Surfaces of Solids. XXI. Areas of Non-porous Solids from Adsorption Isotherms of n-Heptane or n-Hexane

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I. Introduction

The purpose of this paper is to present the results of an investigation into the use of the adsorption isotherms of n-heptane or n-hexane for the determination of the areas of solids by the Brunauer, Emmett and Teller[1] (BET) and the Harkins–Jura[2] (HJ) relative methods of calculation. These results appear to indicate that the values for the areas of numerous non-porous solids calculated by the HJ relative method from the absorption isotherms of n-heptane or n-hexane are consistent with those calculated by the BET method from the same data. This is true provided the BET method is standardized by means of a solid whose area has been determined by the HJ absolute method.

The area of several non-porous solids calculated from the adsorption isotherms of n-heptane or n-hexane by these two methods are in satisfactory agreement with the values for these solids obtained by the HJ absolute method[3] or by the HJ relative or BET method using nitrogen adsorption isotherms.

II. Experimental

The apparatus and procedure for the determination of the isotherms of n-heptane and n-hexane have been described in an earlier paper.[4] Stock valves or mercury-sealed stopcocks lubricated with a mixture composed of glycerol, dextrin and mannitol were used in the adsorption system. The n-heptane isotherms at 25° consisted of about 35 experimental points over a relative pressure range of 0.0003 to 0.985; the n-hexane isotherms at 0° consisted of fewer points over a less extensive range.

The n-heptane used was Bureau of Standards grade obtained from Westvaco Chlorine Products Company. The n-hexane used was of technical grade obtained from the Phillips Petroleum Company. The hexane was distilled from sodium hydride through a high efficiency fractionating column. The fraction which boiled at 67.9° at 744 mm. was used. The liquids were dried over sodium wire for one month and then distilled into reservoirs on the vacuum line. The liquids were degassed thoroughly by repeated freezing and boiling in vacuo.

Untreated metals were those which possess a coating of oxide or sulfide formed by exposure to the air at room temperature. They were degassed in vacuo for at least sixteen hours at a temperature below that at which sintering occurs. Reduced metals were produced by passing dry hydrogen through untreated metal powders, maintained at a temperature high enough to allow reduction yet not cause sintering. The oxides and sulfides were degassed for at least sixteen hours at 450°, except in the case of unstable compounds for which lower degassing temperatures were used.

(1) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

(2) W. D. Harkins and G. Jura, ibid., **66**, 1366 (1944).

(3) W. D. Harkins and G. Jura, ibid., **66**, 1362 (1944).

(4) G. Jura and W. D. Harkins, ibid., **66**, 1356 (1944).

III. Results and Discussion

A solid of known area (Σ) and the adsorption isotherm of a given vapor on this solid are necessary for the determination of the HJ value of k for this vapor. The solid chosen is anatase, the area of which is 13.8 m.^{2} g.$^{-1}$ as determined by Harkins and Jura using their absolute method. The adsorption isotherms of n-heptane at 25° (Fig. 1) and of n-hexane at 0° on this standard anatase were obtained and the data plotted according to the equation

$$\log p = B' - (A/V^2) \text{ or } \log (p/p_0) = B''(A/V^2) \quad (1)$$

in which A and B' are constants and V is the volume of gas (S. T. P.) per gram of solid adsorbed at pressure p. In the case of n-heptane on anatase at 25°, which is shown in Fig. 1, a straight line is obtained for the relative pressure range of 0.08 to 0.56. Its equation, $\log p =$
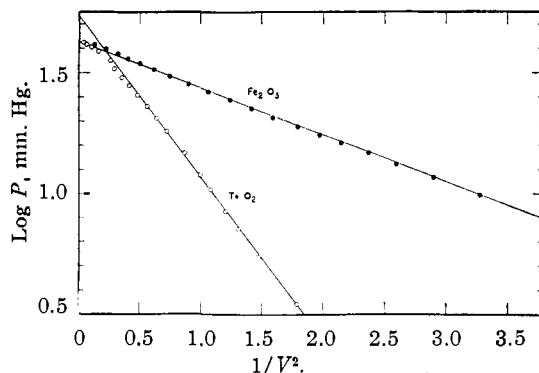

Fig. 1.—HJ plots: n-C$_7$H$_{16}$ on anatase (TiO$_2$) at 25°, $\log p = 1.739654 - 0.669967 (1/v^2)$; n-C$_7H_{16}$ on iron oxide (Fe$_2$O$_3$) at 25°, $\log p = 1.626693 - 0.192568 (1/v^2)$. If k for n-C$_7H_{16}$ at 25° = 16.9, the area of Fe$_2$O$_3$ is 7.42 m.^{2} g.$^{-1}$.

