211. *Kinetics of the Reaction of Potassium Ferrocyanide and Nitrosobenzene: the Catalytic Action of Mercuric Ions and Ultra-violet Light.*

By S. Ašperger, I. Murati, and O. Čupahin.

The kinetics of the reaction of potassium ferrocyanide with nitrosobenzene in aqueous solution were studied spectrophotometrically by measuring the extinction of the violet complex ion $Fe(CN)_5,C_6H_5{\cdot}NO^{3-}$. The absorption spectrum of its solution was determined. The solutions follow the Beer–Lambert law. The approximate value of the activation energy for the reaction $Fe(CN)_6^{4-} \xrightarrow{H_2O} Fe(CN)_5,H_2O^{3-} + CN^-$ was calculated as 19·8 kcal./mole.

Mercuric ions accelerate the reaction very strongly, even at a concentration of 10^{-7}M. This action is specific for mercuric ions and could be utilised for the determination of traces of Hg^{++} in distilled water. In the presence of mercuric ions the reaction shows a negative salt effect.

The action of ultra-violet light leads to the same reaction product as the action of Hg^{++}. The kinetics of the process in ultra-violet light was studied photoelectrically. Mercuric ions accelerate the process in the light very considerably. Cyanide ions suppress the reaction. The reaction mechanism is discussed.

Previous investigations of the decomposition velocity of aqueous solutions of potassium ferrocyanide in ultra-violet light (Ašperger, *Trans. Faraday Soc.*, 1952, **48**, 617) confirmed the reaction mechanism proposed by Baudisch (*Ber.*, 1929, **62**, 2706) and Iimori (*Z. anorg. Chem.*, 1927, **167**, 157); small quantities of $Fe(CN)_5,H_2O^{3-}$ arise in the first phase of decomposition. Its absorption does not differ much from that of the ferrocyanide ion, so it is difficult to observe small quantities of $Fe(CN)_5,H_2O^{3-}$ directly in excess of ferrocyanide. But since pentacyanides give coloured complexes with aromatic nitroso-compounds (Baudisch, *loc. cit.*) the decomposition of aqueous ferrocyanide solutions can be studied by adding nitrosobenzene, for instance. In this case, according to earlier investigations, the following reaction mechanism can be supposed:

$$Fe(CN)_6^{4-} \overset{H_2O}{\rightleftharpoons} Fe(CN)_5,H_2O^{3-} + CN^- \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$Fe(CN)_5,H_2O^{3-} + C_6H_5{\cdot}NO \longrightarrow \underset{\text{violet}}{Fe(CN)_5,C_6H_5{\cdot}NO^{3-}} + H_2O \quad . \; . \; . \; . \quad (2)$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The equilibrium of reaction (1), in the dark, is shifted almost completely towards the left; but if we prevent the reaction between $Fe(CN)_5,H_2O^{3-}$ and CN^- by inducing the relatively fast irreversible process (2) we can measure the velocity of decomposition of ferrocyanide into aquopentacyanide. This process has not yet been studied. The decomposition of ferrocyanide into pentacyanide, being very slow, controls the velocity of the whole process, which was followed by measuring the extinction of the violet complex.

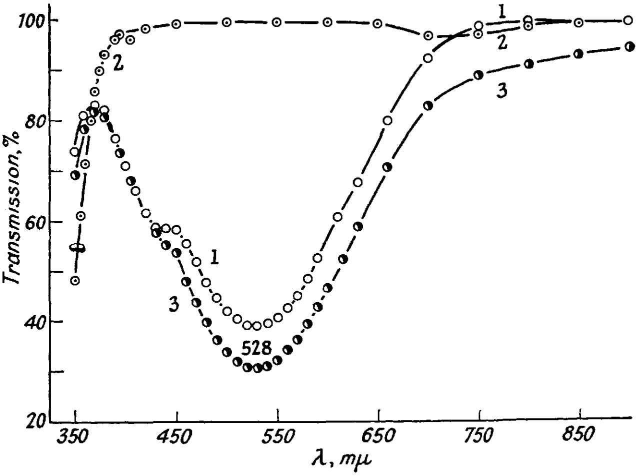
Experimental

Materials.—Nitrosobenzene was prepared according to Bamberger (*Ber.*, 1894, **27**, 1555). A stock solution was made by dissolving 0·666 g. in 1 l. of distilled water at 70°. The light green solution is stable for a few days; then it becomes turbid and cannot be used. The molar concentrations given always relate to the monomeric form. Potassium ferrocyanide trihydrate was Merck's analytical grade.

