

TABLE. Oxidation of ammonia on platinum adsorbed on silica gel.

Temp., °C	Absolute productivity, r_1 , mol. sec ⁻¹ × centre ⁻¹	No. of regions of migration, z_0	Size of migration region in atomic areas, $10^{18} p_j$, cm ²	E , cal mole ⁻¹
300	0.575	$2.14 \cdot 10^{18}$	140	10700
350	1.21	$1.75 \cdot 10^{18}$	170	

The good linear plots of $\log a_n$ against N (see Figure) show that a monatomic ensemble of platinum [Pt]₁ on the carrier is the active centre for the oxidation of ammonia, as for other oxidising reactions, and Eqn.(2) becomes

$$\log a_1 = \log r_1 - 0.434 \frac{N}{z_0} \quad (3)$$

At low degrees of surface coverage ($N = 2.43 \times 10^{18}$) too high a value was obtained for the activity, and this occurred also in the oxidation of sulphur dioxide on the same catalysts³, which was explained by the non-uniformity of the carrier surface. From the graph and Eqn.(3) it is easy to determine the chief parameters of the process — the number z_0 of regions of migration on the surface of 1 g of carrier and the absolute productivity r_1 of an active centre (dimensions of r_1 mol. sec⁻¹ centre⁻¹). The calculated values are given in the accompanying Table. The apparent activation energy computed from the absolute productivities at 300° and 350° was 10700 cal mole⁻¹.

SUMMARY

The structure of a platinum active centre in the oxidation of ammonia has been studied by the method of the theory of active ensembles. The curve of total activity against surface coverage passes through a maximum, and is well represented by the equation of the theory. As with other catalytic oxidation-reduction processes, the chief active centre in the oxidation of ammonia is the monatomic platinum ensemble Pt/SiO₂.

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IRREVERSIBILITY OF REDUCTION OF IRON AT A DROPPING MERCURY ELECTRODE

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Continuing work on the influence of various factors on the kinetics and mechanism of the reduction of ferrous ions at a dropping mercury electrode¹, in order to estimate the degree of irreversibility of this process, we have applied the fundamental Meiman-Bagotskii equation² for an irreversible polarographic wave

$$I = 4\pi a^2 i = \frac{4\pi r^2}{\beta} c_0 \theta(\mu) t^{1/2} \quad (1)$$

where I is the current on the drop, c_0 the concentration of ions in the bulk of the solution, and t the time of existence of the drop†. The correction factor $\theta(\mu)$ for $\mu < 1$ is the series

$$\theta(\mu) = 1 - a\mu + b\mu^2 - c\mu^3 \quad (2)$$

where $\mu = t^{1/2}\beta k$, $\beta = \exp(\alpha nF/RT)\varphi$, and $k = \sqrt{\frac{2}{3}} nFD^{1/2}$ (φ being the electrode potential, D the diffusion coefficient, and α the transfer coefficient); $c_0\theta(\mu) = c(t, 0)$ is the concentration of ions adjacent to the electrode at time t . From values of the Meiman function μ it is easy to obtain, after substitution for β and k and taking logarithms, the expression

$$\frac{\alpha nF}{RT} \varphi = \ln \frac{1}{\sqrt{\frac{2}{3}} nFD^{1/2} t^{1/2}} + \frac{1}{2} \ln t \quad (3)$$

Since $\mu = \mu_0 \S$ at $t = \tau$, and since also $I/I_d = 0.5$ and $\mu_0 = 0.748$ at $\varphi = \varphi_1$, Eqn.(3) gives a criterion of irreversibility which we have termed the first Meiman-Bagotskii criterion

$$\varphi_{1/2} = \text{const} + RT/2n\alpha F \ln \tau$$

or

$$\varphi_{1/2} = \text{const}' + \frac{0.029}{\alpha n} \log \tau \quad (4)$$

The experimental dependence of $\varphi_{1/2}$ on $\log \tau$ for the reduction of iron with 1N KCl as supporting electrolyte is plotted in Fig.1. The value $\alpha = 0.29$ obtained from this relation agrees well with results obtained by other methods (Table 1). In the case of irreversible processes the variation of I with t for an individual drop in the initial part of the polarographic wave is governed mainly by electrochemical kinetics. At the start of the wave with $I/I_d \ll 1$, Meiman's results show that μ_0 is very small, so that $\theta(\mu)$ approaches unity. In this case $c \approx c_0$, and the current on the drop is proportional to $t^{1/2}$, i.e. to the expanding surface of the drop, and hence

$$\log I = \text{const}'' + \frac{1}{2} \log t \quad (5)$$

We have called this relation the second Meiman-Bagotskii criterion of irreversibility. In the case of an irreversible process, the slope of the straight line (5) on the initial portion of the wave should be 0.66. The experimental results plotted in Fig.2 give 0.625, which is close to the theoretical

† This equation has been derived on the assumption that discharge of the ion is the slow stage and is a first-order reaction.