$1.740_0 - (0.670_0/V_2)$, was determined by a least squares treatment of the data. The area per gram of solid, Σ, is related to A, the slope of the line obtained in the above plot, by the equation

$$\Sigma = kA^{1/2} \quad (2)$$

If V is expressed in cc. of gas (S. T. P.) the value of k for n-heptane at 25° is 16.9. A similar treatment for n-hexane at 0° yields a k value of 14.3.

If the adsorption isotherms of these vapors on other solids are plotted according to equation (1) and if a linear relation is exhibited (indicating that the adsorbed film forms a condensed phase), the areas of the solids may be determined by

equation (2). The plot of n-heptane on ferric oxide shown in Fig. 1 is a typical HJ plot for n-heptane on a solid.

Brunauer, Emmett and Teller[1] have suggested that if low temperature adsorption data are plotted according to the equation

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c-1)}{v_m c}\left(\frac{p}{p_0}\right) \qquad (3)$$

a straight line is obtained over a relative pressure range extending from about 0.05 to 0.35. v_m represents the volume of adsorbate required to form a monolayer over the solid adsorbent; v is the volume of gas adsorbed at relative pressure p/p_0; and c is a constant. The BET plots of n-heptane on standard anatase and on iron oxide, exhibited in Fig. 2, are typical of those obtained in this work. The number (N) of adsorbate
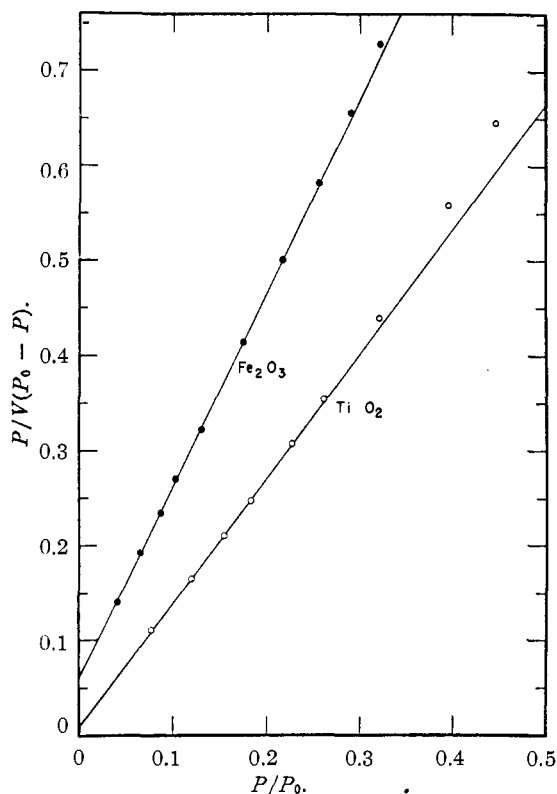

Fig. 2.—BET plots: n-C$_7$H$_{16}$ on anatase (TiO$_2$) and iron oxide (Fe$_2$O$_3$) at 25°. If σ_m for n-C$_7$H$_{16}$ at 25° is 64 sq. Å., the area of Fe$_2$O$_3$ is 8.18 m.^{2} g.$^{-1}$.

molecules necessary to complete a monolayer on one gram of the solid may be calculated from v_m. If (N) and Σ, the area per gram of the solid, are both known, the effective cross-sectional area per molecule (σ_m) is given by the relation

$$\sigma_m = \Sigma/N \qquad (4)$$

From the adsorption isotherms of n-heptane at 25° and n-hexane at 0° on the standard anatase ($\Sigma = 13.8$ m.^{2} g.$^{-1}$) the values of σ_m were calculated to be 64 sq. Å. for n-heptane at 25°

and 58.9 sq. Å. for n-hexane at 0°. This method of obtaining the value of σ_m differs from that used by Emmett's group. This will be discussed later. The BET value for the area (Σ) of the solid is obtained by the multiplication of the number of molecules in the monolayer (N) by σ_m.

In Table Ia are given the values for the areas of 21 non-porous solids, ranging in area from 8 m.^{2} g.$^{-1}$ to 0.09 m.^{2} g.$^{-1}$, as calculated from the adsorption isotherms of n-heptane at 25° by the BET method (standardized with anatase) and by the HJ relative method. The slopes of the HJ and BET lines and the intercepts of the BET lines were determined by the least squares treatment of the experimental data. The range of relative pressure (p/p_0) over which each of the relations is linear is also given. The areas calculated from the adsorption data of heptane at 25° by the two methods agree well, the average difference being about 2.1%, which is excellent agreement for such small areas.

