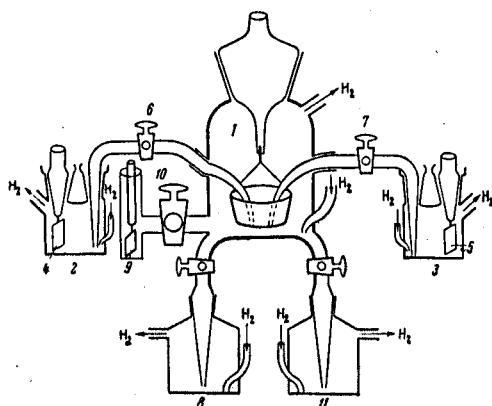


INFLUENCE OF THE DIFFUSION OF ATOMIC HYDROGEN ON THE KINETICS OF ITS ELECTROCHEMICAL EVOLUTION

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Study of the Transmission of Overvoltage through the Walls of an Iron Vessel

Our earlier studies¹⁻⁴ on the influence of diffusing hydrogen on the kinetics of its electrochemical evolution had been carried out at an iron membrane clamped between two vessels. The edge of the diaphragm was smeared with vacuum grease to ensure water-tightness and to avoid electrolytic contact between the two sides of the membrane. An apparatus thus constructed enabled quantitative measurements on the rate of diffusion of hydrogen to be carried out. The close proximity of the electrode and the grease, however, was an undesirable feature and the possible effect of the grease could not be entirely discounted*. It seemed desirable, therefore, to verify, however qualitatively, whether diffusing hydrogen had an effect on η under cleaner experimental conditions.



The apparatus shown in Fig. 1 was therefore constructed. A capsule of 2 cm in diameter, about 1 cm in height, and with 0.1–0.07 mm wall thickness, stamped out of Armco iron, was welded to a platinum contact at its iron handle. The outer surface of the capsule was used as the polarisation side, the inner as the diffusion side.

After cell 1 had been flushed with hydrogen, a 1N NaOH solution, saturated with hydrogen, was forced into the capsule from vessels 2 and 3. A cathodic polarisation was applied to the inner surface of the capsule by means of the platinum anode 4 and the potential φ_d of the diffusion side relative to that of the reference electrode 5 was measured at regular intervals. Stopcocks 6 and 7 were closed. The depth of liquid in the vessel was about 2–3 mm. When φ_d had reached a steady value, a 2N H₂SO₄ solution, saturated with hydrogen, was transferred from vessel 8 into cell 1*. The acid contained a trace of Pb(NO₃)₂, and was made to touch the bottom of the capsule, which was subjected to brief anodic polarisation by means of auxiliary electrode 9 through tap 10, followed by cathodic polarisation with a current of 1×10^{-2} A**. Hydrogen was continuously bubbled through the solution in cell 1. To discontinue diffusion of hydrogen, the acid solution touching the lower surface of the capsule was replaced by hydrogen-saturated alkali from vessel 11, and the cathodic polarisation was interrupted. When it was required to re-establish hydrogen diffusion, the alkaline solution in cell 1 was once again replaced by acid, and the outer surface was activated by anodic polarisation followed by cathodic polarisation. In the present apparatus it was impossible to measure the quantity of diffused hydrogen since the inner and the outer surface of the capsule were in contact via the gas phase. Experiments were performed with mercury-poisoned iron as well as with unpoisoned Armco iron. As in the previous work, the iron capsule was degreased with benzene and by boiling in strong alkali, and then reduced in hydrogen at 700° and vacuum-outgassed at 850°. For the experiments with mercury-poisoned iron, a capsule, prepared as above, was etched in a solution of HCl and cathodically polarised by a current of 0.5 A applied for 10 min in a 5N NaOH solution saturated with HgO. The mercury deposit was wiped off the outer surface of the capsule with a wad of cotton wool moistened with HCl, and the capsule was carefully washed with doubly distilled water and dried.

