

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

## Liquid and Vapor Curves in the System Ethyl Alcohol-Benzene-Carbon Tetrachloride at Constant Pressure

BY A. N. CAMPBELL AND W. J. DULMAGE

While the constituent binary systems of the system alcohol-benzene-carbon tetrachloride have been investigated repeatedly, only an imperfect study of the ternary system exists. This is that of Schreinemakers,<sup>1</sup> who determined by a dynamic method the boiling temperatures under different pressures of ternary mixtures of these substances. From the pressure-temperature curves thus obtained, he deduced the pressure-concentration relations and, more important to the present work, the temperature-concentration relations. The latter data when plotted on a plane triangle give the projection of the boiling point surface for different constant pressures, and this diagram, given by Schreinemakers, is similar to Fig. 3 of this paper. Despite the rather crude method used by Schreinemakers, his results are in qualitative, and rough quantitative, agreement with ours.<sup>2</sup>

Although Schreinemakers' treatment of the vapor pressure relations is adequate, liquid-vapor composition data are necessarily lacking, since his experimental method was incapable of giving such information. Hence, the vapor surface corresponding to Schreinemakers' liquid surface was unknown. It was the aim of the present study to complete Schreinemakers' work, by an investigation of the liquid-vapor equilibria under isobaric conditions. The pressure chosen was that of the standard atmosphere (760.0 mm. at 0°) and the boiling points of all mixtures were determined, although, for reasons detailed later, we claim no greater absolute accuracy than  $\pm 0.05^\circ$  for the temperature measurements.

For the sake of completeness, the binary systems were also investigated, although two of these systems, *vis.*, alcohol-benzene and alcohol-carbon tetrachloride, have been investigated previously in an exhaustive manner: as is well known, these systems show azeotropic minima on their boiling point curves. Considerable doubt has existed hitherto regarding the system benzene-carbon tetrachloride. Because of the closeness of the boiling points of the constituents and the close similarity in composition between liquid and equilibrium vapor, and other criteria, it has been suggested that this system may exhibit an azeotropic mixture of minimum boiling point very close to the carbon tetrachloride end of the curve. Indeed, Young<sup>3</sup> states that "it is certain that ben-

zene and carbon tetrachloride form such a mixture" (of minimum boiling point); and again (ref. 3, p. 92.) "these two liquids can form such a mixture, though the difference between the maximum pressure and the vapor pressure of carbon tetrachloride is probably too small to be determined by direct experiment." Hildebrand,<sup>4</sup> however, states, without authority, that carbon tetrachloride does not form a minimum boiling point mixture with benzene. Lecat,<sup>5</sup> whose work is considered definitive up to the year of its publication, leaves the question open. We show in this paper that, despite an apparent minimum of about  $0.05^\circ$ , which the inaccuracy of our temperature measurements deprives of significance, the vapor phase is never richer in benzene than the liquid phase, over a range from 1 to 99% benzene; that is, there is no reversal of composition, as there would be in passing through an azeotropic point.

## Experimental

The apparatus used for the establishment of equilibrium was that of Scatchard.<sup>6</sup> The advantages of Scatchard's equilibrium still are that traditional difficulties such as superheating of liquid, reflux condensation and entrainment of vapor, and lack of equilibrium are eliminated by the use of a Cottrell-type pump, a double boiler, and a hold up trap. This still simplifies the removal of liquid and condensed vapor samples from the inner boiler and the condensate trap, respectively. The barostat, shown in Fig. 1, was modelled on that of Matthews and Faville,<sup>7</sup> but modified by the introduction of two controlled stages, as shown in Fig. 1. In the first stage, which was controlled simply by an ordinary magnetic relay, the pressure was kept by the pump at about 20 mm. above that in the second stage, which was controlled by the device of Leroy,<sup>8</sup> using an electronic relay which operated when the circuit broke. The mercury column in stage 2 was thermostatically controlled and of such a length as to correspond to 760.0 mm. of mercury at 0°. The final adjustment was made by boiling pure water in Scatchard's apparatus under barostatic control, and altering the pressure in stage 2 by small additions and removals of mercury until the water boiled at  $100.00^\circ$ .

