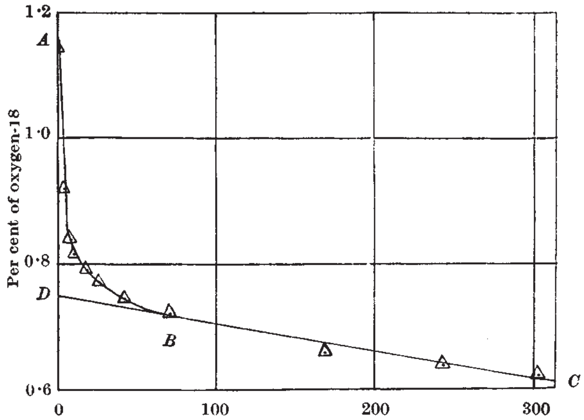

Fig. 1. Experiment 56. $T = 460°$ C

leak connected the reaction vessel to the ionization region of the mass spectrometer, and thus a continuous record of the change of oxygen-18 content of the gas with time was obtained. The quantities of gas bled off from the reaction system for purposes of analysis were small, being about 10^{-4} gm. of oxygen per hour; thus the concentrations of the two reactants remained sensibly constant throughout each run.

The exchange reactions we have measured are all first order with respect to concentration of oxygen-18, as indeed all simple isotopic exchange reactions should be (cf. H. A. C. McKay[2]). We have examined in some detail the exchange reactions of magnesium oxide and chromium trioxide using oxygen gas pressures between 4 and 14 cm. of mercury. We quote here a few results obtained with magnesium oxide. Fig. 1 shows a plot of a typical experiment; the exchange reaction clearly falls into two parts, one fast, *AB*, and the other slow, *BC*. The former might plausibly be exchange with the oxide surface, and the latter might be due to slow diffusion into the lower layers of the oxide. By extrapolation of *BC* back to the point *D*, we can separate roughly the two reactions and hence obtain a first-order plot such as is shown in Fig. 2. Table 1 shows the first-order velocity constant so obtained to be independent of oxygen gas pressure for magnesium oxide over the pressure range studied; this is also the case for chromium trioxide.

From the amounts of oxide and oxygen used, the initial oxygen-18 content, and that at *D* (Fig. 1), it is possible to calculate the amount of 'surface' exchangeable oxygen which takes part in the reaction *A*—*B*. We find that the velocity constant and 'surface' oxygen concerned with the portion *A*—*B* vary considerably with the previous heat treatment of the oxide and with the temperature at which the reaction is studied. From the surface oxygen determined as above, we can calculate the approximate figure for the 'reactive surface area of the oxide' assuming the reactive oxygen to be spread as ions one layer deep, and using a diameter of 1·4 A. We find that the surface areas so obtained are of the same order as those calculated from low-temperature nitrogen adsorption isotherms by the Brunauer, Emmett and Teller method, provided the samples have had a similar heat treatment. Some figures are given in Table 2. The fact that such parallelism exists between the two methods is added evidence that the fast reaction is concerned with, and is probably characteristic of, the surface.

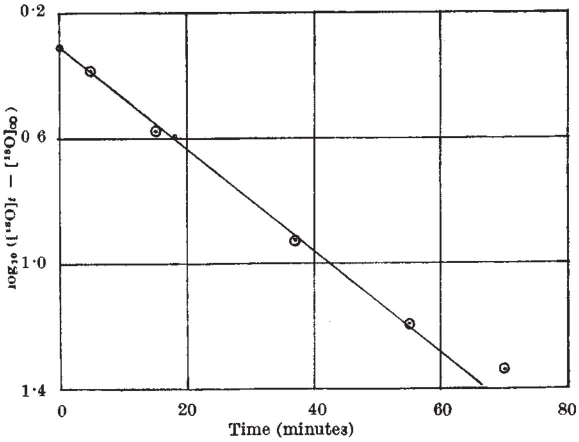

Fig. 2. Experiment 3. $T = 507°$ C.

Table 1

Pressure (mm. Hg)	Velocity constant at 492° C. (min.$^{-1}$)
40·7	0·0283
79·7	0·0290
83·5	0·0292
147·3	0·0286

Table 2

Heat treatment	Surface area (sq. metres/gm.)	
	Nitrogen adsorption	Oxygen exchange
400–500° C. for 14 hr.	61·9	27·5–68·4 at 450–500°
640° C. ,, ,, ,,	—	18·7 ,, 460°
750° C. ,, ,, ,,	—	10·1 ,, 460°
860° C. ,, ,, ,,	21·8	2·76 ,, 460°

Qualitative examinations have been made of the exchange reactions with aluminium, thorium, titanium and zinc oxides, and the exchange of nitrogen-15 between nitrogen and magnesium nitride is under examination. A fuller account of this work is in course of preparation.

G. Houghton
E. R. S. Winter

Chemistry Department,
Imperial College of Science and Technology,
London, S.W.7.
July 27.

---

[1] *Nature*, **164**, 142 (1949).

[2] *Nature*, **142**, 997 (1938).

Preparation of Mono-Halogen Substituted Compounds of Sulphur Nitride

Demarçay[1] first prepared the compound S_4N_3Cl from sulphur nitride, S_4N_4, and sulphur chlorides. Muthmann and Seitter[2] later reported its formation by refluxing sulphur nitride with acetyl chloride. The latter preparation was repeated, diacetamide and sulphur dioxide being found as by-products.

