

ELECTROCHEMICAL AND CATALYTIC STUDIES
AT ELECTRON-CONDUCTING SURFACES

by

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Theoretical expressions have been derived for the catalytic rate (u'_{cat}) and the catalyst potential (E_{cat}) for redox reactions catalysed by a noble metal. The model assumed that the catalysis occurred by electron transfer through the metal, and that the individual current-potential curves of the reacting couples were additive. The cases considered were: (a) two irreversible couples with partial mass transport control, and (b) two reversible couples that remain in equilibrium at the surface.

Experimental tests of the model were made with the reaction between ferricyanide and iodide ions in aqueous potassium nitrate solutions with large rotating disk catalysts. On an oxide-covered platinum disk the catalysis was found to follow all the theoretical predictions of case b as shown by the dependence of u'_{cat} and E_{cat} on the rotation speed of the disk, on the concentration of reactants and products, and on temperature. Moreover, E_{cat} and $2Fu'_{\text{cat}}$ agree well with the mixture potential and mixture current obtained by purely electrochemical experiments.

On oxide-free platinum, iodide was irreversibly adsorbed and partially blocked the surface for the reduction of ferricyanide in the mixed system. Here too, the catalysis followed the electron transfer path but the additivity principle was not obeyed.

Catalytic experiments carried out on a glassy carbon disk catalyst fitted the rotation speed dependence predicted by case a.

Despić et al. (1979), recently claimed that a new kind of "non-faradaic" electrocatalysis, brought about by pulsing gold and silver electrodes in the double layer region, produced large increases in the rate of hydrolysis of t-butyl acetate. Their experiments have been checked by a pH-stat method, and the solvolysis of t-butyl bromide on pulsed silver electrodes has also been investigated. No evidence to substantiate this new catalytic phenomenon was found for either reaction.

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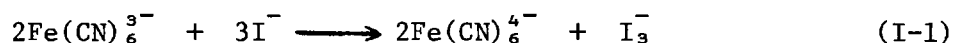
## CHAPTER ONE

### ELECTRON TRANSFER AT INTERPHASES

#### I.1. General Introduction.

The catalysis of redox reactions in solution is very common.<sup>1</sup> An electrochemical mechanism has been proposed for such catalytic activity by Spiro<sup>2</sup>: according to this the electron transfer between the reactants occurs through the solid conducting phase. During the reaction the catalyst acquires a well defined non-equilibrium potential  $E_{\text{cat}}$  which is determined by the rate of electron transfer and by thermodynamic quantities. This potential can be measured against any suitable reference electrode. This model can be predictive if the additivity principle of Wagner and Traud,<sup>3</sup> originally devised to explain the dissolution of metals in acid is introduced. This principle states that when several electroactive couples are simultaneously present at an electrode, the net current density of the mixture at a given potential is the algebraic sum of the curves of each individual couple. The catalytic situation is described in the particular case in which, over a common potential domain, two electroactive couples show currents of opposite polarity: in the absence of an external current source the potential of the electrode adjusts itself to a value in that domain  $E_m$ , at which the two partial currents are equal and opposite in sign. Their absolute value is the mixture current density,  $i_m$ . A catalytic situation also requires the electrode material being inactive, save for its rôle as a medium for electron transfer.

Spiro and Griffin<sup>4</sup> have shown quantitatively that the reaction between ferricyanide (also referred to as Feic, in this thesis) and iodide ions proceeds through the electrochemical mechanism on platinum:



Spiro<sup>5</sup> has produced an expression for the catalytic rate in the case of two irreversible electrochemical couples, when  $E_m$  is in the Tafel region of each couple, and also for the case in which it lies in the limiting current region of one of them. These ideas have allowed Miller et al.<sup>6</sup> to account for the mechanism of the catalytic reduction of water by a potential mediator in the presence of platinum, gold and silver colloids. More recently, in the field of corrosion, a phenomenon also subject to mixed potential control, Ritchie et al.<sup>7,8</sup> have independently developed expressions for the dependence of  $E_m$  on the stirring of the solution in order to obtain diagnostic criteria for the influence of mass transport limitations in the open circuit dissolution of metal disks. There is therefore, considerable current interest in the concepts of mixed potential and mixed current. Moreover, mixed electrochemical processes, particularly on colloidal metal catalysts, would appear to be more properly studied "in toto", as it is not always possible to study the individual couples separately. Therefore the development of theoretical concepts and experimental techniques for their study which allow their electrochemical nature to be pinpointed, would be most useful.

The main goal of this work has been to study the catalytic rate of reaction (1) under a variety of experimental conditions and to interpret the results in terms of the electrochemical model. In this context, theoretical expressions for the catalytic rate have been

obtained to cover the cases of reversible couples and partial mass transport control of irreversible couples. The catalytic work has been complemented by electrochemical studies of the individual couples concerned.

## 1.2. Thermodynamics of the Metal/Solution Interphase.

The chemical potential  $\mu_j^\alpha$  of a species,  $j$ , inside a phase,  $\alpha$ , is defined as

$$\begin{aligned}\mu_j^\alpha &= \left( \partial G^\alpha / \partial n_j^\alpha \right)_{n_k (k \neq j), T, P, \text{ etc.}} \\ &= \mu_j^{\circ \alpha} + RT \ln a_j^\alpha\end{aligned}\quad (\text{I-2})$$

$G^\alpha$  is the Gibbs free energy,  $n_j^\alpha$  are the numbers of moles of  $j$ ,  $a_j^\alpha$  is the activity and  $\mu_j^{\circ \alpha}$  is the value of  $\mu_j^\alpha$  at unit activity. Chemical reactions are only possible if the chemical potential of the products is not equal to that of the reactants.  $\mu_j^\alpha$  is a measure of the energetic value of  $j$  in its chemical interactions with other species that dwell in the phase. If the species bear an algebraic electronic charge,  $Z_j$ , in a phase  $\alpha$  with electrical potential,  $\phi^\alpha$ , the extra electrostatic energy is taken into account by introducing the electrochemical potential,  $\bar{\mu}_j^\alpha$ , devised by Guggenheim<sup>9</sup> and defined as:

$$\bar{\mu}_j^\alpha = \mu_j^\alpha + Z_j F \phi^\alpha \quad (\text{I-3})$$

When two phases are brought into contact, like a metal (M) and an electrolyte solution (S), the condition of equilibrium is expressed as:

$$\Delta \bar{\mu}_j = \bar{\mu}_j^S - \bar{\mu}_j^M = 0 \quad (\text{I-4})$$

for each species,  $j$ , capable of crossing the interphase (e.g.,  $j$  = electron, for redox electrodes;  $j$  = metal ion, for metal-ion electrodes).

Eq. (3) effects an artificial separation between the "chemical" and "electrical" interactions that contribute to the free energy of a substance; but it is a sound concept in the sense that it defines  $\phi^\alpha$  unequivocally, and that no inconsistencies result from its use.<sup>10a</sup> Moreover,  $\phi^\alpha$  coincides with the concept of electrostatic potential.<sup>10b</sup> It is known as the inner (or Galvani) potential of the phase. It is impossible to measure because no operation can be prescribed by which a test charge brought from vacuum into the phase can test  $\phi^\alpha$  only, while not experiencing all the "chemical" influences of the phase. The same argument applies to the absolute potential difference,  $\Delta\phi$ , between two phases ( $\phi^\alpha - \phi^\beta$ ); also, the need to have a probe inside one of them creates an additional interphase and an additional  $\Delta\phi$  that enters into the measurement.<sup>11a</sup> However, changes in  $\Delta\phi$  can be measured, provided that the potential difference generated by the probe does not change upon imposition of a voltage,  $V$ , from an external power source.<sup>11a</sup> In effect (Figure 1), according to Kirchhoff's first law:

$$\Delta\phi_1 - \Delta\phi_2 + V = 0 \quad (\text{I-5})$$

Taking differentials and assuming that  $\Delta\phi_2$  is independent of  $V$ , gives:

$$d\Delta\phi_1 = -dV \quad (\text{I-6})$$

(It is assumed in eq. (6) that the S phase has a negligible ohmic resistance; it is valid, however, if  $dV$  does not lead to a current flow. This would not be true if the interphase is in contact with a redox system, see below).

For a redox couple Ox/Red with charges  $Z_{\text{Ox}}$  and  $Z_{\text{Red}}$ , respectively in contact with a metal electrode:



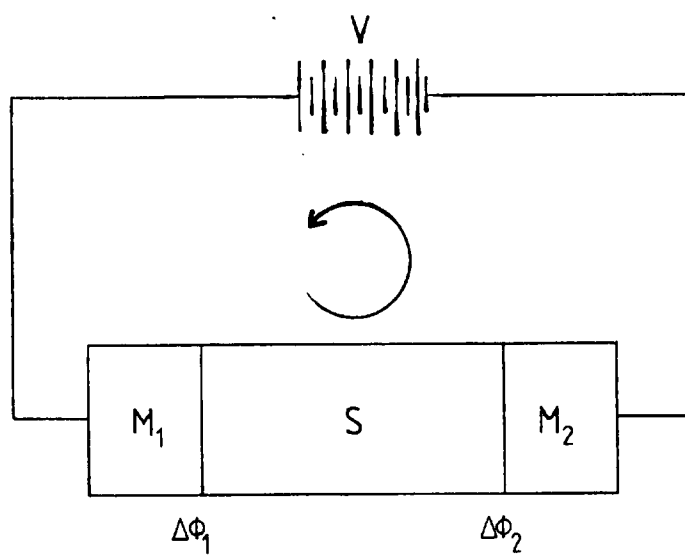


Figure I-1

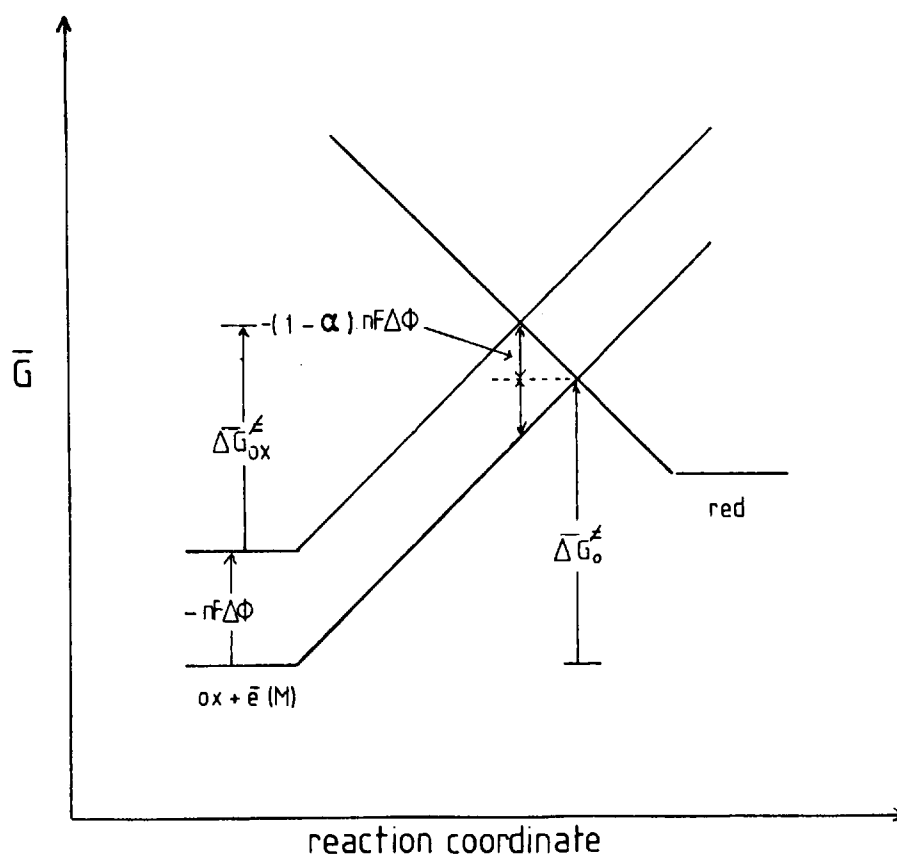


Figure I-2

At equilibrium use of eq. (3) yields:

$$0 = n\bar{\mu}_e^S - n\bar{\mu}_e^M = (\bar{\mu}_{\text{red}}^S - \bar{\mu}_{\text{ox}}^S) - n\bar{\mu}_e^M \quad (\text{I-8})$$

Combining eqs. (2) and (3) for each species, and remembering that  $Z_{\text{ox}} - n = Z_{\text{red}}$ , one obtains<sup>12</sup>:

$$E = \Delta\phi = \phi^M - \phi^S = \Delta\phi^0 + (RT/nF)\ln(a_{\text{ox}}/a_{\text{red}}) \quad (\text{I-9})$$

$$\text{where } E^0 = \Delta\phi^0 = -(\mu_{\text{red}}^0 - \mu_{\text{ox}}^0 - n\mu_e^0)/nF \quad (\text{I-10})$$

Eq. (9) is the Nernst equation for the partial reaction (7).  $\Delta\phi$  and  $\Delta\phi^0$  can be referred to a common arbitrary reference potential. For redox systems at equilibrium the Nernst equation (9) is equivalent to the equality of the electrochemical potentials. The inference follows that if  $\Delta\phi$  is made to depart from its Nernstian value, the electrons in the metal will not be in equilibrium with the electrons in the solution and a net flow of them will occur across the M/S interphase. The non-equilibrium situation is outside the realm of thermodynamics.

