of z_d given by the periodic terms will be small. It will, moreover, be oscillatory in value, and the mean value of the drift will be given by using the particular integral of η.

To get a first approximation we include the $Q_1^{(j)}$, but disregard the $Q_2^{(j)}$, and it turns out that the $Q_2^{(j)}$ are actually negligible in the final solution. As a matter of fact only the $Q_1^{(1)}$ and the $Q_1^{(2)}$ need be included, and of these only $Q_1^{(1)}$ appears in η. This approximation to the drift gives

$$z_d = \int_0^t u \int_0^t \frac{(\lambda - 1)\, Cwq_1}{\lambda h u}\, dt^2. \qquad (31)$$

For δ small, $(\lambda - 1)/\lambda h$ reduces, according to (29) and (30), to f_L/rf_M, and it is easily shown that in this case (31) is identical with the formula for drift given by equations (4·203) and (4·204) of the paper cited.

The Indirect Measurement of the Aqueous Vapour-Pressure of Capillary Systems by the Freezing-point Depression of Benzene.

By Edward Mortimer Crowther and Amar Nath Puri, Soil Physics Department, Rothamsted Experimental Station.

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In the study of the soil-water system a knowledge of the variation of vapour-pressure with water content is of prime importance. The water content of soils in equilibrium with atmospheres of varying humidity can be readily obtained by prolonged exposure over sulphuric acid—water mixtures, preferably in vacuum desiccators. Indeed, the application to soils of the methods used by van Bemmelen (1) in his classical work on silica gel might have prevented much of the confusion that has arisen in certain soil studies. For certain purposes interpolation from other water contents is undesirable, but the direct measurement of vapour pressure on soils of defined water content is either laborious or inaccurate. Tensimetric methods are even more unreliable than with salt hydrates or gels, whilst the saturation of an air current requires large amounts of carefully-prepared soil and is extremely difficult with samples of low humidity.

Several investigators have had recourse to the measurement of other properties thermodynamically connected with the vapour-pressure. The deteration of the freezing-point of moist soils is practicable only at relative pour-pressures greater than about 80 per cent. to 90 per cent., whilst the atometric method involves measurements at widely different temperatures fairly dry soils.

The measurement of the vapour-pressures of salt hydrate mixtures affords similar and simpler problem. For this purpose several investigators have ed distribution methods, combined with some physical method of deterning the concentration of water in the liquid phase. Wilson (2) and Noyes d Westerbrook (3) brought salt hydrates into equilibrium with amyl alcohol, d determined the concentration of dissolved water by colorimetric comrison with cobalt chloride solutions, or by the conductivity of the solutions ter the addition of excess of potassium thiocyanate. The water concentraon at equilibrium was not proportional to the vapour-pressure, since the lutions obtained were not sufficiently dilute to be regarded as of constant ermodynamic environment.

Sidgwick (4) showed that the freezing-point of benzene is depressed by 100° C. by saturation with water, and that the efficiencies of the solid drying gents normally used in the organic chemistry laboratory could be ascertained the freezing-point depression (F.P.D.) of the benzene in equilibrium with em. By assuming that the concentration of dissolved water was proporonal to the aqueous vapour-pressure of the drying agent, Sidgwick ascribed alues to these. No other vapour-pressures were given for comparison, and ufficient data cannot be obtained from the literature, owing to the indefinite ature of some of the hydrates used.

The measurement of vapour-pressures by the F.P.D. of benzene in equilirium with the substances in question possesses the advantage that the slight olubility of water in benzene (0·03 per cent.) results in the transference of ery small amounts of water, and renders possible its application to small uantities of materials of low water content. The validity of the assumption hat dissolved water in benzene behaves as an ideal solution, and that the oncentration of water, as measured by the F.P.D., is proportional to the relative vapour-pressure of the added substance, is established by the experiments on sulphuric acid—water mixtures described below. For such solutions, and for salt hydrates, the method is both rapid and accurate. The essential features of the method appeared to render it suitable for the study of the vapour-pressure of soils, especially for those of low water content.