To obviate the possibility of a flutter in the mercury surface we introduced the second slow leak  $L_1$ , the effective orifice of which was such as to give approximate balance between the two leaks,  $L_1$  and  $L_2$ . Under these conditions no tremor of the mercury could be detected in the field of vision of a telescope and the boiling point of pure benzene remained absolutely constant as measured by a Beckmann thermometer.

**Temperature Measurement.**—As we possessed neither a multiple junction thermocouple nor a resistance thermometer, we were obliged to measure temperature with a

(1) F. A. H. Schreinemakers, *Z. physik. Chem.*, **47**, 445 (1903); **48**, 257 (1904).

(2) Cf. Table 7 of Schreinemakers' paper,<sup>1</sup> **48**, 275, where the data are given (in weight per cent.) for plotting the isotherms at  $p = 760$  mm.

(3) Young, "Distillation Principles and Processes," 1st ed., MacMillan and Co., London, 1922, p. 47.

(4) Hildebrand, "Solubility," 2nd ed., Reinhold Publishing Corporation, New York, N. Y., 1936, p. 129.

(5) "La Tension de Vapeur des Mélanges de Liquides: l'Azeotropisme," Lamertin, Brussels, 1918.

(6) G. Scatchard, C. L. Raymond and H. H. Gilman, *THIS JOURNAL*, **60**, 1275 (1938).

(7) J. H. Matthews and K. E. Faville, *J. Phys. Chem.*, **22**, 3 (1918).

(8) D. J. Leroy, *Ind. Eng. Chem.*, **17**, 652 (1945).

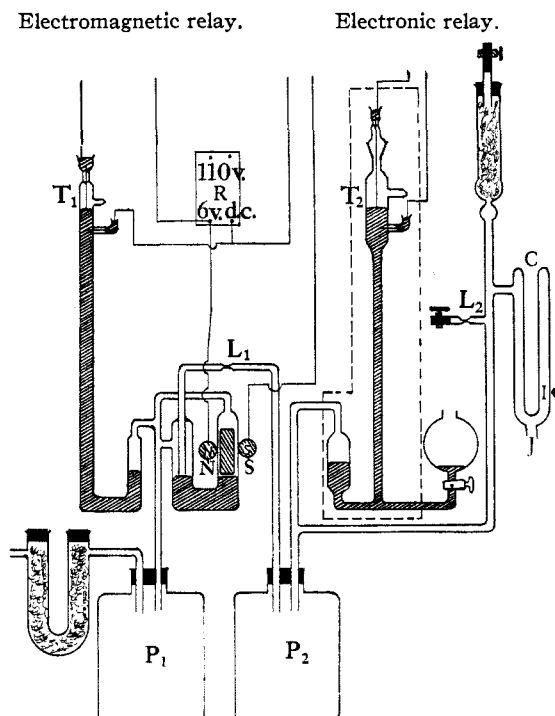


Fig. 1.—Barostat apparatus:  $T_1$ ,  $T_2$ , mercury and tungsten contacts;  $P_1$ ,  $P_2$ , carboys acting as buffers; NS, electromagnet;  $L_1$ , leak from crude to sensitive barostat;  $L_2$ , leak to atmosphere; I, condenser of Scatchard apparatus.

mercury-in-glass thermometer, graduated to  $0.1^\circ$ . Such is the uncertainty of the exposed stem correction, that we do not feel justified in claiming a higher absolute accuracy than  $\pm 0.05^\circ$ , although the agreement between consecutive determinations on the same day is no doubt better than this. About two hours of boiling were allowed for the attainment of equilibrium in each determination. After the reading of temperature, samples were removed from "liquid" and "vapor" chambers for analysis. There is a small, and probably inevitable, error introduced when using Scatchard's apparatus at pressures above that of the laboratory. Since sampling must be done immediately boiling is discontinued, on opening the apparatus there is a tendency for boiling to recommence when the pressure falls. This may produce a small amount of distillation, and the resulting disturbance of equilibrium can be detected.

