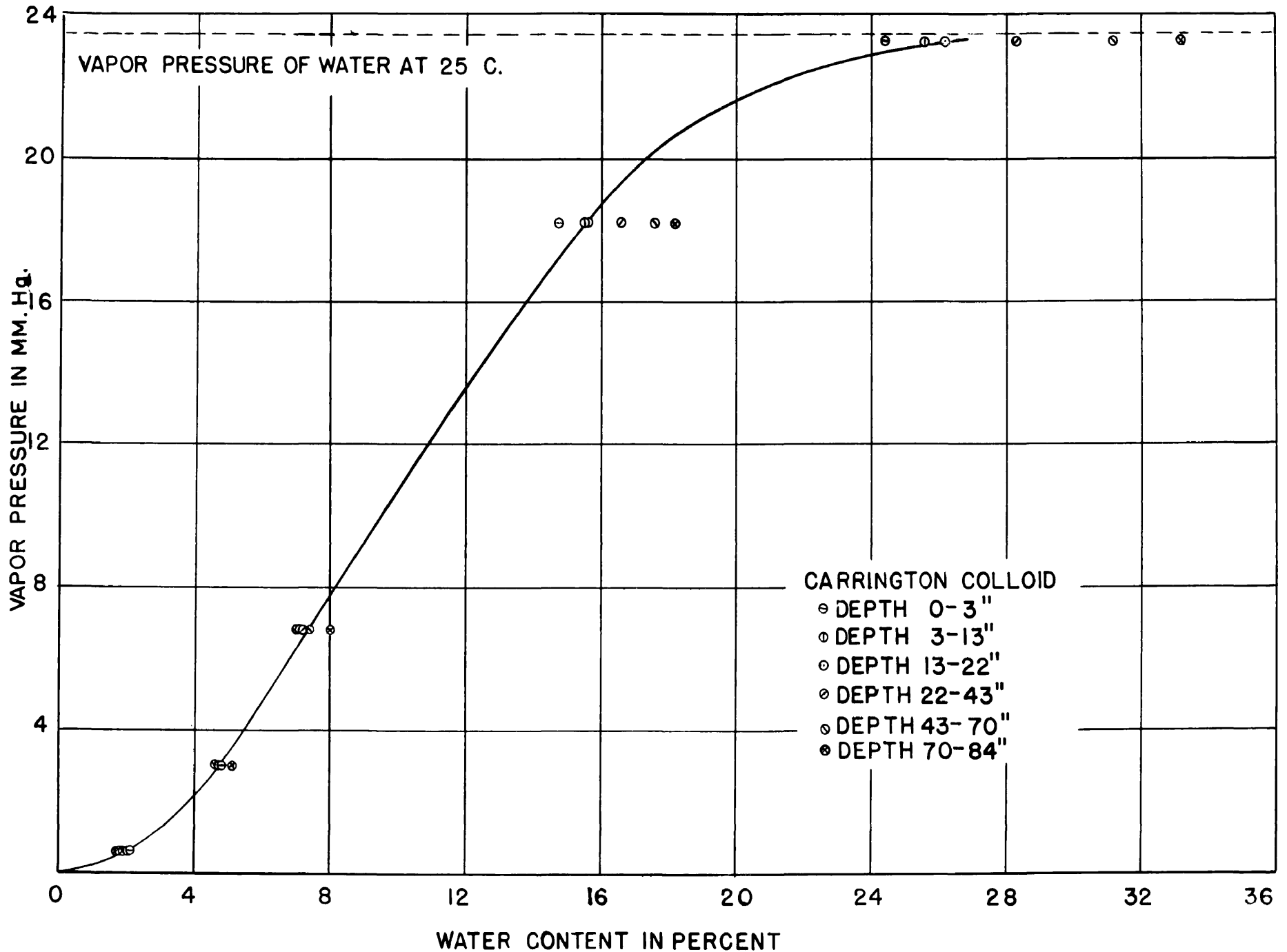


FIG.-8. VAPOR PRESSURE WATER