It was found, however, that equilibrium was reached only slowly in the case of soils, and that the method was therefore not a convenient one for systematic work. Further, soils differed from sulphuric acid—water mixtures and salt hydrates, in that the F.P.D. was not proportional to the relative vapour-pressure as measured in air or *in vacuo*; the apparent relative vapour-pressure, corresponding to the observed F.P.D., was greater by an amount which was the same for soils of very different types, when these were compared at the same relative vapour-pressures in air. The deviation arises apparently from the introduction of an additional liquid phase, benzene, and may therefore throw light on the manner in which water is held in relatively dry soils. By assuming a fine capillary structure and considering the changes in surface energy brought about by the addition of benzene, it was possible to derive an expression connecting the relative vapour-pressure in air with the apparent vapour-pressure in benzene, or with the F.P.D. The agreement of the experimental results with this expression suggests that some, and possibly the greater part, of the soil water may be regarded as existing in such fine capillaries.

Experimental.

The purest sample of benzene that could be obtained was recrystallised several times until the freezing-point of the dried sample was constant. This recrystallisation was found necessary because the earlier samples showed a steady rise in freezing-point if kept frozen for some time, due apparently to the escape of some volatile impurity. The measurements of the freezing-point depression were made with the usual Beckmann technique; the cooling chamber being kept at 2–3° C. by floating lumps of ice in a large quantity of water, which was kept well stirred in a heavily lagged bath. For each determination 50 c.c. of benzene were taken from a stock bottle containing metallic sodium, and before each series, measurements were made on two samples, treated respectively with water and phosphorus pentoxide. In all cases the difference in freezing-points was $0 \cdot 100 \pm 0 \cdot 001°$ C., as recorded by Sidgwick. The tube was open to the air only through the narrow glass tube through which the stirrer passed. There was therefore the possibility of traces of water being picked up from the air, but no appreciable error was introduced in this way, since measurements were made in every case in the presence of an excess of a material, whose vapour-pressure would not be changed perceptibly by these small amounts of water.

Preliminary experiments with varied amounts of sulphuric acid—water mixtures showed that 4 c.c. of the mixture was sufficient to give constant results. After each reading the benzene was melted and well stirred, and the process repeated several times. With sulphuric acid—water mixtures there as occasionally a change of 0·002° C. between the first and second readings, ad no subsequent change in some dozen readings. To test the possibility any interaction between the sulphuric acid and benzene, especially with the ore concentrated acids, samples were left overnight in contact with the nzene, and in no case was any change in F.P.D. found. The observed eezing-point depressions and those calculated from the vapour-pressure of e acids are given in Table II, cols. 1-3, and show very good agreement, so at the method is proved to be both rapid and accurate for systems such s solutions or salt hydrates, in which no interaction with or disturbance by e benzene is probable.

Measurements on Soils.

Whereas the sulphuric acid—water mixture came rapidly to equilibrium with e benzene, soils gave constant readings only after several repetitions of the eezing and melting. Successive readings of the freezing-point increased y 0·004–0·001° C. for the first three or four repetitions, and then became eady. All the results quoted are the means of some successive 6–10 readings, hich did not vary by more than 0·002° C. The F.P.D. resulting from the ldition of successive lots of 2 gms. of soil to 50 c.c. of benzene, showed that further change took place after the addition of 10 gms. of soil, and that e freezing-point depression was the same for either dry or wet samples of enzene. 10 gms. of soil were used for all the subsequent experiments. At e end of each series of readings water was added in excess and the freezing-oint thus obtained was in every case identical with that of the original wet mple of benzene. This is definite proof that nothing was dissolved from e soil by the benzene. Parker (5), working with dry soil and benzene in arious proportions, found that the freezing-point was reduced only when the mount of benzene added was a small fraction of the amount of soil.

Several 10 gm. lots of oven-dried soil (Harpenden Common) were brought to ifferent moisture contents by exposure to a moist atmosphere for varying mes and similar samples were exposed to air currents of known humidities as to obtain data for a vapour-pressure curve. Table I gives the observed eezing-point depressions compared with those derived from the vapour-ressures obtained by interpolation on the vapour-pressure curve. Since enzene saturated with water gives a F.P.D. of 0·100° C., the calculated .P.D. is taken as 0·1 × the relative vapour-pressure.

Table I.