The results of measurements on unpoisoned and on mercury-poisoned iron are presented in Figs. 2 and 3 respectively. Black and open circles correspond respectively to η values without and with hydrogen diffusion. The figures show that hydrogen diffusion in unpoisoned iron is accompanied, over the range of polarisations considered, by an increase in the potential of the diffusion side, $\Delta\eta$, which is decreased by increasing the cathodic polarisation. On mercury-poisoned iron, on the other hand, hydrogen diffusion lowers η by an amount which increases with the cathodic polarisation of the electrode. The fact that the two effects are of opposite sign proves that they are unrelated to any electrolytic contact between the diffusion and polarisation sides of the capsule. The results are in

* It should be noted that in our experiments grease was present near the electrode whether or not hydrogen diffusion happened to be taking place. Changes in the electrode potential took place only as a result of the appearance of diffusing hydrogen on the side towards which diffusion was directed (diffusion side). Furthermore, the effect of this particular grease on η in a solution of H₂SO₄ was assessed as follows. The overvoltage η at an iron electrode welded to a platinum lead, immersed in pure H₂SO₄ solution, was followed as a function of time. A glass rod smeared with the grease was then introduced into the solution, and the measurements of η were continued, the solution being continuously stirred by a stream of hydrogen. No significant change in η was caused by the introduction of the greased rod.

* A solution of H₂SO₄, rather than HCl, was used in cell 1 in the hope of decreasing the likelihood of an electrolytic contact between the two sides of the capsule.

** A brief anodic polarisation followed by cathodic polarisation is known, from our earlier work², to induce a rapid onset of hydrogen diffusion. Traces of Pb(NO₃)₂ also favour the diffusion of hydrogen.

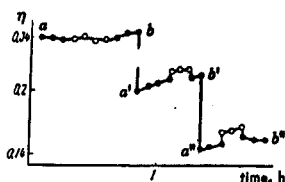


Fig. 2. Effect of diffusing hydrogen on η at an unpoisoned iron surface in 1N NaOH at different cathodic polarisations: $ab - i_0 = 1.6 \times 10^{-4}$ A/cm²; $a'b' - i_0 = 1.6 \times 10^{-5}$ A/cm²; $a''b''' - i_0 = 0.4 \times 10^{-5}$ A/cm².

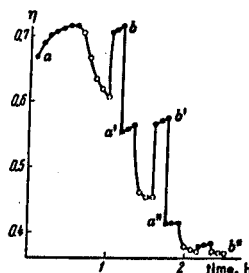


Fig. 3. Effect of diffusing hydrogen on η at a mercury-poisoned iron surface in 1N NaOH at different cathodic polarisations: $ab - i_0 = 1.6 \times 10^{-4}$ A/cm²; $a'b' - i_0 = 1.6 \times 10^{-5}$ A/cm²; $a''b''' - i_0 = 0.4 \times 10^{-5}$ A/cm².

qualitative agreement with our findings when an iron diaphragm was used, but quantitatively the effects are somewhat smaller, and the influence of cathodic polarisation of the diffusion side on the transmission of overvoltage is no longer so clear-cut, especially in the case of unpoisoned iron. This is obviously because the diffusion currents of hydrogen are small due to the low cathodic polarisation of the polarisation side*. Furthermore, the diffusion of traces of oxygen from the gas phase to the inner surface of the capsule must have interfered with the measurements on the iron capsule (the gas volume in cell 1 was large, about 120 cm³, and the layer of electrolyte in the capsule was relatively shallow, 2–3 mm). This probably explains our failure to detect any transmission of overvoltage when the diffusion side was not cathodically polarised, i.e. under steady-state potential conditions.

Determination of the Increase in the Rate of Electrochemical Evolution of Hydrogen at Constant η under the Influence of Diffusing Hydrogen

We have previously carried out a qualitative study⁴ of the accelerating effect of the diffusion of atomic hydrogen

* Since in these experiments the diffusion and the polarisation sides were in contact through the gas phase, measurements were carried out with tap 10 closed. The accessible cathodic polarisation was therefore relatively modest, and the density of current flowing through the outer surface of the capsule was less than in the diaphragm experiments.