Stability of Aqueous Solutions of Potassium Ferrocyanide.—The pH of a freshly prepared 0·1M-solution increased from 6·42 to 7·70 during 4 days in a closed vessel in the dark, and became constant at *ca.* 8 after 15 days. The measurements are not readily reproducible, although an increase in pH is always found. This change is probably due to reactions (1) and (3). The measurements were performed by a glass electrode on a Doran pH Meter M. 4981. The same instrument was used for all further pH measurements.

Absorption Spectrum of $Fe(CN)_5,C_6H_5{\cdot}NO^{3-}$.—An aqueous solution of potassium ferrocyanide ($5{\cdot}0 \times 10^{-2}$M) and nitrosobenzene ($5{\cdot}2 \times 10^{-5}$M) was exposed to ultra-violet light for about 5 hours. The ultra-violet light accelerates the otherwise very slow process. After termination of the reaction, which is irreversible, the violet solution had almost the unchanged initial concentration of potassium ferrocyanide, and approximately 5×10^{-5}M-$Fe(CN)_5,C_6H_5{\cdot}NO^{3-}$. The absorption ~~spectrum of the violet solution was measured by means~~ of the Unicam S.P. 500 Quartz Spectrophotometer; a $5{\cdot}0 \times 10^{-2}$M-solution of potassium ferrocyanide was taken as a standard. The absorption maximum is situated at 528 mμ (Fig. 1, curve 1). Unused nitrosobenzene cannot impair the measurements since it scarcely absorbs in the visible region, as shown by curve 2, Fig. 1. All the subsequent spectrophotometric measurements were made at 528 mμ, *i.e.*, at the maximum of absorption. The violet solutions of $Fe(CN)_5,C_6H_5{\cdot}NO^{3-}$ obey the Beer–Lambert law. The mixture of 0·10M-ferrocyanide and approximately 6×10^{-4}M-nitrosobenzene was exposed to ultra-violet light for several hours. The extinction was measured against 0·10M-$K_4Fe(CN)_6$ standard. The solution was then repeatedly diluted with the standard solution, and the extinction measured. A linear dependence between extinction and concentration of $Fe(CN)_5,C_6H_5{\cdot}NO^{3-}$ was established; the same linear dependence was obtained even when the dilution was carried out with distilled water (Fig. 2). This shows, at the same time, that the absorption of potassium ferrocyanide at 528 mμ and under the above conditions is so small that it may be neglected.

FIG. 1. *Transmission curves*: (1) $Fe(CN)_5,C_6H_5{\cdot}NO^{3-}$, ca. 5×10^{-5}M, *obtained by action of ultra-violet light on a solution containing* $5{\cdot}0 \times 10^{-2}$M-$K_4Fe(CN)_6$ *and* $5{\cdot}2 \times 10^{-5}$M-*nitrosobenzene*; (2) *nitrosobenzene*, $4{\cdot}2 \times 10^{-4}$M, *in distilled water*; (3) $Fe(CN)_5,C_6H_5{\cdot}NO^{3-}$, ca. 5×10^{-5}M, *obtained by action of* Hg^{++} *on a solution containing* $5{\cdot}0 \times 10^{-3}$M-$K_4Fe(CN)_6$ *and* $5{\cdot}2 \times 10^{-5}$M-*nitrosobenzene. Thickness of layer* = 1 *cm.*



Velocity of Reaction of Potassium Ferrocyanide with Nitrosobenzene in the Dark.—A mixture of freshly prepared aqueous solutions of ferrocyanide and nitrosobenzene was kept in a water thermostat (±0·05°) in the dark. Samples were taken at definite reaction times in faint yellow light, and the extinction of the violet product measured; the standard was a solution of potassium ferrocyanide of the same concentration as in the original solution. It was found that the initial reaction velocity (= extinction in the tenth minute) depends on the concentration of potassium ferrocyanide, which was varied from $5{\cdot}0 \times 10^{-4}$M, at which the reaction is scarcely perceptible, up to $5{\cdot}0 \times 10^{-1}$M, where, after 100 minutes, distinctly violet solutions were obtained. The temperature and the initial concentration of nitrosobenzene (20°; $4{\cdot}2 \times 10^{-4}$M) were kept constant. The initial velocity also depends on the concentration of nitrosobenzene, but only up to *ca.* $1{\cdot}4 \times 10^{-3}$M; then the dependence rapidly disappears, because reaction (1) takes over control of the velocity of the total process.