**Method of Analysis.**—The method of analysis, which is very accurate, has been described elsewhere.<sup>9</sup> The method consists in the determination of refractive indices and densities, and yields an analytical accuracy of 0.3% of the total of each component, using pure materials. Our liquid and vapor curves are therefore correct to this limit. In the binary systems, density determinations only were made, and here the accuracy is still higher. Unfortunately, the flatness of the boiling point curves and the uncertainty of our temperature measurements renders a precise comparison of our data with existing data impossible, but there is no doubt the agreement is very good for the two well established systems, alcohol-benzene and alcohol-carbon tetrachloride.

**Purity of Materials.**—All materials were purified by the methods used by Campbell and Miller<sup>9</sup> when they calibrated the analytical curves.

(9) A. N. Campbell and S. I. Miller, *Can. J. Research*, **B25**, 228-242 (1947).

**Distillation Curves.**—After determining the liquid-vapor relations in the ternary system (Fig. 3) and knowing the boiling temperature of each point plotted, it is an easy matter to draw a diagram descriptive, in a qualitative manner, of the course of distillation, that is, the direction in which the residue will change its composition with rising temperature. This has been done in Fig. 4. A few rough experiments were carried out to confirm this. Certain typical mixtures were submitted to distillation through a fractionating column, and successive distillates, and occasionally the residue, analyzed. Barostatic control was not imposed and the results therefore correspond to an average laboratory pressure of 740 mm.

## Results

The results for the equilibrium concentrations of liquid and vapor are expressed numerically in Table I and graphically in Figs. 2 and 3, where concentrations are expressed in mole per cent.: the figures for the well-known binary systems:

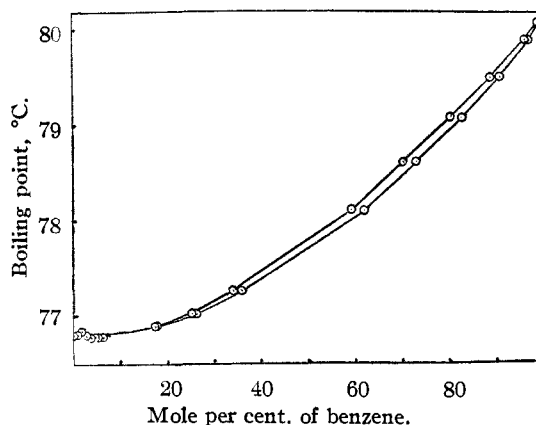


Fig. 2.—Boiling point-composition diagram for the system benzene-carbon tetrachloride.

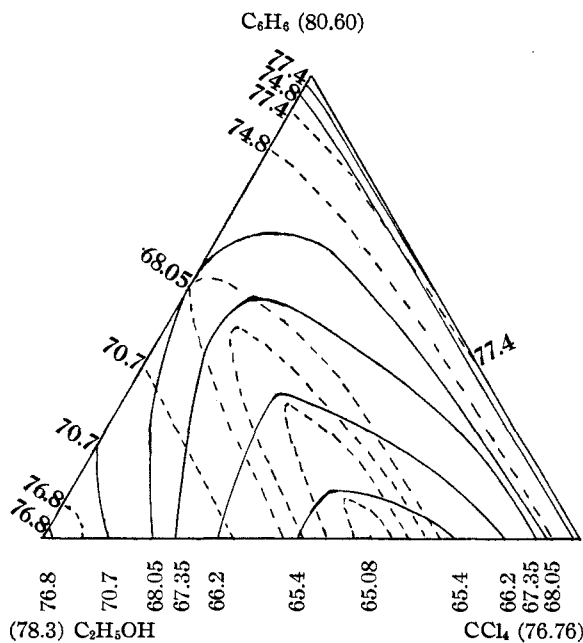


Fig. 3.—Liquid and vapor isothermals in the ternary system (concentrations in mole per cent.).