on the electrochemical evolution of hydrogen. The work was based on measurements of the change in electrode potential at constant cathodic polarisation resulting from hydrogen diffusion. It was shown that as the cathodic polarisation of a mercury-poisoned iron electrode in alkaline solution is increased the positive potential change $\Delta\eta$ initially grows, for a constant ratio i'/i_0 , but eventually tends towards a limiting value (i' is the rate of diffusion of atomic hydrogen, and i_0 the cathodic polarisation of the electrode). For high values of η , when $\Delta\eta$ is independent of η at constant i'/i_0 , $\Delta\eta$ at first increases with i' and then tends towards a limit. In the light of Frumkin's theory⁵ the decrease in overvoltage, $\Delta\eta$, due to diffusing hydrogen at high electrode polarisations and low hydrogen-diffusion currents, such that the reverse reactions can be neglected, should be given by

$$\Delta\eta = b \log (1 - i'/i_0).$$

The experimental value of $\Delta\eta$ proved to be higher than the theoretical by an amount corresponding to an approximate doubling of the hydrogen diffusion current. In other words, each diffusing hydrogen atom can facilitate the discharge of two water molecules. This experimental finding is not readily explainable on the basis of existing theoretical models. A direct determination of the increased rate of electrochemical evolution of hydrogen, Δi , induced by diffusing hydrogen at constant overvoltage, therefore appeared desirable. Interest also attached to quantitative work on other electrodes, also capable of showing an enhanced electrochemical evolution of hydrogen under the influence of diffusing hydrogen. For work of this type we chose an iron electrode coated with a galvanic deposit of zinc.

The Armco iron electrodes were reduced in hydrogen at 700° and vacuum-outgassed at 850° before being plated. Poisoning with mercury was carried out as before⁴ by cathodic polarisation of the electrode in 5N NaOH + HgO at a current density of 0.01 A/cm² for 10 min. Before zinc plating the diffusion side of the diaphragm, the polarisation side was coated with a layer of paraffin wax. The diaphragm was then etched in HCl and a galvanic layer of zinc was deposited on it at a cathodic current density of 0.02 A/cm² applied for 20 sec, 2, 10, or 40 min, using a galvanic bath free from surface-active materials⁶. The wax was then mechanically removed, the polarisation side was cleaned with hydrochloric acid, and the membrane was washed in doubly distilled water and dried. Measurements on mercury-poisoned iron were taken in 0.5N and 3N NaOH solutions; those on the zinc plated electrode were taken in 0.5N and in 4N NaOH. The solutions were prepared by decomposing sodium amalgam in redistilled water. The measurements were carried out in an apparatus already described^{3,4}. As soon as the alkaline solution touched the diffusion side of the diaphragm, a cathodic polarisation was applied to the latter by a current of 1×10^{-3} A/cm², and the electrode potential was measured. Throughout this work the reference electrode was a mercury-mercuric oxide electrode in a 5N NaOH solution.

When the electrode potential had reached the steady value ϕ_d at a given cathodic polarisation, the hydrogen diffusion was begun. It was invariably accompanied by a positive shift of ϕ_d . After the diffusion of hydrogen was interrupted, the potential of the diffusion side of the electrode was usually found to be more positive than its initial value, to which it failed to return on standing. The phenomenon is probably connected with partial loss of zinc and mercury from the electrode surface or with the dislocation of the electrode lattice by the diffusing hydrogen. After two

or three diffusion cycles the effect decreases and the difference between the initial and the final values of φ_d is no more than 1–2 mV.

A direct demonstration of the accelerated electrochemical evolution of hydrogen (Δi) under the influence of diffusing hydrogen at constant φ_d was achieved as follows. After the start of hydrogen diffusion, the potential of the electrode, treated as above, was held constant and the current i , flowing at the electrode for a given rate of hydrogen diffusion i' , was measured. Throughout the duration of the experiment φ_d was directly controlled by means of a compensation circuit. The value of i' was set by the cathodic polarisation on the polarisation side. The amount of diffused hydrogen was determined by comparing the volumes of hydrogen evolved during a 5 min period, with and without diffusion, from the diffusion side of the diaphragm. To express hydrogen diffusion rates in electrical units, use was made of the quantity of hydrogen evolved at a given cathodic polarisation in the absence of hydrogen diffusion from the diffusion side of the diaphragm. The air-tightness of the apparatus was checked at the end of the experiment by noting the position of the meniscus of the solution in a horizontal burette at $i_0 = 0$ and verifying its constancy. With the mercury-poisoned electrode the measurements were carried out with $i' \ll i_0$ and at values of η such that the decrease due to diffusing hydrogen attains a limiting value⁴ and does not continue to grow with further increase in η .