### I.3. The Butler-Volmer Equation.

#### a) Simple Electrode Reactions.

An expression for the rate of electron transfer across the metal/solution interface when  $\Delta\phi$  is made to depart from its Nernstian value  $\Delta\phi_{\text{rev}}$  was obtained by J.A.V. Butler<sup>13</sup> and independently by M. Volmer.<sup>14</sup> As a first approximation<sup>15</sup> the cathodic and anodic rate constants  $k_{\text{ox}}$  and  $k_{\text{red}}$ , respectively [see eq. (7)] can be obtained from the absolute reaction rate theory<sup>11b</sup>:

$$k_{\text{ox}} = (kT/h) \exp(-\bar{\Delta G}_{\text{ox}}^\ddagger/RT) \quad (\text{I-11a})$$

$$k_{\text{red}} = (kT/h) \exp(-\bar{\Delta G}_{\text{red}}^\ddagger/RT) \quad (\text{I-11b})$$

where  $k$  is the Boltzmann constant, and  $h$  is the Planck constant. The net

current density is:

$$i = F k_{ox} C_{ox} - F k_{red} C_{red} \quad (I-12)$$

Figure 2 shows the electrochemical free energy  $\bar{G}$  of reactants and products, measured from some arbitrary value. The only step in consideration is the charge transfer; any other process like transport of Ox and Red to the electrode or metal-ligand bond formation are either absent or in equilibrium. A change in  $\phi^S - \phi^M$  will displace both curves if both reactants and products are charged. The electrochemical free energy of the species are:

$$\bar{G}_{ne-}^M = nG_{e-}^M - nF\phi^M \quad (I-13a)$$

$$\bar{G}_{ox}^S = G_{ox}^S + Z_{ox}F\phi^S \quad (I-13b)$$

$$\bar{G}_{red}^S = G_{red}^S + Z_{red}F\phi^S \quad (I-13c)$$

The displacement of the reactant curve relative to the displacement of the product curve effected by the existence of  $\phi$  is:

$$(-nF\phi^M + Z_{ox}F\phi^S) - Z_{red}F\phi^S = -nF\Delta\phi \quad (I-14)$$

This is why in Figure 2 only the reactant curve has been displaced upwards by an amount,  $-nF\Delta\phi$  (meaning that  $\Delta\phi$  has been made more negative). From there it seems clear that at the crossing point of the curves this contribution is only  $\alpha nF\Delta\phi$ , with  $0 < \alpha < 1$ ;  $\alpha$  is known as the symmetry factor. If  $\Delta G_0^\ddagger$  is the activation energy in the hypothetical case when  $\Delta\phi = 0$ , then

$$\bar{\Delta G}_{ox}^\ddagger = \bar{\Delta G}_{o,ox}^\ddagger + \alpha nF\Delta\phi \quad (I-15a)$$

$$\bar{\Delta G}_{red}^\ddagger = \bar{\Delta G}_{o,red}^\ddagger - (1-\alpha)nF\Delta\phi \quad (I-15b)$$

Introducing eqs. (15) in eqs. (11) and in (12):

$$i = \vec{F}k C_{\text{ox}} \exp(-\alpha n f \Delta\phi) - \overleftarrow{F}k C_{\text{red}} \exp[(1-\alpha) n f \Delta\phi] \quad (\text{I-16})$$

where  $\vec{k} = (kT/h) \exp(-\bar{\Delta}G_{\text{o,ox}}^\ddagger/RT)$  (I-17a)

$$\overleftarrow{k} = (kT/h) \exp(-\bar{\Delta}G_{\text{o,red}}^\ddagger/RT) \quad (\text{I-17b})$$

$$f = F/RT$$

Eq. (16) is known as the Butler-Volmer equation. When  $\Delta\phi = \Delta\phi_{\text{rev}}$  then  $i = 0$  since the backward and forward rates must be equal. Thus, we can introduce the exchange current density,  $i_0$ , by:

$$i_0 \equiv \vec{F}k C_{\text{ox}} \exp(-\alpha n f \Delta\phi_{\text{rev}}) = \overleftarrow{F}k C_{\text{red}} \exp[(1-\alpha) n f \Delta\phi_{\text{rev}}] \quad (\text{I-18a})$$

The standard exchange current density,  $i_{00}$ , is the value of  $i_0$  when all the species are at unit activity:

$$i_{00} = \vec{F}k \exp(-\alpha n f \Delta\phi^0) = \overleftarrow{F}k \exp[(1-\alpha) n f \Delta\phi^0] \quad (\text{I-18b})$$

Introducing eq. (18a) into (16):

$$i = i_0 (\exp(-\alpha n f \eta) - \exp[(1-\alpha) n f \eta]) \quad (\text{I-19})$$

where the overpotential  $\eta$  is defined as:

$$\eta \equiv \Delta\phi - \Delta\phi_{\text{rev}} \quad (\text{I-20})$$

The shape of a steady state current-voltage curve according to eq. (19) is shown as a broken line in Figure 3. The current grows almost exponentially with  $\eta$  if  $|\eta| \geq \text{ca. } 0.1/n \text{ V}$ . In practice, as the electron transfer becomes faster and faster, the slower mass transport rate begins to hold up the current until it reaches a limiting value (see section I.5.a).

b) Consideration of Pre-Equilibria.

K.J. Vetter,<sup>16a</sup> has introduced the possibility of fast chemical or electrochemical steps preceding a slow rate-determining step (r.d.s). The derivation given by Bockris and Reddy,<sup>11c</sup> will be followed here.

Suppose that reaction (7) goes through the following sequence:



where  $S_r$  and  $S_{r+1}$  are intermediate species. Reaction 21b is the r.d.s. which occurs  $v$  times when the overall reaction (7) occurs once.  $v$  is the stoichiometric number of the reaction. During the r.d.s.  $p$  electrons are transferred at once. Reactions (21a) and (21c) are assumed to be so fast that they are effectively in equilibrium at the electrode potential  $\Delta\phi$ . They can occur through a sequence of steps in which electrons may or may not be transferred (each step being also at equilibrium). From eq. (7) and from the sequence (21) it follows that:

$$\vec{p} + \overleftarrow{p} + vp = n \quad (\text{I-22})$$

Applying eq. (16) to the r.d.s. in (21):

$$i = \vec{Fk}_{\text{rds}} C_r \exp(-\alpha pf\Delta\phi) - \overleftarrow{Fk}_{\text{rds}} C_{r+1} \exp[(1-\alpha)pf\Delta\phi] \quad (\text{I-23})$$

Since (21a) is in equilibrium during the forward reaction and (21c) during the backward reaction, the Nernst equation may be applied to each of them to obtain the concentration of the intermediates  $S_r$  and  $S_{r+1}$ .

Therefore:

$$C_r = \vec{K}^{1/\nu} C_{ox}^{1/\nu} \exp[-(\vec{p}/\nu) f \Delta \phi] \quad (I-24a)$$

$$C_{r+1} = (C_{red}^{1/\nu} / \hat{K}^{1/\nu}) \exp[(\hat{p}/\nu) f \Delta \phi] \quad (I-24b)$$

where

$$\vec{K} = \exp(\vec{p} f \Delta \phi^0), \text{ and } \hat{K} = \exp(\hat{p} f \Delta \phi^0) \quad (I-25)$$

Introducing eqs. (24) into (23):

$$i = F \vec{k} C_{ox}^{1/\nu} \exp[-(\alpha p + \vec{p}/\nu) f \Delta \phi] - F \hat{k} C_{red}^{1/\nu} \exp\{[(1-\alpha)p + \hat{p}/\nu] f \Delta \phi\} \quad (I-26)$$

where

$$\vec{k} = \vec{k}_{rds} \vec{K}^{1/\nu}, \text{ and } \hat{k} = \hat{k}_{rds} \hat{K}^{1/\nu} \quad (I-27)$$

By analogy with eq. (16) the anodic and cathodic transfer coefficients  $\hat{\alpha}$  and  $\vec{\alpha}$ , respectively, are defined as:

$$\vec{\alpha} = \alpha p + \vec{p}/\nu, \text{ and } \hat{\alpha} = (n - \vec{p})/\nu - \alpha p \quad (I-28)$$

and

$$\vec{\alpha} + \hat{\alpha} = n/\nu \quad (I-29)$$

Use has been made of eq. (22) to obtain  $\hat{\alpha}$ . Similarly to eqs. (18) the exchange current density, and the standard exchange current density are:

$$i_o = F \vec{k} C_{ox}^{1/\nu} \exp(-\vec{\alpha} f \Delta \phi_{rev}) = F \hat{k} C_{red}^{1/\nu} \exp(\hat{\alpha} f \Delta \phi_{rev}) \quad (I-30)$$

$$i_{oo} = F \vec{k} \exp(-\vec{\alpha} f \Delta \phi^0) = F \hat{k} \exp(\hat{\alpha} f \Delta \phi^0) \quad (I-31)$$

Substitution of eq. (30) in (26), and using eq. (20):

$$i = i_o [\exp(-\vec{\alpha} f \eta) - \exp(\hat{\alpha} f \eta)] \quad (I-32)$$

This is the more general form of the Butler-Volmer equation, when all the steps other than the r.d.s. are in equilibrium, in the absence of mass transport limitations and of adsorption of reactants or intermediates at the electrode surface. Since in principle any number of substances can enter in the pre-equilibria, several  $C_j$  can appear in eq. (26), not just  $C_{ox}$  and  $C_{red}$ . Their exponents will vary too and will not necessarily be  $1/\nu$ , but any number,  $W$ .

c) The Tafel Approximation.

If  $\eta$  is sufficiently negative, the second exponential term in eq. (32) can be ignored with respect to the first. Thus, in logarithmic form eq. (32) assumes the form known as the Tafel equation:

$$\eta = \frac{2.303}{\bar{\alpha}f} \log i_0 - \frac{2.303}{\bar{\alpha}f} \log i, \text{ if } \eta \ll 0 \quad (\text{I-33a})$$

$$\eta = -\frac{2.303}{\bar{\alpha}f} \log i_0 + \frac{2.303}{\bar{\alpha}f} \log (-i), \text{ if } \eta \gg 0 \quad (\text{I-33b})$$

The usefulness of the Tafel equations is obvious since plots of  $\eta$  vs.  $\log|i|$  are linear; the slope yields  $\bar{\alpha}$  or  $\bar{\alpha}$ , depending on which region of  $\eta$  is being considered, and the intercept provides the exchange current density. As a rule of thumb, the Tafel region should occur if  $|\eta| > 0.1$  V for one electron reactions, or if  $|\eta| > 0.05$  V for a two-electron reaction. If the reaction does not strictly follow eq. (32), i.e., in the presence of "complications", this is more likely to be detected in the Tafel plots in the form of curvatures, of disagreement between the anodic and cathodic  $i_0$  values, or in failure of  $\bar{\alpha} + \bar{\alpha}$  to comply with eq. (29).

d) Approximation at Low Overpotentials.