CONTENT RELATION FOR THE COLLOID OF THE MIAMI PROFILE

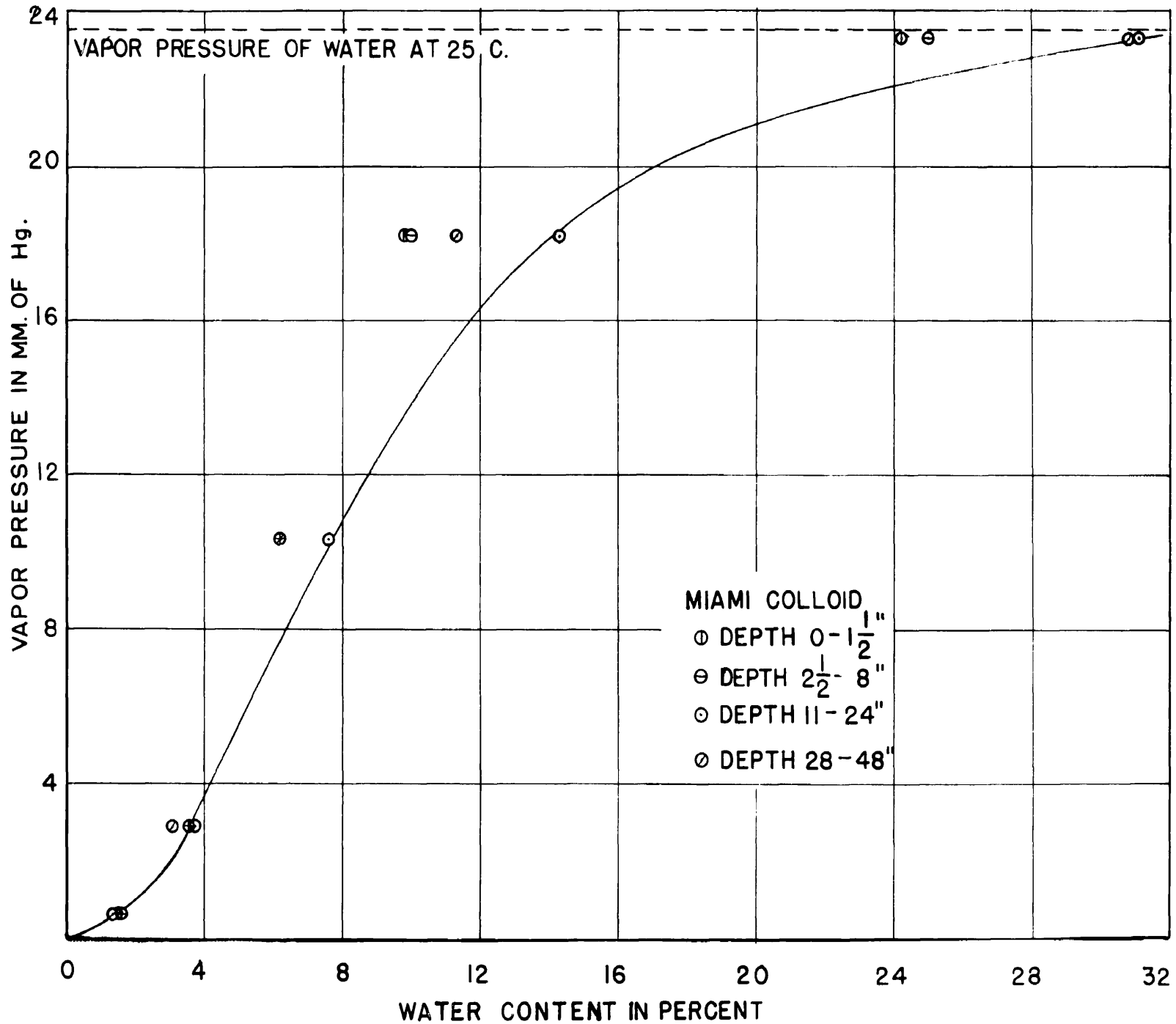
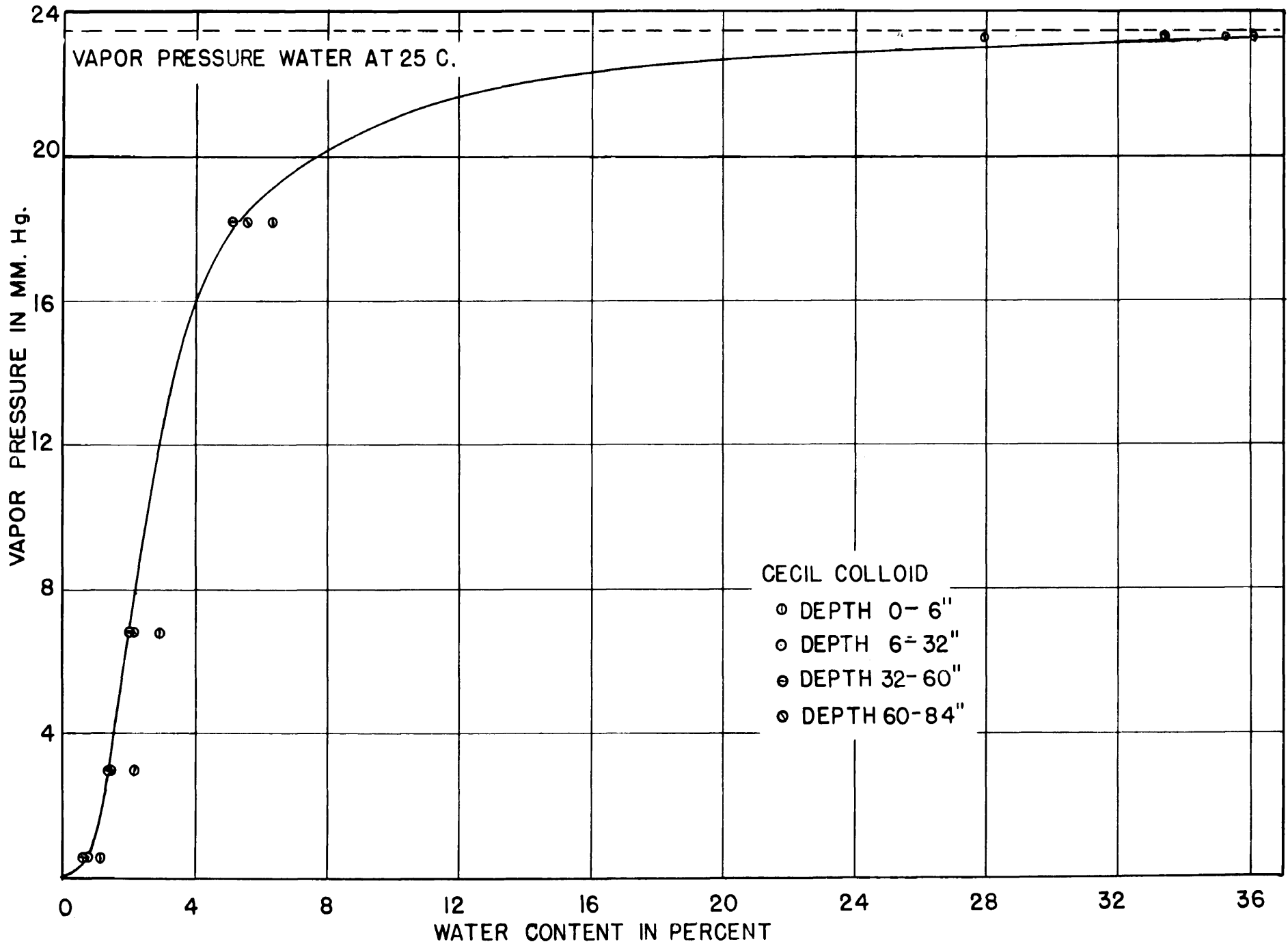