Electrode	Solution	Thickness of deposit, cm	η *	$(\Delta i/i')_{av}$
Fe + Hg	3N NaOH	**	0.800	1.72
	0.5N NaOH		0.790–0.875	1.37
Fe + Zn	4N NaOH	$1.8 \cdot 10^{-5}$	0.610	0.24
		$1.1 \cdot 10^{-4}$	0.770	0.33
			0.675–0.685	0.24
			0.725–0.735	0.22
			0.760	0.23
		$5.4 \cdot 10^{-4}$	0.730	0.25
			0.780	0.29
		$2.1 \cdot 10^{-3}$	0.720	0.03
	0.5N NaOH	$1.8 \cdot 10^{-5}$	0.690	0.1
			0.800	0.16

* The potential of the mercury-mercuric oxide electrode in 5N NaOH relative to that of a hydrogen electrode in alkaline solutions of various concentration was determined experimentally.

** The quantity of mercury deposited on the iron cannot be assessed because the greater part of the current used for poisoning the electrode was consumed by hydrogen evolution.

The results of measurements of $(\Delta i/i')_{av}$ *, characteristic of the activity of diffusing hydrogen at the given electrode, are given in the Table, averaged over a large number of experiments. The tabulated data show that $\Delta i/i'$ at mercury-poisoned iron is greater than unity and increases with alkali concentration. On electro-deposited

* As was remarked above, the electrode potential at constant cathodic polarisation was 1–2 mV more positive than its initial value when hydrogen diffusion was stopped. This is equivalent to an increase in i_0 following the interruption of hydrogen diffusion in a potentiostatic experiment. The value of i_0 used for calculating Δi was therefore the mean of the values before and after diffusion.

zinc, on the other hand, $\Delta i/i'$ was in every case less than unity*. The growth in η , under otherwise comparable conditions, was not accompanied by a well defined increase in $\Delta i/i'$. This indicates that our measurements on plated zinc deposits were carried out at a value of η high enough for $(\Delta i/i')_{i_0 = \text{const}}$, and therefore also $(\Delta i/i')_{\eta = \text{const}}$, to have reached their limiting values, independent of η . A 30-fold increase in the thickness of the zinc deposit (from 1.8×10^{-5} to 5.4×10^{-4} cm) in 4N NaOH had practically no effect on the value of $\Delta i/i'$, and only by further increasing the thickness of the zinc deposit could an appreciable increase in $\Delta i/i'$ be brought about. An analogous behaviour was noted with the mercury-poisoned iron electrode. When the iron electrode is very heavily poisoned with mercury the passage of diffusing hydrogen no longer causes a decrease in η at $i = \text{const.}$, and consequently no increase in the electrode current is observed at $\eta = \text{const.}$ The low values of $\Delta i/i'$ at relatively high levels of mercury and zinc on the electrode are probably due to the fact that in these circumstances practically the whole of the diffusing atomic hydrogen can recombine in deep surface cracks and fails to reach the site of the electrochemical reaction. A similar explanation may apply to the decrease in $\Delta i/i'$ as the alkali concentration is lowered, since the wetting of the surface is then somewhat inhibited**. It should be stressed that the constancy of $\Delta i/i'$ over quite a wide range of thicknesses of the zinc deposit is evidence of a high mobility of the hydrogen atoms on the electrode surface, such that these atoms are able to diffuse from the sites at which they emerge from the iron to the sites of electrochemical reaction, since metallic zinc and mercury are impervious to atomic hydrogen. The discrepancy between $(\Delta i/i')_{\eta = \text{const}} \approx 1.37$ –1.72 and $(\Delta i/i')_{i = \text{const}} \approx 2$ (according to Frumkin⁴) may possibly arise from an error in $(\Delta i/i')_{i = \text{const}}$ due to the inaccuracy of the available value of the b coefficient. It should also be noted that the experiments on $(\Delta i/i')_{i = \text{const}}$ were conducted in ordinary "C. P." alkali without any further purification.

