If ion solvation in the mixture is primarily by water rather than methanol molecules, and if the Debye–LaMer diameter is a true measure of the diameter of the solvated ions, this would account for the surprising agreement between the values of *a* in the two cases. It would still leave unexplained, however, the decreased ion conductances in the mixture as compared with those predicted by the Walden rule, unless some additional factor, significant only in the transport process, is postulated, *e. g.*, hydrogen bonding between the water molecules in the hydrated sheath about the ions and the "free" methanol molecules of the solvent.

Secondly, it should be observed that the *a* value found here is considerably less than the critical Bjerrum[11] distance, given for 1:1 electrolytes by $e^2/2DkT = 5.6$ Å. for a solvent of dielectric constant 50 at 25°. Thus on the Bjerrum picture there should be considerable ion-pair formation, yet the form of the ion conductance *vs.* concentration curves[5] for this salt shows that association must be slight.

A consideration of the data presented here and of the ion conductances suggests (to us at any rate) that the use of a mixed solvent complicates the problem considerably, and that measurements in a one-component non-aqueous solvent may yield data which are more easily interpreted.

Summary

1. The e. m. f. of the cell with transference Ag,AgCl/NaCl(m_1)//NaCl(m_2)/AgCl,Ag, with 50 mole per cent. aqueous methanol as solvent, has been measured at 25° for sodium chloride concentrations from 0.003 to 0.08 *M*.

2. The precision and reproducibility of the results are comparable with those obtained with this type of cell for aqueous solutions. The bias potential between stable pairs of electrodes is 0.03 mv. or less, and is independent within one or two microvolts of the electrolyte concentration, just as is the case when water is solvent.

3. The activity coefficients, computed from the e. m. f. data and the known transference numbers, were extrapolated by means of the Gronwall, LaMer and Sandved extension to the Debye-Hückel equation, which represents the coefficients up to 0.025 *M* when the value selected for the mean ionic diameter is 4.45 Å. For higher concentrations, the observed values lie below those predicted by the equation.

4. The value found for the ionic diameter is in fortuitously exact agreement with that for this salt in water, and is definitely less than the critical Bjerrum distance for this solvent. The significance of the mean ionic diameter in its relation to the ion conductances for the salt in water and in methanol–water solution is discussed.

TORONTO, CANADA RECEIVED MARCH 13, 1948

[11] Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY]

Mixed Adsorption of Radon and Argon on Silica Gel

BY BENJAMIN P. BURTT[1] AND J. D. KURBATOV

Mixed adsorption studies using radon in various gases at 1 atm. have been made by Siebert[2] at −80°, by Francis[3] with silica gels of various states of hydration, by Becker and Stehberger[4] and, using charcoal, by Nikitin and Joffe.[5]

The present work lies in the general field of mixed gas adsorption. The adsorbent was silica gel and all the experiments were conducted at 25 ± 3°. Adsorption isotherms of radon in air, in carbon dioxide and in argon at near atmospheric pressure were obtained. Approximately 1×10^{-16} g. atom of radon at partial pressures around 1×10^{-10} mm. was used.

Adsorption isotherms for air, argon and carbon dioxide were determined under the same experimental conditions as for radon. A brief study was also made of the mixed adsorption of carbon dioxide and air using conventional pressure–volume methods with subsequent analysis of the gas. A more thorough study was made of the mixed adsorption of argon and carbon dioxide applying both methods of conventional analysis and radioactive tracer technique. The adsorption of argon from air was investigated using radioactive argon as a tracer.

Description of the Apparatus and Procedure

The apparatus shown in Fig. 1 was constructed for mixed adsorption studies using radioactive gases. It was also suitable for the measurement of the simple adsorption of gases by pressure–volume methods.

The mixture of radioactive gas and the gas accompanying it is stored in buret S. Chosen volumes of the mixture can be transferred to the evacuated system as well as to the ionization chamber for analysis. The ionization chamber was connected to a Wulf bifilar electrometer. The gas is confined during adsorption in the system, A and E (total volume 26 cc.). About 0.8 g. of silica gel is placed in the removable adsorption flask E. With-

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[2] W. Siebert, *Z. physik. Chem.*, **A180**, 169 (1937).

[3] M. Francis, *Kolloid-Z.*, **59**, 292 (1932).