For small values of  $\eta$  one can expand the exponential terms in eq. (32) in series. If the terms in  $\eta$  of order higher than one are ignored:

$$i = i_0 [1 - \frac{n}{v} f \eta - (1 + \frac{n}{v} f \eta)] = -(n/v) i_0 f \eta \quad (\text{I-34})$$

Apart from some obvious utilitarian aspects, eq. (34) offers a glimpse of the intimate workings of the electron transfer in the context of the absolute reaction rate theory. Thus, for example, a small departure from  $\Delta\phi_{\text{rev}}$  causes a linear increase in the number of reactant particles capable of producing an activated complex, hence a linear increase in  $i$ . It is also seen that the more often the r.d.s. has to be performed, the lower the current is (other factors being equal), because the  $n$  electrons have to be milled  $v$  times in succession through the slow r.d.s. Another aspect is the absence of any symmetry factors, which are related to the relative slope of the energy profiles in Figure 2 at the intersection point. At equilibrium, the activated complex crosses the top of the activation barrier with the same frequency in both directions; therefore the actual slopes of the free energy curves have no importance. For small departures from equilibrium one would expect this obliviousness w.r.t. the slopes to be preserved, because the forward and backward frequencies are still essentially the same.

I.4. Electrochemical Reaction Orders and Activation Energies.

The electrochemical reaction orders,  $W_j$ , were first introduced by K.J. Vetter.<sup>16b</sup> By analogy with ordinary chemical reactions:

$$W_j^T = (\partial \ln i / \partial \ln C_j)_{T, P, \Delta\phi, C_k (k \neq j)} \quad (\text{I-35})$$

The condition of constant  $\Delta\phi$  is due to the potential dependence of  $i$ . According to eq. (35) the  $W_j^T$  are the exponents of the concentrations in the pre-exponential terms of eqs. like (26). It follows that they should be measured in the Tafel region, otherwise they become  $\Delta\phi$ -dependent. The superscript  $T$  stands for "an" or "cath", depending on whether the anodic or cathodic Tafel regions are being considered. Another definition of  $W_j$  is:

$$W_j' = (\partial \ln i / \partial \ln C_j)_{T, P, \eta, C_k (k \neq j)} \quad (I-36)$$

These  $W_j'$  are the reaction orders of the exchange current density [see eqs. (32) and (30)], and since  $\eta = \text{const.}$ , the  $W_j'$  contain the concentration dependence of  $\Delta\phi_{\text{rev}}$ . Unlike  $W_j^T$ ,  $W_j'$  can be measured at any  $\eta$  value, provided that it is constant, and  $W_j'$  will not depend on  $\eta$  or on  $\Delta\phi$ . The relation between  $W_j^T$  and  $W_j'$  is, from consideration of eq. (30):

$$W_j' = W_j^{\text{an}} + \frac{\alpha}{n} \nu_j \quad \text{or} \quad W_j' = W_j^{\text{cath}} - \frac{\alpha}{n} \nu_j \quad (I-37)$$

The value of the  $W_j'$  do not depend on which Tafel region is being used.  $\nu_j$  is the stoichiometric coefficient of  $j$  in the overall reaction (positive for oxidants, negative for reductants). The  $W_j^T$  have a direct kinetic value in the sense that they appear in the kinetic laws as a direct consequence of the operating mechanism, while the  $W_j'$  may be seen as a consequence of mathematical handling of equations like (26).

The electrochemical activation energy  $E^\ddagger$  is defined as<sup>17a</sup>:

$$E_{\text{ox}}^\ddagger = - R [\partial \ln k_{\text{ox}} / \partial (1/T)]_{C_j, P, \Delta\phi} \quad (I-38a)$$

$$E_{\text{red}}^\ddagger = - R [\partial \ln k_{\text{red}} / \partial (1/T)]_{C_j, P, \Delta\phi} \quad (I-38b)$$

Using eqs. (11) and (15):

$$E_{\text{ox}}^\ddagger = RT + \Delta G_{\text{o,ox}}^\ddagger + \alpha n F \Delta\phi \quad (I-39a)$$

$$E_{\text{red}}^{\neq} = RT + \Delta G_{\text{o,red}}^{\neq} - (1-\alpha)F\Delta\phi \quad (\text{I-39b})$$

Setting  $E^{\neq} = E_{\text{rev}}^{\neq}$  when  $\Delta\phi = \Delta\phi_{\text{rev}}$ :

$$E_{\text{ox}}^{\neq} = E_{\text{ox,rev}}^{\neq} + \alpha n F \eta \quad (\text{I-40a})$$

$$E_{\text{red}}^{\neq} = E_{\text{red,rev}}^{\neq} - (1-\alpha)n F \eta \quad (\text{I-40b})$$

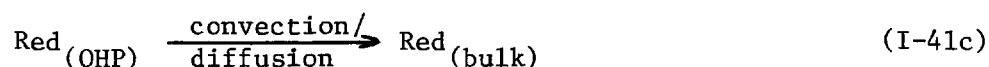
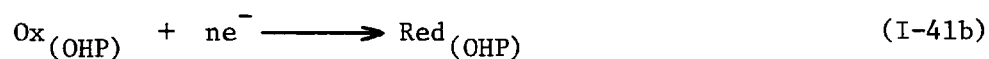
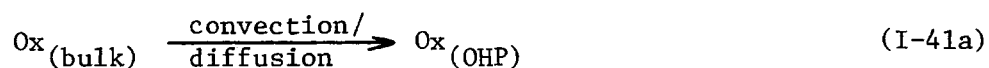
Because  $\Delta\phi_{\text{ref}}$  varies with temperature, correction must be made to eqs.

(40) for the temperature coefficient of  $\Delta\phi_{\text{rev}}$ . As expected,  $E_{\text{rev}}^{\neq}$  decreases for the cathodic reaction if  $\eta$  is made negative; the same happens to the anodic reaction if  $\eta$  is made positive.

#### I.5. Corrections to the Butler-Volmer Equation.

##### a) Effect of Mass Transport Limitations.

When the rate at which the reactants can reach the electrode or at which the products can leave it is not fast compared with the electron transfer itself, these steps must be introduced in the reaction scheme and their rate allowed for. Therefore, reaction (7) which occurs through a sequence like (21) must be described as:



In this sequence "bulk" means that the chemical is positioned just outside the diffusion layer at which its concentration equals  $C_j$ , i.e., its bulk concentration. It is assumed that the electron transfer proceeds

when  $j$  is at the outer Helmholtz plane (see section I.5.c) at which its concentration is  $C_j^\sigma$ . It is assumed that none of the major steps in (41a-c) is in equilibrium. Step (41b), however, is still described by the sequence (21). In the steady state the rate of each step is the same. Therefore:

$$\text{Rate of (41a)} = i = nFD_{\text{ox}}(C_{\text{ox}} - C_{\text{ox}}^\sigma)/\delta_{\text{ox}} \quad (\text{I-42a})$$

$$\text{Rate of (41c)} = i = -nFD_{\text{red}}(C_{\text{red}} - C_{\text{red}}^\sigma)/\delta_{\text{red}} \quad (\text{I-42b})$$

The rate of (41b) is also  $i$ , given by eq. (26), except that  $C_j^\sigma$  must be used. Solving for  $C_j^\sigma$  in eq. (42) and introducing them into eq. (26) and using eq. (30):

$$i = i_o \left[ (1-i/L_{\text{ox}})^{w_{\text{ox}}^{\text{cath}}} \exp(-\alpha f \eta) - (1-i/L_{\text{red}})^{w_{\text{red}}^{\text{an}}} \exp(\alpha f \eta) \right] \quad (\text{I-43})$$

The  $L_j$  are the limiting current densities, defined by:

$$L_{\text{ox}} = nFD_{\text{ox}} C_{\text{ox}}/\delta_{\text{ox}}, \quad L_{\text{red}} = -nFD_{\text{red}} C_{\text{red}}/\delta_{\text{red}} \quad (\text{I-44})$$

Eq. (43) will yield curved Tafel plots in the  $|\eta| > 0.1/n$  region. If  $w_{\text{ox}}^{\text{cath}}$  (or  $w_{\text{red}}^{\text{an}}$ ) = 1, then at constant  $\eta$ :

$$1/i = 1/L_{\text{ox}} + 1/i_k, \quad i_k = i_o \exp(-\alpha f \eta) \quad (\text{I-45})$$

$L_{\text{ox}}$  can be controlled by varying the stirring of the solution (see Chapter II), and a plot of  $1/i$  vs.  $1/L_{\text{ox}}$  yields  $i_k$  at infinite stirring. With several plots at different  $\eta$  each, a mass transport-free Tafel plot is obtained from  $\eta$  vs.  $\log i_k$ . If  $w_{\text{ox}}^{\text{cath}}$  (or  $w_{\text{red}}^{\text{an}}$ )  $\neq 1$ , the corresponding plot, at constant  $\eta$  is:

$$\ln i = w_{\text{ox}}^{\text{cath}} \ln (1-i/L_{\text{ox}}) + \ln i_k \quad (\text{I-46})$$

from which  $i_k$  as well as  $w_{\text{ox}}^{\text{cath}}$  can be obtained.

A different situation occurs when all the electron transfer steps in (41) are much faster than mass transport [therefore (41b) can no longer be represented by (21)] and the Butler-Volmer equation cannot be used. In the steady state, the rate of (7) is that of the slow steps (41a) and (41c), given by eqs. (42), while (41b) is in equilibrium at the electrode potential  $\Delta\phi$ . Thus, with reference to reaction (7);

$$\begin{aligned}\Delta\phi &= \Delta\phi^{\circ} + \frac{1}{nf} \ln(C_{\text{ox}}^{\sigma}/C_{\text{red}}^{\sigma}) \\ &= \Delta\phi_{\text{rev}} + \frac{1}{nf} \ln[(1-i/L_{\text{ox}})/(1-i/L_{\text{red}})]\end{aligned}\quad (\text{I-47})$$

where  $\Delta\phi_{\text{rev}}$  is given by the Nernst equation. According to eq. (20):

$$\eta_c = \frac{1}{nf} \ln[(1-i/L_{\text{ox}})/(1-i/L_{\text{red}})] \quad (\text{I-48})$$

$\eta_c$  is called the diffusion or concentration overpotential,<sup>16c</sup> and the couple Ox/Red is termed "reversible". In this situation no kinetic information can be gained from the study of  $i$ - $\Delta\phi$  curves. Or, put in a positive way, no such knowledge is required to describe reversible electrochemical systems.

#### b) Migration of Ions.

Charged reactants and/or products can also reach the electrode by migrating in the electric field between the electrodes. Migrational effects hinder the reduction of anions and assist their oxidation and vice versa for cations. Because a travelling ion in solution contributes to the current being passed, the fraction of the current carried by the ion is represented by its ionic transference number  $t_j$ <sup>16d</sup>:

$$t_j = \frac{|Z_j| u_j c_j}{\sum_k |Z_k| u_k c_k}, \text{ and } \sum_k t_k = 1 \quad (\text{I-49})$$

where  $u_j$  is the ionic mobility of ion  $j$ . The summation takes into account all of the other species in the solution. If  $j$  is the species whose electrode kinetics are under scrutiny, then the complicating effect of its electrical migration can be effectively avoided by adding a large excess of supporting electrolyte. This is a salt that does not undergo electron transfer in the same potential range as does  $j$ , but being dissociated into ions and present in large amounts compared to  $j$ , it is capable of carrying most of the current through the solution. According to the example of hydrogen evolution from  $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$  solutions cited by Vetter,<sup>16</sup> migration effects on the  $\text{H}^+$  ion are almost completely eliminated for  $[\text{Na}_2\text{SO}_4]/[\text{H}_2\text{SO}_4]$  ratios as low as unity. It seems reasonable to assume that the same order of magnitude for the ratio  $[\text{sup. electrolyte}]/C_j$  should apply generally. However, there are other reasons for preferring ratios 2 and 3 orders of magnitude higher as it is always done in practice, in order to maximise the conductivity of the solution (see Chapter IV) and to minimise double layer effects (see next section). It also keeps activity coefficients constant, which affect formal electrode potentials.<sup>17</sup>

### c) Double Layer Effects.

The consideration of double layer effects was originally made by Frumkin.<sup>18</sup> The situation is sketched in Figure 4, where the metal/solution potential difference  $\Delta\phi$  has been broken down into several sections corresponding to the various layers of ions.

