Electrochemical Methods in Kinetic Studies of Isotopic Exchange Reactions. I. Application to Systems of the Type $RI + I^{*-} \rightleftharpoons RI^* + I^-$

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A new method for the measurement of the isotopic exchange between organic and inorganic iodides has been investigated. The procedure used is as follows. From a mixture of the organic and inorganic components in the solvent used, small fractions of the iodide ions (I^--131) are deposited anodically on silver electrodes at certain times. The radioactivity of the thin layers of radioactive silver iodide is measured. From the activity values, and from the concentration of the components, it is possible to calculate the rate constant.

The anodic formation of silver iodide was performed at constant current. To prevent discharging of any other component than the iodide ions, it is necessary to keep the current density below the limiting current density for the discharge of iodide ions. The limiting current density was measured, at sharply defined conditions, for sodium iodide in water, methanol and an ethanol-water mixture. Linearity was found between the concentration of sodium iodide and the limiting current density.

The method described was used to study the reaction $CH_3I + NaI^* \rightarrow CH_3I^* + NaI$ in dry methanol. The value of the second order rate constant was found to be 33.5×10^{-4} l·mole⁻¹sec⁻¹ at 25.0°C.

The application of this method to the study of rapid reactions is discussed.

Even at moderate concentrations, the isotopic exchange between some organic iodides and alkali iodides is rapid in certain solvents. From the value of the rate constant for the isotopic exchange between methyl iodide and sodium iodide [1] in acetone at 25°C, *viz.* 6 l.mole⁻¹sec⁻¹, it can be calculated that, with an equal concentration for both components of 0.05 mole.l⁻¹, the half-life of the reaction is about 1 sec. For benzyl iodide, under the same conditions, the half-life is of the same order of magnitude [2].

With the separation methods hitherto used for the reacting components, *viz.* extraction, which is most frequently used, distillation and precipitation, it is clear that one is restricted to the study of isotopic exchange under such conditions that the half-life of the reaction is rather long, say at least 10 sec,

in order to obtain accurate results. Otherwise the time of separation becomes too long in comparison with the time of reaction. Hence it would be of value to extend the time range available for the study of isotopic exchange reactions of the type discussed.

The purpose of this investigation was to develop an electrolytical separation method which, after certain improvements, may make it possible to study reactions with half-lives as short as a few thousands of a second.

The method has been described briefly in a previous paper [5]. The present article gives a more detailed account of the work. The electrolytic deposition reaction has been studied in some respects and the method has been applied to the investigation of the system, methyl iodide + sodium iodide in dry methanol, at such concentrations of the reacting species that the half-life of the reaction was longer than 10 min.

GENERAL PRINCIPLES OF THE METHOD

The course of the reaction, which can be written

$$RI + I^{*-} \rightleftharpoons RI^{*} + I^{-} \tag{1}$$

where RI is an organic iodide * and the asterisk indicates a radioactive iodine atom, is followed by depositing small fractions, about 1 ‰, of the total amount of iodide ions electrolytically on silver anodes at different times of the reaction. Thin layers of radioactive silver iodide are thereby formed. If the amount of current is equal for all the anodes, their radioactivity will be proportional to the specific activity of the iodide ions in the reaction mixture at the time in question. From the change in radioactivity of the anodes with the time of reaction and from the known concentrations of the reactants, it is then possible to calculate the rate constant.

In the conventional methods the iodides are completely separated and the distribution of radioactivity between the organic and inorganic iodides is determined. Since the amount of electrodeposited iodine can be made very small, the sample is almost unaltered even after several depositions have been carried out. In this respect the method can be compared with non-destructive analytical ones, e.g. spectrophotometric, thermal etc.

If a number of electrode pairs are placed at various points in the observation tube of a flow apparatus of the type used by Hartridge and Roughton [3], it would be possible to perform measurements a few thousands of a second after the reactants have been mixed. This means that the method would permit an extension of the observable time range [4] for exchange reactions of this type by a factor of about 10 000.

Reactions which are too slow for the Hartridge-Roughton technique but too rapid for ordinary analytical work might be studied by anyone of the following methods.

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* There is no reason why the method could not be extended to systems involving bromides or chlorides or other systems where it is possible to precipitate one of the reactants electrolytically without affecting the other one.