Effect of Hydrogen Diffusion Rate i' , of Cathodic Polarisation, and of pH on $\Delta \eta$ at an Unpoisoned Iron Electrode and at a Galvanic Deposit of Nickel in Alkaline Solution

In view of the high activity of diffusing atomic hydrogen in accelerating the electrochemical evolution of hydrogen at mercury-poisoned iron in alkaline solutions, a quantitative study of the increase in overvoltage brought about by diffusing hydrogen appeared desirable. Armco iron at low cathodic polarisation and a galvanic deposit of nickel on iron, at its steady-state potential in alkali, were studied, since they show large overvoltage effects under the influence of diffusing hydrogen. The techniques of measurement and of electrode preparation remained the same as in the previous experiments.

* On zinc deposits the increase in the rate of electrochemical evolution of hydrogen Δi , was studied at rates of hydrogen diffusion, i' , not very different from the cathodic polarisation current of the electrode, i_0 .

** An alternative explanation of the decrease in $\Delta i/i'$ with decreasing alkali concentration may be sought in terms of the recombination reaction $H_{ad,1} + H_{ad,2} \rightarrow H_2$. An increased rate of recombination will lead to a decrease in the concentration of atomic hydrogen available to the electrochemical desorption reaction.

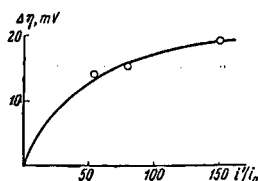


Fig. 4. Increase in overvoltage, $\Delta\eta$, as a function of hydrogen diffusion current at constant cathodic polarisation of an iron electrode at $i_0 = 2.6 \times 10^{-6}$ A/cm² ($\eta = 0.130$) in 1N NaOH.

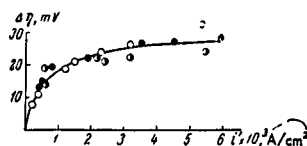


Fig. 5. Negative shift of the steady-state potential of electrodeposited nickel on iron as a function of the quantity of diffusing hydrogen (i') in 1N NaOH. The points refer to different experiments.

The galvanic deposit of nickel was plated on to the diffusion side of the electrode from a bath free from surface-active agents⁶. The polarisation side was coated with a layer of paraffin wax. The thickness of the nickel deposit was about 1×10^{-4} cm. The experiments with iron were carried out in alkali of "C. P." grade, those with plated nickel in alkali prepared by decomposing sodium amalgam in doubly distilled water.

With the nickel-plated electrode in solutions of "C. P." grade alkali, a rapid growth of $\Delta\eta$ with time was noticed. This was probably caused by the deposition of iron from the solution on to the electrode surface, "C. P." alkali being known to contain appreciable amounts of iron salts*. Measurements on iron electrodes, on the other hand, gave practically identical results whether the alkaline solution was prepared from "C. P." alkali or from sodium amalgam. Since we were unable to measure hydrogen diffusion currents below 2×10^{-4} A/cm² and the experiments were carried out at low cathodic polarisations of the electrode, when $\Delta\eta$ is relatively large, a much larger value of i' was used in the investigation. Figs. 4 and 5 show the variation of $\Delta\eta$ with rate of hydrogen diffusion i' at an iron electrode held at a constant cathodic polarisation by a current of 2.6×10^{-6} A/cm² ($\eta = 0.130$) and at a nickel deposit at its steady-state potential**. It can be seen that for a constant cathodic polarisation of the electrode the excess overvoltage on iron and plated nickel initially increases

* The increase of overvoltage due to diffusing hydrogen in alkaline solutions is higher at a pure iron electrode than at a galvanic nickel deposit.

** Measurements on electrodeposited nickel were taken only at the steady-state potential, because the effect of diffusing hydrogen on overvoltage, even at low cathodic polarisations, became so small that quantitative study was impossible.