It is assumed that the electron transfer takes place when the reacting ion is positioned in the OHP. Two results follow. The first, apparent from the figure, is that the acting potential difference is not  $\Delta\phi$ , but only  $\Delta\phi - \Delta\phi_{\text{OHP}}$ . The second is that the electric field in the diffuse

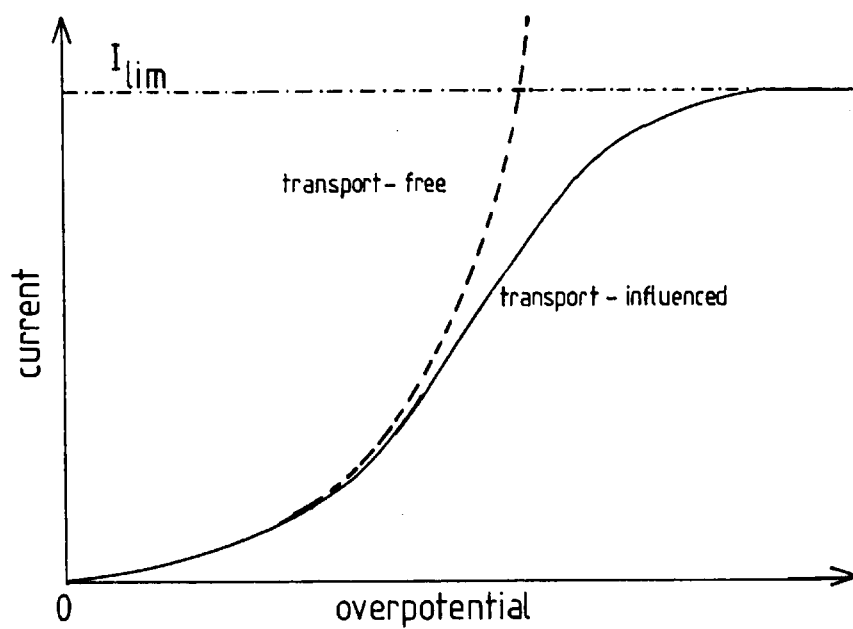


Figure I-3

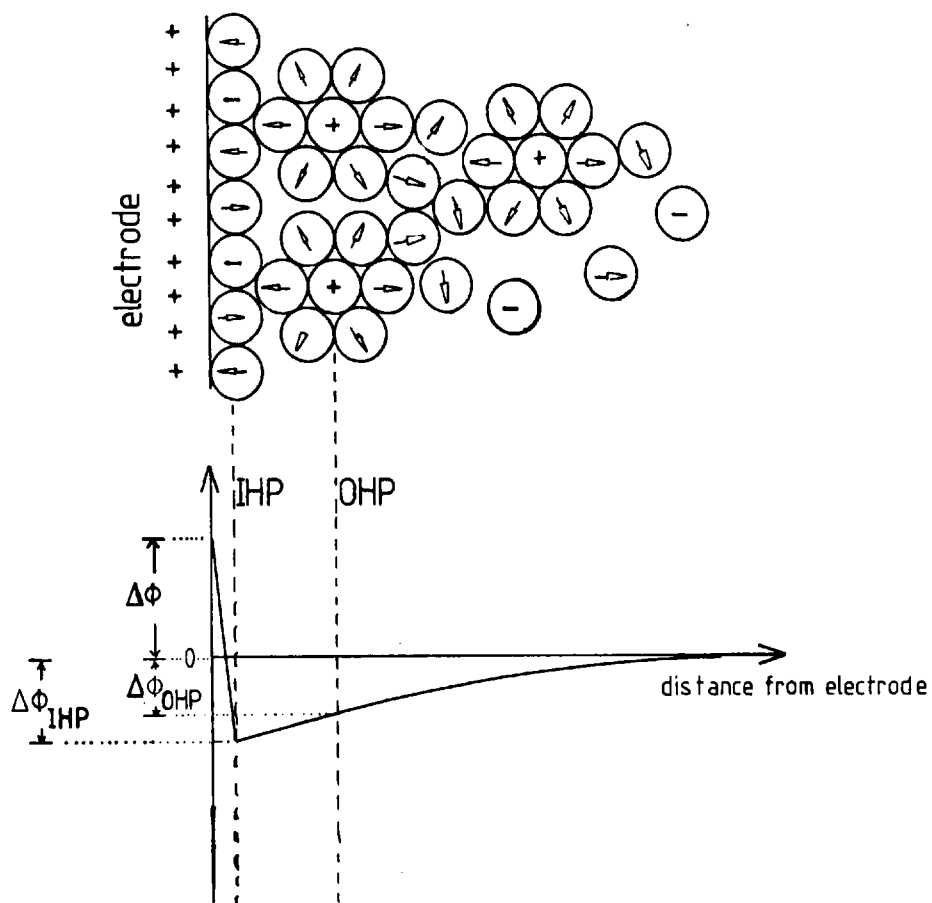


Figure I-4

double layer imparts to the charged species,  $Ox$ , an extra energy (compared to the bulk of the solution) which makes its concentration at the OHP depart from the bulk value. Thus, according to the Boltzmann distribution law:

$$C_{ox}^{OHP} = C_{ox} \exp(-Z_{ox} f \Delta\phi_{OHP}) \quad (I-50)$$

Eq. (16) must be modified accordingly to contain only the relevant  $\Delta\phi$  s and  $C$  s. Therefore (for the cathodic reaction only):

$$i = \vec{F}kC_{ox} \exp(-Z_{ox} f \Delta\phi_{OHP}) \cdot \exp[-\vec{\alpha}nf(\Delta\phi - \Delta\phi_{OHP})] \quad (I-51)$$

At the reversible potential,  $\Delta\phi_{OHP} = \Delta\phi_{OHP}^{rev}$ , because  $\Delta\phi_{OHP}$  depends on  $\Delta\phi$ . Thus,

$$i'_o = \vec{F}kC_{ox} \exp(-Z_{ox} f \Delta\phi_{OHP}^{rev}) \exp[-\vec{\alpha}nf(\Delta\phi_{rev} - \Delta\phi_{OHP}^{rev})] \quad (I-52)$$

Introducing (52) into (51);

$$i = i'_o \exp[(\vec{\alpha}n - Z_{ox})f(\Delta\phi_{OHP} - \Delta\phi_{OHP}^{rev})] \exp(-\vec{\alpha}nf\eta) \quad (I-53)$$

where  $i'_o$  is given by eq. (18). Generally  $\Delta\phi_{OHP}$  depends on  $\Delta\phi$  through complicated expressions involving the capacitance of the diffuse and compact double layers, as well as the dependence of the contact-adsorbed charge with the charge on the metal. In treatments like this, the validity of applying the equilibrium concepts used in double layer theory to the non-equilibrium process of charge transfer must be considered. Double layer effects are likely to arise in dilute electrolyte solutions where the diffuse layer is well developed, but in concentrated supporting electrolyte, the diffuse layer is almost completely squeezed against the OHP, which reduces the double layer effects. Even in those solutions, however, if the reacting ion is large, e.g., ferricyanide, this creates a new plane further into the solution than the OHP of the supporting electrolyte. This introduces the need for certain corrections, which may, however, be difficult to evaluate numerically.

d) Adsorption.

Adsorption on the electrode is an important and widespread phenomenon. Two general situations may be considered: adsorption of participants or intermediates in electrochemical reactions, and adsorption of foreign (often organic) electroinactive substances which may affect the kinetics of electrode reactions. In the former case, it is difficult to introduce adsorption in a general scheme like eqs. (21) since adsorbed intermediates may react to give new adsorbed substances; simultaneous discharge from species in the solution and combination with adsorbates may occur too. Strong adsorption of a reactant may speed the electron transfer step because closer contact with the electrode must greatly increase the probability of electron tunnelling, but too strong an adsorption of the product may block the electrode, thus decreasing the rate of the reaction. Where adsorption is present, the reaction usually presents more than average sensitivity to the structure of the electrode surface. A brief account will be given of the kind of mathematical modelling normally used.<sup>17b</sup> Let us assume that reaction (7) proceeds through the following sequence:



where the subscript S means an adsorbed chemical. If the desorption step is rate-determining the current is given by:

$$i = fk\theta \quad (\text{I-55})$$

where  $\theta$  is the degree of coverage by Red. If (54a) is very fast, then by the assumption of equilibrium the forward and backward electronation rates must be equal:

$$\vec{k}(1-\theta)C_{ox} \exp(-\alpha f \Delta \phi) = \hat{k} \theta \exp[(1-\alpha) f \Delta \phi] \quad (I-56)$$

The term  $(1-\theta)$  arises because Ox can only discharge on the part of the surface not yet covered by Red. From eq. (56) the Frumkin adsorption isotherm is obtained:

$$\theta/(1-\theta) = K C_{ox} \exp(-f \Delta \phi) \quad (I-57)$$

where the adsorption equilibrium constant K is given by:

$$K = \vec{k}/\hat{k} = K_o \exp(-g\theta/RT) \quad (I-58)$$

Here K has been expressed under the Temkin condition of linear increase in the standard free energy of adsorption with coverage. The parameter, g, is related to lateral interactions between the adsorbed Red molecules. If the molecules attract each other laterally in the monolayer, then K increases with  $\theta$ . This would be reflected in a negative g. In the opposite case, lateral repulsions, K must decrease with  $\theta$  to reduce the "loathed" crowding at high coverage and g is positive. The Langmuir isotherm is obtained for  $g = 0$  at constant potential. Introducing (57) into (55):

$$i = \frac{kK C_{ox} \exp(-f \Delta \phi)}{1 + KC_{ox} \exp(-f \Delta \phi)} \quad (I-59)$$

The Tafel plots will thus fail to produce straight lines. If the electron transfer step is the slow one,  $\theta$  is bound to be small and independent of  $\Delta \phi$ , and its effects on the kinetics will be small too.

#### e) The Transfer Coefficient, $\alpha$ .

According to Figure 2, the transfer coefficient represents the fraction of the applied electrical free energy that is used to change the height of the activation barrier. Or:

$$\alpha = [ \partial \bar{\Delta G}^\ddagger / \partial (nF\Delta\phi) ] \quad (\text{I-60})$$

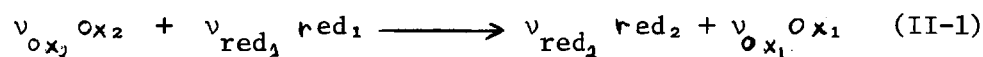
$\alpha$  must have a value between zero and one. The actual value is determined by the relative slopes of the free energy curves at the intersection point. If reactants and products are chemically very similar their curves will be also of similar shape and slopes. Under these conditions  $\alpha \approx 0.5$  and will be nearly independent of  $\Delta\phi$ .<sup>11e</sup> The latter indicates that the intersection occurs high in the branches of the curves where the slopes change less drastically. Thus, for high activation reactions (slow reactions),  $\alpha$  is nearly constant, while it changes with  $\Delta\phi$  for fast reactions which show a low activation energy so that the intersection takes place in the lower part of the curves. The exact dependence of  $\alpha$  on  $\Delta\phi$  depends on the theoretical treatment used to describe the free energy curves. Modern electron transfer theories<sup>15,19,20</sup> emphasise the rôle of the solvation sheath around the ion in bringing the electron energy levels of the reactant to an intermediate stage at which an electron in the metal with the same energy can tunnel through the double layer to the ion. The theory at present only applies to reactions not involving breaking or forming of chemical bonds or strong changes in metal-ligand interactions during the electron transfer. Verification of the theory is being currently attempted in two main lines of research: correlation between rate constants for homogeneous electron transfer reactions and heterogeneous electrochemical rate constants,<sup>21</sup> and in the measurement of  $\alpha$  as a function of potential.<sup>22</sup> Although changes in  $\alpha$  have been measured, the cause of their variation is not undisputed, double layer effects being the most serious correction that need to be applied. In any case, these changes are small and within the experimental uncertainties in the ordinary conditions of most electrochemical work, other reasons for changes in the slopes of the Tafel plots being more important.