0 10 20 30 40 50 mm

Fig. 1. Electrolysis cell,

1. Aluminium vessel;
2. Water jacket (the tangential inlet and outlet for water from a thermostat bath are not shown in the figure);
3. Teflon lid;
4. Gasket;
5. Teflon holder for the anode;
6. Teflon cone for tightening the silver wire inlet. The tightening cone is pressed downwards by a screw, 7;
8. Silver anode soldered to a copper wire;
9. Silver cathode attached to a silver wire;
10. Rotating magnetic bar.

The vessel was thermally insulated.
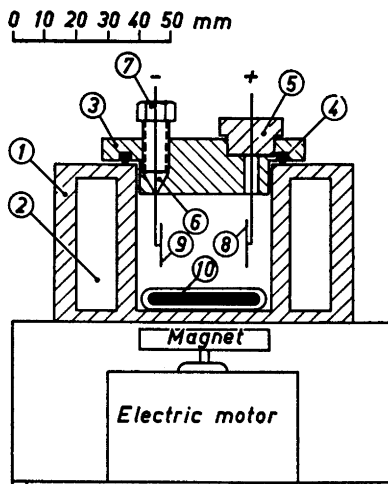
If a silver anode, in the form of a band, is drawn with a constant speed through the reaction mixture during electrolysis, the specific activity of the iodide ions could be continuously registered as a function of the time of reaction. The activity at various points of the band, together with information concerning the concentrations of the reactants, would then make it possible to calculate the rate constant.

It might also be possible to use a method in which the electrolytic precipitation is performed between stationary electrodes during such a long time that the composition of the reaction mixture alters appreciably. This method, in the following referred to as "the integral method", will receive a more detailed account at the end of the article.

Another possibility is the capacity flow method [13] in which a uniform and steady state is created in a reactor vessel. After the steady state has been attained, electrolysis could be performed between electrodes mounted in the vessel.

EXPERIMENTAL DETAILS

The reaction vessel. The cylindrical electrolysis cell shown in Fig. 1 was used for determining the limiting current density and for the kinetic experiments. It consisted of a water-jacketed aluminium vessel of 50 ml volume. The inside of the vessel was covered with the plastic fluorocarbon material [14] Kel-F to prevent any contamination of the reaction mixture due to corrosion of the vessel. The teflon lid was provided with a gasket which made the vessel tight. The lid was kept in position by six screws. Stirring was provided by means of a magnetic stirrer. The cylindrical, teflon-covered stirring rod was 38 mm long and 8 mm in diameter. Its rate of revolution was measured using a stroboscope.

The electrodes. The circular electrodes were symmetrically located in the vessel at a distance of 30 mm from each other. The silver cathode, which had an area of 1.5 cm², was attached to a silver wire by spot welding. The wire was inserted in a hole in the lid and was kept in position by a teflon cone which was forced down by means of a screw.

The anode * was stamped from thin sheet-silver (0.1 mm) which had been previously polished with emery paper ("Emery Polishing Paper 3/0"). It was soldered to a copper

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* Each anode was used for only one deposition and was then replaced by a new one.
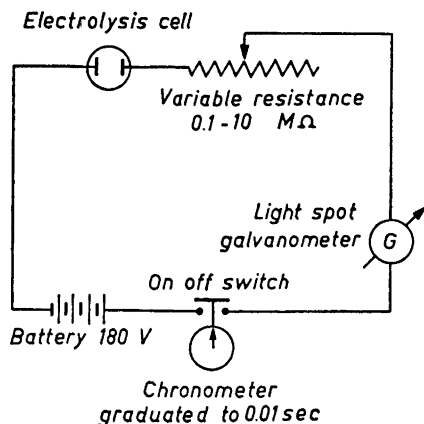
Electrolysis cell

Fig. 2. Circuit used for accurate measurement of the amount of current.

wire. This wire was inserted in a narrow hole in a holder made out of teflon. When the holder was put in the lid, as Fig. 1 indicates, the anode was kept in its correct position and was easily exchangeable.

The back of the anode, the sharp edges along its periphery and the copper wire were covered with paraffin wax to prevent electrodeposition on these parts.

It is of extreme importance that the surface of the anode should be perfectly clean. Otherwise reproducible results are not obtained. Washing with liquid detergent and thorough rinsing with distilled water gave a satisfactorily clean electrode surface.

The circuit. The radioactivity of the anode is proportional to the amount of current and the specific activity of the iodide ions. To get reproducible results it is thus necessary to determine the amount of current very exactly. The circuit used for this is shown in Fig. 2. By means of a large series resistance, which compensated for the change in the cell resistance due to polarization, the current strength could be kept practically constant during the electrolysis.