‡ [$\theta(\mu) = 1 - a\mu + b\mu^2 - c\mu^3$ (Ed. of Translation).]

§ Values of μ_0 are given by Meiman² in a special table as a function of I/I_d (along the polarographic wave).

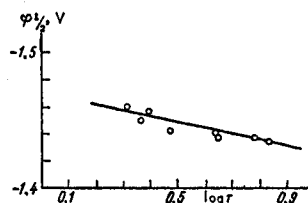


Fig. 1. Dependence of ϕ_1 on $\log \tau$ for 10^{-3} N Fe^{2+} + 1.0 N KCl.

TABLE 1.

1 N KCl + 10^{-3} N	α from dependence of				log k_0 from dependence of	
	i_0 on i	i on t	$\log k_f$ on ϕ	oscillogram	$\log k_f$ on ϕ	oscillographic curves
H^+	0.5	—	0.48	—	-14.1	—
Fe^{2+}	0.3	0.29	0.29	0.25	-15.0	-14.6
Co^{2+}	0.35	—	—	0.23	—	-11.6

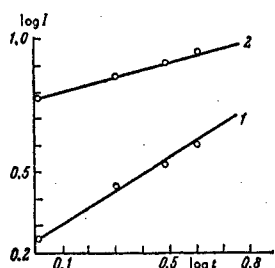


Fig. 2. Dependence of $\log I$ on $\log t$ for 10^{-3} N Fe^{2+} + 1.0 N KCl:

- 1) at start of wave (slope 0.625);
- 2) at end of wave (slope 0.26).

value. Thus both criteria have confirmed our ideas on the irreversibility of the process. In order to obtain a quantitative estimate of the degree of irreversibility of the process, let us calculate the formal reaction rate constants k_0 and k_s by exploiting the potentialities of the Meiman-Bagotskii theory, taking the normal hydrogen potential as the origin of the potential scale: $\phi_H^0 = 0$. All potentials measured on other scales will therefore be converted to the hydrogen scale. Since the rate of an electrochemical reaction (disregarding the ψ_1 -potential) is $i = k_0 c \exp[-(\alpha n F / RT) \phi]$, we have $i = k_0$ and $\phi = \phi_H^0 = 0$ if $c = 1$. At other values of ϕ and c we have $i = k_f c$, where

$$k_f = k_0 \exp\left(-\frac{\alpha n F}{RT} \phi\right), \quad (6)$$

c here being the concentration of ions adjacent to the electrode. Consequently k_0 can be determined by extrapolating

the linear plot of $\log k_f$ against ϕ to $\phi = 0$. The intercept made on the ordinate axis will give k_0 . From the slope α of the straight line we can determine the transfer coefficient $\alpha = (RT/nF) \tan \sigma$. But the dependence of k_f on potential can be determined if tabulated values of the Meiman function μ_0 are known, the latter being in turn determined from the I/I_d ratios at different potentials along the polarographic wave. After values of the constant k_f have been determined for each value μ_0 from the relation

$$k_f = \frac{\mu_0 D^{1/4}}{1.3 \tau^{1/4}}, \quad (7)$$

they must be plotted against ϕ , α determined, and then k_0 calculated. The rate constant k_s of the process at the normal electrode potential of the M^{n+}/M^0 system is readily found on putting $k_f = k_s \exp[(-\alpha n F / RT)(\phi - \phi_c^0)]$, where

$$k_s = k_0 \exp\left(-\frac{\alpha n F}{RT} \phi_c^0\right), \quad (8)$$

ϕ_c^0 here being the normal electrode potential. Calculated values of k_0 and α for the reduction of several ions at a dropping mercury electrode are given in Table 1, which includes for comparison values determined by other methods, for example by Gokhshtein's method³ from oscillographic polarograms. This involved use of the equation $I_{\text{max}}^{1/2} / I_{0.2} = 2.62 \sqrt{\alpha n}$, where $I_{0.2}$ is the value of I at a distance of 200 mV beyond the current maximum, and the equation

$$k_0 = 0.45 \times 10^{-4} \frac{I_{\text{max}}}{n n c_0} \times 10^{16.82 n \phi_p}, \quad (9)$$

ϕ_p being the potential of the peak. The very low values of k_0 in Table 1 also indicate that the process is irreversible. Several kinetic characteristics of an electrode process can be obtained by measuring the polarisation resistances R_F and the pseudocapacitance of the process C_F . However, the methods for calculating the reaction parameters k_s , i_0 , and α from R_F and C_F , described in many papers⁴, are applicable only with sufficiently reversible processes.