## CHAPTER TWO

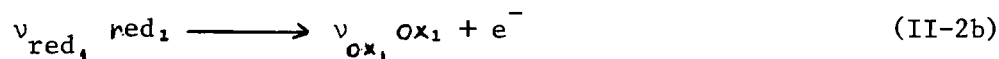
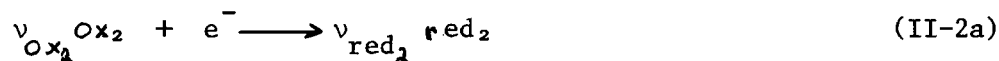
### THE HETEROGENEOUS CATALYSIS OF REDOX REACTIONS

#### II.1. Introduction.

Figure 1 illustrates the additivity principle of Wagner and Traud,<sup>3</sup> as explained in Section I.1. The same figure may serve to illustrate either the dissolution of a metal in acid or the reaction between an oxidant and a reductant in the presence of an inert electrode. In both cases the net transformation:



is decomposed into two partial reactions of concerted occurrence:



(It is convenient to represent these as one electron reactions which means that the stoichiometric coefficients  $v'_j$  have been divided by  $n_j$ ; thus  $v_1 = v'_1/n_1$ , and  $v_2 = v'_2/n_2$ ). The resultant  $i$ - $E$  curve is displayed as a broken line in Figure 1. The salient feature of this type of chemical process is that at  $E = E_m$ , although the net current is zero, a net chemical change is occurring, which does not necessarily require physical adsorption of the reactants onto the catalyst. It was a major advance to have realised that the dissolution process corresponds to that single point in the net curve. The extension of the principle to the catalysis of redox reactions by Spiro<sup>2</sup> seems a natural one, and a useful one too because it places the phenomenon in the context of hetero-

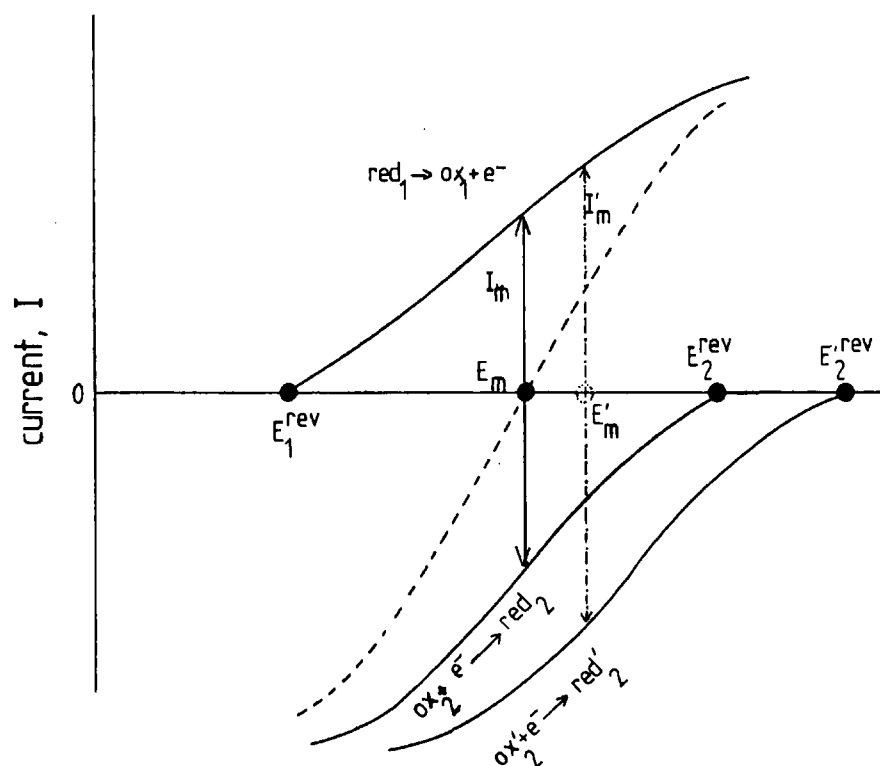


Figure II-1

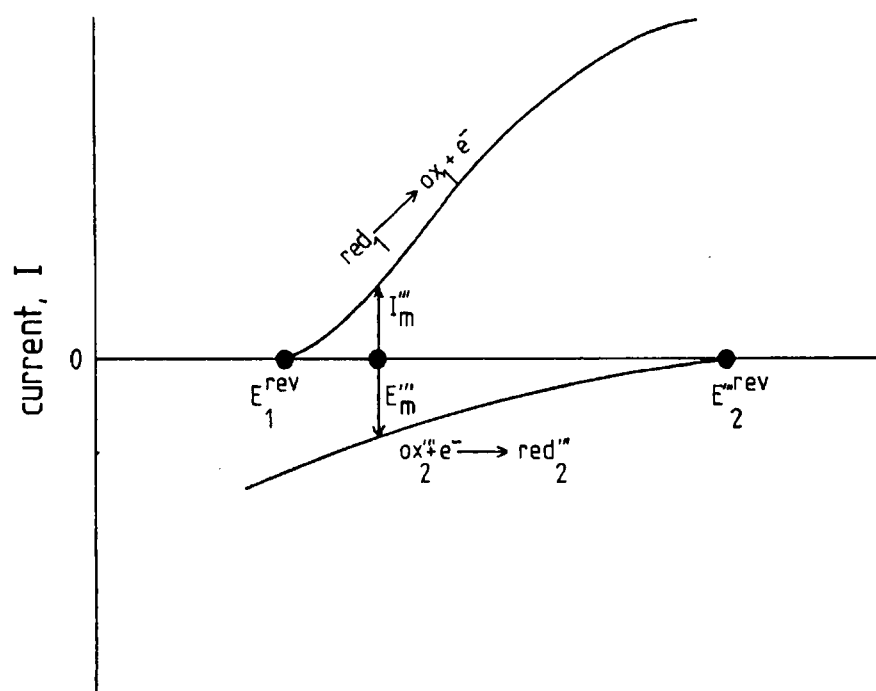


Figure II-2

geneous catalysis where it can be used by researchers who are not necessarily acquainted with electrode kinetics. Of course, when two electroactive species are present at an electrode and specially if both became adsorbed, interactions other than electron transfer through the metal are conceivable, like direct electron transfer between adsorbed species or the appearance of new reaction paths. A 100% electrochemical mechanism cannot therefore be taken for granted.

Spiro and Ravnö<sup>1</sup> have pointed out qualitative conditions in which catalysis by the electrochemical mechanism could be expected. With reference to Figure 1 a large positive difference  $E_2^O - E_1^O$  would cause the curves to intercept at higher current values. The effect is enhanced if the reactant/product ratio is kept as high as possible. In the case of a highly irreversible couple  $ox^{III}/red^{III}$  which possesses a small  $i_0$  value the mixture current is small and so is the catalytic rate. A survey<sup>1</sup> of over 80 solution reactions in the presence of platinum bear out this theory.

In their original paper<sup>3</sup> Wagner and Traud pointed out some experimental procedures that proved helpful in their study of zinc amalgam dissolution in acid, and the reduction by  $H_2$  of oxygen,  $K_2S_2O_8$ ,  $H_3AsO_4$  and nitrophenol in the presence of platinised platinum.

a) The slope of the net polarisation curve is measured in the neighbourhood of  $E_m$ . If one of the couples is very reversible (say  $E_m \approx E_1^{rev}$ ) the mixture current is calculated according to the expression:

$$i_m \approx (E_1^{rev} - E_m) \left( \frac{\partial i}{\partial E} \right)_{E=E_m} \quad (II-3)$$

The calculated value can then be compared with the experimental rate of dissolution of the metal, or of consumption of a reactant  $dN/dt$  (in moles per unit time), according to

$$dN/dt = i_m / nF \quad (II-4)$$

If  $E_m$  does not fall too close to any of the  $E_j^{\text{rev}}$  the Tafel or the Butler-Volmer equations are used to derive a relation between  $dN/dt$  and  $(\partial i / \partial E)_{E=E_m}$ . Assuming first order dependence on reactants and products, the final expression is:

$$dN/dt = \frac{1}{nF} \left( \frac{\partial i}{\partial E} \right)_{E=E_m} / [\bar{\alpha}_1 + \bar{\alpha}_2 + B_1/(1-B_1) + 1/(1-B_2)] \quad (\text{II-5})$$

where

$$B_j = \exp[-(\bar{\alpha}_j + \bar{\alpha}_j') f \eta_j] \quad (\text{II-6})$$

The subscript  $j$  refers to the couple  $\text{ox}_j/\text{red}_j$ ;  $\eta_j$  is defined according to eq. (I-20) for each couple.

b) The potential of the mixed system can be forced (e.g., potentiostatically, or galvanostatically) to acquire the value  $E_1^{\text{rev}}$  or  $E_2^{\text{rev}}$  in which case the transformation rate for the couple concerned should cease, if only the electrochemical mechanism is operating.

The advantage of these methods is that the electrochemical measurements are performed at the mixed electrode, except in cases where eq. (5) is applied because some assumptions have to be made about the value of the  $\alpha$  values in the mixed system. In the second method, if the reversible potential being enforced happens to lie in the limiting current density region of the other couple, then any non-electrochemical surface reaction will disappear, as  $C_j^{\sigma} = 0$  for the species under limiting current situation, thus giving the impression that the electrochemical mechanism is being followed. It is conceivable in the catalytic situation that the  $E_j^{\text{rev}}$  might fall in a region where the catalyst ceases to be electrochemically inert, creating the possibility of more reactions between the components of the system. More generally, it could be said that since the concentrations of reactants and products are changing during the reaction, so do the values of  $E_m$  and  $E_j^{\text{rev}}$ .

An alternative experimental approach used by Spiro and Griffin<sup>4</sup> is that of obtaining the separate steady state  $i$ - $E$  curves of each couple, and comparing the resulting  $i_m$  and  $E_m$  with the experimental catalytic rate  $u_{cat}$  and with the catalyst potential  $E_{cat}$  at zero time. The same electrode surface, treated in identical ways, must be used in both sets of experiments. This approach gave surprisingly good results in the case of reaction (I-1) catalysed by platinum. It constitutes the basis of the theoretical treatment in the following sections in which expressions for  $i_m$  are obtained under several experimental conditions.

## II.2. Quantitative Model of the Catalytic Rate.

### a) Assumptions.

The catalytic rate  $v_{cat}$  is the value of the overall rate,  $v_{obs}$ , less the value of the rate  $v_{hom}$  in the absence of the catalyst:

$$v_{obs} = v_{cat} + v_{hom} \quad (II-7)$$

It will be assumed that  $v_{cat}$  and  $v_{hom}$  are independent of each other (but see Appendix 1). The relation between  $v_{cat}$  (in  $\text{mol l}^{-1} \text{min}^{-1}$ ) and the specific catalytic rate  $u_{cat}$  (in  $\text{mol per unit area per unit time}$ ) is

$$v_{cat} = Au_{cat} / V \quad (II-8)$$

$$\text{and } u_{cat} = i_m / F, \quad v_{cat} = Ai_m / FV \quad (II-9)$$

It will also be assumed that the whole of the catalyst surface area is available to the reactants. Therefore, it is immaterial to refer to current densities,  $i_m$ , or to net currents.  $i_m$  will be used all the time, but it will be made clear when net current is being referred to. The mixture current is given by the sum of the currents of the individual isolated couples. Positive sign will be given to both anodic and

cathodic currents. The catalyst is taken to be in the form of a rotating disk at which the Levich equation for the limiting current density applies<sup>23</sup>:

$$L_j = 0.620 \, n F D_j^{\frac{2}{3}} \nu^{-\frac{1}{6}} \omega^{\frac{1}{2}} C_j \quad (\text{II-10})$$

where  $n$  represents the number of electrons transferred,  $D_j$  is the diffusion coefficient,  $\nu$  is the kinematic viscosity of the solvent (= viscosity divided by the density),  $\omega$  is the angular velocity of the disk, and  $C_j$  is the bulk concentration of the species undergoing electron transfer. The mass transport rate constant  $k_j$  and the parameter,  $\sigma_j$  are defined by:

$$L_j = k_j C_j \quad (\text{II-11})$$

$$L_j = \sigma_j \omega^{\frac{1}{2}} C_j \quad (\text{II-12})$$

It follows from eq. (10) that

$$k_j = 0.620 \, n F D_j^{\frac{2}{3}} \nu^{-\frac{1}{6}} \omega^{\frac{1}{2}} \quad (\text{II-13})$$

and

$$\sigma_j = 0.620 \, n F D_j^{\frac{2}{3}} \nu^{-\frac{1}{6}} \quad (\text{II-14})$$