[4] A. Becker and K. H. Stehberger, *Ann. Physik*, [5] **1**, 529 (1929).

[5] B. A. Nikitin and E. M. Joffe, *Bull. acad. sci. U. R. S. S., Classe sci chim.*, **1944**, 210–215 (English Summary).

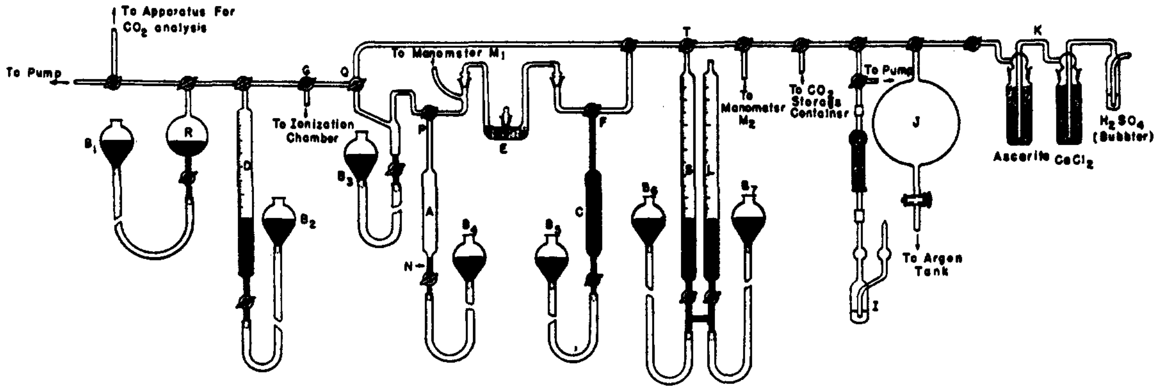

Fig. 1.—Apparatus for adsorption of gases.

out disturbing the equilibrium established, the sample of gas in pipet A is isolated from the system and removed to the ionization chamber for analysis.

To measure simple adsorption, a known quantity of gas was added to the evacuated system; after equilibrium had been established the quantity remaining in the gas phase was determined from the final pressure, volume and temperature.

In the experiments on the mixed adsorption of carbon dioxide with air, and with argon, the amount of carbon dioxide at equilibrium was determined by removing the gas in pipet A into a gas buret for absorption in potassium hydroxide.

Experimental Results

The Adsorption of Air, Argon and Carbon Dioxide on Silica Gel at 25°.—The adsorption isotherms of air, argon and carbon dioxide are plotted in Fig. 2. It was found in agreement with previous work, that carbon dioxide is adsorbed to a greater extent than air or argon. Air is adsorbed only slightly more than argon.

The data for the three isotherms were fitted by the method of least squares to the Freundlich equation

$$y = kx^{1/n} \tag{1}$$

where y is the number of gram moles adsorbed per gram of gel and x is the number of gram moles per cc. in the gas phase. The data also conform to the Langmuir equation

$$y = y_m b'x/(1 + b'x) \tag{2}$$

In these equations x and y have the same meanings as in the Freundlich equation, y_m is the number of gram moles of gas adsorbed per gram of silica gel when the surface is covered with a unimolecular layer and b' is the adsorption coefficient.

An estimate of the heat of adsorption of a gas can be made from the value of the adsorption coefficient b'. Laidler, Glasstone and Eyring[6] derived an expression for b' in terms of the heat of adsorption per molecule E. With some approximations the value of E can be calculated from b'. For carbon dioxide b' and y_m are obtained by plotting equation (2) in the form

$$\frac{1}{y} = \frac{1}{y_m b'x} + \frac{1}{y_m} \tag{3}$$

The isotherms of argon, air, and radon were experimentally linear and b' could not be obtained in this way. However, an approximate value of b' is calculated for these gases from the adsorption isotherms and estimated surface area of the adsorbent as follows. Brunauer and Emmett[7] found the area of silica gels with 6 to 9% water to be about 600 sq. m. per gram. The silica gels in this work averaged 6.27% water and the surface area is assumed to be of the same order of magnitude. The values of y_m are estimated using the above surface area for silica gel. These values of y_m are then used to calculate the adsorption coefficients b' from the adsorption isotherms. By this method the heat of adsorption of radon in air or argon is evaluated to be of the order of 9000 calories per mole (a 50% error in estimating the surface area would produce an error of about 350 cal./mole). It may be seen that this method gives values of the correct order of magnitude. The calculated value for argon is 5,500 calories per mole