benzene-alcohol and carbon tetrachloride-alcohol are not given. In the ternary figure (Fig. 3) the full curves represent liquid solutions and the dotted curves equilibrium mixtures of vapor; the pairs are identified by the temperatures which are given at the end of each curve. To avoid confusion, no tie-lines have been drawn, but these can be put in by the reader from the data of Table I.

TABLE I  
LIQUID AND VAPOR COMPOSITIONS SYSTEM CARBON TETRACHLORIDE-BENZENE

B. p., °C.	Liquid compn. Mole % C <sub>6</sub> H <sub>6</sub>	Vapor compn. Mole % C <sub>6</sub> H <sub>6</sub>
80.12	100.00	100.00
80.05	99.28	99.15
79.88	97.13	96.55
79.48	90.92	88.84
79.06	82.96	80.59
78.58	73.07	70.37
78.09	61.98	59.16
77.26	35.56	34.01
77.02	26.00	25.01
76.87	17.62	16.90
76.78	5.05	4.97
76.76	6.02	5.93
76.77	4.67	4.62
76.77	3.60	3.58
76.81	3.39	3.35
76.80	2.47	2.41
76.84	1.54	1.54
76.81	0.65	0.65
76.79	0.00	0.00

67.98	53.6	1.2	53.7	1.5
67.91	9.5	84.2	7.1	67.0
67.86	29.9	6.9	39.7	11.3
67.66	60.6	16.0	48.0	15.4
67.60	15.5	14.4	23.5	26.4
67.50	44.1	41.1	32.9	35.2
67.37	54.5	13.9	46.0	14.6
67.36	40.2	9.6	42.8	12.8
67.28	43.4	10.9	43.8	13.4
67.02	43.6	14.5	40.1	18.3
66.62	3.1	26.9	4.7	47.2
66.58	22.6	21.3	25.7	30.1
66.34	28.7	27.3	27.3	31.3
66.33	33.9	32.6	28.9	32.7
66.24	32.3	26.8	29.9	29.6
66.22	29.4	29.3	25.9	31.8
66.10	9.1	30.7	11.2	44.7
65.89	23.0	36.8	21.0	39.3
65.77	20.1	40.5	18.0	42.5
65.73	19.4	41.2	17.8	43.2
65.68	12.2	63.2	9.9	55.6
65.54	6.8	42.2	7.1	52.3
65.41	8.6	46.7	8.9	51.3
65.39	9.0	56.8	8.4	53.2
65.41	7.1	65.5	6.6	59.2
65.38	9.0	57.3	7.6	54.8

From the data of Table I, the distillation diagram (Fig. 4) has been deduced. The results of experimental distillations, conducted under laboratory pressure and without barostatic control, were in qualitative agreement with the predictions of Fig. 4.

SYSTEM ALCOHOL-BENZENE-CARBON TETRACHLORIDE

B. p., °C.	Liquid compn.		Vapor compn.	
	Mole % C <sub>2</sub> H <sub>5</sub> OH	Mole % CCl <sub>4</sub>	Mole % C <sub>2</sub> H <sub>5</sub> OH	Mole % CCl <sub>4</sub>
78.33	95.1	4.1	91.5	4.5
77.37	78.8	21.0	74.0	23.0
76.96	0.49	1.33	0.89	6.63
76.79	94.2	3.9	87.2	4.4
76.62	54.0	46.0	50.2	47.4
76.62	1.4	1.1	4.5	4.8
76.55	78.2	21.0	77.2	17.8
75.70	4.1	0.9	11.2	3.4
75.59	50.3	48.7	46.0	49.2
75.46	48.8	49.3	44.5	50.4
74.79	11.7	87.6	11.4	83.8
74.00	0.84	5.13	1.97	18.5
73.18	92.2	3.2	76.2	3.3
72.95	9.8	88.7	9.4	80.9
72.83	2.5	4.4	10.3	13.9
72.32	50.3	47.2	45.9	43.8
72.21	10.2	1.6	24.2	4.7
70.65	7.7	6.9	17.4	19.2
69.70	23.4	0.4	40.3	0.9
69.50	71.5	19.1	54.0	17.5
69.47	15.0	2.5	34.7	7.6
69.11	2.11	15.4	5.11	47.1
69.00	80.3	2.1	61.8	2.0
68.25	40.4	0.8	49.3	1.3
68.08	64.5	1.7	57.0	2.0
68.02	61.5	1.5	56.0	1.7