#### b) Case of Two Irreversible Couples.

This case has been considered by Spiro,<sup>5</sup> assuming that  $E_m$  lies in the Tafel region of each couple. If subscript 1 stands for the couple that undergoes a net oxidation and 2 for the one that undergoes a net reduction:

$$i_1 = i_{o1} \exp[(1-\alpha_1)Z_1 f(E-E_1^{\text{rev}})] \quad (\text{II-15a})$$

$$i_2 = i_{o2} \exp[-\alpha_2 Z_2 f(E-E_2^{\text{rev}})] \quad (\text{II-15b})$$

where  $Z_j$  is the number of electrons divided by the stoichiometric number and  $\alpha_j$  is the transfer coefficient of each couple. At the mixture potential,

$$E = E_m, i_1 = i_2 = i_m \quad (\text{II-16})$$

The expression for  $i_m$  obtained<sup>5</sup> was:

$$i_m = i_{001}^{r_1} i_{002}^{r_2} \exp[\alpha_2 Z_2 r_1 f(E_2^o - E_1^o)] \left( \prod_{j_1} C_{j_1}^{r_1 W_{j_1}^{\text{an}}} \right) \left( \prod_{j_2} C_{j_2}^{r_2 W_{j_2}^{\text{cath}}} \right) \quad (\text{II-17})$$

$$r_1 = \frac{(1-\alpha_1)Z_1}{(1-\alpha_1)Z_1 + \alpha_2 Z_2}, \quad r_2 = \frac{\alpha_2 Z_2}{(1-\alpha_1)Z_1 + \alpha_2 Z_2} \quad (\text{II-18})$$

$i_{00j}$  are the standard exchange current densities, and the  $W_j^T$  are the electrochemical reaction orders. Eq. (17) shows that the catalytic rate will be larger the larger  $E_2^o - E_1^o$  and the larger  $i_{00j}$ . Another feature is that since the  $r_j$  are in general fractional numbers, it follows that the reaction orders will not be in general whole numbers. Spiro has pointed out that this behaviour may give the superficial impression that reaction (1) proceeds through a Langmuir-Hinshelwood mechanism with  $\text{ox}_2$  and  $\text{red}_1$  adsorbed by Freundlich isotherms, the r.d.s. being the interaction between neighbouring adsorbed species.

b) Partial Control by Mass Transport to the Catalyst.

Using relations previously mentioned (Section I.5.a.), and assuming that only one reactant species\* is affected by mass transport, the following equations are obtained in the Tafel region:

$$i_m = (1 - i_m / L_{\text{red}_1})^{W_{\text{red}_1}} i_{01} \exp[(1-\alpha_1)Z_1 f(E_m - E_1^{\text{rev}})] \quad (\text{II-19a})$$

$$i_m = (1 - i_m / L_{\text{ox}_2})^{W_{\text{ox}_2}} i_{02} \exp[-\alpha_2 Z_2 f(E_m - E_2^{\text{rev}})] \quad (\text{II-19b})$$

(Thus, it is not necessary to specify the Tafel region in which the  $W_j$  s are being considered).

---

\* of each couple

In logarithmic form:

$$\ln i_m = \ln i_{o1} + W_{red_1} \ln(1 - i_m/L_{red_1}) + (1 - \alpha_1) Z_1 f(E_m - E_1^{rev}) \quad (II-20a)$$

$$\ln i_m = \ln i_{o1} + W_{ox_2} \ln(1 - i_m/L_{ox_2}) - \alpha_2 Z_2 f(E_m - E_2^{rev}) \quad (II-20b)$$

To eliminate  $E_m$ , multiply eq. (20a) by  $\alpha_2 Z_2$  and eq. (20b) by  $(1 - \alpha_1) Z_1$ , add them and divide by  $(1 - \alpha_1) Z_1 + \alpha_2 Z_2$  throughout:

$$\begin{aligned} \ln i_m = \ln(i_{o1}^{r_2} i_{o2}^{r_1}) + \ln[(1 - i_m/L_{red_1})^{r_2 W_{red_1}} (1 - i_m/L_{ox_2})^{r_1 W_{ox_2}}] + \\ + r_1 \alpha_2 Z_2 (E_2^{rev} - E_1^{rev}) \end{aligned} \quad (II-21)$$

Now, if  $\omega \rightarrow \infty$ , then  $L_j \rightarrow \infty$  and  $i_m \rightarrow i_{m,\infty}$ . Therefore:

$$\ln i_{m,\infty} = \ln(i_{o1}^{r_2} i_{o2}^{r_1}) + r_1 \alpha_2 Z_2 (E_2^{rev} - E_1^{rev}) \quad (II-22)$$

$i_{m,\infty}$  is given by Spiro's eq. (17). Eq. (22) is an equivalent expression.

Introducing eq. (22) into (21), rearranging and eliminating the logarithms:

$$\frac{i_m}{i_{m,\infty}} = \left(1 - \frac{i_m}{L_{red_1}}\right)^{r_2 W_{red_1}} \left(1 - \frac{i_m}{L_{ox_2}}\right)^{r_1 W_{ox_2}} \quad (II-23)$$

The binomial expansion can be applied to the bracketted terms. If

$i_m \ll L_j$  only the first order terms in  $i_m/L_j$  need be considered. Thus:

$$\boxed{\frac{1}{i_m} = \left( \frac{r_2 W_{red_1}}{\sigma_{red_1} C_{red_1}} + \frac{r_1 W_{ox_2}}{\sigma_{ox_2} C_{ox_2}} \right) \frac{1}{\omega^2} + \frac{1}{i_{m,\infty}}} \quad (II-24)$$

Eq. (24) allows the determination of the rate of the surface reaction by extrapolating plots of  $1/\omega_{cat}$  vs.  $1/\omega^2$  to infinite rotation speed.

Still under the assumption  $i_m/L_j \ll 1$ :

$$\ln(1-i_m/L_j) \approx -i_m/L_j \quad \text{--- (II-25)}$$

If eq. (25) is used in eqs. (20), and if (20b) is subtracted from (20a) to eliminate  $\ln i_m$ , then  $E_m$  can be solved for:

$$E_m = E_{m,\infty} + \frac{r_2}{\alpha_2 Z_2 f} \left( \frac{W_{red_1}}{\sigma_{red_1} C_{red_1}} - \frac{W_{ox_2}}{\sigma_{ox_2} C_{ox_2}} \right) \frac{i_m}{\omega^{\frac{1}{2}}} \quad \text{(II-26)}$$

where

$$E_{m,\infty} = r_1 E_1^{rev} + r_2 E_2^{rev} + \frac{r_2}{\alpha_2 Z_2 f} \ln \left( \frac{i_{o2}}{i_{o1}} \right) \quad \text{(II-27)}$$

According to eq. (26) the catalyst potential should vary linearly with the ratio  $u_{cat}/\omega^{\frac{1}{2}}$ , if the electrochemical mechanism is operating. The sign of the slope should be governed by the chosen experimental system. It is possible to obtain an explicit dependence of  $E_m$  on  $\omega$  by introducing expression (24) into (26) but the resulting equation is not easy to use in practice. However, solving for the ratio  $i_m/\omega^{\frac{1}{2}}$  in eq. (24) and introducing it into eq. (26) gives

$$E_m = E_{m,\infty} + (a/b)(1-i_m/i_{m,\infty}) \quad \text{(II-28)}$$

where  $a$  is the slope in eq. (26) and  $b$  the slope in eq. (24). Thus, a linear relationship between  $E_{cat}$  and  $u_{cat}$  as  $\omega$  is changed is predicted for the electrochemical model. Since eq. (28) is a relation between  $E_m$  and  $i_m$  it seems that compliance with it would provide important evidence in favour of the electrochemical mechanism, if the system satisfies all the assumptions made.

### Comments.

Equations similar to (24) are bound to appear also for any non-electrochemical mechanism subject to partial mass transport control. But the slope depends on the mechanism, and in the case of mixed potential control it could be compared with the slope calculated from the electrochemical kinetics of each couple. It is most useful to determine the value of the surface reaction rate  $u_{\text{cat},\infty}$  under different conditions.

It is very unlikely that  $E_m$  would follow eqs. (26) or (28) in the case of a non-electrochemical mechanism, and compliance with either of these equations would be strong evidence in favour of the mechanism.

Preliminary experimental tests should be made to check whether the assumptions of the model are correct. The limiting current densities of all the species should be compared with  $u_{\text{cat}}$ , i.e., the ratio  $F u_{\text{cat}} / L_j$  calculated to see whether the binomial expansion admits truncation after the second term.  $E_{\text{cat}}$  should lie in the Tafel region when the individual  $i$ - $E$  curves are obtained. However, since the reactions are usually carried out without the products being initially present, then  $E_1^{\text{rev}} \longrightarrow -\infty$  and  $E_2^{\text{rev}} \longrightarrow +\infty$  at zero time. Thus, as least in theory it is always true that a Tafel approximation can be used, since only the initial catalytic rate is being measured (because the slopes of the concentration vs. time plots are always extrapolated to zero time).

### c) Reversible Couples.

In this case the rate of diffusion across the diffusion layer is so slow compared with the kinetics of electron transfer, that the latter reactions are in equilibrium at the mixture potential (see Section I.5.a.). Thus, applying the Nernst equation to reaction (2):

$$E = E_1^0 + (1/f) \ln \left[ (C_{ox_1}^\sigma)^{v_{ox_1}} / (C_{red_1}^\sigma)^{v_{red_1}} \right] \quad (II-29a)$$

$$E = E_2^0 + (1/f) \ln \left[ (C_{ox_2}^\sigma)^{v_{ox_2}} / C_{red_2}^\sigma \right]^{v_{red_2}} \quad (II-29b)$$

where  $E$  is the electrode potential. At the mixture potential  $E = E_m$ ,  $i = i_m$ . Solving for the  $C_j^\sigma$  in eqs (I-42) and remembering that all the currents are positive:

$$E_m = E_1^0 + \frac{1}{f} \ln \left[ \frac{(1 + i_m/L_{ox_1})^{v_{ox_1}} C_{ox_1}^{v_{ox_1}}}{(1 - i_m/L_{red_1})^{v_{red_1}} C_{red_1}^{v_{red_1}}} \right] \quad (II-30a)$$

$$E_m = E_2^0 + \frac{1}{f} \ln \left[ \frac{(1 - i_m/L_{ox_2})^{v_{ox_2}} C_{ox_2}^{v_{ox_2}}}{(1 + i_m/L_{red_2})^{v_{red_2}} C_{red_2}^{v_{red_2}}} \right] \quad (II-30b)$$

Multiplying by  $f$ , re-arranging and taking exponentials:

$$\left[ \frac{C_{ox_2}^{v_{ox_2}} C_{red_1}^{v_{red_1}}}{C_{ox_1}^{v_{ox_1}} C_{red_2}^{v_{red_2}}} \right] \exp[f(E_2^0 - E_1^0)] = \frac{K}{Q} = h(i_m) \quad (II-31)$$

where  $K$  is the equilibrium constant and  $Q$  is the reaction quotient.

The function  $h(i_m)$  equals

$$h(i_m) = \left[ \frac{(1 + i_m/L_{ox_1})^{v_{ox_1}} (1 + i_m/L_{red_2})^{v_{red_2}}}{(1 - i_m/L_{ox_2})^{v_{ox_2}} (1 - i_m/L_{red_1})^{v_{red_1}}} \right] \quad (II-32)$$

If the measurement of  $u_{cat}$  is constrained to the initial rate,  $C_{ox_1}$  and  $C_{red_2}$  will both be very small. Then:

$$i_m/L_{ox_1} \gg 1, \text{ and } i_m/L_{red_2} \gg 1 \quad (II-33)$$

Furthermore, let us assume that for the reactants  $ox_2$  and  $red_1$ ,

$$i_m/L_{red_1} \ll 1, \text{ and } i_m/L_{ox_2} \ll 1 \quad (II-34)$$

Introducing (33) and (34) into (32):

$$h(i_m) \approx (i_m/L_{ox_1})^{v_{ox_1}} (i_m/L_{red_2})^{v_{red_2}} \quad (II-35)$$

Solving for  $i_m$ , taking (31) and (11) into account

$$i_m = \left[ k_{ox_1}^\phi v_{ox_1} k_{red_2}^\phi v_{red_2} C_{red_1}^\phi v_{red_1} C_{ox_2}^\phi v_{ox_2} \right] \exp[\phi f(E_2^0 - E_1^0)]$$

(II-36a)

where  $\phi = 1/(v_{ox_1} + v_{red_2})$

A less severe approximation is obtained if the denominator of  $h(i_m)$  is binomially expanded, neglecting all terms in  $i_m/L_j$  of order larger than unity. The resulting expression for  $i_m$  is:

$$1/i_m = 1/W + \phi(v_{ox_2}/L_{ox_2} + v_{red_1}/L_{red_1}) \quad (II-36b)$$

where  $W$  is the expression for  $i_m$  in eq. (36a).

