

Physics. — *On the rate of reaction in the system mineral oil/oxygen and the mechanism of the influence of copper and tin on this system.* By D. J. W. KREULEN and D. TH. J. TER HORST. (Communication from the Laboratory for Coal- and Oil Research at Rotterdam and from the Physical Laboratory of the University of Utrecht.) (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of December 30, 1939.)

For the measurement of the rate of reaction in the system liquid/gas two methods are available.

A. The method originating from A. TITOFF¹⁾. It is characterized by the application of a pure homogeneous medium. In this method the gas (in our case oxygen) is introduced into the liquid till saturation is obtained. Then the liquid is completely separated from the gas-phase and it is allowed to react at the temperature which is wanted. One is able to calculate the velocity constant K of the reaction from the equation:

$$K = \frac{1}{t} \lg \frac{A}{A-x}$$

A being the quantity of the gas in gm. molecules per litre at the beginning of the test and $(A-x)$ that at the time t . As the active mass of the liquid remains practically constant the monomolecular law is followed. In our case this method has a disadvantage on account of the small solubility of oxygen in oil. Thus the original concentration of the oxygen is small and the problem is to estimate these relative small quantities with sufficient accuracy.

B. The method originating from R. LUTHER and J. PLOTNIKOW²⁾. In this method as well the liquid- as the gas-phase is present during the reaction. Both together form one closed system; precaution is taken to prevent any escape of gas from it. The gas-phase is continually stirred into the liquid-phase. To obtain this a hollow glass stirrer of special construction is used. The lower part of it has the form of a SEGNER's water wheel; it serves to divide the gas into the liquid. At the top of the hollow glass-spindle a couple of small openings is made through which the gas-phase is allowed to enter into the stirrer. When the stirring velocity is increased the gas-phase is more intensely introduced into the liquid. A mercury-seal enables to drive the stirrer from outside the reacting system by a small electromotor.

¹⁾ Ztschr. f. Phys. Chemie, XLV, 1903, pag. 641—648.

²⁾ Ztschr. f. Phys. Chemie, LXI, 1908, pag. 513—544.

During the reaction the oxygen in solution will have a tendency to decrease. One has to choose that stirring velocity which corresponds with a large supply of oxygen in comparison with the decrease of concentration resulting from the reaction. Only in this case comparable oxidation velocities are measured.

For the study of the system mineral oil/oxygen, method A is but used in one series of investigations³⁾. We consider this work as essentially correct. Moreover in technics a great many "ageing tests" exist as f.i. the I.P.T. test; the British Air Ministry test; the B.S.I. test; the Indiana oxidation test e.s.o. In all these tests either air or oxygen is passed at a certain rate through the oil which is maintained at an arbitrary chosen temperature. After a certain period of heating the alteration of one or more constants is determined.

Thus these tests correspond to the B-method. However in no case the *conditio sine qua non*: solution velocity > reaction velocity is fulfilled. This was proved by the following experiments. We used the method and apparatus introduced by LUTHER and PLOTNIKOW in the modification as described by W. REINDERS and S. I. VLES⁴⁾. In this apparatus a medicinal paraffin oil was oxidized at 100 deg. cent.

The increase of the dipole moment was followed as a function of the oxidation time. Measuring the dielectric constant we used the ordinary high frequency-method.

To indicate the reaction velocity we choosed the tangent from the line giving the dipole moment as a function of time.

In figure 1 the reaction velocity is plotted as a function of the velocity of stirring. It is clear that the measured velocities are independent of the

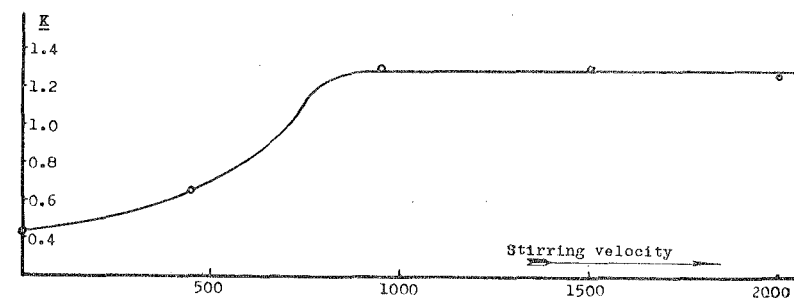


Fig. 1.

intensity of stirring when this is higher than 1000 revs. p. min. To be absolutely sure, in the further experiments a velocity of 1500 revs. p. min. was applied. Then the reacting system is a milk white liquid in consequence of many small oxygen bubbles which are divided in the liquid.