FIG. 9- VAPOR PRESSURE-WATER CONTENT RELATION FOR THE COLLOIDS OF THE CECIL PROFILE





## DISCUSSION

The data obtained on the nature of the vapor pressure-water content curves of four of the great soil groups have considerable bearing on a number of problems related to soils.

## RELATION TO SOIL CLASSIFICATION

The system of soil classification used in the United States is based primarily on the characteristics of the soils themselves. One of the accomplishments of the soil chemists has been the finding of a chemical basis for the differences observed in the field. The most commonly used criteria are the formula ratios of silica to sesquioxides, and of silica to alumina of the colloid. These ratios are open to the objection that we cannot, with our present knowledge, obtain these colloids in a pure state. A comparatively small percentage of mineral which is not weathered may alter the chemical relationships very greatly without materially affecting the properties of the soil from which the colloid was obtained. For example, the values for the two ratios mentioned above, shown in Tables 1 - 4, show the Miami colloid to have higher silica alumina and silica sesquioxide ratios than the Garrington. From soil characteristics observed in the field, however, we know that the Miami is a more weathered soil than the Garrington. Its characteristics are intermediate between those of the Cecil and Garrington; an examination of the chemical analysis shows an unusually high percentage of potassium.

One might infer that there was present some unweathered mineral of the type of orthoclase which has the formula  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ . McCaughey and Fry (16) have found considerable quantities of unweathered feldspars such as orthoclase in the coarser fractions of soils derived from glacial till. While there is no proof that these minerals also carry over into the colloid, it seems reasonable that such may be the case.

Since unweathered ground minerals such as orthoclase do not hold water appreciably in the hygroscopic range, they should, if present as an impurity, serve merely as a diluent, and hence affect the vapor pressure curves only slightly. An examination of the curves in Fig. 3 shows that the Miami falls nicely into its proper relation between the Carrington and Cecil and not between the Barnee and Carrington as its silica sesquioxide and silica alumina ratios would predict.

The differentiation shown by this family of curves between the four groups of soils covered in this investigation is sharp and of even distribution. It appears that the hygroscopic moisture of the colloid is a characteristic function of the factors which determine the field characteristics of the soil. Further investigation may reveal some curves out of place, just as some of the ratios are out of place, but this will not invalidate the use of these curves as criteria of soil properties. It is possible that rectification of the curves would reveal that some one or two determinations could be made to give this characterization.

Keen (13) has suggested the use of the amount of moisture held at 50 percent relative humidity, but it seems that this alone would not be adequate.

#### RELATION TO WEATHERING PROCESSES

A mineral such as orthoclase or anorthite ground in a plate mill to pass a 100-mesh sieve, has no combined water and little or no hygroscopic water. If this 100-mesh mineral is ground in a ball mill to colloidal dimensions and the bases removed by electro dialysis, it will have both combined water and hygroscopic water. Roughly three or four molecules of water are added as combined water for each molecule of base removed. The bases are quickly removed from the surface of the ground mineral by electro dialysis and the conductivity soon drops to a very low value. Further grinding will present new surface either by crushing the mineral or by stripping off the hydrolyzed portion, thus exposing more bases.

In Nature the same thing happens except much more slowly. In northern latitudes it may be that the freezing and thawing of water is the force which breaks the particles apart. The pressure so developed could also be pictured to strip off the coat of hydrolyzed mineral or colloid. In the southern latitudes we do not have this freezing and thawing, but hydrolysis proceeds at a much faster rate than in the north. In fact, in parts of the Piedmont region there are deposits of hydrolyzed material as much as 100 feet thick which have been formed from crystalline rocks.

If this material were formed without the aid of some mechanical force to break the rock apart and keep the colloid coatings stripped off, it should consist of solid cores of unweathered mineral coated by highly weathered hydrous material, with intervening layers only partially weathered. If one should remove by gentle treatment the outermost coat of colloid, and then by more vigorous treatment the next layer, and so on, the various fractions so obtained should vary enormously in chemical composition. Such is not the case. While there is some difference in composition between the easily and difficultly removed colloid of a soil, the colloid extracted from a given soil has almost the same composition whether a small portion is extracted or a complete extraction made (7).