Because of the definition of  $k_j$  in eq. (11), it follows that the net order in  $\omega^{\frac{1}{2}}$  is unity.

$$i_m = \left[ \sigma_{ox_1}^\phi v_{ox_1} \sigma_{red_2}^\phi v_{red_2} K^\phi C_{red_1}^\phi v_{red_1} C_{ox_2}^\phi v_{ox_2} \right] \omega^{\frac{1}{2}} \quad (II-37)$$

Therefore, a plot of  $i_m$  vs.  $\omega^{\frac{1}{2}}$  will be a straight line passing through the origin. The slope contains only transport and equilibrium parameters, so that the same expression could have been obtained if one had started from the equilibrium equation for reaction (1), regardless of the nature of the mechanism. In this case one must prove that the only equilibrium in existence is the electrochemical one, for example by obtaining the  $i$ - $E$  curves of the separate couples and showing that within experimental error  $u_{cat} \approx i_m/F$ , and  $E_{cat} \approx E_m$ . The effect of stirring on  $E_m$  should be tested too. In effect, according to eqs. (30) because  $i_m$  and  $L_j$  are both directly proportional to  $\omega^{\frac{1}{2}}$ ,  $E_m$  should be independent of  $\omega$ , other conditions being kept constant. The dependence of  $E_m$  on the concentration of the reactants can be tested too, although the analysis as given here may be under conditions that are too restrictive. Assuming eqs. (33), and also assuming that

$$i_m/L_{red_1} \approx 0, \text{ and } i_m/L_{ox_2} \approx 0 \quad (II-38)$$

then one obtains from eq. (30a):

$$E_m \approx E_1^0 + \frac{1}{f} \ln \left[ (i_m/k_{ox_2})^{v_{ox_2}} / C_{red_1}^{v_{red_1}} \right] \quad (II-39)$$

Introducing the expression for  $i_m$  in eq. (36):

$$E_m \propto \frac{1}{f} \ln \left( [C_{red_1}^{\phi_{red_1}} C_{ox_2}^{\phi_{ox_2}}]^{v_{ox_1}} / C_{red_1}^{v_{red_1}} \right) \quad (II-40)$$

Therefore,

$$\left( \frac{\partial E_m}{\partial \ln C_{red_1}} \right)_{C_{ox_2}} \approx (\phi_{ox_1} - 1) v_{red_1} / f \quad (II-41a)$$

$$\left( \frac{\partial E_m}{\partial \ln C_{ox_2}} \right)_{C_{red_1}} \approx \phi_{ox_1} v_{ox_2} / f \quad (II-41b)$$

Such an approach allowed Spiro et al.<sup>24</sup> to show that reaction (I-1) came to a rapid equilibrium on platinum electrodes, which suggested that the mechanism involved electron transfer through the metal. [The same result can be obtained starting with, e.g., (30b). However, in practice one must choose the equation that is more likely to satisfy condition (38), i.e., that in which the more concentrated reactant appears].

It is possible to obtain an explicit expression for  $E_m$ . Assuming eqs. (33) and (34), and multiplying eq. (30a) by  $1/v_{ox_1}$  and (30b) by  $1/v_{red_2}$ , adding them and multiplying by  $v_{ox_1} v_{red_2}$  throughout:

$$\begin{aligned}
 E_m = & \phi(v_{red_2} E_1^0 + v_{ox_1} E_2^0) + (\phi v_{ox_1} v_{ox_2} / f) \ln C_{ox_2} - (\phi v_{red_1} v_{red_2} / f) \ln C_{red_1} + \\
 & + (\phi v_{ox_1} v_{red_2} / f) \ln(k_{red_2} / k_{ox_1}) + (\phi v_{ox_1} v_{ox_2} / f) \ln(1 - i_m / L_{ox_2}) - \\
 & - (\phi v_{red_1} v_{red_2} / f) \ln(1 - i_m / L_{red_1})
 \end{aligned} \tag{II-42}$$

The situation described so far is valid only as long as the concentration of the products is kept low during the reaction. The kinetic law will now be analysed for high product concentrations.

Case 1: Consider first the addition of large amounts of the product  $red_2$ , while  $ox_1$  is kept low. The rate will be very much depressed so that:

$$i_m / L_{red_1} \ll 1, \text{ and } i_m / L_{ox_2} \ll 1 \tag{II-43}$$

also

$$i_m / L_{red_2} \ll 1 \tag{II-44}$$

Since the other product  $ox_1$  is not initially present:

$$i_m / L_{ox_1} \gg 1 \quad (II-45)$$

Therefore,  $h(i_m)$ , eq. (32) becomes

$$h(i_m) \sim (i_m / L_{ox_1})^{v_{ox_1}} \quad (II-46)$$

Introducing eq. (46) into (31), and solving for  $i_m$ :

$$i_m = k_{ox_1} \left[ C_{ox_2}^{v_{ox_2}} C_{red_1}^{v_{red_1}} C_{red_2}^{-v_{red_2}} \right]^{1/v_{ox_1}} \exp[f(E_2^0 - E_1^0) / v_{ox_1}] \quad (II-47)$$

Case 2: Consider now a large addition of  $ox_1$  while  $red_2$  is kept low.

Eq. (43) still holds, but now

$$i_m / L_{ox_1} \ll 1, \text{ while } i_m / L_{red_2} \gg 1 \quad (II-48)$$

Therefore:

$$h(i_m) \sim (i_m / L_{red_2})^{v_{red_2}} \quad (II-49)$$

Therefore:

$$i_m = k_{red_2} \left[ C_{ox_2}^{v_{ox_2}} C_{red_1}^{v_{red_1}} C_{ox_1}^{-v_{ox_1}} \right]^{1/v_{red_2}} \exp[f(E_2^0 - E_1^0) / v_{red_2}] \quad (II-50)$$

Case 3: Both products  $ox_1$  and  $red_2$  are added in large quantities, but the concentration of one of them at least does not exceed the final equilibrium value in the bulk of the solution. Therefore:

$$i_m / L_j \ll 1 \quad (II-51)$$

for all  $j$ . Thus,  $h(i_m)$  can be expanded binomially, neglecting all terms of order larger than one in  $i_m/L_j$ , to yield

$$h(i_m) \approx 1 + i_m/L_0 \quad (\text{II-52})$$

where

$$1/L_0 = v_{ox_1}/L_{ox_1} + v_{ox_2}/L_{ox_2} + v_{red_1}/L_{red_1} + v_{red_2}/L_{red_2} \quad (\text{II-53})$$

Solving for  $i_m$  in eq. (31) gives

$$i_m = L_0 \left[ \frac{C_{ox_2}^{v_{ox_2}} C_{red_1}^{v_{red_1}}}{C_{red_2}^{v_{red_2}} C_{ox_1}^{v_{ox_1}}} \exp[f(E_2^0 - E_1^0)] - 1 \right] \quad (\text{II-54})$$

### Comments.

Two curious consequences follow from the addition of large amounts of one of the products: the rate becomes dependent on the concentration of that product, although it remains independent of the concentration of the other product, and the reaction orders of the reactants change. The rate constant also changes but the rate remains proportional to  $\omega^{\frac{1}{2}}$ . This has been summarised in Table 1.

It is also interesting to look at the mixture potential. At high  $red_2$  concentration (Case 1),  $E_m$  from eq. (30a) is:

$$E_m = E_1^0 + \frac{v_{ox_1}}{f} \ln[(i_m/k_{ox_1})/C_{red_1}^{v_{red_1}}/v_{ox_1}] \quad (\text{II-55a})$$

For Case 2:

$$E_m = E_2^0 - \frac{v_{red_2}}{f} \ln[(i_m/k_{red_2})/C_{ox_2}^{v_{ox_2}}/v_{red_2}] \quad (\text{II-55b})$$

Therefore  $E_m$  and  $i_m$  appear in a Tafel-like logarithmic relation. Alternatively, one could insert the expression of  $i_m$  in eq. (47) into eq. (55a), and that from eq. (50) into (55b), thus providing the dependence between

$E_m$  and  $C_j$ . The study of the dependence of  $E_m$  and  $i_m$  on the  $C_j$  in these limiting conditions provides further evidence of the operation of the electrochemical mechanism.

TABLE II-1. KINETIC PARAMETERS PREDICTED FOR TOTAL MASS TRANSPORT CONTROL.

| Condition              | Reaction orders w.r.t.                  |                                          |                               |                               | Rate Constant                                        |
|------------------------|-----------------------------------------|------------------------------------------|-------------------------------|-------------------------------|------------------------------------------------------|
|                        | <u>Reactants</u>                        |                                          | <u>Products</u>               |                               |                                                      |
|                        | ox <sub>2</sub>                         | red <sub>1</sub>                         | red <sub>2</sub>              | ox <sub>1</sub>               |                                                      |
| No Added Product       | $\frac{v_{ox_2}}{v_{ox_1} + v_{red_2}}$ | $\frac{v_{red_1}}{v_{ox_1} + v_{red_2}}$ | 0                             | 0                             | $(k_{ox_1}^{v_{ox_1}} k_{red_2}^{v_{red_2}} K)^\phi$ |
| Added red <sub>2</sub> | $\frac{v_{ox_2}}{v_{ox_1}}$             | $\frac{v_{red_1}}{v_{ox_1}}$             | $-\frac{v_{red_2}}{v_{ox_1}}$ | 0                             | $k_{ox_1} K^{1/v_{ox_1}}$                            |
| Added ox <sub>1</sub>  | $\frac{v_{ox_2}}{v_{red_2}}$            | $\frac{v_{red_1}}{v_{red_2}}$            | 0                             | $-\frac{v_{ox_1}}{v_{red_2}}$ | $k_{red_2} K^{1/v_{red_2}}$                          |

A minor point should be mentioned here. It is that  $E_m$  is not the same as the final potential that would be reached when the reaction reaches equilibrium in the bulk of the solution too. The reason is that the surface concentrations are dictated partly by the rate of mass transport. Thus, for example, if one starts with zero initial concentration of products, their relative surface concentration at any given time

$C_{red_2}^\sigma / C_{ox_1}^\sigma$  is not  $v_{red_2} / v_{ox_1}$ , but  $[(1 + i_m / L_{red_2}) / (1 + i_m / L_{ox_1})] v_{red_2} / v_{ox_1}$ .

### Limiting Current Region.

This situation has been discussed by Spiro.<sup>5</sup> It arises when the mixture potential is in the limiting current region of one of the couples.

The rate is then given by the Levich equation (10). The main features of the catalytic rate are:  
 (i) linear dependence of  $u_{\text{cat}}$  on  $\omega^{\frac{1}{2}}$ ; (ii) first order dependence of the rate on the concentration of the transport-limited reactant;  
 (iii) independence on the concentration of the other reactant. Such behaviour would add value to the hypothesis of an electrochemical mechanism. The ideal proof would lie in obtaining the full  $i$ - $E$  curve of one of the reactants from  $i_m$ - $E_m$  data alone, by continuous variation of the concentration of the other reactant. This curve should coincide with the electrochemical  $i$ - $E$  curve.

### e) Suggested Tests for the Electrochemical Mechanism.

Some simple qualitative tests could be performed. Catalysis should be observed if each couple in turn is replaced by another couple known to indulge in the electrochemical mechanism with other reaction partners. The substitute couple should be similar to the one replaced in  $i_0$  and  $E^0$  values. The rationale for this test is that the electrochemical mechanism does not require interactions between the reactants other than the ability to receive and donate electrons to an electrode.