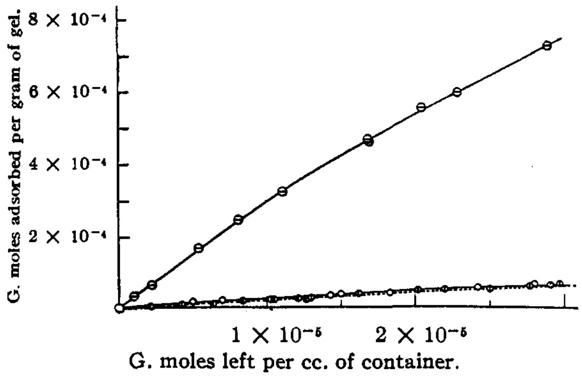

Fig. 2.—Adsorption isotherms of air, argon and carbon dioxide on silica gel, temp. 25°, wt. gel. = 0.8216 g.: -⊖-⊖-⊖- CO$_2$, -⦶-⦶-⦶-- A, -○-○-○- air.

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[6] K. J. Laidler, S. Glasstone and H. Eyring, *J. Chem. Phys.*, **8**, 659 (1940).

[7] S. Brunauer and P. H. Emmett, THIS JOURNAL, **59** 2682 (1937).

while data in the literature range from 2,500 to 3,600.[8,9,10,11,12] The value for carbon dioxide calculated from a plot of equation (3) is 7,700 calories per mole. The value calculated using the estimated surface area is 7300 calories per mole, whereas values from 6,900 to 7,900 are reported by other investigators.[8,10,13] The calculated value for air is 5,500 calories per mole and the values in the literature for oxygen and nitrogen are from 3,000 to 5,500 calories per mole.[10,13,14,15]

In addition to the per cent. adsorbed, a distribution coefficient α (the quantity of gas adsorbed per gram of adsorbent divided by the quantity of gas per cc. of space) is calculated. Slight unavoidable variations in the weight of the gel and the volume of the system from one experiment to the next do not affect α, whereas they may affect the per cent. adsorbed.

The results of the calculation are given in Table I for each gas at the same concentration in the gas phase (corresponding to a pressure of 557 mm.).

TABLE I

Gas	G. mole per cc. of space $\times 10^6$	G. mole adsorbed per gram gel $\times 10^6$	α	% of total gas adsorbed
Argon	3	6.52	2.1	6.5
Air	3	6.89	2.3	6.8
Carbon dioxide	3	78.20	26.1	45.4

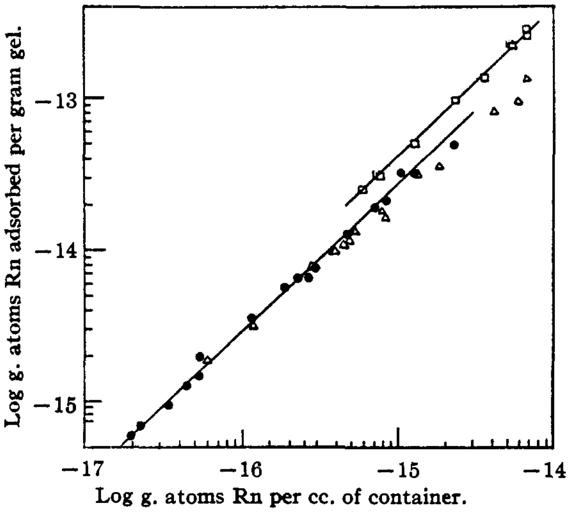

Fig. 3.—Mixed adsorption of radon on silica gel with air, carbon dioxide and argon: ●, Rn + Air at 740 mm.; △, Rn + CO_2 at 704 mm.; □, Rn + Argon at 697 mm. temp. 25°; av. wt. gel., 0.75 g.

Mixed Adsorption Studies with Radon—Radon and Air.—The adsorption isotherm for radon in air at near atmospheric pressure is given in Fig. 3. The log-log plot is linear and of approximately unit slope. Decreasing the pressure of the accompanying air to 120 mm. produces no measurable change in the adsorption of radon. The value of the distribution coefficient α of radon obtained from the plot is 28.5. Approximately 50% of the total radon is adsorbed, the variations being due to slight differences in the weight of gel and the volume of the system.