Now by the technical tests mentioned before a quantity of gas varying

³⁾ C. JANSSEN Czn. Archiv f. Electrotechn. 25, 567 (1930); L. S. ORNSTEIN, C. KRIJGSMAN and D. TH. J. TER HORST, Physica (II) 3, 1935, pag. 201.

⁴⁾ Recueil des Travaux Chimiques des Pays Bas. XLIV, 1925, pag. 1.

from 2- till 15 liters per hour is passed through the oil. It is obvious that in this case, even in approximation, the critical solution velocity is not realized. Therefore, both for the measurement of reaction velocities as well from the standpoint of exactness one is obliged to reject these tests.

The oil with which the experiments were carried out had the following constants: molecular weight 445; density 20/4 0.8833; refractive index $D/20$ 1.4828; aniline point (critical solution temperature) 109.0 deg. cent; specific dispersion

$$\frac{(N_G - N_C) 10^4}{d} = 158;$$

surface tension at 20 deg. cent. 32.1 dyne/cm.

According to J. C. VLUGTER, H. I. WATERMAN, H. A. VAN WESTEN and J. J. LEENDERTSE⁵⁾ we are able to get from these constants an idea with regard to the average constitution of the oil molecules. So we found: aromatic rings 0%; naphthenic rings 37%; paraffinic side chains 63%; extra tertiary carbon atoms 5 (which corresponds with a very moderate branching of the paraffinic side chains) and average number of rings per molecule = 2.8. The figure for the average number of rings per molecule is absolutely exact if one takes the average molecular weight into account. In order to calculate the percentage of naphthenic rings and paraffinic side chains a supposition has to be made. In our case we have assumed that we had to do with polycyclic 6-ring naphthenes.

The dipole moment was estimated as the difference between the molecular polarisation and the molecular refraction at a temperature of 20 deg. cent. according to the equation:

$$\bar{\mu} = 0.0127 \cdot 10^{-18} \sqrt{(P - P_0) T}$$

where $\bar{\mu}$ is the average dipole moment; P the molecular polarisation; P_0 the molecular refraction and T the absolute temperature. If we assume ϵ the dielectric constant, N the refractive index, M the molecular weight and d the density we have:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \text{ and } P_0 = \frac{N^2 - 1}{N^2 + 2} \cdot \frac{M}{d}$$

For the unaltered oil, in which no polar compounds are present, we found for P , in first approximation, the same value as for P_0 (143.21 respectively 143.82). We corrected for this small difference at the beginning of the experiments.

Now during the oxidation the average molecular weight did not change; in each case the variations which were found are within the accuracy of the experiment. The accuracy of $\bar{\mu}$ is therefore dependent from the reliability with which the density, the dielectric constant and the refractive

⁵⁾ J. Inst. Petroleum Techn. 21, 661—701 (1935); Ibid. 24, 16 (1938).

index can be measured. The density and the refractive index are reliable to within 2 pro mille. The dielectric constant however is only reliable to within $\frac{1}{2}$ %.

Now about fifty experiments showed us that a simple relation exists between the increase of the density and that of the dielectric constant. In figure 2 the dielectric constant is plotted against the density. A straight-

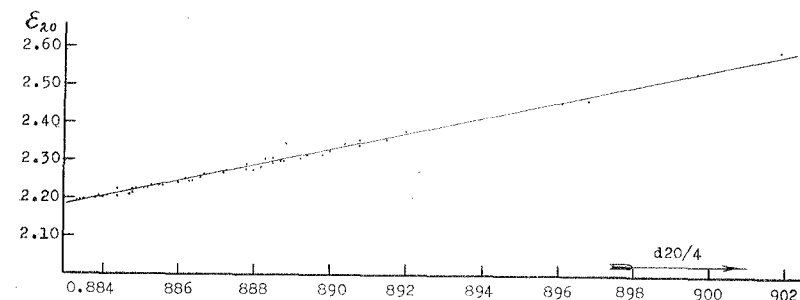
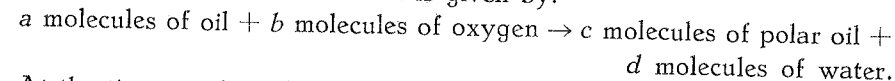


Fig. 2.

line relationship is obtained, the deviations from the average line are lying well within the accuracy of the experiment.