What then is the force which does the mechanical work of splitting the rocks into fragments and the mechanical mixing of the colloid? It may be the pressure referred to on page 28. The swelling pressure at 99 percent humidity is very great and it is certain that the colloid is dried below this point during the summer drouths at and near the surfaces. Whether this swelling is a factor down as low as the water table is uncertain, but it seems probable that it is a factor near and at the surface.

It is interesting to note that the values for water held at 99% humidity vary progressively from top soil colloid to subsurface soil colloid. It would seem that there are some factors operating at the surface of these soils which lower progressively the amount

of water held at high vapor pressures. This cannot be charged to progressive weathering since the value for water held by the Carrington surface colloid is less than the corresponding figure for the Cecil. The organic matter content decreases from top to bottom of the profile and may be responsible for the observed phenomenon, but this change from top to bottom is more probably due to the irreversible wetting and drying mentioned by Brown, Rice, and Byers (9). Indeed, Brown and Byers (8) have found experimentally that the water held at this relative humidity is progressively decreased by alternate wetting and drying. The data given for the colloids extracted from these four soil profiles are not sufficient either to establish the generality of the phenomenon observed, or to determine the primary cause of it.

#### RELATION TO THE WILTING COEFFICIENT

The wilting coefficient is defined by Briggs and Shantz (6) as "the moisture content of the soil (expressed as a percentage of the dry weight) at the time when the leaves of the plant growing in that soil first undergo a permanent reduction in their moisture content as the result of a deficiency in the soil moisture supply. By a permanent reduction is meant a condition from which the leaves can not recover in an approximately saturated atmosphere without addition of water to the soil." These investigators reached the conclusion that the wilting coefficient depended on the "moisture retentiveness" of the soil. They apparently attribute the "moisture retentiveness" to the texture of the soil.

Veihmeyer and Hendrickson (23) found a great variation (from 1.41 percent to 19.03 percent) in the wilting coefficients of different soils. No information is given as to the nature of the soils which gave these percentages, however. Recently Bodman and Edlefsen (5) published vapor pressure-water composition curves for "sand" and "clay". They designate on these curves the point at which permanent wilting occurs. These points correspond to 99 percent relative humidity at 30°C. This means that the wilting coefficient is a point on the vapor pressure-water composition curve. The lowest value for water held at 99 percent humidity among the colloids used in this investigation is 24.4 percent in the Carrington surface soil colloid, and the highest value is 36.5 percent in the subsurface colloid of the Barnes. Thus it is seen that soils of the same texture but having different kinds of colloid would have different wilting coefficients. This is in accord with the experimental evidence.

Livingston and Koketsu (14) have arrived at a more dynamic concept of the soil-water relations at the wilting point. They have developed the "water-supplying power" of a soil as the critical factor at the wilting point. They find this to be independent of the nature of the physical make-up of the soil. This must mean that the transfer of water takes place in the vapor state at the wilting point. This would be predicted if the vapor pressure of a soil is less than that of pure water at the wilting point, as found by Bodman and Edlefsen.

## THE NATURE OF THE HYGROSCOPIC WATER

Mattson (15) has pictured the hygroscopic water as a film or shell of water around the colloid particles. He attributes the heat liberated on wetting the soil colloid as due to compression. This conclusion is reached because soil colloids (1) (3) have been shown to have a small<sup>er</sup> specific volume in water than in liquids like toluene and petroleum ether. The compression is assumed to be due to molecular attraction of the colloid for water.

Baver and Horner (4) have pointed out that it is not logical to pick an arbitrary point, 110°C, and call all water not driven off at this temperature, combined water. They prefer to call combined water, that water which is a part of the crystal lattice. Measurements indicate that this water is considerably less than what is ordinarily termed combined water. They would put a portion of the combined water in the same class as hygroscopic water, which they consider as being held by adsorption.