The results of this work are in agreement with the Langmuir theory of mixed adsorption. The equations derived by Markham and Benton[16] predict that a decrease in air pressure produces no appreciable change in the adsorption of radon under these experimental conditions. No change in the adsorption of radon is observed with a decrease in air pressure.

Radon and Carbon Dioxide.—Figure 3 shows the adsorption of radon from carbon dioxide and from air at near atmospheric pressure to be the same at concentrations of radon below 3×10^{-16} g. atom/cc. At higher concentrations of radon its adsorption is less from mixtures with carbon dioxide than from mixtures with air at one atmosphere total pressure.

Studies were made of the adsorption of radon from radon-air-carbon dioxide mixtures when the total pressure of the gases was approximately one atmosphere. The adsorption of radon in mixtures containing as much as 25% carbon dioxide was not measurably different from the adsorption of radon in air alone.

The Langmuir equations predict a straight line of unit slope for the log-log plot as long as the concentration of radon is very small compared to that of carbon dioxide. In this experimentation the slope of the isotherm was slightly less than unity even though the concentration of radon was negligible. This could be partially explained by postulating that the surface of the gel is heterogenous and the adsorption of radon takes place primarily on the points of greatest unsaturation. Upon increasing the concentration of radon in the gas phase above 3×10^{-16} g. atom/cc., the active points on the gel become more nearly saturated and further increases in the partial pressure of radon do not result in a proportional increase in the amount adsorbed per gram of silica gel.

Radon and Argon.—The adsorption isotherm of radon from radon–argon mixtures at near atmospheric pressure is also given in Fig. 3. The log–log plot is experimentally linear, of approximately unit slope and lies considerably above the corresponding isotherm of radon in air.

At the same partial pressure of radon in the gas phase approximately 50% more radon is adsorbed in the presence of argon than in the presence of

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(8) F. Dewar, *Proc. Roy. Soc. (London)*, **A74**, 122 (1904).

(9) E. Hückel, "Adsorption and Kapillarkondensation," Leipzig, 1928, p. 22.

(10) W. Kalberer and C. Shuster, *Z. physik. Chem.*, **A141**, 270 (1939).

(11) F. G. Keyes and M. J. Marshall, THIS JOURNAL, **49**, 156 (1927).

(12) A. Lendle, *Z. physik. Chem.*, **A172**, 77 (1935).

(13) W. Kalberer and H. Mark, *Z. physik. Chem.*, **A139**, 151 (1928).

(14) S. F. Gregg, *J. Chem. Soc.*, 1494 (1927).

(15) A. Mangus, *Z. physik. Chem.*, **A142**, 401 (1929).

(16) E. C. Markham and A. F. Benton, THIS JOURNAL, **53**, 497 (1931).

air. Decreasing the pressure of argon decreases the adsorption of radon. From Table II it can be seen that α, the distribution coefficient for radon in argon, decreases simultaneously with the pressure of the argon.

TABLE II

MIXED ADSORPTION OF RADON AND ARGON

G. atoms Rn to system × 10⁶	Pressure argon, mm.	α, Radon
35.1	704	42.8
133	701	42.7
360	690	42.4
74.6	684	39.5
133	345	38.6
52.7	280	37.1
384	114	35.6
42.6	105	34.9

These observations indicate that the adsorption of radon is enhanced by the presence of argon.

The Langmuir theory predicts that the plot of the amount adsorbed per gram of gel against the amount per cc. in the gas phase should be linear. In this respect the data agreed with the theory of mixtures. The Langmuir theory also predicts that for the argon–radon mixtures approximately 1% more radon should be adsorbed than from a mixture with air.

A comparison of the adsorption of radon in air, in argon and in carbon dioxide is made in Table III showing the amount of radon adsorbed per gram of silica gel corresponding to a given partial pressure of radon in the gas phase in each of the three accompanying gases.