Influence of temperature. With $5{\cdot}0 \times 10^{-4}$M-potassium ferrocyanide and $4{\cdot}7 \times 10^{-3}$M-nitrosobenzene, reaction is still perceptible at 20°. At a definite reaction time several ml. of solution were withdrawn and poured into a dry vessel, cooled below 0°; the solution was thus rapidly cooled to about 5°, at which temperature the reaction practically stops, and the extinction was measured. A standard solution identical in composition with the original reaction mixture was freshly prepared every 30 minutes and kept constantly at 5°. The results of the measurements with freshly prepared ferrocyanide solutions are shown in Fig. 3.

If we plot logarithms of the extinctions measured in the tenth minute ($\log_{10} E_{10}$) against $1/T$, we obtain a straight line, whose slope corresponds to an activation energy of 19·8 kcal./mole (Fig. 4). This value is only approximately that of the activation energy of the slowest process (1). The velocity constants could not be determined since the violet complex slowly decomposes at a higher temperature; this can be neglected initially, but becomes considerable during the course of a long run.

Measurements analogous to those of Fig. 3 were carried out with ferrocyanide solutions 3—4 days old. The velocity of reaction with old ferrocyanide solutions is always somewhat smaller, but the activation energy is approximately the same as reported above.

Catalytic Action of Mercuric Ions on Velocity of Reaction.—The catalytic action of mercuric ions on the decomposition of aqueous potassium ferrocyanide in acid solution, and the accelerated production of Prussian-blue, was described by Pinter [*Farm. Vjesnik*, 1940, 3 (Zagreb, Croatia)]. We added a small quantity of very dilute mercuric chloride solution to a weakly acid, neutral, or weakly alkaline mixture of aqueous solutions of potassium ferrocyanide and nitrosobenzene, and observed that the violet complex was formed very quickly.

The violet compound, obtained by action of ultra-violet light or by action of mercuric ions in the dark, has the same absorption spectrum in both cases. This was shown as follows. Reaction in a solution of $5{\cdot}0 \times 10^{-3}$M-$K_4Fe(CN)_6$, $5{\cdot}0 \times 10^{-5}$M-$C_6H_5{\cdot}NO$ and $5{\cdot}0 \times 10^{-5}$M-$HgCl_2$ was generally complete after 15 hours, and then the absorption spectrum of the violet complex, of concentration approximately equivalent to that of the original nitrosobenzene, was determined; a solution of ferrocyanide of the same concentration as in the reaction mixture was taken as a standard. Curve 3, Fig. 1, was obtained, and it is analogous to curve 1, Fig. 1, where the violet compound was produced by the action of ultra-violet light, in absence of mercuric ions.

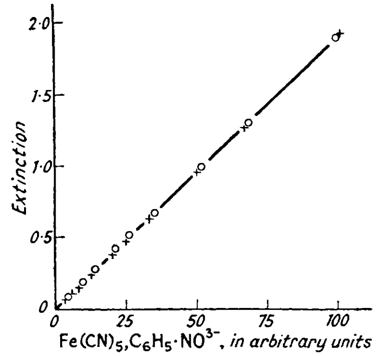


FIG. 2. *Dependence of the extinction* ($\lambda = 528$ mμ) *on the concentration of* $Fe(CN)_5{\cdot}C_6H_5NO^{3-}$: $\times$, *dilution with* $0{\cdot}10$M-$K_4Fe(CN)_6$; o, *dilution with* H_2O. *Thickness of layer* = 1 *cm.*

The velocity of reaction of potassium ferrocyanide and nitrosobenzene in presence of mercuric ions depends on pH, being a maximum at pH 3·5 (Fig. 5). The pH required was produced by addition of a few drops of sodium hydroxide or of hydrochloric acid to a mixture of nitrosobenzene and mercuric chloride solutions; the solution of ferrocyanide was brought to the same pH. The reaction solutions were separately placed in the thermostat at 20° in the dark, and after they had acquired this temperature they were mixed. After 30 minutes, the extinction E_{30} was measured against a standard of freshly prepared potassium ferrocyanide and nitrosobenzene solutions of the same concentrations as in the original reaction mixture. The foregoing measurements showed that the extinction of the standard solution does not change in these circumstances. (Extremely dilute solutions of mercuric chloride must be prepared just before use, since the salt is slowly adsorbed on glass.)