The data shown in this paper indicate that the hygroscopic water of the soil colloids is held in the same manner as the water of swelling in gelatin and in wood. The vapor pressure-water composition curves are also very similar to those for sulfuric acid-water mixtures. It is true that a portion of the water in these mixtures is held with greater tenacity than the hygroscopic water of the soil colloids but the difference is one of degree.

Probably the most illuminating treatment of hygroscopic water in elastic gels is that of Peirce (18). He proposes a "two-phase" theory of absorption of water by cotton cellulose which has water content-vapor pressure isothermals very similar to those of soil colloids.

According to the Peirce theory the hygroscopic water can be considered as occurring in two different phases, or states, on the cellulose. The first of these is the (a) phase which is held to be chemically bound by the hydroxyl groups of the hexose units of the cellulose. The second or (b) phase is the water molecules attracted by the water molecules of the (a) phase and by the colloid surface which is not reactive toward water. From theoretical considerations he arrives at the following formula for the vapor pressure-water content isotherms for cotton and starch.

$$1 - \frac{P}{P_0} = (1 - kC_a)e^{-BC_b}$$

where P is the water vapor pressure of the cellulose ( $xH_2O$ )

$P_0$  is vapor pressure of water at the same temperature

k is a constant characteristic for each sample

$C_a$  is concentration of moisture in the (a) phase

B is another constant characteristic of each sample

$C_b$  is the concentration of water in the (b) phase

This equation is similar in many respects to the equation arrived at on page 20 for the soil colloids. Peirce pointed out that the equation would be applicable only to pure substances.



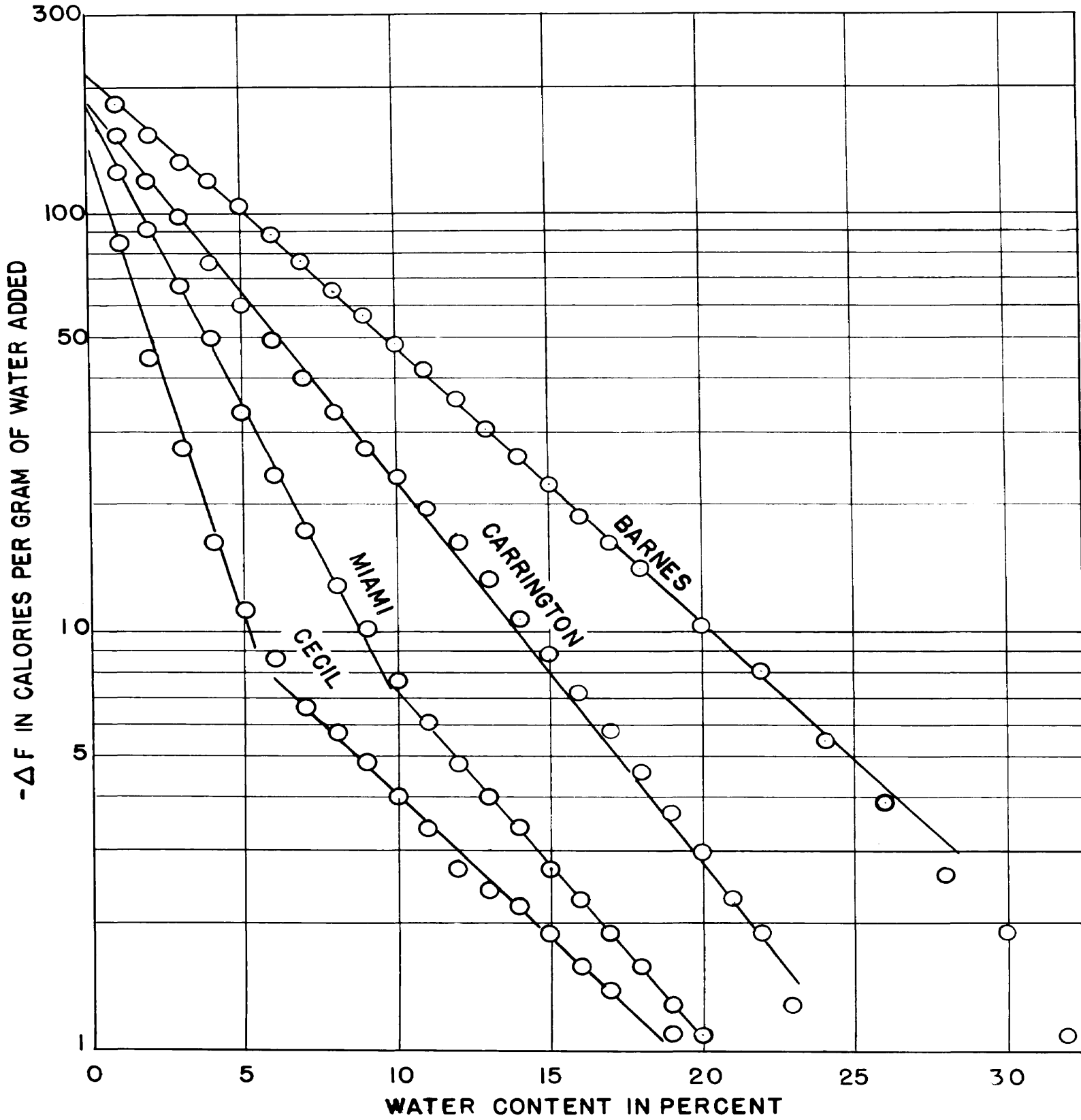
It is probable that the failure of the curves for free energy as a function of water content, to rectify, as shown in Fig. 10, is due to some contaminating colloid which does not exert a noticeable lowering of the vapor pressure in the lower moisture content ranges, but which does make itself noticeable in the higher moisture content ranges. Iron oxide is a contaminant to which we may attribute this behavior.