It is possible to explain this straight-line relationship.

The general scheme of reaction is given by:



At the time $t=0$ we have from the oil n particles and at the time $t=t$ we have from the oil $(n-x)$ particles. Thus the density of the oxidized oil $s = (n-x)m_0 + \frac{c}{a} x m_p + \frac{d}{a} x m_w$; m_0 , m_p and m_w being respectively the mass of an oil-, polar oil- and watermolecule.

As $a m_0 + b m_{O_2} = c m_p + d m_w$ we get $x = \frac{\Delta s}{m_{O_2}} \cdot \frac{a}{b}$; Δs being the increase in density.

Now

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{4\pi}{3} n A_0$$

(A_0 being the polarisation per oil-molecule) and

$$\frac{\epsilon_t - 1}{\epsilon_t + 2} = \frac{4\pi}{3} (n-x) A_0 + \frac{4\pi}{3} \cdot \frac{c}{a} x A_p + \frac{4\pi}{3} \cdot \frac{d}{a} x A_w$$

thus:

$$\frac{\epsilon_t - 1}{\epsilon_t + 2} - \frac{\epsilon_0 - 1}{\epsilon_0 + 2} = 3 \frac{\Delta \epsilon}{(\epsilon_0 + 2)^2} = \frac{4\pi a}{3 b m_{O_2}} \Delta s \left[\frac{c}{a} A_p + \frac{d}{a} A_w - A_0 \right].$$

Now A_w is known, A_0 follows from our experiments and with regard to A_p we made an estimation.

In our experiments we found $\frac{\Delta\epsilon}{\Delta s}$ to be 20.77 (figure 2). Thus one comes to the result that $2a + 2b = 4c + 1d$ which is acceptable if we assume an average scheme of reaction in which the oil is as well converted into alcohols, ketons, water as acids.

Consequently it is possible to increase the accuracy with which the average dipole moment can be estimated by the following procedure. The dielectric constant which is found is used to check whether the relationship between the density and the dielectric constant holds. This being the case we calculate the average dipole moment with that value of ϵ which is obtained from the more exact density with the aid of the line given in figure 2.

It is desirable to state that already W. N. STOOPS⁶⁾ realized that the decomposition in transformer oils may be followed rather closely by measuring the dielectric constant of the oils as they deteriorate in service.

Also by J. L. HIDDINK⁷⁾ the change in polar characteristics of transformer oil was measured in laboratory tests.

A more extensive and systematical research however was not yet carried out. In connection with this we remember of the remark made in 1936 by L. S. ORNSTEIN, D. TH. J. TER HORST and G. H. FREDERIK: "it might be important to point out that one is able to follow chemical reactions measuring the dipole moment as function of time"⁸⁾.

We too set much value on the introduction of the average dipole moment to characterize the degree of oxidation which is reached by an oil. For if an oxygen molecule takes hold of an oil molecule, the first result will be the introduction of a polar group into the system. Moreover the average dipole moment includes all the oxidation stages while other figures as f.i. the acid value, represent but one oxidation stage. In figure 3 the increase of the dipole moment is plotted as a function of time. The experiments were carried out at 100 deg. cent.

From figure 3 one sees that not until an induction period (or initial period of slow reaction) is passed an appreciable increase in polar compounds can be observed.

Beyond this induction period there exists a straight line relationship between μ and the time of oxidation. During our experiments we got the impression that the introduction of polar compounds in the system does not begin suddenly but that a slight and increasing reaction exists in the latter part of the induction period. Although this observation is very probable correct, the reaction itself is so small that the phenomenon is quite within the accuracy of the experiment. We are therefore only allowed to mention it as an indication in this direction.