The time of electrolysis, which varied between 1 and 30 sec, was measured by a chronometer graduated to 0.01 sec. A switch was attached to the starting button of the chronometer and was adjusted so that the latter was started and stopped at the instant when the circuit was closed and broken respectively. This device permitted the time of electrolysis to be determined with an accuracy of $\pm$ 0.02 sec (checked against a rapid recorder (Mingograf 230)).

The counting equipment. The activity of the anodes was measured by a proportional flow-counter provided with a mylar window. Propane was used as counting gas. The counting equipment consisted of a University Series Proportional Counting System which comprises a Scaler Assembly 4125 and a Model 821 B Flow Counter in a Model 800 D Low Background Shield.

Calculation of the electrode activity. The activities measured by the flow counter were corrected for the background and the decay of the iodine (half-life 8.07 days)[16]. The corrected activity values were then converted to equal amounts of current.

Reagents for the kinetic experiments. "Analytical reagent" methanol was refluxed for 2 h with magnesium methoxide[15] and was then distilled in an atmosphere of dry nitrogen. Merck's purest methyl iodide was distilled over silver foil in a 450 mm high Vigreux Column. "Analytical reagent" sodium iodide was dried at 110°C. Carrier-free NaI—131 in a dilute solution of sodium thiosulphate was obtained from The Radiochemical Centre, Amersham, England. The solution was evaporated to dryness and the radioactive sodium iodide was dissolved in dry methanol.

Reagents for the other experiments. Sodium nitrate, of analytical reagent grade, was used as supporting electrolyte in the measurements of limiting current density in water, methanol and an ethanol-water mixture. The distilled water had a specific conductivity of 1.0×10^{-6} ohm^{-1}cm^{-1}. The methanol was of analytical reagent grade and was not

further purified. To the commercial ethanol used, water was added to make the support-
ing electrolyte sufficiently soluble. The ethanol-water mixture contained 10 % water
by volume.

Preparations of solutions and methods of analysis. Stock solutions (about 0.01 M) of
sodium iodide in the different solvents were prepared. The concentration was determined
by titration with standard silver nitrate solution with eosin as indicator. From the stock
solutions, 10 ml portions were transferred to volumetric flasks, sodium nitrate was added,
in the cases where a supporting electrolyte was necessary, and the solvent in question
was added to the correct volume. The solutions used for the kinetic experiments were
made up at 25.0°C in volumetric flasks which had been calibrated at this temperature.
The other solutions were made up at room temperature.

Methyl iodide was added to the sodium iodide solution just before the kinetic experi-
ments were carried out. The concentration of methyl iodide was determined by accurately
weighing the liquid into a known volume of the sodium iodide solution, and the concentra-
tion was checked by gravimetric analysis (precipitation of the iodine with silver nitrate).

DETERMINATION OF LIMITING CURRENT DENSITY FOR THE ANODIC DEPOSITION OF IODIDE IONS

General remarks. A prerequisite for a successful application of the electro-
lytic method is that the anodic precipitation reaction, which is written

$$Ag + I^{*-} \rightarrow AgI^* + e^-, \qquad (2)$$
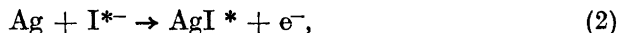
is able to occur with a 100 % current efficiency. That this is the case, provided
that the anode potential is kept within a certain range, was demonstrated
by Lingane [6] who determined halide ions by coulometric techniques.

When the electrolytic precipitation is performed according to the "con-
stant current" technique, which is the case in this investigation, it is necessary
to keep the current density below a limiting value. Otherwise the anode poten-
tial will exceed the oxidation potential for some other electrode reaction.
It is therefore necessary to determine this limiting current density. To be of
the greatest value, the determination must be carried out under accurately
defined conditions.

Definition of the stirring efficiency. The stirring efficiency will be specified
here by stating the following data: The size and shape of the stirring rod and
electrolysis vessel, the number of revolutions of the rod and the location of the
anode. The dimensions of the electrolysis vessel and stirring rod and the loca-
tion of the anode have been given under "Apparatus".

Factors governing the limiting current. If diffusion is the current-controlling
factor, it can be shown [7] that the limiting current, i_1, is given by the expression:

$$i_1 = \frac{n \cdot F \cdot D \cdot A \cdot C}{\delta} \qquad (3)$$

where

    n = number of electron equivalents per molar unit of the reaction
    F = Faraday's constant
    D = diffusion coefficient
    A = electrode area
    C = concentration in the bulk of the solution
    δ = thickness of the diffusion layer.