When processes are irreversible, a constant polarising potential must be superimposed in order to reach the potentials at which measurable currents are achieved. The theory of this method has been discussed for the case of Faraday currents⁵. For a series arrangement of the reaction impedance $Z_F = R_F + 1/\omega C_F$ the following expression linking R_F and C_F with k_s , α , and i_0 was obtained

$$\cot \Phi_{\text{max}} = \omega R_F C_F = 1 + \sqrt{2} \frac{V \omega}{k_s f^{1-\alpha} (D^{1-\alpha}) [\alpha / (1-\alpha)]^2}, \quad (10)$$

where i_0 is the exchange current, ω the angular velocity, f the activity coefficient, and $\cot \Phi_{\text{max}}$ the value of the function $\omega R_F C_F$ at its maximum. With reversible processes $\Phi_{\text{max}} = \phi_1$. With irreversible processes $\Phi_{\text{max}} \neq \phi_1$. The value of α can be determined from the expression

$$\Phi_{\text{max}} = \phi_1 + \frac{RT}{nF} \ln \frac{\alpha}{1-\alpha}.$$

If k_s is determined from Eqn. (10), the reaction can be regarded as irreversible at $D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, $f = 1$, $\alpha = \beta = 0.5$, and $T = 298^\circ \text{K}$ if $k_s < 3 \times 10^{-5} \text{ cm sec}^{-1}$. The method has been tested by Tamamushi and Tanaka⁶ for the reduction of cadmium and zinc. However, they showed that R_F and C_F cannot be determined for a completely irreversible process (the reduction of Ni). We have made a similar test of the method for the reduction of iron (Fe^{2+}). In this case only the capacitance C_p and resistance R_p of the reaction could be calculated. It was not possible

TABLE 2.

Ion	$C_p, \mu F\ cm^{-2}$	$R_p, \Omega\ cm^2$	$C_F, \mu F\ cm^{-2}$	$R_F, \Omega\ cm^2$	Ref.
Cd ²⁺	101	1.45	219	0.78	6
Zn ²⁺	0.131	29	230	28.9	6
Fe ²⁺	0	150			own results
Ni ²⁺		not determined			

to convert them to R_F and C_F , since $C_p \rightarrow 0$ at $\varphi = \varphi_1$. In order to compare our results with those of Tanaka and Tamamushi, we converted their values of R_F and C_F (series arrangement) for Cd and Zn to values of R_p and C_p for the reaction (parallel arrangement), and compared them with our results for iron (see Table 2). The decrease in C_p and increase in R_p for the reaction indicate a considerable increase in the irreversibility of the processes on passing from cadmium to iron.

SUMMARY

1. Methods are considered for analysing the degree of irreversibility of polarographic processes.
2. The electrochemical reduction of Fe²⁺ ions is irreversible. Discharge of the ion is the slow stage, and obeys a first-order kinetic equation.

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AUTOMATIC ANALYSIS OF OZONE

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The method based on a comparison of thermal conductivities has been widely used in gas analysis¹⁻⁴, but the use of heater filaments is of little value for the determination of ozone and other reactive gases, since reaction with the filament gradually alters the electrical properties of the

measuring circuit with loss of stability⁵. This shortcoming may be eliminated by the use in catharometers of semiconductor thermoresistors covered with a thin protective glass film.

This work covered the determination of ozone in ozone-oxygen and ozone-air mixtures. Two types of detector were studied: No.1 was a semi-flow design using SF-3 thermistors and made from a brass block (Fig.1a), while No.2 was a full-flow design using TSh-1 thermistors and made of molybdenum glass (Fig.1b). The ozone was obtained from the apparatus previously described, in which the pressure was maintained constant within 0.2 mm Hg.⁶ Fig.2 shows the analyser layout. A small fraction of the gas, drawn off from the main stream at the input to the ozone generator 8, passes through the needle-valve 1, is purified and dried with fused KOH in the column 2, and reaches the comparator cell of the catharometer 4 after passing the manostat 3, which maintains a constant velocity. Then the gas passes through the six-way sampling tap 5, into the measuring cell of the catharometer, and finally escapes to the atmosphere through the flow meter 6 which establishes the flow rate. The calcium chloride tube 7 with fused KOH is placed at the outlet of the system in order to decompose the ozone. Fig.3 shows the electrical circuit of the analyser. The bridge formed by thermistors X1 and X2 and wirewound resistors R1 and R2 is supplied from a 6 V accumulator. The current is measured by a

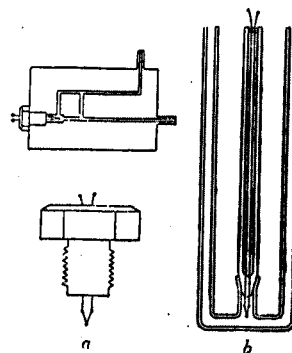


Fig. 1. Layout of catharometers: a) semi-flow cell; b) full-flow cell.

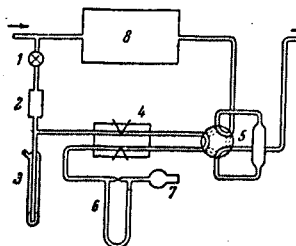


Fig. 2. Overall layout of automatic ozone analyser.