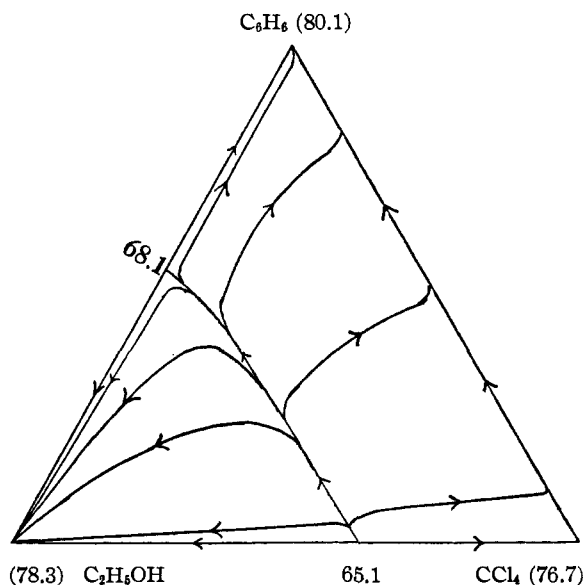


Fig. 4.—Course of the distillation: the arrows represent the direction of rising temperature.

Discussion

Nothing need be said about the binary systems: alcohol-benzene and alcohol-carbon tetrachloride except that our results were in good agreement

with published data and better than most in respect of composition, though not of temperature. The disputed system benzene-carbon tetrachloride does not show an azeotropic minimum on the boiling point curve, despite the fact that our own results appear to show a minimum temperature about  $0.05^\circ$  below the boiling point of carbon tetrachloride: this temperature difference is the error of measurement. The evidence against the minimum rests on our very accurate method of analysis. No matter how low the benzene content the tie-lines never reverse; that is, the vapor is a ways richer in carbon tetrachloride. It is admitted that if there were any azeotropic mixture it could not contain more than ten mole per cent. benzene, and from 10 to 2.47% benzene our results show a higher content of carbon tetrachloride in the vapor, while for 1.54 and 0.65 mole per cent. the vapor appears to have the same composition. This apparent identity is due to our inability to read the analytical curve to any higher degree of accuracy than, say, 0.02%; the density determinations themselves still indicated a higher carbon tetrachloride content in the vapor.

The ternary diagram shows the existence of a trough of minimum boiling point running across the diagram from  $65.08^\circ$  and about 39 mole per cent. alcohol, in the alcohol-carbon tetrachloride system, to  $68.05^\circ$  and about 45 mole per cent. alcohol, in the alcohol-benzene system. This trough has itself no minimum of temperature and therefore the liquid and vapor curves coincide only at its ends. The method of investigation actually used was to proceed across the diagram from the alcohol corner along lines of approximately constant benzene:carbon tetrachloride ratio. Proceeding in this way, the following behavior of the tie-lines is general over the diagram. At first, *i. e.*, for mixtures rich in alcohol, the vapor is much richer in benzene and carbon tetrachloride, the direction of the tie-line being symmetrical with respect to the sides of the triangle. As the content of alcohol decreases, the tie-line shortens and changes direction as it approaches the trough. A liquid mixture lying in the trough (which is almost, though not quite, a straight line) has a tie-line also lying almost in the trough, but the slightest change in liquid composition causes the tie-line to deviate considerably in one or the other direction. The experimentally determined tie-lines lying over the trough, of which there are several, were obtained by proceeding along the trough itself, a difficult procedure involving much trial and error. Proceeding along a line of constant benzene-carbon tetrachloride ratio, after crossing the trough, the tieline turns rapidly to assume a position at almost  $180^\circ$  to its former position; that is, the vapor is now richer in alcohol. In the solid model, the temperature slope from the trough to the benzene-carbon tetrachloride side is much steeper than the corresponding slope from the trough to the alcohol apex and, as Fig. 4 shows,