Eqn. (3) has been deduced on the assumption that the concentration in the diffusion layer is a linear function of the distance from the surface of the electrode. If, for a given solvent, the electrode area, stirring rate and temperature are kept constant but the concentration is varied, then eqn. (3) can be written

$$i_1 = \text{const} \cdot C \tag{4}$$

In eqn. (4), the variation in the value of the diffusion coefficient with concentration is neglected.

The limiting current density for a certain electrode process is for different solvents, if all other conditions are constant, a function of the diffusion coefficient and the thickness of the diffusion layer. In this case, eqn. (3) becomes

$$i_1 = \text{const} \cdot \frac{D}{\delta} \tag{5}$$

Eqn. (3) is valid for the case where diffusion is the current-controlling factor. If (electrical) migration contributes to the current, then the limiting current, for anion oxidation, is given by the expression [9],[11]

$$i_1 = \frac{n \cdot F \cdot D \cdot A \cdot C}{(1-t)\,\delta} \tag{6}$$

where t = transport number of the anions.

Experimental determination of the limiting current density. The limiting current density was determined under various conditions by measuring the current density as a function of the applied cell voltage [8]. When the limiting current has been reached, a further increase in the cell voltage does not cause any increase in the current until the decomposition potential of another component has been attained.

Determinations were performed for sodium iodide in three solvents, *viz.* water, methanol and an ethanol-water mixture, at 25.0°C and at two stirring rates, *viz.* 400 and 1 000 rpm. Sodium nitrate was used as a supporting electrolyte at such concentrations that the transport number of the iodide ions was effectively reduced to zero. The vessel was completely filled with the solution. The anode was made comparatively small (area 0.48 cm²) to keep down the total deposition of iodide ions. The amount deposited never exceeded 1 % of the total quantity. After taking each current-cell voltage curve, both the solution and the anode were replaced by fresh samples.

The temperature, which was determined with an accuracy of ± 0.05°C, was measured using a calibrated thermometer obtained from "Deutsches Amt für Mass und Gewicht".

The circuit employed is shown in Fig. 3. The cell voltage, which was measured by a vacuum tube voltmeter with an internal resistance of 11 MΩ, was increased stepwise by means of a variable resistance. The electrolysis current could be read off directly on the galvanometer because practically no current passed through the voltmeter.

When a supporting electrolyte was not added to the electrolyte, an almost straight line was obtained upon plotting the current against the cell voltage
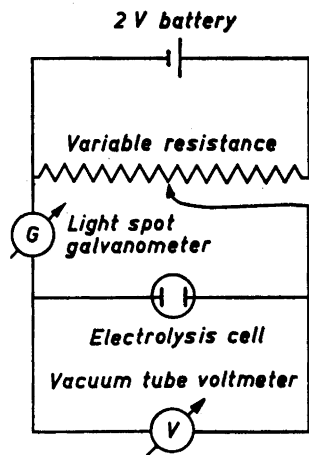
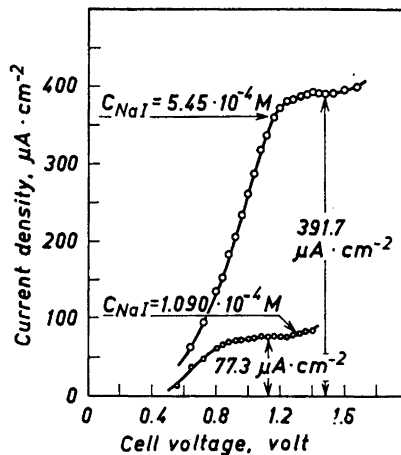Fig. 3. Circuit used for measurement of limiting current density.

Fig. 4. Current-cell voltage curves obtained for anodic deposition, of I^- from a solution of NaI in methanol. Supporting electrolyte, 0.10 M $NaNO_3$; Stirring rate, 400 rpm; Temp. 25.0°C; Anode area, 0.48 cm².

and it was thus not possible to read off the limiting current from the diagram. The fact that the current efficiency for reaction (2) becomes less than 100 % when the limiting current is exceeded was used to determine this quantity in a pure sodium iodide solution by means of a radioactive method. This method, which is comparatively laborious, was restricted to one experiment only for the purpose of demonstration, and was carried out as follows.

