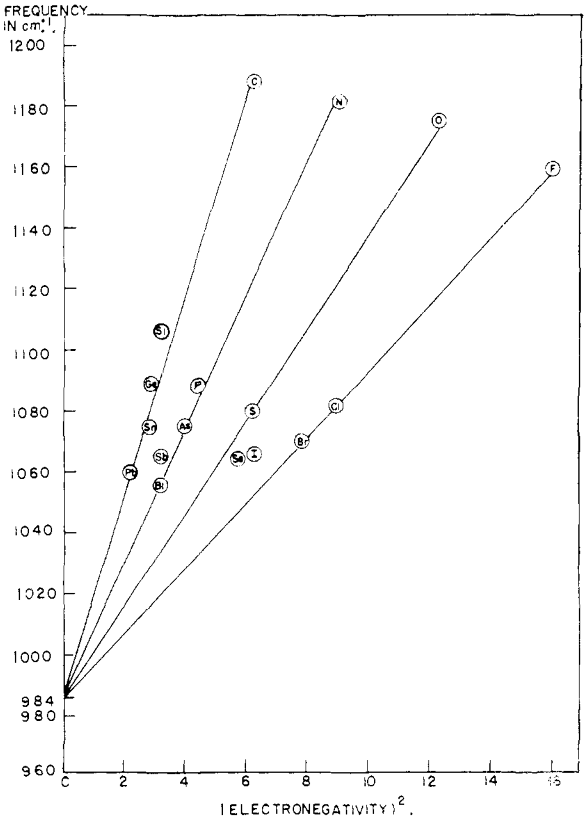

Fig. 2.—Relation between vibration frequency and electronegativity of substituent element.

Fig. 1, this suggests that the published electronegativity value for iodine may be slightly erroneous.

TABLE II

ELECTRONEGATIVITY VALUES

Element	Calcd.	Pauling	Others	Element	Calcd.	Pauling	Others
F	4.00	4.0		As	2.00	2.0	
Cl	3.00	3.0		Sb	1.89	1.8	
Br	2.75	2.8		Bi	1.79	..	1.8[6]
I	2.65	2.5	2.6[6]				1.8[7]
O	3.42	3.5		C	2.51	2.5	
S	2.48	2.5		Si	1.93	1.8	
Se	2.26	2.4		Ge	1.79	1.7	
N	2.96	3.0		Sn	1 66	1.7	
P	2.14	2.1		Pb	1.52	..	1.5[7]

An equation relating the slopes of all of the four lines in Fig. 2 in terms of the valence of the substituent is

$$\text{Slope} = 2^{n/2}[7.70 + (n - 1)0.15] \qquad (1)$$

Incorporating this expression into the general equation for a straight line involving slope and intercept, an equation was obtained which yields electronegativity values directly from knowledge of the corresponding frequency and the valence of the substituent. It is (for the B group elements investigated)

$$E = 2^{-n/4}\left(\frac{\nu - 984}{7.70 + (n - 1)0.15}\right)^{1/2} \qquad (2)$$

Table II shows the good correspondence of electronegativity values obtained from the above equation with those listed by Pauling and others. It should be noted that Haissinsky's value for the electronegativity of iodine is more in agreement with the value obtained in this research, and is probably more nearly correct. The values obtained for germanium and tin also appear more accurate than those of Pauling, since in his table both elements have the same values, which is somewhat unlikely.

An interesting application of equation 2 arises in the case of deuterium. In view of the simple electronic configuration of the hydrogen isotopes, deuterium can be considered as either a group 1 or group 7 element. Since the A and B subdivisions of the groups begin in the fourth period, deuterium can be thought of as the highest member of the halogen series, and thus equation 2 should apply to its phenyl compound, monodeuterobenzene. Comparison of the spectrum of that compound[3] with the spectra of the other monosubstituted benzenes indicates that the monodeuterobenzene band at 1030 cm.$^{-1}$ is the appropriate one to use in equation 2. The calculation leads to an electronegativity of 2.06 for deuterium, which is close to the 2.13 value listed[7] for hydrogen. It should be noted that the 1030 cm.$^{-1}$ band has been assigned fairly conclusively to a C–H planar bending vibration,[8] and since this band varies in position depending on the substituent, the evidence points to the fact that the "X-sensitive vibration" arises from a C–H planar mode.