Table Ib was obtained by the rearrangement of the values in Table Ia (columns 8, 7 and 5) according to the order of increasing or decreasing values of c of the BET theory. What this table indicates is that with n-heptane at 25° the *condensed phase* of the film forms in general at lower values of p/p_0 at the higher values of the BET constant c, than at the lower values listed. Also the per cent. difference (column 7 of Table Ia) usually moves in the positive direction for lower values of c. In other words: at higher values of c, the BET method tends to give slightly smaller values for areas than does the HJ relative method; at lower values of c, the BET method tends to give slightly larger areas than the HJ method.

Since few HJ plots have been published, several additional diagrams are presented here. In Fig. 3 that for Fe$_2$O$_3$ is given for comparison with those of ferric oxide (Fe$_2$O$_3$), silver sulfide (Ag$_2$S) and reduced silver (Ag). In Fig. 4 those for n-heptane on lead sulfide (PbS), for graphite of less than 0.004% of ash and of 0.46% of ash.
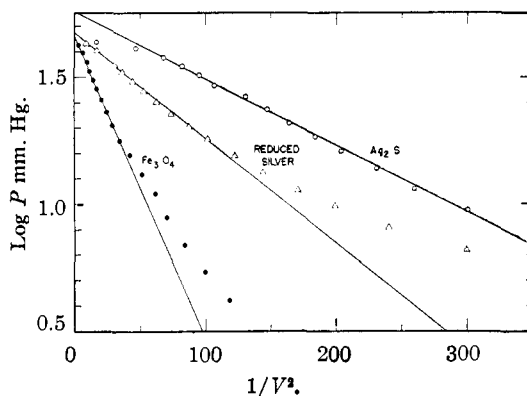

Fig. 3.—HJ plots of n-C$_7$H$_{16}$ on silver sulfide (Ag$_2$S), iron oxide (Fe$_3$O$_4$) and reduced silver at 25°.

TABLE Ia

COMPARISON OF AREAS OF TWENTY-ONE POWDERS BY n-HEPTANE ADSORPTION CALCULATED BY THE HJ RELATIVE METHOD AND THE STANDARDIZED BET METHOD

k = 16.9, σ_m = 64 sq. Å.; areas of powders in sq. meters per gram; vapor pressure of n-heptane at 25° 45.77 mm.

Solid material	Standardized BET area[a]	Applicable p/p_0 range	HJ area	Applicable p/p_0 range	Difference (2–4)	% difference	c (BET Theory)
Fe_2O_3	8.18	0.04 to 0.28	8.04	0.18 to 0.75	+0.14	+1.8	37
Rutile (TiO_2)	7.81	.04 to .35	8.12	.07 to .81	− .31	−3.9	127
Graphite (ash 0.46%)	6.85	.05 to .35	6.97	.18 to .54	− .12	−1.7	167
SnO_2	6.84	.05 to .30	6.89	.07 to .76	− .05	−0.7	97
PbS	6.47	.04 to .27	6.41	.14 to .85	+ .06	+ .9	155
Graphite (ash <0.004%)	4.39	.05 to .35	4.37	.13 to .86	+ .02	+ .5	174
CuO	3.47	.04 to .22	3.33	.16 to .78	+ .14	+4.1	46
CuS	2.17	.04 to .23	2.24	.15 to .73	− .07	−3.2	149
Fe_3O_4	1.83	.05 to .45	1.84	.39 to .98	− .01	−0.5	38
Ag (untreated)	1.20	.05 to .35	1.15	.45 to .89	+ .05	+4.3	21
Ag (reduced)	1.15	.05 to .33	1.12	.38 to .76	+ .03	+2.6	19
Ag_2S	0.821	.03 to .30	0.865	.11 to .77	− .044	−5.4	81
Cr (untreated)	.516	.05 to .37	.500	.42 to .91	+ .016	+3.1	42
PbO	.285	.03 to .30	.273	.10 to .95	+ .012	+4.3	61
Sn (untreated)	.274	.05 to .35	.278	.28 to .94	− .004	−1.4	32
Fe (untreated)	.185	.04 to .35	.189	.04 to .93	− .004	−2.1	112
Fe (reduced)	.183	.06 to .27	.181	.10 to .98	+ .002	+1.1	108
Fe (oxidized)	.178	.05 to .24	.180	.14 to .90	− .002	−1.1	151
Sn (M. D.)(untreated)	.161	.06 to .32	.170	.12 to .32	− .009	−5.4	108
Pb (untreated)	.1006	.05 to .25	.0991	.11 to .92	+ .0015	+1.5	90
Pb (reduced)	.0926	.05 to .30	.0931	.13 to .85	− .0005	−0.5	101

[a] The areas are 35% smaller by the BET–EB method; i. e., when Emmett and Brunauer's value of 44 sq. Å., is used for the n-heptane molecular area.