⁶⁾ Physics, Vol. II, 1932, pag. 322.

⁷⁾ Diss. Utrecht 1932.

⁸⁾ Proc. Kon. Akad. v. Wetensch., Amsterdam, 39, 325 (1936).

In figure 3 besides $\bar{\mu}$ also the increase of the acid value is given as a function of time. One sees that it is difficult to conclude from the latter

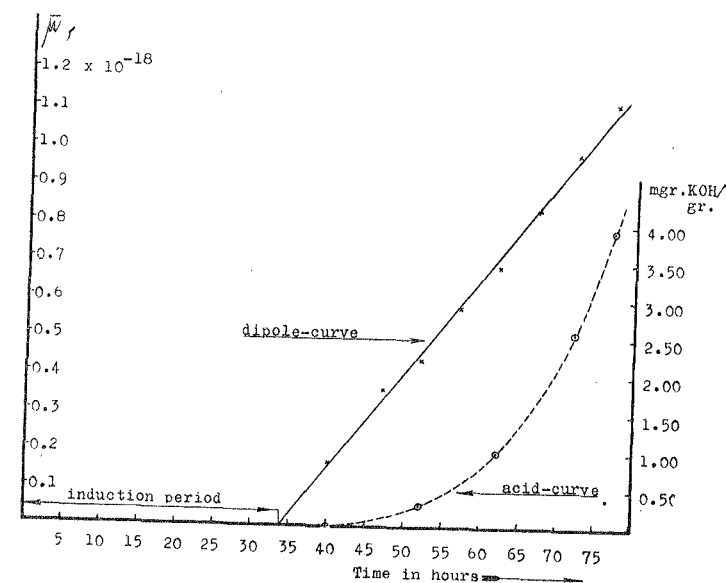


Fig. 3.

curve where the period of induction comes exactly to an end. Similar phenomenons are inhaerent in the curves which represent the alteration of other quantities as a function of time. Thus the superiority of $\bar{\mu}$ for the estimation of the length of the period of induction will be obvious.

The existence of a period of induction includes that any judgment of oils which is but founded on the alteration of a certain constant, after a fixed time of reaction, is incorrect. With regard to this we refer to figure 4.

Oil 1 possess a larger reaction velocity than oil 2 as $tg a_1 > tg a_2$. Yet one would be obliged to conclude to quite the reverse if only one measure-

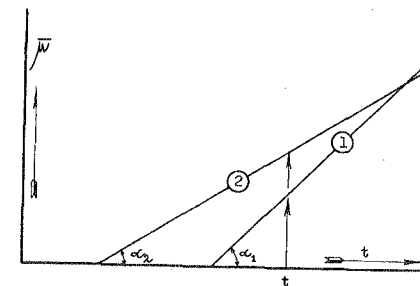


Fig. 4.

ment at the time t was taken. This is caused by the different length of the period of induction of the two oils.

For the determination of reaction velocities in our system it is therefore necessary to measure during the whole test; the induction period included.

We now pass on to the influence of metals on the rate of reaction. In a series of experiments copper filings (electrolytic copper) were used. These filings passed a sieve with 400 openings pro sq. cm. Tests were carried out without any addition of the metal; subsequently with oils containing an increasing quantity of metal. The progress of $\bar{\mu}$ was measured for every period of five hours and so it was possible to deduce at the end of the experiment both the length of the period of induction and the reaction velocity. The magnitude of the reacting surface of the filings is directly proportional to the number of grams which are added. After that the reaction velocity was definitely established in the presence of the metal (dotted lines in figure 5) the experiment was discontinued. The oil was divided among four centrifuge tubes and centrifugated at a rate of 1500 rvs. per min. With the supernatant oil, in which no solid metal was present, the experiment was then continued (drawn lines in figure 5).

The lines marked D_{6a} and D_{6b} refer to experiments with oil without any metal but with different quantities of oil (respectively 250- and 125 cm³).