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New Microcatalytic-Chromatographic Technique for Studying Catalytic Reactions

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For several years the analysis of gases and hydrocarbons of low molecular weight by gas chromatographic or thin film chromatographic techniques has been in successful use.[1–7] It has proved especially valuable for the analysis of hydrocarbon in the C_1–C_8 range. The method of operation of such an analytical column is well known and has been described in detail on several occasions.[1–6] It involves adding 1 to 10 mg. of the mixture that is to be analyzed to a stream of some suitable carrying gas such as H_2, He or N_2 and passing it through a chromatographic column (see Fig. 1) packed with a

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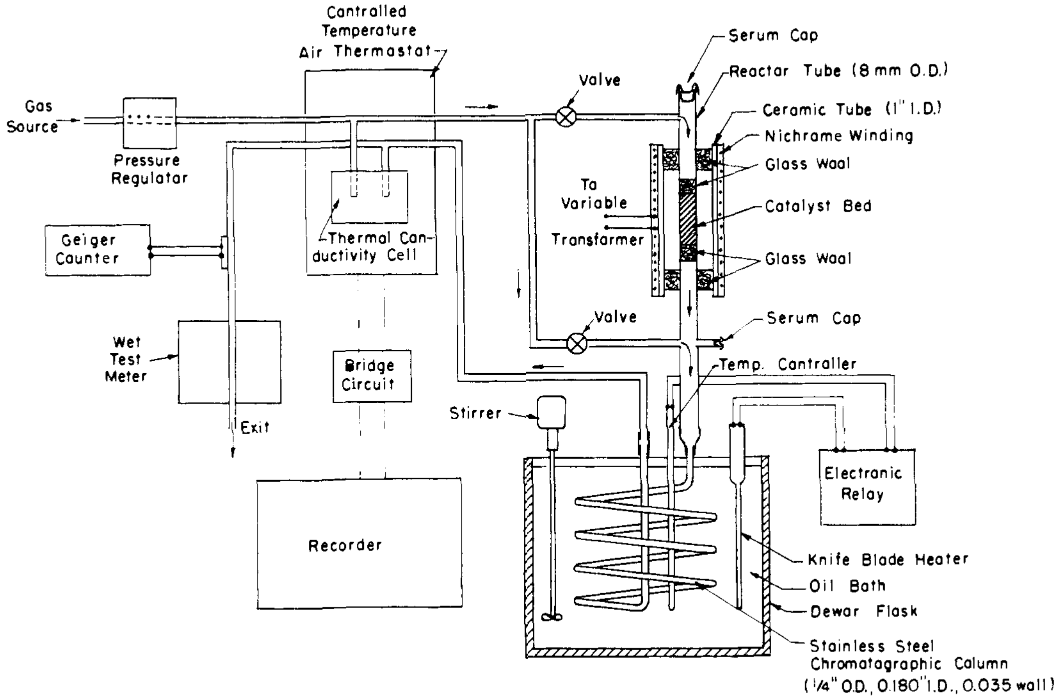

Fig. 1.—Microreactor and chromatographic product analyzer unit.

finely divided adsorbent or with a finely divided solid coated with a suitable solvent such as paraffin oil or dioctyl phthalate. Each component of the sample has a definite and characteristic time of passage through a given column because each component will in general spend a different length of time in an adsorbed or dissolved state in passing through the column. A thermal conductivity cell at the exit of the column can be connected to a standard recorder to trace a curve of the thermal conductivity of the exit gas as a function of time. The resulting plot or chromatogram will contain relatively sharp peaks for each component of the mixture. The area under a peak is a measure of the amount of a component present; the time at which the peak appears can serve to identify the component. The curve in Fig. 2 and the dashed curve in Fig. 3 are both typical chromatograms. Recently, it occurred to us that by attaching a reactor unit to the top of a chromatographic column, one could inject small quantities of reactant into a suitable carrying gas, pass the mixture over a catalyst and analyze the exit gas from the reactor by passing it directly into a chromatographic column. We have now successfully completed a number of catalytic runs by this technique. The present note is a brief description of the apparatus used, the results obtained, and the potential application of this procedure.

Figure 1 is a rough sketch of the equipment. The catalyst reactor contained 1 cc. of M-46 Houdry type cracking catalyst. By proper manipulation of the stream of hydrogen that was used as a carrying gas, samples of hydrocarbons could be injected as liquids or gases through the serum caps above the catalyst and passed through the chromatographic column, or such samples could, for calibration purposes, be inserted in the lower serum cap and passed directly into the column. The exit gases from the column were passed through a thermal conductivity unit connected to one pen of a two pen recorder; and then, if radioactive components were present, through a Geiger counter connected to the second pen of the recorder.

A typical reaction that has been studied in testing this "one shot" microcatalytic method is the decomposition of 2,3-dimethylbutane. The results of a cracking experiment in which 0.027 cc. of the liquid reactant was injected into a stream of hydrogen (38.5 cc. per minute) and passed through the 1 cc. of catalyst are shown in Fig. 2. Peaks marked A, B, C, D, E, F, G, etc., correspond, respectively, to C_2; C_3; i-C_4H_{10}; n-C_4H_{10}, i-C_4H_8 or n-C_4H_8-1; *cis-* and *trans-*C_4H_8-2; 2-methylbutane and a trace of 2,2-dimethylbutane or 2-methyl-2-butene. The peak H at 31.8 minutes is that of the unreacted 2,3-dimethylbutane; the small peak at I is probably an isomerization product 2-methylpentane though it might also be either of two hexenes. A comparison of the products formed is in satisfactory agreement with the cracking runs of Greensfelder and Voge[8] on this hydrocarbon. It is at once apparent that by properly selecting the chromatographic column, one can obtain as complete identification as desired of the amounts and nature of the products formed.