If then we carry over the two-phase theory of Peirce to soil colloids, we may picture the (a) phase water as being combined with the aluminosilicic acid complex, with the tendency toward further hydration as the attracting force. The (b) phase water is held on the surface of the colloid not occupied by (a) phase water and as outer layers on the (a) phase water.

Concerning the (a) phase water, one must conclude that in the little hydrolyzed soils of the chernozem group the tendency to hydrate is very great, and that in the lateritic Cecil series the tendency is very small. The (b) phase water does not appear to be a function of the chemical composition of the colloid, but probably is determined by specific surface. Further investigation is necessary to determine the quantitative relations between these two kinds of hygroscopic water. The equation of Peirce given above offers a very attractive possibility in this direction.

This idea of the two kinds of hygroscopic water is easily harmonized with the work of Anderson and Mattson (3) and of Bayer and Horner (4) on the effect of exchangeable ions on the hygroscopicity of colloids. It is interesting to note that the colloids

FUNCTION OF WATER CONTENT AT 25°.



having high base exchange capacities are the ones having such attraction for the (a) phase water. It is possible that the base exchange phenomena and absorption of (a) phase water are due to the same chemical affinity, that is secondary valence, or it may be that the base exchange bases are held by primary valence bonds. Further investigation along this line should lead to the designation of one of these as being responsible for the phenomena.

#### SUMMARY

1. A study has been made of the detailed vapor pressure-water content curves of four typical soil colloids. The curves are shown to be characteristically different for the different soil groups. The chemical composition of the colloids of four soil profiles is given.
2. A study has been made of the variation of the vapor pressure-water content curves for the different colloids of a given profile.
3. The change of free energy as a function of water content has been calculated and the total free energy change on wetting has been determined approximately.
4. Data have been presented to show that the swelling pressures of soil colloids even at relatively high water content is great.

The relation of this swelling pressure to weathering processes has been pointed out.

5. The connection between the vapor pressure curves and wilting of plants is discussed.

6. The relation of the characteristic vapor pressure curves to soil classification is shown.

7. The two phase theory of absorption of water by cellulose of Peirce is used to picture the nature of the hygroscopic water of soil colloids.

8. The results of this investigation indicate a fruitful field of investigation in the thermodynamics of the moisture relations of soil colloids below the saturation point.

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