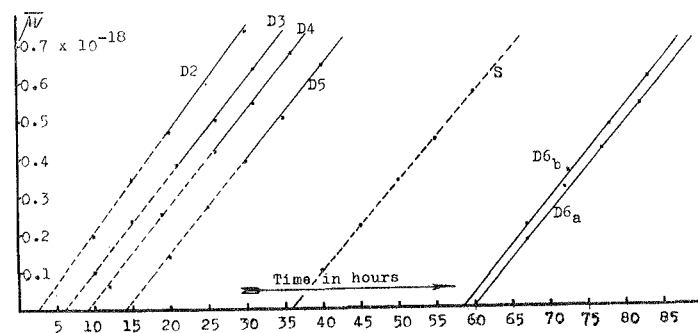


Fig. 5.

The lines marked D_2 , D_3 , D_4 and D_5 refer to such in which to 250 cm³ of oil respectively 10-, 5-, 2½ and 1¼ grms of copper filings are added. Line S refers to an experiment with tin which is mentioned below. The magnitude of the tin surface in this test is comparable with the copper surface added in test D_4 .

In figure 6 the length of the induction period is plotted as a function of the number of grams of copper filings which are added. It appears that the first quantities of surface, which are added, are the most active. This suggests the possibility of an adsorption phenomenon.

To verify this assumption a same quantity of copper filings (2½ grams) were brought into contact with the oil for different spaces of time. This contact was realized within the usual conditions; thus at 100 deg. cent. applying stirring. After the choosen space of time the experiment was discontinued. The copper filings were centrifuged and the work was continued with the supernatant pure oil.

Now it appeared that the length of the period of induction was quite the

same, either for a time of contact of say one hour or for a time of contact agreeing with the complete induction period.

Figure 7 is a common curve of adsorption. To be absolutely sure an experiment was carried out in which the contact of metal and oil was realized in a nitrogen atmosphere for two hours. In this case too the

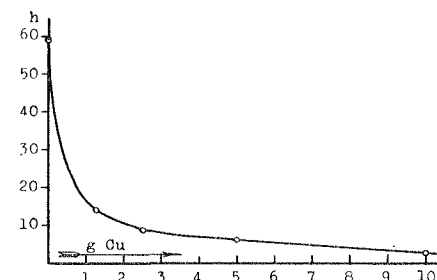


Fig. 6.

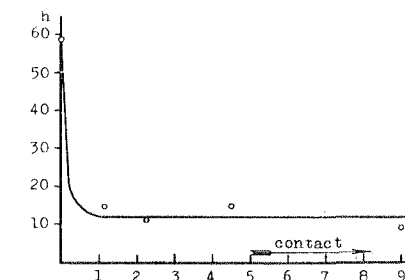


Fig. 7.

induction period decreased and well from 60 hours for the original oil to 17 hours. This proves that we are justified to speak in our case from adsorption.

According to MOUREUX and DUFRAISE⁹⁾ the existence of an induction period is the result of the presence of antioxydants which are often able to exercise their influence in rather small quantities. If we accept this theory to be correct then it is evident that, a metal surface being present, the length of the induction period is a function of the time necessary to destruct that part of the antioxydant which is not adsorbed. The largest quantity of antioxydant is adsorbed by the first sq. cms of metal surface which are added (largest concentration of antioxydants). This explains why the first quantities of metal exert such a great effect. The subsequent quantities of metal meet with lower concentrations of the antioxydant, thus the adsorption, and consequently the effect on the length of the induction period, decreases.

After the induction period no influence whatever is exerted by electrolytic copper. With regard to the reaction velocity this metal is thus completely inert; it is entirely unjustified to speak about a catalytic effect in our case.

Thus when previous workers concluded that the reaction in question is catalyzed by copper, they were very probably deceived by the influence of copper on the length of the induction period (figure 4). Especially in experiments carried out at relative low temperatures, where the length of the induction period is of great importance, neglecting this phenomenon leads to serious mistake.

A corresponding experiment was carried out with Chempur-tin. Here

⁹⁾ Chim. Ind. Tôme 18, pag. 3, 1927; Premier Congrès de la Sécurité aérienne, t. 1, 1931, pag. 55; Bull. Soc. d'Encourag. à l'Ind. Nat. février 1934.

too the same result was obtained; a shortening of the induction period and no influence on the reaction velocity. It appeared that tin is less active than copper. So for the original oil, without any supply of metal, the induction period was found to be 60 hours. By supplying a certain surface of copper filings this time was reduced to 8 hours. Using the same surface of tin however we got an induction period of 36 hours. As most of the anti-oxidants contain polarisable nitrogen containing groups¹⁰⁾ this experiment affirms the well known fact of a higher relative affinity of adsorption for these compounds in the case of copper as in that of tin.