NOTE ADDED JUNE 28, 1950.—In an important, extensive investigation in this laboratory Dr. M. L. Corrin has done much to make clear the previously obscure relations between the BET and the HJ methods for the determination of the area of a solid. These are important in understanding what is presented in Table I. His experimental work was carried out with solids of high area: 65 to 250 sq. meters per gram. This allowed a much higher accuracy to be attained than with the low area solids of the table, as low as 0.1 sq. meter per gram.

Isotherms were obtained for 10 solids with 4 vapors: nitrogen, argon, n-pentane and pentene-1, and from these the areas were calculated by both the HJ and the BET methods, thus giving 80 values and 40 comparisons. The results exhibited remarkable agreement between the 2 methods and the 4 vapors.

1. For any one vapor the molecular area, σ, in the complete monolayer was found to be independent of the variation in the nature of the subphase.

2. The HJ linear isotherm exhibited 3 slopes and 3 constants: k_1, k_2, k_3 and presumably a fourth. In Table I, k = 16.9 is used, except this times 1.08 or 18.2 for ferric oxide, untreated tin, and graphite (ash 0.46%).

The value of k increases with molecular size but for any one size $k_3 = 1.08k_1$ and $k_2 = 1.08k_3$ and $k_2 = 1.16k_1$.

The import of these relations will be considered in a later paper.

The writers wish to thank Dr. George Jura for his help before the measurements were begun.—WILLIAM D. HARKINS.

In Table II are given the values of the areas of a smaller number of the same solids as calculated from the adsorption isotherms of n-hexane at 0° by the HJ relative method and by the standardized BET method. The slopes of the HJ and BET lines and the intercepts of the BET lines were obtained by the graphical method. The agreement between the area values calculated by the two methods using the adsorption data of nitrogen at −195.8° of n-heptane at 25° and of n-hexane at 0° indicate the general applicability of the methods for the determination of the areas of non-porous solids when these vapors are the adsorbates. The values for the area of graphite and rutile obtained by the HJ absolute method are included in Table II for purposes of comparison.

In their earlier papers Emmett and his co-workers calculated the effective cross-sectional area of the adsorbed molecules in a completed

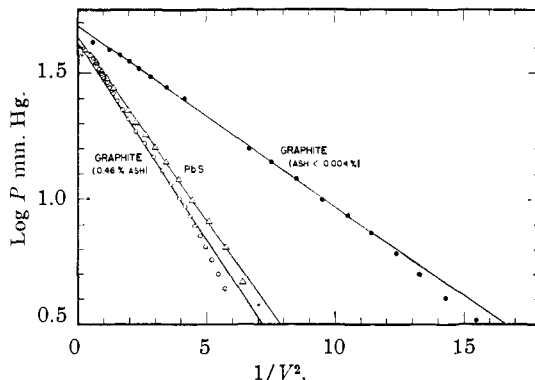monolayer from the density of the liquid or solid

Fig. 4.—HJ plots of n-C_7H_{16} on graphite (0.46% ash), graphite (less than 0.004% ash) and lead sulfide (PbS) at 25°.

TABLE Ib

PER CENT. DIFFERENCE AND RANGE OF p/p_0 AS RELATED TO LOW AND HIGH VALUES OF THE BET c

c, BET theory	% Col. 7 of Table Ia	Applicable p/p_0 range of HJ plot
	Lower c values	
19	+2.6	0.38 to 0.76
21	+4.3	.45 to .89
32	−1.4	.28 to .94
37	+1.8	.18 to .75
38	−0.5	.39 to .98
42	+3.1	.42 to .91
46	+4.1	.16 to .78
	Higher c values	
174	+0.5	.13 to .86
167	−1.7	.18 to .54
155	+0.9	.14 to .85
151	−1.1	.14 to .90
149	−3.2	.15 to .73
127	−3.9	.07 to .81
112	−2.1	.04 to .93
108	+1.1	.10 to .98
108	−5.4	.12 to .32
101	−0.5	.13 to .85
97	−0.7	.07 to .76
90	+1.5	.11 to .92
81	−5.4	.11 to .77
61	+4.3	.10 to .95