The effect of a current of dry hydrogen chloride on a saturated solution of sulphur nitride at room temperatures was then investigated, and it was found that in the presence of a trace of moisture a very rapid reaction took place. A reddish-brown substance was precipitated after three to four minutes, and gradually changed during the next ten minutes to a pale yellow equimolecular mixture of

S_4N_3Cl and ammonium chloride. The $(S_4N_3)^+$ radical could be separated from this by dissolving the mixture in water and precipitating the insoluble S_4N_3I by potassium iodide.

The decomposition of the red precipitate to form the chlorine-substituted compound is evidently catalysed by hydrogen ions, for if no trace of water is present the reaction will not continue past the intermediate red precipitate stage. A volatile oxidizing agent, some of which is carried over in the current of hydrogen chloride, is formed during the reaction. This could be explained by a reaction such as the following:

$$S_4N_4 + 4HCl \xrightarrow{H^+} S_4N_3Cl\downarrow + NH_4Cl\downarrow + Cl_2\uparrow .$$

It was reported by Demarçay[1,3] that chlorine combines with sulphur nitride, and if allowance is made for reaction between the liberated chlorine and unchanged sulphur nitride, then the yields are approximately theoretical.

The formation of S_4N_3Cl from sulphur chlorides and acetyl chloride is therefore apparently due to traces of hydrogen chloride which are always present in these liquids, and not to any specific property of the reagents themselves. In this case, the replaced nitrogen is removed not as ammonium chloride but as diacetamide. Hydrogen bromide and hydrogen iodide also appear to react with sulphur nitride, under similar conditions, to give precipitates of S_4N_3Br and S_4N_3I respectively.

From this it would appear that the constitution of sulphur nitride and its mono-halogen substituted compounds must be similar, for the replacement, as shown, takes place readily under very mild conditions.

Research is still taking place on this subject. I wish to thank Mr. A. D. Monro for his invaluable assistance and active interest in this work.

A. G. MacDiarmid

Chemistry Department,
Victoria University College,
Wellington, N.Z.
July 14.

[1] Demarçay, *C.R. Acad. Sci.*, **91**, 854, 1066 (1880).

[2] Muthmann and Seitter, *Ber.*, **30**, 627 (1897).

[3] Demarçay, *C.R. Acad. Sci.*, **92**, 726 (1881).

A New Method for the Separation of Hydrocarbons by Selective Adsorption

The separation of hydrocarbons can be effected by different methods, for example, crystallization, distillation and solvent treatment. A particular type of the last method is that of fractional precipitation from solution in light hydrocarbons such as propane by the use of methane and other gases under high pressure[1].

Recently selective adsorption has become of increasing importance as another method for the separation of different groups of hydrocarbons contained in mineral oil fractions[2]. Analytical methods of this type have been elaborated for testing gasolines[3], and attempts have been made to separate lubricating mineral oils using the principle of chromatography. Allibone percolated a solution of mineral oil in light petroleum through a column of silica-gel and collected about twelve fractions differing in specific gravity[4]. Similar results were obtained at the same time in Germany, fullers' earth being used as adsorptive material[5]. The characterization of the composition of mineral oils by these methods must be regarded as inadequate, as there is no clear demarcation between the fractions obtained.

I have also investigated the resolution of mineral lubricating oils by selective adsorption. The method has been improved and new principles for the rapid characterization of different hydrocarbons have been found. It enables clear-cut fractions to be obtained representing different groups of compounds. The results obtained may be compared to some extent with fractional distillation of high efficiency, a broken curve being their graphic representation.

The important new feature of this work is the use of an indicator which, when deposited on silica-gel, produces a colour reaction with hydrocarbons containing an aromatic nucleus. Trinitrobenzene, trinitrotoluene, trinitrophenol and many other nitro compounds may be used as indicators. At the moment, trinitrobenzene has proved to be the most useful indicator; when deposited on silica-gel it produces a colour in contact with the solution of most aromatic hydrocarbons. This reaction is very sensitive, and the colour produced is the result of the formation of the addition product between the hydrocarbon and nitro compound. The colour is dependent mainly on the structure of the hydrocarbon and varies from yellow to dark red or violet. About thirty pure hydrocarbons and twenty different nitro compounds have been examined for this reaction, and a relationship roughly established between constitution and the colour produced.

This new colour reaction on the surface of silica-gel can be usefully applied not only for quick characterization of different hydrocarbons but also for very sharp resolution of some hydrocarbon mixtures on the chromatographic principle. Characteristic colours of different hydrocarbons can be observed during the percolation of mineral oil dissolved in light petroleum, for example, *n*-hexane, when silica-gel containing trinitrobenzene is used as adsorptive material. With the right conditions, a red zone is formed at the top of the column, a yellow zone blending smoothly into the red in the middle, and a colourless zone at the bottom. Hydrocarbons contained in the different zones can be collected separately. Such visual indication of specific types of hydrocarbons in the column admits of their separation and converts what has been previously a 'blind' adsorption into a serviceable chromatography.

Adopting this principle, it is possible now to isolate four fractions which contain different classes of compounds: (1) A fraction containing hydrocarbons from the colourless zone, which are practically non-adsorbed by silica-gel. Their characteristic feature is that they do not change the colour of silica-gel containing the indicator. This fraction is water-white. When the chromatogram is properly developed, hydrocarbons of this type may be estimated quantitatively, reproducibility of results being good. (2) A fraction containing hydrocarbons which change the colour of silica-gel containing trinitrobenzene to yellow and deep orange, brown or red. They can be eluted from the column by *n*-hexane, used in large excess. They are colourless or yellow. (3) A fraction consisting of hydrocarbons which can only be eluted with difficulty by *n*-hexane, but easily by the use of benzene. These hydrocarbons react readily with trinitrobenzene or trinitrophenol deposited on silica-gel, giving intensely coloured addition compounds. The colour of this fraction varies