In this investigation not only the alteration of the dipole moment but also that of peroxides, acid value, saponification number, density and viscosity was measured. All these quantities are absolutely independent from the presence of copper or tin, provided one takes the induction period into account. It may be possible that an influence on the reaction velocity exists if one adds such compounds as f.i. copper stearate getting thus a homogeneous system. However such an influence, if it exists, must be regarded as a phenomenon of induced oxydation. It is therefore that we consider the addition of soluble organic metal compounds for the study of specific metal actions as incorrect.

Finally we also tried to get an idea about the mechanism of the oxidation of our oil. Therefore the number of particles which were estimated respectively as peroxides, acids and saponifiable compounds, were plotted on a logarithmic scale as a function of the time of oxidation. For small values of the time straight lines were obtained which show the tangent 1.0 for peroxides (indicating a first oxidation stage) and 2.9 for acids (third oxidation stage).

For the increase of the saponification number however we found in this way the tangent 1.4; a value which is difficult to explain.

Acknowledgement. First of all we wish to express our sincere thanks to Prof. Dr. L. S. ORNSTEIN for his interest in our work. It was this interest which enabled us to obtain the desired apparatus for the measurement of the dielectric constant.

We are also indebted to Mr. G. H. FREDERIK for his disinterested help in connection with the construction of the apparatus.

Then we wish to thank Dr. W. P. JORISSEN who kindly furnished us with the oxidation apparatus. The costs of construction of this apparatus were defrayed out of an endowment supplied by the "Hoogewerff-fonds".

Finally we wish to mention the intensive co-operation in the experimental part of this work of Mr. J. C. HEYNRAETS.

Rotterdam, }
Utrecht, } December 1939.

¹⁰⁾ E. VELLINGER and N. SAITO, 2e Congrès Mondial du Pétrole. Paris, juin, 1937.

Physics. — *The decay of the penetrating cosmic rays.* III. By E. M. BRUINS. (Communicated by Prof. J. CLAY.)

(Communicated at the meeting of December 30, 1939.)

§ 1. *The GROSZ-reduction.*

The relation between the unidirectional intensity ψ and the total intensity I of cosmic rays has been discussed by B. GROSZ¹⁾, the fundamental assumptions being:

1. the primary rays are isotropic
2. the absorptionfunction is the same in any direction
3. the intensity is a unique function of the mass per cm² traversed.

This well-known GROSZ-reduction, normalising ψ in such a way that at the top of the atmosphere $\psi = I$, is given by

$$\psi = I - x \frac{dI}{dx} \dots \dots \dots (1)$$

x being the depth below the top of the atmosphere in gr per cm².

The conditions 2 and 3 do not hold for the penetrating cosmic rays. Therefore the GROSZ-reduction cannot be correct; neither in the atmosphere nor in a layer of absorbing material. It is easy to prove, that for non-isotropic rays, obeying the conditions 2 and 3 the relation (1) has to be replaced by (see § 3 and § 4)

$$\psi = I - \frac{1}{p+1} x \frac{dI}{dx} \dots \dots \dots (2)$$

the intensitydistribution of the primary rays with the zenith angle ϑ being:

$$F_{\vartheta} = F_0 \cos \vartheta^p.$$

§ 2. We wish to stress an important relation between the correction-factors K_{ϑ} for the decay in different directions. Suppose the differential energyspectrum in the direction ϑ at the height H , where the penetrating rays are created, is $F_{\vartheta}(E)$. Then the energy spectrum at a depth h below this layer will be²⁾:

$$N(E-\Delta E, h) = F_{\vartheta}(E) \cdot K_{\vartheta}(E)$$

¹⁾ B. GROSZ, Zs. f. Physik 83, 214 (1933).

²⁾ These relations have been deduced and used in these Proceedings 42, 54 and 740 (1939).