From 250 ml of a solution of sodium iodide in methanol containing 5 μC NaI—131, 50 ml portions were transferred to the electrolysis cell. Depositions were performed on a number of anodes (area 1.50 cm²) at different current densities. Each 50-ml portion of the electrolyte was used for three depositions. On each anode, 0.4 % of the total amount of iodide was deposited. Thus the maximum reduction was 1.2 %. The electrolysis times were adjusted so that the amount of current was nearly equal for all the anodes. After the usual corrections, the electrode activities were plotted against the current density (Fig. 6).

Results. In Fig. 4, the current density has been plotted against cell voltage for two concentrations of sodium iodide in methanol. The height of the steps represents the magnitude of the limiting current densities. According to eqn. (4), these should be proportional to the concentration of the iodide ions. From the data given in the diagram, it can be calculated that the ratio between the two concentrations is 5:1.00 and that the ratio between the corresponding limiting current densities, which should theoretically be the same, is 5:0.99. Thus there is good agreement between the theoretical and experimental values.

Fig. 5 shows a plot of the limiting current density against the concentration of sodium iodide in three solvents and at two stirring rates. According
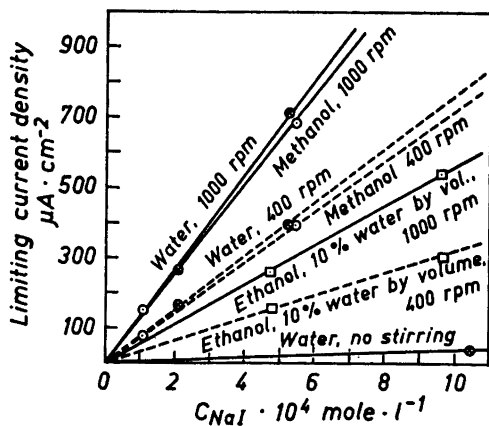
Fig. 5. Limiting current density as function of NaI concentration in different solvents at 25.0°C and two stirring rates. The concentration of the supporting electrolyte (sodium nitrate) is 0.1 M in water and methanol and 0.05 M in ethanol.
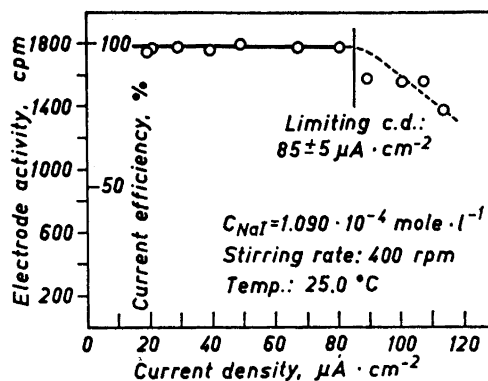
Fig. 6. Current efficiency as function of current density for anodic formation of silver iodide.

to eqn. (4), the points should fall on straight lines passing through the origin. This was in fact the case to within rather small errors.

The thickness δ of the diffusion layer at the electrode surface, for the various solvents used, can be calculated by eqn. (3) and the data given in Fig. 5. The results are summarized in Table 1.

Table 1. Estimated thickness of the diffusion layer for anodic deposition of iodide ions from solutions of sodium iodide in different solvents at 25°C and at various stirring efficiencies.

Solvent	Supporting electrolyte	$D°_{I^-} \times 10^5$ cm^2 . sec^{-1}	δ cm (no stirring)	δ cm (400 rpm)	δ cm (1 000 rpm)	Temp °C
Water	0.1 M NaNO$_3$	2.05	0.050	0.0026	0.0015	25.0
Methanol	0.1 M NaNO$_3$	1.68	—	0.0022	0.0013	25.0
Ethanol (10 % water by vol.)	0.05 M NaNO$_3$	0.81	—	0.0024	0.0014	25.0

The diffusion coefficients used in the calculations have been estimated [12] by the formula $D° = \dfrac{RT}{nF^2} \cdot \lambda°$. The $\lambda°$-values used were: 76.8 for water [18], 62.8 for methanol [19] and 30.4 for the ethanol-water mixture [20]. The last value was computed by interpolation between values given for pure ethanol and for ethanol containing 25 % water by volume.