method. Recently Davis, DeWitt and Emmett[6] have assigned cross-sectional areas of krypton, butane, freon-21 and 1-butene which gave agreement between the surface areas of various adsorbents as measured by these adsorbates and those obtained by the nitrogen isotherms, using the BET procedure and the cross-sectional area of 16.2 sq. Å. for nitrogen. These corrected values of σ_m for the various adsorbates were about 1.3 to 1.5 times larger than those obtained by the density calculations. At present, the difference between our method of utilizing the BET theory in the determination of the area of non-porous solids and that of the Emmett group appears to be in the choice of the standard for the calibration of σ_m. In the application of the σ_m values for the determination of areas by the BET method it is assumed that σ_m of a given adsorbate is constant, i. e., its value is independent of the type of surface on which the vapor may be adsorbed. It it is assumed that the HJ relative method gave accurate values for the areas of the non-porous solids listed in Table Ia, it is obvious that the effective cross-sectional area of the n-heptane molecule in a completed monolayer on these solids, with the possible exceptions of ferric oxide, silver sulfide and untreated tin, does not vary greatly from the value of 64 sq. Å.

TABLE II

AREAS OF POWDERS IN SQUARE METERS PER GRAM

Determined by the H. J. absolute method or from adsorption data by the H. J. relative method and the B. E. T. method. The values of k and σ_m are calculated according to Section III by use of the standard solid anatase, whose area (Σ) is 13.8 sq. meters per g. as determined by the absolute method of Harkins and Jura.

Solid material	HJ absolute method	HJ relative method Nitrogen at −195.8°, k = 4.06	n-C$_6$H$_{14}$ at 0°, k = 14.3	n-C$_7$H$_{16}$ at 25°, k = 16.9	BET Nitrogen at −195.8°, σ_m = 16.2 Å²	Standardized BET method n-C$_6$H$_{14}$ at 0° σ_m = 58.9 Å²	n-C$_7$H$_{16}$ at 25° σ_m = 64 Å²
Anatase	13.8						
Graphite (ash <0.004%)	4.40 ± 0.6[c]	4.22	4.06	4.37	4.31		4.42
Rutile (TiO$_2$)	7.96 ± .15[a]			8.12	8.14[a]		7.81
Graphite (ash 0.46%)		6.22[b]		6.47	6.22[b]		6.85
Iron oxide (Fe$_2$O$_3$)		7.51[a]	7.07	7.42	7.51[a]		8.18
Silver (untreated)		1.22[b]	1.05	1.15		1.19	1.20
Copper sulfide (CuS)			2.24	2.24		2.33	2.17
Lead oxide (PbO)			0.265	0.273		0.297	0.285
Lead sulfide (PbS)			7.12	6.92		7.78	6.47

[a] Determinations made by P. R. Basford. [b] Determinations made by G. Jura. [c] P. R. Basford, G. Jura and W. D. Harkins, THIS JOURNAL, 70, 1444 (1948). The adsorption data for n-hexane are not as precise as those for n-heptane and therefore the area values are not as accurate.

adsorbate. Harkins and Jura[2] and Beebe, Beckwith and Honig[5] have shown that the effective cross-sectional area of the adsorbed molecule in a completed monolayer (σ_m) for various adsorbates may be somewhat larger than that obtained by the method of Emmett and Brunauer. Our calculated values for σ_m, based on the calibration with a standard surface, are 64 sq. Å. for n-heptane at 25° and 58.9 sq. Å. for n-hexane at 0° as compared to 44 sq. Å. and 39 sq. Å. calculated by the Emmett and Brunauer density

The HJ relative method for determining the area of a porous or non-porous solid is dependent upon the presence of a condensed phase in the adsorbed film over a considerable pressure range and upon the knowledge of the constant k for the particular adsorbate. Livingston[7] and Emmett[8] have discussed the relation between the constant c of the BET isotherm and the relative pressure range over which the HJ relative plot is applicable.

(5) R. A. Beebe, S. B. Beckwith and J. M. Honig, THIS JOURNAL, 67, 1554 (1945).

(6) R. T. Davis, Jr., T. W. DeWitt and P. H. Emmett, J. Phys. Colloid Chem., 51, 1232 (1947).

(7) H. K. Livingston, J. Chem. Phys., 12, 462 (1944).