Since the catalytic action of Hg^{++} is a maximum at pH 3·5, we examined the dependence of the reaction velocity on the concentration of Hg^{++} at this pH. The concentrations of potassium ferrocyanide and nitrosobenzene being kept constant at $5{\cdot}0 \times 10^{-4}$ and $4{\cdot}2 \times 10^{-4}$M, respectively, the concentration of mercuric chloride was varied from 10^{-7}M to 10^{-4}M. After a reaction time of 30 minutes (at 20°), the extinction E_{30} was measured. The results are shown in Fig. 6. It is evident that the catalytic action of Hg^{++} is so large that it can be observed even at the concentration of 10^{-7}M, for at this concentration the absorption in a 1-cm. layer, measured in the 30th minute (A_{30}) was 1·3%. At 5×10^{-7}M-mercuric chloride the violet colour of the complex is distinctly visible. On the basis of the catalytic action of mercuric ions on the reaction, a method for the determination of traces of mercuric ions in distilled water was developed. The catalytic action is strictly specific for mercuric ions. Other metal cations do not interfere with this reaction unless they cause a turbidity. $AgNO_3$, $SnCl_2$, and $CdSO_4$ in concentration less than 10^{-4}M did not produce any turbidity; $Pb(NO_3)_2$ and $ZnCl_2$ gave a slight, constant turbidity at 10^{-4}M, but were dissolved clearly at 10^{-5}M. 10^{-5}M-$CuCl_2$ gives a clear, slightly reddish-brown solution of cupric ferrocyanide which causes a constant absorption of 1·4% at 528 mμ and $d = 1$ cm.

The reaction of ferrocyanide and nitrosobenzene in presence of mercuric ions shows a negative salt effect. Addition of 0·7M-KNO_3 reduces the extinction E_{30} by 41% at concentrations $K_4Fe(CN)_6$ 5·0 × 10^{-4}M, $C_6H_5{\cdot}NO$ 4·2 × 10^{-4}M, and $HgCl_2$ 6·66 × 10^{-4}M. This is in agreement with Brönsted's theory, since the charges of ferrocyanide and mercuric ions are of opposite signs.

Fig. 3. *Dependence of the velocity of reaction in the dark on temperature*: $K_4Fe(CN)_6$ 5·0 × 10^{-4}M; *nitrosobenzene* 4·7 × 10^{-3}M.

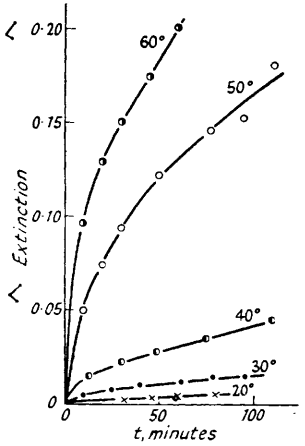


Fig. 4. *Influence of temperature on the reaction in the dark.*

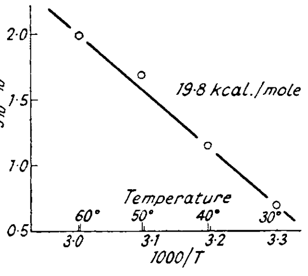


Fig. 5. *Dependence of velocity of reaction in presence of mercuric ions on* pH. E_{30} = *extinction in the* 30*th minute at* 528 mμ; 5·0 × 10^{-4}M-$K_4Fe(CN)_6$; 4·2 × 10^{-4}M-$C_6H_5{\cdot}NO$; 6·66 × 10^{-6}M-$HgCl_2$, 20°.

