

but may rather be described as being looped, since the sudden reduction in the rate seems always to be followed by a rapid recovery.

It will now be clear that phenomena, which are generally accepted as criteria of chain mechanism, are observed in both cases. In the case of acetaldehyde, the initial rate of decomposition is considerable, and we must suppose that the main process is carried forward both by the formation of new primary centres, and to a very material extent by chain mechanism. In the case of ethylene oxide, the rate of formation of primary centres is obviously very small, and the main process is carried forward mainly through the operation of the chain mechanism. In this case, surface does not influence the rate of the main reaction.

In both cases the secondary process conforms to the main reaction, and when breaks occur in the graphs representing the latter, they also appear simultaneously in the graphs representing the former. It would appear therefore that the *breaking of chains*, at the walls or in the gas phase, does not merely involve the dispersal of energy, but also the formation of new primary centres, of the kind referred to by Semenoff as *degenerate*, from which the secondary process originates. Three-body collision must obviously play an important part in these processes.

We have made a further study of the influence of neutral gases, such as hydrogen and methane, on the rates of reaction. The phenomena are much more complex than was indicated by our first experiments. The work is being continued, and will, we hope, throw light on the phenomena associated with the breaks in the rate graphs.

This work, and investigation carried out with Mr. P. F. Gay on the thermal decomposition of dimethyl-ether into methane and formaldehyde, and other similar experiments, seem to be leading definitely to the conclusion that in all spontaneously occurring processes of this kind, the probability that the process will be continued by a chain mechanism is never zero. Semenoff has referred to the free energy of the process as giving a measure of the probability of the continuation of the process by chain mechanism. The term 'free energy' can only be used qualitatively, but so far as our work goes the principle seems to be well established.

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Initial Formation of Methyl Alcohol in the Oxidation of Methane

ALTHOUGH a paper published about a year ago from our research laboratories, by Dr. D. M. Newitt and Mr. P. Z. Szego¹, described experiments in which large yields (up to 50 per cent of the theoretical) of methyl alcohol had been obtained by the slow reaction of methane-air mixtures at 430° and 50 atmospheres pressure, up to then no direct evidence had been obtained of its formation during the slow combustion of methane at atmospheric pressure.

Since then, however, further experiments by Dr. Newitt and Mr. J. B. Gardner have resulted in the isolation of methyl alcohol from the reaction products of a $2\text{CH}_4 + \text{O}_2$ mixture at 450° and atmospheric pressure, in contact with a porcelain surface, proof also being forthcoming of its formation preceding that of formaldehyde.

Such result led Dr. J. Bell to repeat some former experiments upon the explosions of a $5\text{CH}_4 + 2\text{O}_2$ mixture at initial pressure of about 50 atmospheres in a bomb (1 litre capacity), so arranged that the burning medium would be suddenly cooled by expansion after bursting a disc at a point (320 atmospheres) during the actual combustion period short of the maximum pressure of 430 atm., and that the cooled products would be retained in a large expansion chamber for subsequent analysis. Later examination of the suddenly cooled products has proved the presence therein of about 0.13 per cent of methyl alcohol and 0.03 per cent of formaldehyde, the alcohol having been isolated and identified as methyl 3:5 dinitro benzoate, m.p. 107.5°.

In none of the experiments referred to could even the faintest sign of 'peroxide' formation be detected.

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Radioactivity of Oil-Waters in Czechoslovakia

PROF. V. J. VERNADSKY has directed attention to the investigations of Chlopin, Kurbatov¹ and other Russian scientific workers on the radium and mesothorium content of the brine of the Russian oil districts. In general, the radium content was found to be much higher than the normal content of surface waters (10^{-15} gm. radium per gm. water). The maximum was found in the water of the oil beds of Novyj Groznyj in the Northern Caucasus, with 1.46×10^{-10} gm. radium per gm. water. In several places the mesothorium content was likewise considerably higher, though there were scarcely any traces of thorium.

Later, O. Hahn and H. J. Born² put forward the view that the high radium content of the waters of the oil beds would account for the occurrence of helium in sylvine, as the alkali chlorides form mixed crystals with lead. During its secondary formation, the sylvine might therefore receive the isotope of lead, radium D, from underground waters rich in radium.

In connexion with these questions and also to ascertain how far the higher radium content of the oil-waters depends upon the kind of oil and the place of its occurrence, a preliminary survey has been made of the radium content of the brine of two oil beds in Czechoslovakia, at Gbely (Slovakia) and at Jasina (Carpathian Ruthenia).

Technically important occurrences of naphtha and natural gas are found in Czechoslovakia only in the Carpathian system. Compared with the other Carpathian countries—Poland and Rumania—the naphtha resources of the country are at present neither so important nor so well explored (Fig. 1). We find here two types of naphtha beds: beds of a light paraffinic naphtha limited to the Carpathian flysh belt (Cretaceous and Palæogene beds), and beds of a heavy naphtha without paraffin and without asphalt, of the naphthenic series, occurring in the Neogene of the Vienna basin. Light naphtha is met with in Moravia at Bohuslavice nad Vlárrou and at Ratiskovice, in Western Slovakia at Turzovka and at Popradné in the Trenčín district, in Eastern Slovakia at Komárník na Dukle, at Miková,