(8) P. H. Emmett, THIS JOURNAL, 68, 1784 (1946).

In Table Ia are given the c values for heptane on various non-porous solids and also the pressure ranges over which the HJ plots were found to be applicable. These c values range from 19 to 174. Although, as pointed out by Emmett, the lower relative pressure limit at which the HJ plot is linear lies above $p/p_0 = 0.35$ when c is about 25 or less, nevertheless a straight line HJ plot is obtained over a considerable range at higher pressures (Fe_3O_4, Ag (untreated), Ag (reduced), Cr (untreated) and Sn (untreated) are examples). The range of linearity is in general considerably larger for the HJ than for the BET method. Furthermore, the slopes of these HJ plots yield area values which are in moderately good agreement with those obtained by the standardized BET method. Emmett[3] states, "good agreement between BET (using 16.2 sq. Å. as the cross-sectional area of the nitrogen molecule) and the Harkins–Jura plots will be obtained *only* for c values between 100 and 150." The experimental data for n-heptane on the 21 non-porous solids included in this paper appear to indicate that this is not the exact criterion for the c values when n-heptane is used.

During the course of this work with n-heptane a number of area determinations have been made on samples whose total areas were only 1 sq. meter. It appears probable that a moderately accurate area measurement could be obtained on a sample whose total area is about 0.25 sq. meter.

IV. Summary

1. The values for the areas of 21 non-porous solids calculated from n-heptane adsorption isotherms at 25° by the Harkins–Jura (HJ) relative method and by the Brunauer, Emmett and Teller (BET) method (standardized by use of a solid of known area as determined by the HJ absolute method) are in satisfactory agreement, although the BET values of c vary from 19 to 174. The value of k, the constant used in the HJ relative method, is 16.9 (or 18.2 more rarely) for n-heptane at 25°. The effective cross-sectional area (σ_m) of n-heptane at 25° used in the calculation of areas by the BET method is, as determined by us, 64 sq. Å.

2. Similar agreement for a smaller number of solids is obtained using the isotherms of n-hexane at 0°. The value of k for n-hexane at 0°, 14.3, and of σ_m, 58.9 sq. Å., are probably less accurate than those for n-heptane.

3. The values for the areas of several non-porous solids calculated from the adsorption isotherms of n-heptane or n-hexane are in satisfactory agreement with those calculated from the adsorption isotherms of nitrogen and with those obtained by the HJ absolute method.

4. The method is described for the calculation of the effective molecular cross-sectional area of an adsorbate (σ_m).

5. With higher values of the BET constant c the condensed phase of the HJ method forms at relatively low values of p/p_0 for n-heptane, and at low values of c at higher values of p/p_0.

The Locus of the Initiation in an Emulsion Polymerization Recipe Containing Ferrous Iron and Benzoyl Peroxide*

BY I. M. KOLTHOFF AND MADOLYN YOUSE

In recent years several papers[1] have been published on the emulsion polymerization of butadiene (75) and styrene (25) using an organic peroxide which is soluble in monomers and some reducing system in the aqueous layer. In these systems the free radicals which initiate polymerization are produced by the reaction of ferrous iron with the organic peroxide. In some recipes ferrous iron is the only reducing substance present while in other recipes a reducing organic substance such as a reducing sugar is present. The main function of sugars such as glucose or fructose is to reduce continuously the ferric iron formed; on the other hand, it has been shown in this Laboratory that with more active sugars, such as dihydroxyacetone or scylloinosose, the direct reaction between the sugar and the peroxide may be of major importance in initiating polymerization. The peroxides which have been used most successfully are cumene hydroperoxide (denoted below as CHP) and benzoyl peroxide (BP). One of the notable differences in these two peroxides is that cumene hydroperoxide is soluble in water to the extent of 13.9 grams per liter (0.0914 molar), while benzoyl peroxide is practically insoluble in aqueous solutions. From work carried out in this Laboratory[2] it is evident that with CHP, the locus of formation of free radicals is the aqueous layer. It has been proposed by Wall and Swoboda[3] that with BP the locus of the reaction is the organic layer, the

(1) W. Kern, Die Makromoleculare Chem., 1, 199 (1948); E. J. Vandenberg and G. E. Hulse, Ind. Eng. Chem., 40, 932 (1948).

(2) I. M. Kolthoff and A. I. Medalia. J. Polymer Sci., in press.
(3) F. T. Wall and T. J. Swoboda, THIS JOURNAL, 71, 919 (1949).