Eqn. (5) indicates that the difference in magnitude of the limiting current density for different solvents is due to differences in the quotient D/δ. From Table 1 one can see that, at a given stirring rate, the difference in thickness of the diffusion layers for the solvents used is not very great and that the limiting current density is mainly determined by the value of the diffusion coefficient. The magnitude of δ is in agreement with previous experience that the thickness of the diffusion layer tends to a minimum value [10] of about 0.001 cm in well-stirred solutions. The calculated value for δ in an unstirred solution of sodium iodide in water is 0.05 cm. This is also a plausible value.

In Fig. 6, the current efficiency for the anodic formation of radioactive silver iodide from a solution of sodium iodide in methanol has been plotted against the current density. From this curve, the limiting current density $85 \pm 5 \ \mu A \cdot cm^{-2}$ can be read off. This is to be compared with the value 77 $\mu A \cdot cm^{-2}$ which, according to Figs. 4 and 5, is obtained when a supporting electrolyte is present. The higher value obtained for the pure sodium iodide solution is due to the contribution of a migration current to the diffusion current according to eqn. (6). This positive effect is, however, counteracted by a decrease in the value of the diffusion coefficient * so that the overall net effect is only a slight increase in the limiting current density.

ELECTROLYSIS TIME

When the kinetic experiments are performed by electrolytic deposition on a number of electrodes at stated intervals, the electrolysis time should be short compared with the total observable time range. Otherwise the composition of the reaction mixture changes too much during the deposition. It is therefore of interest to know how short one can make the electrolysis time without causing a serious deterioration is the reproducibility. This was investigated as follows. From a radioactive solution of sodium iodide in methanol, depositions were carried out on a number of anodes under the same experimental conditions and the activities were measured. The mean value was computed, after the usual corrections and recalculation of the individual activity values to equal amounts of current. The electrolysis times were then successively shortened to a minimum value of 1 sec, but the current density was kept unchanged.

In Table 2, the results obtained are given together with the experimental conditions. All activities are converted to 6 000 μQ which was approximately the total amount of current after 30 sec. electrolysis. The discrepancy in the individual activities, from the mean value, is after 30 sec. electrolysis in most cases less than 1 %. The accuracy is acceptable down to an electrolysis time as short as about 5 sec. This minimum may probably be shortened still more after further development of the method.

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* The diffusion coefficient, estimated to be $1.68 \times 10^{-5} \ cm^2.sec^{-1}$ at 25°C for iodide ions in the presence of a supporting electrolyte, is reduced to about $1.2 \times 10^{-5} \ cm^2.sec^{-1}$ for the pure sodium iodide solution. This latter value has been estimated from the value [17] $1.0 \times 10^{-5} \ cm^2.sec^{-1}$ given at 14°C whereby it has been assumed that the temperature coefficient [12] for the diffusion coefficient is 2 % deg^{-1}.

Table 2. Influence of electrolysis time on reproducibility of anodic deposition of radio-active silver iodide.

Electrolysis time, sec.	Activity, cpm, after recalculation to 6 000 μQ		Deviation (in %) of the activity from the mean value (12 647)	Experimental conditions
30.06	12 570		−0.6	Initial composition of the elec-
30.12	12 486		−1.3	trolyte: 0.000272 M NaI in
30.45	12 654		+0.1	methanol.
30.13	12 690	Mean	+0.4	4 μC NaI * in 50 ml sample.
30.48	12 564	value	−0.6	
30.16	12 690	12 647	+0.4	
30.17	12 402		−1.9	Temp.: 25.0°C
30.13	12 684		+0.3	
29.98	12 906		+2.1	Stirring rate: 400 rpm.
30.20	12 822		+1.4	
				Current density:
20.18	12 606		−0.3	130 $\mu A \cdot cm^{-2}$
7.03	12 120		−4.2	
5.06	12 618		−0.2	Anode area: 1.50 cm^2
3.08	11 784		−6.8	
2.06	11 610		−8.2	
1.07	13 800		+9.1	

HETEROGENEOUS EXCHANGE BETWEEN THE SILVER IODIDE-COVERED ELECTRODE SURFACE AND THE REACTION MIXTURE

If heterogeneous exchange occurs between the silver iodide-covered surface of the anode and the methyl iodide in the reaction mixture, an error will be introduced. On the other hand, an exchange between the electrode and the iodide ions in the solution will cause no error because the ratio between the number of active and inactive iodine atoms is equal * for the silver iodide layer and for the sodium iodide in the solution. Thus any heterogeneous exchange between these components will not change the radioactivity of the electrode.