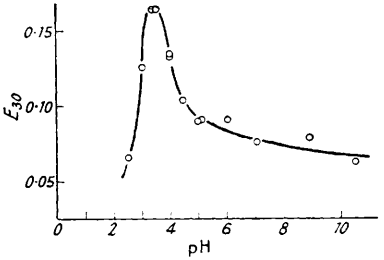
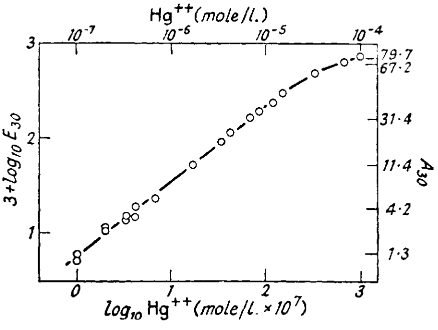


Fig. 6. *Dependence of extinction and absorption in the* 30*th minute* (E_{30} *and* A_{30}) *on the concentration of* Hg^{++}: 5·0 × 10^{-4}M-$K_4Fe(CN)_6$; 4·2 × 10^{-4}M-$C_6H_5{\cdot}NO$; pH = 3·5; t = 20°; λ = 528 mμ.



Velocity of Reaction in Ultra-violet Light.—Apparatus. A glass cell (5 × 5 × 1 cm.) containing the mixture of aqueous solutions of potassium ferrocyanide and nitrosobenzene was placed in an air-thermostat (±0·3°). The solution was stirred vigorously. A Philips Philora lamp HO 2000 was used as a source of light. A second glass cell, containing distilled water, served as a thermal filter. Close behind the reaction vessel, screened by an orange filter OG2, Schott und Gen., Jena, there was a selenium photo-element. The extinctions were measured by means of a Lange reflection galvanometer.

Photoactive light. Our earlier investigations (*loc. cit.*) showed that with the above lamp the photoactive light for ferrocyanide solutions is represented by a group of lines of mean wavelength 365·5 mμ; the other Hg lines do not come into consideration as photoactive light. The violet complex ion $Fe(CN)_5,C_6H_5{\cdot}NO^{3-}$ absorbs the photoactive light relatively weakly, because the maximum of transmission is situated just at 370 mμ (Fig. 1, curves 1 and 3). This absorption is particularly weak initially, when the extinctions E_{20} were read.

The aqueous solutions of nitrosobenzene absorb the photoactive light rather strongly (Fig. 1, curve 2). In these experiments the initial concentration of nitrosobenzene was always the same ($3{\cdot}1 \times 10^{-3}$M). At the time of measurement of E_{20}, the change in concentration of nitrosobenzene is small so that its absorption could be regarded as constant.

Light used for measurements. The OG2 filter transmitted the yellow mercury lines 579·07 and 576·96 mμ. The orange Hg lines 607·3, 612·3, and 623·4 mμ are so weak that they could not be observed spectroscopically through the filter. Nitrosobenzene and potassium ferrocyanide practically do not absorb yellow light (Fig. 1), wherefore the change in extinction is caused only by change in concentration of the violet complex.

Influence of temperature on the velocity of reaction. On the supposition that the photodecomposition of ferrocyanide into pentacyanide is the slowest process in the system (1), (2), and (3), one would expect but a slight dependence of the total reaction velocity on temperature. The velocities of reaction were measured at 15°, 25°, and 35° (Fig. 7). The mean temperature coefficient Q_{10}, determined by means of the extinctions E_{20}, is 1·2; this value is, of course, only approximate, because the velocity constants could not be determined. The value obtained for Q_{10} corresponds to a photo-reaction. Now, since reaction (1) is the slowest process in the irradiated system, it is certainly by far the slowest as a thermal reaction.

FIG. 7. *Dependence of the velocity of reaction in light on the temperature. The velocity of reaction in the dark:* $K_4Fe(CN)_6$ $7{\cdot}50 \times 10^{-2}$M; $C_6H_5{\cdot}NO$ $3{\cdot}1 \times 10^{-3}$M.