The technique here described can also be readily adapted to tracer experiments. For example, a 50-50 mixture of C_3H_6 and radioactive C_2H_4 passed in a stream of hydrogen over the cracking catalyst at 400° yielded the chromatographic tracings shown in Fig. 3. The dashed curve represents the relative amounts of the various products expressed in terms of millivolts unbalance in a thermal conductivity cell at the exit of the chromatographic column. The

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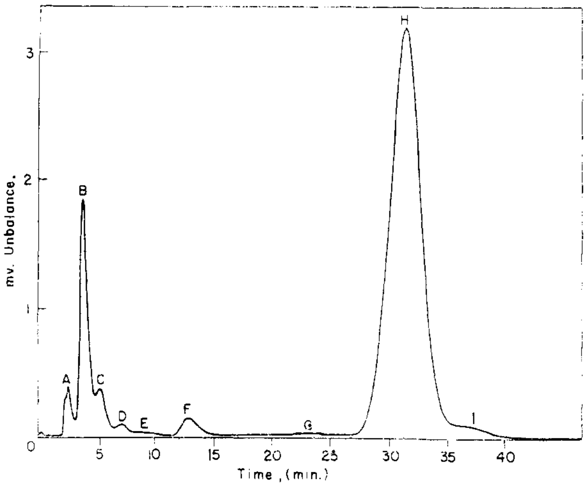

Fig. 2.—Chromatogram of the products obtained by injecting 0.027 cc. of liquid 2,3-dimethylbutane into a stream of hydrogen as a carrying gas and permitting it to pass over 1 cc. of cracking catalyst at 540°. The chromatographic column contained "Celite 545" coated with dioctyl phthalate.

curve drawn as a solid line is the recording for the radioactivity of the product gas as determined by a flow type[9] Geiger counter placed in series with the thermal conductivity cell. It is at once evident that some of the radioactive ethylene takes part in the formation of the C_4, C_5 and C_6 polymerization products (corresponding to the range 5 to 45 minutes in Fig. 3). A quantitative study of this reaction system will be presented at a later date. For the present, Fig. 3 is intended merely to illustrate the effective use that can be made of this new catalytic–chromatographic technique in studying reactions with the help of radioactive tracers.

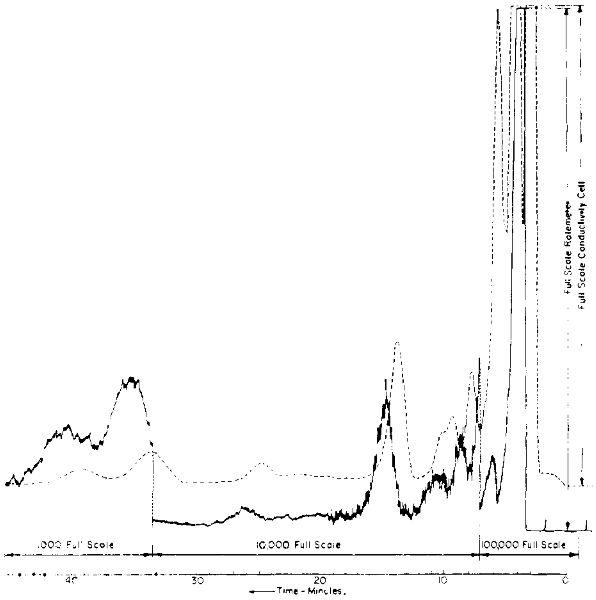

Fig. 3.—Chromatogram (dashed line) and radioactive record (solid line) of the products formed when a mixture of 8 cc. of radioactive ethylene and 8 cc. of non-radioactive propylene was injected into a stream of hydrogen carrying gas and passed over 1 cc. of cracking catalyst at about 400°. The peaks corresponding to the various products and reactants are displaced to as much as 1 minute longer time than the peaks on the dashed line because of several details of operation. The three scales indicated by arrows refer to various settings of the rate meter. The curved (solid line) gives instantaneous counts per minute for the gas in the counting chamber.

The possible applications of this micro-technique are so numerous and obvious as to need little explanation. The catalyst chamber may be replaced by an empty tube for thermal reactions or for reactions in the presence of radiation. The column can be varied according to known techniques to permit the analysis of a variety of products. The apparatus, with a few modifications, could be adapted to high-pressure experiments. This micro-catalytic setup gives promise of being very useful for a great variety of exploratory catalytic work as well as for fundamental studies of the mechanism of catalytic reactions.

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