To find out whether there is any heterogeneous exchange between the methyl iodide in the solution and the electrode, the following experiment was carried out. A silver electrode, with a thin layer of electrolytically formed inactive silver iodide, was dipped into a solution of radioactive methyl iodide ** in methanol which was kept at 25.0°C and stirred at a rate of 400 rpm. After 5 min, the electrode was removed, rinsed and counted. No activity above the background activity was found. Thus there was no measurable exchange between the methyl iodide and the silver iodide-covered electrode under the conditions in question.

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* A condition for this is however that the time of deposition is so short that the change in composition of the reaction mixture can be neglected.

** The radioactive methyl iodide was prepared by adding 1 μC carrier-free NaI−131 to 50 ml 0.03 M methyl iodide + 0.0002 M NaI in methanol. The solution was allowed to stand until equilibrium had been reached.

INVESTIGATION OF THE ISOTOPIC EXCHANGE BETWEEN METHYL IODIDE
AND SODIUM IODIDE IN METHANOL

The experimental technique. The kinetic experiments were performed as follows. The electrolysis cell was completely filled with a solution of inactive sodium iodide and methyl iodide in dry methanol. When the reaction mixture had reached the thermostat temperature, the exchange reaction was started by adding carrierfree NaI—131 in 0.2 ml of the dry solvent. The radioactive solution was added rapidly by means of a syringe. At pre-determined times of reaction, different anodes were dipped into the reaction mixture and electrolysis was carried out. The times of reaction, taken at the middle of the electrolysis, were measured by a stop-watch. After the electrolytic deposition, the anode was immediately removed and replaced by a new one. The silver iodide-covered anode was then treated as follows: After a thorough rinsing with alcohol, the paraffin wax was removed by petroleum ether. The copper wire was cut off near the silver plate. The latter was then mounted in a reproducible manner on a source holder and counted in the flow counter. If counting could not be performed immediately, the electrodes were kept in the dark to prevent any loss of activity due to photochemical decomposition of the radioactive silver iodide.

The rate equation. If the reaction,
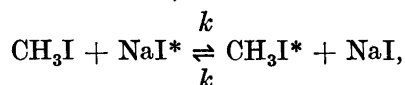
$$CH_3I + NaI^* \overset{k}{\underset{k}{\rightleftarrows}} CH_3I^* + NaI,$$

is of the second order, then the rate equation can be deduced as follows: Let the concentrations of the reacting species at times 0 and t be:

	CH_3I	NaI^*	CH_3I^*	NaI
$t = 0$	a_o	b_o	0	c_o
$t = t$	$(a_o - x)$	$(b_o - x) = b$	x	$(c_o + x)$

Then the reaction rate is given by the expression:

$$\frac{dx}{dt} = k(a_o - x)(b_o - x) - kx(c_o + x) \tag{7}$$

which after integration becomes

$$\log_e \frac{a_o b_o - x(a_o + b_o + c_o)}{a_o b_o} = -k(a_o + b_o + c_o) \cdot t \tag{8}$$

If the organic iodide is used in great excess, c_o can be neglected in comparison with a_o, and since b_o is negligibly small, eqn. (8) reduces to

$$\log_e \frac{b_o - x}{b_o} = \log_e \frac{b}{b_o} = -k \cdot a_o \cdot t \tag{9}$$

Eqn. (9) can be written in the simple form

$$b = b_o \cdot e^{-k't} \tag{10}$$

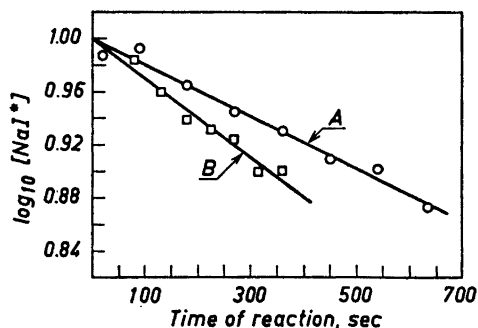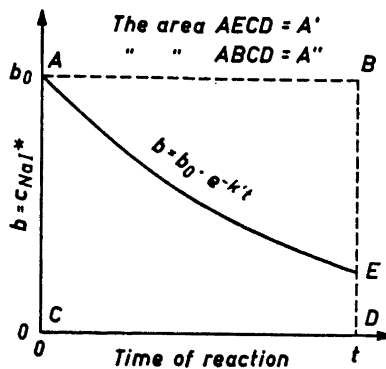where $k' = k \cdot a_o$ is the pseudo-first order rate constant.