the former slope increases very rapidly at the last. In agreement with this, it is found that the tie-line, which now slopes somewhat toward the carbon tetrachloride corner, retains this slope almost till the last and then, as the last trace of alcohol leaves the mixture, undergoes a sharp change to occupy its position in the binary surface benzene-carbon tetrachloride.

This detailed knowledge of the behavior of the tie-lines enables one to predict the course of distillation of any mixture. Referring to Fig. 4, consider a liquid mixture lying in the triangle to the left of the trough. The residue will move in the direction of the arrow, the temperature rising and the mixture becoming richer in alcohol, until pure alcohol is left in the boiler. The first distillate will be poorer in alcohol than the original mixture. Redistillation of distillates will eventually give a mixture lying in the trough: the trough can never be crossed. It might be supposed that a mixture on the trough, lying as it does in an (almost) pseudo-binary system, might be separated by distillation into a distillate of the low boiling azeotrope of the alcohol-carbon tetrachloride system, and a residue of the higher boiling azeotrope of the alcohol-benzene system. This is not true, however, because the projections of liquid and vapor compositions do not quite coincide in the trough of minimum boiling point. Hence, though the distillate will always approximate to the trough, the residue soon deviates from it, because the tie-lines change their direction rapidly on both sides of the trough. It would seem, then, that the final results of fractional distillation of any mixture in the triangle described above would be a residue of pure alcohol and a distillate of the low boiling azeotrope alcohol-carbon tetrachloride; but this obviously cannot describe the fate of the whole mass of the mixture, since the mixture as a whole contains benzene. The benzene is to be found in the middle fractions which approximate more and more to the trough and move up it in the direction of the higher boiling azeotrope. To summarize, a mixture containing benzene, alcohol and carbon tetrachloride in such proportions that the mixture lies to the left of the trough can be separated by distillation into a residue of pure alcohol, a refined distillate of the low boiling azeotrope of the alcohol-carbon tetrachloride system and an intermediate mixture approximating in composition to the higher boiling azeotrope of the alcohol-benzene system. The same result could of course be obtained by using a fractionating column of suitable length and drawing off fractions at suitable heights.

In the quadrilateral area lying between the trough and the benzene and carbon tetrachloride corners, distillation eventually yields a distillate of the low boiling azeotrope, while the residue rapidly approaches in composition the binary system benzene-carbon tetrachloride. But shortly before the last trace of alcohol is removed from the res-

idue, the direction of change of composition of the residue alters abruptly in the direction of the benzene corner, so that when eventually the last trace of alcohol is removed, the binary mixture produced is much richer in benzene than the original mixture. From this binary mixture both benzene and carbon tetrachloride can (theoretically) be obtained by distillation, since the binary mixture benzene-carbon tetrachloride shows neither minimum nor maximum on the boiling point curve. It appears, therefore, that in the quadrilateral area pure benzene, pure carbon tetrachloride and the low boiling azeotrope can be obtained by fractionation. In addition, however, certain of the middle fractions would tend to approximate to the higher boiling azeotrope of benzene-alcohol but, as with the triangular area, it is doubtful whether in practice any of this binary azeotrope, uncontaminated by carbon tetrachloride, would be obtained, because of the strong curvature of the tie-lines around the trough.