Water-content per cent.	0·035	0·81	1·54	2·13	2·66	3·40
Relative vapour-pressure	0·002	0·10	0·305	0·46	0·59	0·74
Calc. F.P.D. °C.	0·000	0·010	0·030	0·046	0·059	0·074
Observed F.P.D. °C.	0·009	0·030	0·058	0·069	0·080	0·090

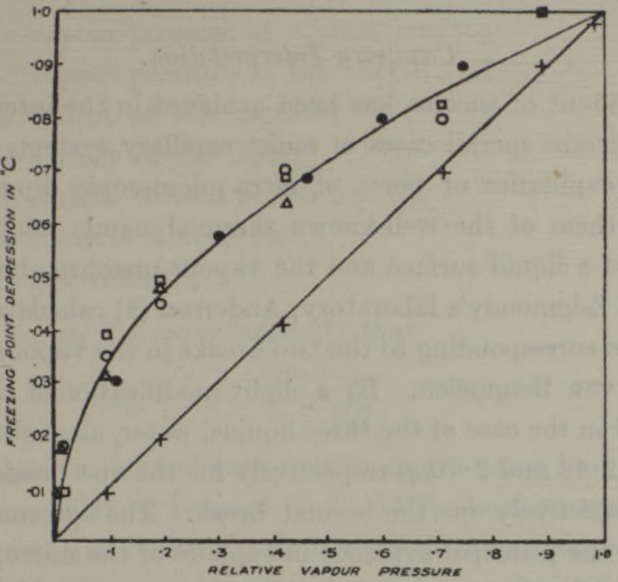
The F.P.D. observed are considerably greater than those calculated from the simple distribution law.

A more direct comparison was obtained by bringing soils into equilibrium with sulphuric acid—water mixtures and then comparing the F.P.D. produced by the soil with that produced by the acid directly. Three soils (a light sand, a heavy loam and a very heavy clay) were selected; the mechanical analyses given in Table II bring out the wide differences in their types. 10 gms. of the finely divided air-dry samples were exposed to the sulphuric acid—water mixtures in a vacuum desiccator for a fortnight; previous experiments had shown that one week was sufficient for the attainment of constant weight. Several replicate samples of the air-dry soils were exposed at the same time over strong sulphuric acid, so as to obtain data for the water contents at the various vapour-pressures. The F.P.D. data refer to 5·5° C. whilst the direct vapour-pressure data are for about 12° C.; other experiments have shown that the temperature coefficient of the relative vapour-pressure is so small that it can safely be neglected for a temperature difference of this order.

Table II.

Relative Vapour-pressure (= 10 × calc. F.P.D.)	Freezing-point Depressions.				Water-content (per cent. of dry sample).			Fraction.	Mechanical Analysis.		
	Sulphuric acid—water mixtures.	Woburn sand.	Rothamsted loam.	Sudan clay.	Woburn	Rothamsted.	Sudan.		Woburn.	Rothamsted.	
0·977	0·098	—	—	—	—	—	—	—	—	—	—
0·885	0·090	0·100	0·100	0·100	1·88	3·98	13·34	Coarse Sand	51·7	11·0	—
0·702	0·070	0·080	0·083	—	1·25	2·88	10·57	Fine Sand	19·9	18·1	16·
0·416	0·041	0·070	0·069	0·064	0·91	2·05	8·25	Silt	10·6	30·7	11·
0·195	0·019	0·045	0·049	0·047	0·60	1·17	5·46	Fine Silt (I)	3·6	9·6	4·
0·095	0·009	0·035	0·039	0·031	0·41	0·87	3·94	Fine Silt (II)....	1·5	3·4	4·
0·015	0·001	0·018	0·009	0·018	0·06	0·30	1·14	Clay	7·3	16·3	42·

The results contained in Tables I and II are represented graphically in fig. 1, hich gives the F.P.D. as a function of the corresponding vapour-pressures



G. 1.—Relation of Freezing-point Depression of Benzene to Relative Vapour-pressure for Sulphuric Acid—Water Mixtures and Soils, with the Theoretical Curves.

\+ Sulphuric Acid—Water Mixtures.
● Harpenden Common Soil.
○ Woburn Soil.
□ Rothamsted Soil.
△ Sudan Soil.

r the sulphuric acid—water mixtures and for the four soils. This graph rings out clearly the good agreement in the case of the acid mixtures and the stematic deviation shown by the soils. In all cases the F.P.D. produced by soil is very much greater than that corresponding to the vapour-pressure. ut the most important result is that the soils all show substantially the same eviations, even though their types differ to such an extent that for any given umidity there is a variation in water-content of from 1 to 9.

The essential difference between the soil-water system and the acid is that e latter consists of a single phase, whilst in the former some portion, at least, f the water is held in small pores or capillaries or is spread out in thin films, that surface energy factors are involved in the equilibrium state. Immersion f the soil in benzene results in replacing the surface tension water/air by that of ater/benzene. In the present state of our knowledge of the soil-water system is not possible to discuss the whole of the rearrangements that may be xpected to result from such a change, but it was found that by making certain simple assumptions as to the state of the water in the soil, it was possible to deduce a relationship between the vapour-pressure in air and the vapour-pressure in benzene which would account for the observed results.