TABLE III

COMPARISON OF THE ADSORPTION OF RADON ON SILICA GEL IN THE PRESENCE OF CARBON DIOXIDE, AIR AND ARGON

Temperature 25°; average weight of gel 0.75

Accompanying gas, at mm.	Concentration of radon in gas phase, g. atoms/cc. × 10¹⁸	G. atoms of radon adsorbed/gram of gel × 10¹⁶
CO_2 at 704	7.00	165.0
Air at 735	7.00	194.0
Argon at 684	7.00	300.0
CO_2 at 704	4.00	100.0
Air at 735	4.00	114.0
Argon at 684	4.00	172.0
CO_2 at 704	1.00	27.0
Air at 735	1.00	29.5
Argon at 684	1.00	43.0
CO_2 at 704	0.70	18.8
Air at 735	0.70	21.0
Argon at 684	0.70	30.2

Mixed Adsorption of Argon—Argon and Carbon Dioxide.—The adsorption of the two gases was measured at various mole fractions of pure argon and carbon dioxide, maintaining a constant total quantity (1×10^{-3} g. mole) of carbon dioxide and of argon. The conventional procedure of analysis for the carbon dioxide content was compared with the use of a radioactive tracer (A^{37}). Isotope A^{37} has a half life of 34.1 days[17] and it was prepared in the Ohio State University cyclotron by bombardment of potassium chloride. The results for the adsorption of carbon dioxide in the presence of argon are shown in Fig. 4. No significant change in the adsorption of carbon dioxide in the presence of argon was detected. The results of the conventional method were slightly higher, in general, than the simple adsorption isotherm for carbon dioxide, while those obtained using A^{37} were slightly below the isotherm. Figure 5 shows the adsorption of stable argon from mixtures with carbon dioxide as determined by the use of radioactive argon. There was no measurable change in the adsorption of argon due to the pressure of carbon dioxide.

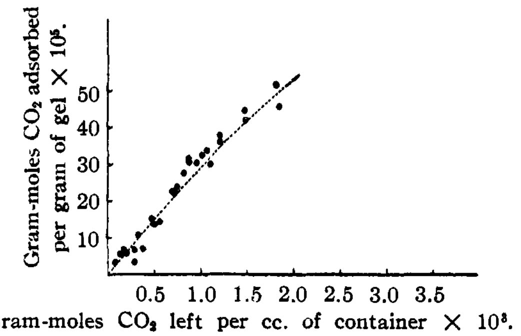

Fig. 4.—Mixed adsorption of argon and carbon dioxide: on silica gel, adsorption of CO_2 from A–CO_2 mixtures compared to adsorption of pure CO_2: total g. moles A + CO_2 = 1×10^{-3}; temp., 25°; av. wt. gel, 0.75 g.; -----, adsorption isotherm of pure CO_2; ⊖, adsorption of CO_2 from A–CO_2 mixtures by pressure change and CO_2 analysis; ●, adsorption of CO_2 from A–CO_2 mixtures by pressure change and use of radioactive argon (A^{37}) as tracer.

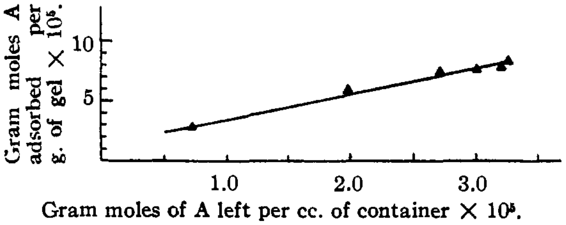

Fig. 5.—Mixed adsorption of argon and carbon dioxide, adsorption of argon on silica gel: adsorption of A from A–CO_2 mixtures, total g. moles A + CO_2 = 1×10^{-3}; temp., 25°, av. wt. gel., 0.75 g.

Argon and Air.—It has been reported that argon and nitrogen, and argon and oxygen mutually increase one another's adsorption at 0°.[18,19] Using radioactive argon similar results were obtained. Radioactive argon is added to

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(17) P. K. Weimer, M. L. Pool and J. D. Kurbatov, *Phys. Rev.*, **66**, 209 (1944).

(18) B. Lambert and H. S. Heaven, *Proc. Roy. Soc.* (*London*), **A153**, 584 (1936).

(19) G. Damkohler, *Z. physik. Chem.*, **B23**, 58, 69 (1933).

air and the adsorption of the stable argon from air is traced. Approximately 13% of the total argon present in air was found to be adsorbed.