The above predictions were borne out in practice by our distillation experiments.

### Summary

The boiling temperatures, under constant pressure, of the binary systems alcohol-benzene, alcohol-carbon tetrachloride, and benzene-carbon tetrachloride, as well as those of the ternary system alcohol-benzene-carbon tetrachloride, have been investigated. The equilibrium concentrations of liquid and vapor for the above systems have been determined, with an accuracy of 0.3 weight per cent.

It is shown that the system benzene-carbon tetrachloride does not exhibit an azeotropic minimum on its boiling point curve. An improved barostat is described.

The liquid-vapor composition diagram is discussed and the course of distillation predicted. The course of distillation has been verified qualitatively by experiment.

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[CONTRIBUTION FROM THE BUREAU OF MINES, DEPARTMENT OF THE INTERIOR]

## Modifications of the Brunauer, Emmett and Teller Equation II<sup>1</sup>

BY ROBERT B. ANDERSON<sup>2</sup> AND W. KEITH HALL<sup>2</sup>

The simple Brunauer, Emmett and Teller equation<sup>3</sup> (hereafter abbreviated to B.E.T.) has been useful in the estimation of surface areas from physical adsorption isotherms. This equation will fit satisfactorily experimental data for almost all isotherms except those of Type I of Brunauer, Deming, Deming and Teller<sup>4</sup> in the relative pressure range of 0.05 to 0.40. Several modifications of the simple B.E.T. equation have extended the range of applicability. In most cases the adsorbent structure is pictured as a series of parallel plates which will permit the adsorption of only  $n$ -layers from each side. An  $n$ -equation derived by B.E.T.<sup>3</sup> and Hill<sup>5</sup> extends the fit to higher relative pressures for most isotherms, but it is somewhat difficult to apply to experimental data.<sup>6</sup> Brunauer, Deming, Deming, and Teller<sup>4</sup> derived a more elaborate  $n$ -equation in which the heat of adsorption of the last layer adsorbed in a condenser plate capillary was higher than the heat of liquefaction. Although this equation can be fitted to the entire isotherm, its application is too difficult to be of any practical value as a method of characterizing isotherms.

Pickett<sup>7</sup> presented a simpler type of  $n$ -equation than that of B.E.T., one which is more easily applicable to adsorption data and probably fits over a greater range. The simplest derivation of this equation assumes that the volume of gas adsorbed in any layer is independent of the molecules adsorbed in higher layers; whereas, the  $n$ -equation of B.E.T.<sup>3</sup> implies that adsorption of molecules in higher layers stabilizes the molecules in underlying layers.

Recently, Anderson<sup>8</sup> suggested that the parallel plate type of pore structure is probably not a good physical picture of most porous adsorbents. A pore structure in which the area available to each subsequent layer is less than the area of the underlying layer is probably a better physical picture. In this paper it was also shown that for isotherms of finely divided, presumably non-porous solids such as carbon black, titania, etc., the modified B.E.T. equation could be fitted to the range of relative pressure of 0.05 to 0.7 by assuming the free energy of adsorption in the several layers after the first to be less than the free energy of liquefaction.

In the present paper, an equation embodying the same assumptions is derived in a manner similar to that of the B.E.T. equation. It can be satisfactorily fitted to isotherms of Type I and those approaching Type I by assuming the free energy of adsorption in the second and subsequent layers

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(3) Brunauer, Emmett and Teller, *THIS JOURNAL*, **60**, 309 (1938).

(4) Brunauer, Deming, Deming and Teller, *ibid.*, **62**, 1723 (1940).

(5) Hill, *J. Chem. Phys.*, **14**, 263 (1946).

(6) Joyner, Weinberger and Montgomery, *THIS JOURNAL*, **67**, 2182 (1945).

(7) Pickett, *ibid.*, **67**, 1958 (1945).

(8) Anderson, *ibid.*, **68**, 686 (1946).