Capillary Interpretation.

A certain amount of success has been achieved in the interpretation of the behaviour of certain special cases of moist capillary systems and gels by the postulation of capillaries or pores of ultra-microscopic dimensions, and the application to them of the well-known thermodynamic relationship between the curvature of a liquid surface and the vapour-pressure above it. Working on silica gels in Zsigmondy's laboratory, Anderson (6) calculated the diameters of the capillaries corresponding to the two breaks in the vapour-pressure curves first studied by van Bemmelen. By a slight modification of the equation used below, he found in the case of the three liquids, water, alcohol and benzene, the values of $2 \cdot 75$, $2 \cdot 42$ and $2 \cdot 70 \mu\mu$ respectively for the first break, and $1 \cdot 38$, $1 \cdot 21$ and $1 \cdot 35 \mu\mu$ respectively for the second break. The agreement is extremely good and forms the principal evidence in support of the micropore hypothesis. Whipple (7) following Sresnevsky (8) has developed a theory of the hair hygrometer by postulating pores of these dimensions. Anderson (6) found a change in the rate of evaporation of water from silica gel at water contents corresponding to the commencement of the removal of water from capillaries of the order of $2 \cdot 5 \mu\mu$, and Fisher (9) has recently suggested that the breaks in the rate of evaporation from wool arise from a similar cause. The micropore hypothesis has an attractive simplicity, but the evidence in its favour is as yet admittedly insufficient to establish the validity of the application to such ultra-microscopic pores of the laws of surface tension deduced from microscopic dimensions. The data given in this paper afford additional support to this micropore hypothesis.

It is assumed that the surface of a capillary system, such as soil, contains pores of various forms and sizes down to the order of $1 \mu\mu$ diameter. For equilibrium with an unsaturated atmosphere, a fraction, not necessarily the whole, of the water is contained in these pores, so as to expose concave surfaces with a curvature sufficient to account for the reduction of the vapour-pressure below that of a plane water surface at the same temperature. It is further assumed that the effect of the added benzene is limited to the replacement of the interfacial tension of water/benzene for the surface tension of water/air, with a consequent reduction of the curvature of the water surface and an increase of the vapour-pressure. The water is then distributed between the soil and enzene, so that the concentration of water in the benzene, as measured by the bserved F.P.D., is proportional to the increased relative vapour-pressure of ater.

If p = the vapour-pressure at a plane surface,
p' = the vapour-pressure at the curved surface,
r = the radius of the capillary,
ρ = the density of the liquid,
T = the surface tension of the liquid,
θ = the absolute temperature,
R = the gas constant,

hen it can be shown thermodynamically that

$$\log_e \frac{p'}{p} = -\frac{2T}{r\rho} \cdot \frac{1}{R\theta} = -k \,.\, T.$$

'he modified equation of Anderson reduces to the same form.

At the melting point of benzene (5·5° C.) the surface tension of water is 5·0 dynes per cm., and the interfacial tension of water and benzene 35·8 dynes er cm. (10). If p'' be the aqueous vapour-pressure at a water/benzene urface for the same capillary, then

$$\log_e p'/p = -75{\cdot}0k$$

$$\log_e p''/p = -35{\cdot}8k$$

$$\log_e p''/p = 0{\cdot}478 \log_e p'/p,$$

r

$$p''/p = [p'/p]^{0{\cdot}478}. \qquad (1)$$

Table III.

Relative Vapour-pressure.		Freezing-point Depression in °C.	
In Air (p'/p).	In Benzene. ($p''/p = [p'/p]^{0{\cdot}478}$).	Calc.	Obs.
0·885	0·943	0·094	0·100
0·702	0·844	0·084	0·082
0·414	0·656	0·066	0·067
0·195	0·458	0·046	0·047
0·095	0·325	0·032	0·035
0·015	0·134	0·013	0·015

Table III gives the values of the relative vapour-pressure for such a capillary system in air and in benzene, together with the values of the F.P.D. calculated in this way, and the mean of those obtained experimentally for the three soils used in the direct experiments. The curve of fig. 1 represents the F.P.D. as calculated from the relative vapour-pressure on the above assumptions. Fig. 2