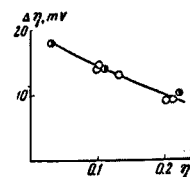


Fig. 6. Variation of the increase in overvoltage, $\Delta\eta$, due to diffusing hydrogen, with cathodic polarisation of an iron electrode in 1N NaOH at $i'/i = 50$.

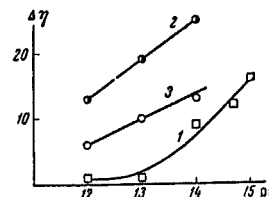


Fig. 7. Influence of pH on the increase in overvoltage $\Delta\eta$: 1) on iron with $\eta = 0.200$ V and $i'/i = 50$; 2) and 3) on a nickel deposit at various hydrogen-diffusion currents [(2) - $i' = 4.1 \times 10^{-3}$ A/cm²; (3) - $i' = 0.4 \times 10^{-3}$ A/cm²].

with i' but eventually tends to a limiting value*. Frumkin's theory predicts that the increase in overvoltage due to diffusing hydrogen will be related to the slow removal of H_{ads} by a recombination mechanism or by electrochemical desorption. It follows that $\Delta\eta$ should show a steady increase with i' provided that $\Delta\eta$ is not too large and that the effect of changes in the electrode potential on $\Delta\eta$ itself, arising from overvoltage transmission, can be neglected. It should be emphasised that the overvoltage increase due to diffusing hydrogen is much less than the growth of overvoltage which would take place if the whole of the diffusing hydrogen were generated on the diffusion side of the electrode by locally increasing the cathodic polarisation. Thus, on iron, with $i'/i_0 = 50$, $\Delta\eta = 19$ mV (Fig. 4), whereas if the cathodic polarisation of the diffusion side is increased 50-fold and $b \approx 0.12$, we find $\Delta\eta = 0.120 \log 50 \approx 200$ mV. Fig. 6 shows the variation of $\Delta\eta$ with η on iron in 1N NaOH with $i'/i = 50$. The Figure shows that, in agreement with theory, $\Delta\eta$ decreases as η at the electrode is increased, owing to the decreased ionisation of H_{ads} . The slope of the curve, $(\partial(\Delta\eta)/\partial\eta)_{i'/i}$, is of the order of 0.05. In view of such a low value of $(\partial(\Delta\eta)/\partial\eta)_{i'/i}$, it can be shown that the fact that $\Delta\eta$ approaches a limit as i' increases (Figs. 4 and 5) cannot be entirely attributed to a decreased overvoltage transmission resulting from the negative shift in electrode potential brought about by the diffusing hydrogen.

The excess overvoltage due to diffusing hydrogen increases with the pH of the solution both in the case of iron and in the case of electrodeposited nickel (Fig. 7).

From the experimental material presented above we can draw the conclusion that the expected analogy between the effects of the amount of diffusing hydrogen and of pH on the

* The decrease in $\Delta\eta$ with increasing η has been observed for iron in 5N NaOH with $i'/i = 5$.

overvoltage at unpoisoned iron, electrodeposited nickel, and mercury-poisoned iron (an increase in the former two cases, a decrease in the latter) has been demonstrated, in spite of the fact that the effects are found to be much smaller than expected. The problem will be re-examined in a later communication.

We would like to express our deep gratitude to Academician A. N. Frumkin for his valuable advice during the course of this work.

SUMMARY

1. A study has been made of the effect of diffusing hydrogen on the overvoltage η at pure and at mercury-contaminated iron electrodes in 1N NaOH solutions in the total absence of vacuum grease. The measurements were carried out using the outer surface of an iron vessel as the polarisation side and the inner surface as the diffusion side. The results are in qualitative agreement with those previously obtained using an iron diaphragm: diffusing hydrogen raises η on an uncontaminated iron surface and lowers it on a mercury-poisoned iron surface.
2. The increase in the rate of the electrochemical evolution of hydrogen in the presence of diffusing atomic hydrogen and at constant η has been directly determined for the case of mercury-poisoned iron and of zinc electrodeposited on iron.
3. It has been shown that on mercury-poisoned iron in alkaline solutions $\Delta i/i'$ is greater than unity, whereas on a galvanic zinc deposit it is less than unity (Δi is the increase in the rate of electrochemical evolution of hydrogen at constant electrode potential brought about by diffusing atomic hydrogen; i' is the rate of hydrogen diffusion). When the alkali concentration is increased, $\Delta i/i'$ likewise increases.
4. The effect of the hydrogen diffusion current, of the electrode potential, and of the pH of the solution on the increase in overvoltage due to diffusing hydrogen has been qualitatively studied on a pure iron electrode and on nickel electrodeposited on iron in alkaline solutions. The increase in overvoltage at constant cathodic polarisation has been shown to tend to a limiting value as the flow of diffusing hydrogen is increased. Increasing η and decreasing the pH of the solution causes a drop in $\Delta\eta$.