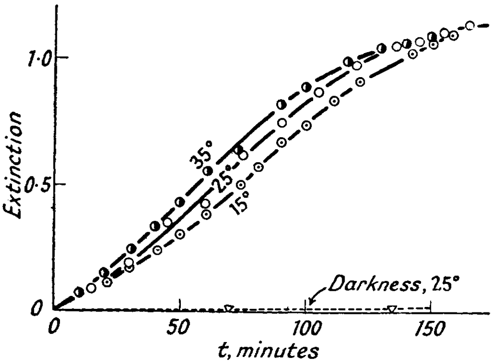
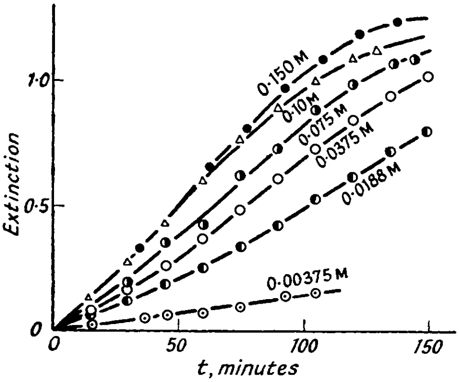


FIG. 8. *The velocity of reaction in light at various concentrations of* $K_4Fe(CN)_6$. $C_6H_5{\cdot}NO$ $3{\cdot}1 \times 10^{-3}$M; $t = 25°$.



In Fig. 7 the velocity of reaction in the dark at 25°, with the same concentrations as in the photoreaction, is also represented (broken curve). The velocity of the reaction in the dark was measured in the following manner: the assembly for the measurement of the photoreaction, described above, was modified by transferring the OG2 filter to the front of the cell containing the reaction mixture. The light of the Philora lamp was screened off by closing the door of the thermostat. At a certain reaction time the door was opened for a short time and inactive yellow light was allowed to pass through the mixture. The extinction was measured analogously as in the case of photoreaction. It is evident from Fig. 7 that the reaction in the dark, under the specified conditions, is so slow that it can be ignored.

Dependence of velocity of reaction on concentration of $K_4Fe(CN)_6$. The dependence is represented in Fig. 8. By calculating the absorption of photoactive light (365·5 mμ), *e.g.*, for 0·0375M-$K_4Fe(CN)_6$ (molecular extinction coefficient, according to our earlier investigations, *loc. cit.*: 76·6; $d = 1$ cm.), we find the value 99·9%. From this concentration upwards, the absorption of photoactive light is practically complete; even at 0·0188M-$K_4Fe(CN)_6$ it is considerable (96·4%). We see nevertheless that the velocity of reaction in the range of total absorption depends on the concentration of $K_4Fe(CN)_6$.

The velocity of reaction also depends on the concentration of nitrosobenzene up to about 2×10^{-3}M; above that it is practically independent of this concentration.

Influence of pH. The velocity of reaction in light depends on pH, being a maximum at pH 4·7 as compared with 3·5 in the presence of mercuric ions.

Influence of foreign electrolytes. The concentrations of reactants were: $K_4Fe(CN)_6$

$7{\cdot}50 \times 10^{-2}$M; $C_6H_5{\cdot}NO$ $3{\cdot}1 \times 10^{-3}$M. 0·25M-Sodium cyanide prevented the photo-process almost completely, and $1{\cdot}2 \times 10^{-2}$M-sodium cyanide reduced the extinction E_{20} by 50%. The action of CN^- consists in the mass-action effect on the equilibrium (1) to favour ferrocyanide. Potassium cyanate had no effect upon the reaction. Mercuric chloride accelerates the process in light, a concentration of $3{\cdot}7 \times 10^{-4}$M making it almost instantaneous. Except for the ions mentioned, the velocity of reaction is mainly independent of ionic strength.

Discussion.—The dependence of the velocity of reaction on the concentration of potassium ferrocyanide in the range of total absorption indicates that the elementary photochemical act does not consist in the direct dissociation of ferrocyanide ion into pentacyanide and cyanide ions, for in such a case Bunsen and Roscoe's law would be followed and the velocity of reaction would be independent of ferrocyanide concentration. Reaction (1), as suggested in our earlier investigations (*loc. cit.*) where the same dependence was observed by a different method, seems to represent the overall equation of a more complicated process.

[*Added in proof*, 12.2.53.] A simple, quick, and sensitive method for determination of mercury vapour and mercury-bearing dust in the atmosphere has recently been developed on the basis of the catalytic action of mercuric ions, and will be reported in due course.

INSTITUTE OF INORGANIC, ANALYTICAL, AND PHYSICAL CHEMISTRY,
FACULTY OF PHARMACY, UNIVERSITY OF ZAGREB,
CROATIA, YUGOSLAVIA.

[*Received, October 17th,* 1952.]