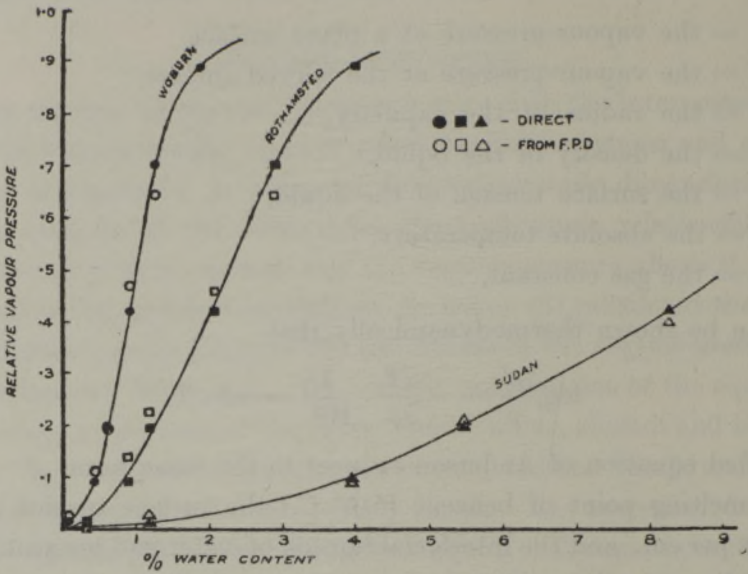


Fig. 2.—Direct and Indirect Vapour-pressure Water-content curves for Soils.

gives the vapour-pressure water-content curves for the three soils as obtained directly in vacuum desiccators, and indirectly from the benzene experiments after correcting the observed values by means of equation (1).

The agreement is very close, and well within the experimental error of the determinations, except in the case of wettest samples.

Confirmatory Experiments.

Semi-quantitative evidence of the increase in the aqueous vapour-pressure of soils on treatment with benzene was obtained in other ways. Soil samples of different moisture-content were left for long intervals in closed vessels, with and without benzene, and uniform pieces of blue cobalt-chloride paper introduced. In an hour or so the papers acquired tints which remained unchanged for several weeks. In every case the sample treated with benzene showed a more complete change towards the pink colour than the untreated sample. Thus, a soil with a relative vapour-pressure of 0·1 gave about the same tint with benzene as one with a relative vapour-pressure of 0·4 in the absence of benzene.

A series of approximate vapour-pressure measurements was made by the dew-point method, using a brightly polished silver test-tube treated with boiling water at one part in the manner described by McBain and Salmon (11) to prevent odensation. It was found possible to obtain approximate readings even in th presence of excess of benzene. A rapid condensation of benzene took plce on the treated portion, but it occasionally happened that no condensation tok place on the untreated portion until a much lower temperature had been rached. This was apparently the dew-point of the water-vapour and was dinitely reproducible. It sometimes happened that the dew-point could be dfined very accurately by the appearance and disappearance of the character-iic colours of thin films. If this temperature is taken as the dew-point crresponding to the water-vapour present in the saturated benzene-vapour, stinct evidence was obtained of the increase in vapour-pressure, as this dew-pint was always higher than that of the untreated soil by an amount similar t that deduced above.

No very great importance is attached to these results, although they were peated many times, since it was found impossible some time later to bring te silver surface into the state necessary for the measurement of the dew-point i the presence of excess benzene. This method is being investigated further.

Some slight confirmation was also obtained from experiments on the sorption of water by hair. A quantity of hair was left in a closed vessel ver soils, with and without benzene, and weighed after exposing it freely for ne minute in the balance case. Definite weights were obtained after the aporation of the benzene, and these weights were always greater in the case samples exposed to soil with benzene.

Summary.

The validity of an indirect method for the measurement of aqueous vapour-ressures has been tested. The freezing point of benzene is depressed by an mount which is strictly proportional to the aqueous vapour-pressure of an nsoluble material with which it is in equilibrium, provided that surface energy not one of the factors determining the vapour-pressure of this material. he method is both rapid and accurate when applied to substances such as ulphuric acid—water mixtures and certain salt hydrates. With capillary ystems such as soil, the equilibrium is reached more slowly and the pparent vapour-pressures show a systematic deviation, which is the same or soils of widely different types.

It is shown that, by assuming that a fraction of the water in such cases is eld in micropores and making allowance for the effects of the changes in urface energy on the introduction of an additional liquid phase, it is possible o account for this deviation. The agreement between the observed values and those calculated on this assumption is taken to afford evidence of the manner in which water is held in moist capillary systems.

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