RELATIVE REACTIVITY OF RADICALS

Kh. S. Bagdasar'yan

Many radical reactions are known which enable the reactivity* of valency-saturated molecules towards a radical** to be determined directly from experimental data. Nearly all the research of this type has been carried out by the method of competing reactions, which does not require a knowledge of the absolute rate constants or activation energies.

No single experimental method has yet been found for the direct determination of the relative reactivities of various radicals with respect to some valency-saturated molecule. To estimate the reactivities of radicals it is necessary to compare absolute values of rate constants or activation energies, which are usually difficult to determine.

Szwarc and his collaborators¹ suggested a method for the indirect comparison of the reactivities of radicals. Szwarc's method is based on the following empirical postulate. Let the relative reactivities of the molecules $A_0, A_1, A_2, \dots$ be known towards the radicals R_1 and R_2 , which undergo reactions of the same type with these molecules. The molecules $A_0, A_1, A_2, \dots$ differ from one another in a substituent which interacts with the reactive centre (a double bond, an active hydrogen atom, an aromatic ring atom, etc.); the radicals R_1 and R_2 may be either of the same type or of different types. Then, as Szwarc and his collaborators have shown in the case of several examples, a linear relationship holds:

$$\log \frac{k_{R_1 A_i}}{k_{R_1 A_0}} = n \log \frac{k_{R_2 A_i}}{k_{R_2 A_0}}, \quad (1)$$

where $k_{R_i A_i}$ is the velocity constant for the reaction of an R_i radical with an A_i molecule, the constants k with other subscripts having an analogous meaning. The quantities $k_{R_1 A_i}/k_{R_1 A_0}$ and $k_{R_2 A_i}/k_{R_2 A_0}$ represent the relative reactivities of the valency-saturated molecules towards the radicals R_1 and R_2 , A_0 being the molecule adopted as the standard of comparison, and n is a constant.

Figs. 1 and 2 give fresh examples of the application of the relationship (1). In Fig. 1 the logarithm of the relative affinity of the polyvinyl acetate radical for aromatic rings² is compared with the logarithm of the methyl affinity of the same molecules¹. Fig. 2 shows an analogous relationship for the reactions of polyvinyl acetate² and poly(methyl acrylate)³ radicals with aromatic nitro compounds. All the data for the polymer radicals were obtained by the method of inhibiting polymerisation of the corresponding monomers.

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2. I. A. Bagotskaya, *ibid.*, **107**, 843 (1956).
3. I. A. Bagotskaya, *ibid.*, **110**, 397 (1956).
4. A. I. Oshe and I. A. Bagotskaya, Zhur. Fiz. Khim., **32**, 1379 (1958).
5. A. N. Frumkin, *ibid.*, **31**, 1775 (1957).
6. V. I. Lainer and N. T. Kudryavtsev, "Osnovy Gal'vanostegii" (Principles of Electrodeposition), 1953.

* The term "reactivity" is employed in the following sense. Let the molecules (radicals) $A_0, A_1, A_2, \dots$ undergo reactions of the same type. The reactivity of the molecule A_1 is taken to refer to any quantity which can serve as a kinetic characteristic of the position of the A_1 molecule in this series. Reactivity can be expressed also by the activation energy or the rate constant at a given temperature. The method of competing reactions leads to an expression for reactivity in relative units.

** The term "radical" is employed here solely in the sense of a free radical.