Fig. 7.

Fig. 8.

Since the radioactivity of the electrodes, at equal amounts of current, is proportional to b, a straight line should be obtained when the logarithm of the electrode activities is plotted against the time of reaction. The slope of the line is equal to $-k'/2.303$.

Results. In Fig. 7 the logarithm of the electrode activities has been plotted against time for two runs. The straight lines have been fitted to the points according to the method of least squares. The experimental conditions and results are summarized in Table 3.

Table 3. Results of exchange experiments between CH_3I and NaI in dry methanol. Experimental conditions, which were equal for A and B: Spec. activity of NaI: 1 $\mu C/50$ ml sample. Current density: 130 $\mu A.cm^{-2}$. Electrolysis time: 12 sec. Stirring rate *: 400 rpm. Anode area: 1.50 cm^2. Total reduction of iodide ions: 1.3 %. Radioactivity of the anodes: 850 — 1 200 cpm.

Expt.	A	B	Previous expts.[5]	
Temp. °C	25.0	25.0	25.0	25.0
a_0 mole·l^{-1}	0.1291	0.2174	0.00736	0.01508
c_0 mole·l^{-1} × 10^4	2.80	2.80	2.00	2.00
Rate constant × 10^4 l·mole^{-1}·sec^{-1}	34.8	31.5	34.2	33.4
		Mean value	33.5	

* The solution was stirred only during the course of the electrolysis.

In experiment A, the total observation time was 10 min. The scattering of the points is not very great and the k-value is in good agreement with the values reported in a preliminary account of this work [5]. In experiment B, the scattering of the points is greater, though the k-value could be accepted.

From the fact that straight lines are obtained when log b is plotted against time and from the fact that a 30-fold change in the concentration of the methyl iodide does not alter the k-value, it is clear that the reaction is of first order with respect to the inorganic iodide as well as the organic iodide. Thus the overall reaction is second order. The k-value obtained by Swart and Le Roux [1], 80×10^{-4} l·mole^{-1}·sec^{-1}, at the same temperature, 25°C, must be too high.

RAPID REACTIONS

It is evident that kinetic measurements can be performed, with good accuracy, by electrodeposition on a number of different electrodes provided that the observable time range is at least about 10 min. At shorter times it is necessary to modify the method. This case will now be discussed. For simplicity, the discussion will refer to pseudo-first order exchange reactions in which the organic iodide is used in great excess.

Without any special modifications the Hartridge-Roughton technique is applicable to reactions with halflives up to 10 sec. This technique could certainly be combined with the electrolytic method in a useful way.

Reactions which are too slow for the Hartridge-Roughton method but too rapid for common work might be studied either by a moving silver band anode, by the integral method or by the capacity flow method. The last method is undoubtly realizable in practice but is, unfortunately, rather laborious and requires comparatively large amounts of liquid since a steady state has to be created before electrolysis can be performed. It would thus be advantageous if one of the other methods proposed could be made successful.

The principle of the integral method will be described using Fig. 8. The curve in the diagram represents a pseudo-first order exchange reaction, $b = b_0 \cdot e^{-k't}$, in which the organic iodide is in great excess. If an electrolytic deposition is carried out with a constant current strength during t sec from the very moment when the exchange reaction is started, the resulting radioactivity, A', of the anode can be represented by the area AECD between the curve and the t-axis. Consequently:

$$A' = \int_0^t b_0 \cdot e^{-k't}\, dt = \frac{b_0}{k'}\,[1 - e^{-k't}] \tag{11}$$

If another deposition from an iodide ion solution of specific activity equal to the initial specific activity of the iodide ions in the reaction mixture is then carried out on a new anode, the electrode activity, A'', obtained after t sec. electrolysis can be represented by the rectangle ABCD. Hence

$$A'' = b_0 \cdot t \tag{12}$$

After elimination of b_0 between eqns. (11) and (12), one obtains:

$$\frac{A'}{A''} = \frac{1 - e^{-k't}}{k't} \tag{13}$$

This equation can thus be used for calculation of k'.

From the experimental data in Table 2, it is obvious that electrode activities of the order of magnitude 1 000 cpm can be obtainèd after a deposition time of a few seconds, even with a rather low specific activity for the sample. Provided that the mixing time can be made short enough, it appears to be possible to study exchange reactions of this type with halflives as short as a few seconds by means of the integral method. This, and the other methods proposed, will be studied in further investigations.

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