In these studies with radioactive argon it has been found that the use of radioactive tracer for mixed gas adsorption is feasible and gives more consistent results than the conventional method. In cases where the chemical analysis of the gas mixture is difficult by ordinary means, the use of a radioactive tracer, if available, provides a convenient method for studying mixed adsorption. It is recognized that the technique described here using separate samples of silica gel for each experiment does not insure that the adsorbent has exactly the same adsorption properties in each experiment. Experiments in which the only variable was the sample of silica gel used showed this error to be of the order of 3%.

Acknowledgment.—The authors greatly appreciate the support given to this research by Professor Alpheus Smith and by Professor M. L. Pool. We also express our thanks to the Alumni Fund for a grant in aid for purchase of equipment.

Summary

1. An apparatus is described suitable for studying binary mixed gas adsorption in which one component is radioactive or contains radioactive atoms as a tracer. The apparatus is also suitable for certain mixed adsorption studies by conventional means. Simple adsorption isotherms were obtained for air, argon and carbon dioxide on silica gel at 25°.

2. Adsorption isotherms for radon in air, in argon and in carbon dioxide on silica gel at 25° were studied. The isotherm in air follows Henry's law and substantiates the Langmuir theory of mixed adsorption as applied to low concentrations. The adsorption of radon is slightly suppressed in carbon dioxide. The studies with radon in argon show that the adsorption of radon is enhanced in the presence of argon even though a very small fraction of the total surface of silica gel is covered by radon.

3. The heat of adsorption of radon in air and in argon was estimated from the data obtained to be of the order of magnitude of 9,000 calories per mole.

4. Methods are described for the use of radioactive argon to follow the adsorption of argon in mixtures with carbon dioxide and with air.

SYRACUSE, N. Y. RECEIVED JANUARY 2, 1948

NOTES

The Reduction of 6-Methyl-8-(4'-diethylamino-1'-methylbutylidene)-aminoquinoline

BY H. J. BARBER, D. H. O. JOHN AND W. R. WRAGG

The recent publication by Elderfield, *et al.*,[1] reporting a study of the synthesis of Plasmochin by the reductive condensation of 1-diethylaminopentanone-4 (I) with 6-methoxy-8-aminoquinoline (II), from which a satisfactory method did not ensue, is of considerable interest to us since we were concerned during the war with a similar process which gave Plasmochin in excellent yield. We wish therefore to record some additional data.

Early in our work we investigated a process revealed by Bergmann[2] for the reductive condensation of 6-methoxy-8-nitroquinoline with (I), following his conditions as closely as practicable (our palladium/barium sulfate catalyst was prepared by the method of Sabalitschka and Moses[3]), but we could not obtain any Plasmochin. A second Bergmann, patent[4] claims, but does not exemplify, the reductive condensation of (I) and (II).

Preparation of the Schiff base, 6-methoxy-8-(4'-diethylamino-1'-methylbutylidene)-aminoquinoline (III), was accomplished by Elderfield, *et al.*,[1] by the interaction of (I) and (II) using ethylbenzene as an entrainer to remove water, but condensation under these conditions was slow and far from complete. The Schiff base may be obtained in almost quantitative yield using the diethyl ketal of (I), instead of (I) itself, (*cf.* van Shelven[5]) by the procedure described[6] for 6-methoxy-8-amino-1,2,3,4-tetrahydroquinoline (IV). The Schiff base, without distillation, could then be reduced in ethyl acetate solution at 60° and 450 lb. hydrogen pressure in the presence of a platinum/charcoal catalyst, but the results were not consistent. Considerable improvement was effected by using an Adams platinum oxide catalyst[7] at the same pressure but at room temperature. Reproducible results were obtained and an 80% over-all yield (calculated on (II)) of distilled Plasmochin base was obtained on a production scale.

In our experience the reduction is very susceptible to minor changes in materials, catalyst or

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(1) Elderfield, Kreysa, Dunn and Humphreys, THIS JOURNAL, 70, 40 (1948).

(2) British Patent 547,302.

(3) Sabalitschka and Moses, *Ber.*, 60, 800 (1927).

(4) British Patent 547,301.

(5) British Patent 388,087, Example 32.

(6) Barber and Wragg, *J. Chem. Soc.*, 610 (1946).

(7) John, *J. Soc. Chem. Ind.*, 63, 256 (1944).