The electrochemical mechanism can be discarded if polarisation of the catalyst a few millivolts away from  $E_m$  produces no appreciable effect on the rate at which product is formed. However, polarisation may alter the surface activity of electrochemically active participants, even in the absence of an electrochemical reaction pathway, which would then produce changes in the rate. For example, many liquid phase catalytic hydrogenation reactions on platinum involve only chemical interactions

between the adsorbed organic stuff and H-atoms, the catalyst potential being close to  $E_{H_2/H}^{rev}$ . Anodic polarisation would probably decrease the H-atom coverage, hence the rate; the effect of cathodic polarisation would depend on whether the increased coverage actually displaces the organic adsorbate, or drives  $\theta_H$  to more favourable values.

f) Final Comments.

There are some problems regarding the use of Butler-Volmer equation in Section II.2.a and b as follows:

Eqs. (15) or (19) describe the initial stages of the reaction, before the back reaction becomes significant enough due to accumulation of products. It is assumed that the products do not intervene in the forward electron rates [eqs. (2)]. Extrapolation to zero time yields the product-free initial rate, if no product was deliberately added. But at zero time the  $E_j^{rev}$  values are not defined, according to eq. (I-9). Therefore, the  $i_{0j}$  are also undefined and meaningless. To overcome the problem one could initially add minute amounts of the products to the reaction mixture (thus providing a token answer) and in practice such amounts are likely to be present as impurities; but it would not dispel doubts about the behaviour of the system as these amounts are reduced to zero.

An unequivocal definition of  $i_m$  and  $E_m$  is provided by the Butler-Volmer equations:

$$i_m = \overleftarrow{Fk_1}[\text{red}_1]_{\sigma}^{W_{\text{red}_1}} \exp[(1-\alpha_1)Z_1 f E_m] - \overrightarrow{Fk_1}[\text{ox}_1]_{\sigma}^{W_{\text{ox}_1}} \exp(-\alpha_1 Z_1 f E_m) \quad (\text{II-56a})$$

$$i_m = \overrightarrow{Fk_2}[\text{ox}_2]_{\sigma}^{W_{\text{ox}_2}} \exp(-\alpha_2 Z_2 f E_m) - \overleftarrow{Fk_2}[\text{red}_2]_{\sigma}^{W_{\text{red}_2}} \exp[(1-\alpha_2)Z_2 f E_m] \quad (\text{II-56b})$$

Eqs. (56) provide a set of two equations with two unknowns ( $i_m$ , and  $E_m$ ), which define these quantities in terms of all the other parameters at any time.  $i_m$  is also contained in the  $C_j^\sigma$  terms if there is partial control by mass transport. Eqs. (56) can be cast in a useful form.

If reaction (1) is allowed to reach equilibrium ( $t = \infty$ ):

$$E_m = \hat{E}, \quad \text{and} \quad C_j^\sigma = \hat{C}_j, \quad i_m = 0 \quad (\text{II-57})$$

The cap indicates that equilibrium quantities are being considered. The equilibrium exchange current densities  $\hat{i}_{oj}$  are:

$$\hat{i}_{o1} = \vec{Fk}_1 [\hat{red}_1]^{W_{red1}} \exp[(1-\alpha_1)Z_1 f \hat{E}] = \vec{Fk}_1 [\hat{ox}_1]^{W_{ox1}} \exp(-\alpha_1 Z_1 f \hat{E}) \quad (\text{II-58a})$$

$$\hat{i}_{o2} = \vec{Fk}_2 [\hat{ox}_2]^{W_{ox2}} \exp(-\alpha_2 Z_2 f \hat{E}) = \vec{Fk}_2 [\hat{red}_2]^{W_{red2}} \exp[(1-\alpha_2)Z_2 f \hat{E}] \quad (\text{II-58b})$$

Introducing these expressions into eqs. (56):

$$i_m = \hat{i}_{o1} [\beta_{red1} \exp[(1-\alpha_1)Z_1 f \Delta E] - \beta_{ox1} \exp(-\alpha_1 Z_1 f \Delta E)] \quad (\text{II-59a})$$

$$i_m = \hat{i}_{o2} [\beta_{ox2} \exp(-\alpha_2 Z_2 f \Delta E) - \beta_{red2} \exp[(1-\alpha_2)Z_2 f \Delta E]] \quad (\text{II-59b})$$

$$\Delta E = E_m - \hat{E}; \quad \beta_j = (C_j^\sigma / \hat{C}_j)^{W_j} \quad (\text{II-60})$$

Both couples may be represented in terms of a single "over-potential",  $\Delta E$ , and  $\hat{i}_{oj}$  values which are constant in time, although all of the  $C_j$  vary during the reaction. This should be an advantage for numerical calculations. Only the  $\beta_j$  and  $\Delta E$  (and of course,  $i_m$ ) are time dependent.

Expressions (59) should also facilitate quantitative consideration of the latest stages of the reaction, because as  $\Delta E$  approaches zero the exponential terms can be linearised.

Eqs. (59) are only a different representation of the Butler-Volmer equation without the ambiguities contained in representations like eqs. (15) or (19). Identical results should arise from their application regarding the dependence of  $i_m$  and  $E_m$  on various experimental parameters.

## CHAPTER THREE

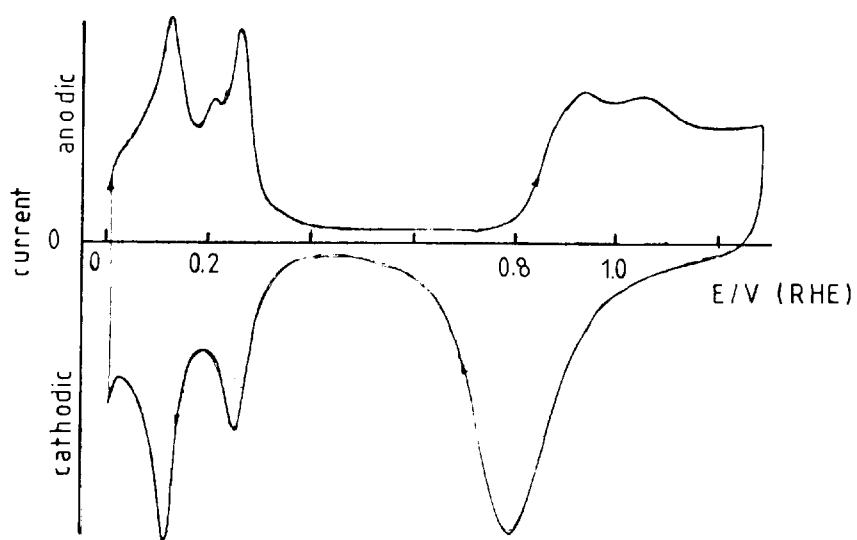
### ELECTROCHEMISTRY ON PLATINUM AND GLASSY CARBON

#### III.1. Introduction.

Part of this work is concerned with the effect that the nature of the catalyst and the state of its surface has on the rate of reaction (I-1). In this chapter the electrochemical properties of platinum and glassy carbon that are of interest for this work will be briefly reviewed: the formation and stability of surface films, and the electrode kinetics of the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  and  $\text{I}^-/\text{I}_2$  couples.

#### III.2. Surface Films on Platinum.

The presence of adsorbed oxygen and hydrogen can be revealed by cyclic voltammetry (see Section IV.2.b). Figure 1 is a typical cyclic voltammogram of platinum in 0.5 M  $\text{H}_2\text{SO}_4$ . Its main features have long since been explained.<sup>e.g., 25,112</sup> Starting from ca. zero volts in the anodic direction, the first three peaks correspond to the oxidation of previously adsorbed hydrogen, followed by the so called "double layer region" in which the low currents are due to double layer charging. In this potential region the surface is free both from adsorbed hydrogen and oxygen. At about 0.8 V the current rises again due to the adsorption of oxygen-containing species from the water to form a layer of so-called platinum oxides, a process which continues beyond 1.4 V. Oxygen evolution starts at about 1.5-1.6 V. There is a large degree of hysteresis between



Cyclic voltammogram.<sup>112</sup> Pt, 0.5 M  $\text{H}_2\text{SO}_4$ , 6 V/min, 25 °C

Figure III - 1

oxide formation and reduction. The latter only happens at  $\sim 0.8$  V after reversal of the sweep into the cathodic direction. The area under the oxide reduction peak (after correction for double layer charging current and IR distortions, see Section IV.3.b) is a useful measure of the amount of oxide formed during the anodic sweep. This peak overlaps with the double layer region, after which there appear the cathodic peaks corresponding to H-atom deposition from the solution.

The main point to observe from this is the wealth of different surface films to be obtained by just holding the potential of the Pt electrode at varying values in acid solution, and to point out the need of considering their possible influence on the catalytic properties of the metal towards redox reactions.

A considerable amount of information now exists regarding the mechanism of formation of the surface films both in acid and alkaline solutions. Hydrogen atoms appear to adsorb on the metal with varying degrees of bond strength, thus giving rise to the appearance of discrete adsorption/desorption peaks in the cyclic voltammogram.<sup>26</sup> About six different forms of adsorbed hydrogen have been observed.<sup>26</sup> They do not appear to be related to particular crystallographic orientations of the metal grains, as multiple adsorption/desorption peaks are observed with single crystal faces.<sup>27</sup> It is believed that the Pt-H bond is dipolar, with the negative end pointing towards the solution. The adsorption of anions tends to destabilise the H-layer, thus reducing the coverage of H atoms, while cations tend to stabilise it.<sup>28</sup> At high H coverages, some of the dipoles change their orientation.

The oxidation of platinum (and of other platinum metals and gold), although much studied, has again been recently investigated by Angerstein-Kosłowska, et al.<sup>29</sup> These workers propose an oxidation mechanisms common to all these metals, the differences between them being due to anion adsorption effects. According to them OH is first adsorbed at about 0.8 V, forming a monolayer at about 1.05 V. Reversibility of the layer decreases as it grows due to the stabilising effect of hydrogen bonding. At higher anodic potentials a place exchange between OH and Pt takes place with simultaneous oxidation to O species and thickening of the oxide film. Anion adsorption acts by displacing OH from their adsorption sites due to lateral repulsion and occupying adsorption sites of the OH species, thus causing them to be adsorbed at higher anodic potentials. This and lateral repulsion increase the rate of place exchange. The anion adsorption tends to stabilise the re-arranged layer, and to change the interfacial electrical field in a way that facilitates place exchange.

More recently, however, Bagotzky and Tarasevich<sup>30</sup> have suggested a model of oxygen adsorption that appears to differ from that of Angerstein-Kosłowska, et al.,<sup>29</sup> mainly in that it does not contemplate place exchange between Pt and O or OH species. Hysteresis in the cyclic voltammograms is due, according to this model, to change in the heat of adsorption of the adsorbed species, manifested through a change in the interaction parameter,  $g$ , in the adsorption isotherms (see Section I.3). One might venture to point out that since oxide grows on Pt, not only as a consequence of increased geometric coverage, but also because of some form of oxygen penetration into the crystal lattice, allowance must be made for this in any model. Both groups seem to agree that

increased irreversibility (hysteresis) of the oxide reduction peak, both with time and with an increase in anodic potential, indicates strengthening of the oxide layer.

In the present work, the platinum electrode was pre-conditioned in  $\text{H}_2\text{SO}_4$  and then transferred to another vessel for further electrochemistry or catalytic experiments (see Chapter VI). Therefore, it is of interest to consider what happens to the surface (whether it has been covered by an oxide layer, H-layer, or laid bare in the double layer region), first, upon returning the potential to open circuit; second, upon exposing the electrode to the air; and third, upon introducing it into the reaction mixture.

The H-layer may well be destroyed by reaction with adsorbed atmospheric oxygen to form water. It would then be replaced by a layer of weakly adsorbed oxygen, just as it would happen if the surface had been "cleaned" in the double layer region.

The fate of the oxide layer is more problematical. In the apparent absence of published data regarding the open circuit behaviour, the best guide would seem the Pourbaix diagram for platinum. However, no definite stoichiometry can be assigned to the surface oxide layer<sup>31</sup>; besides, the activity of surface compounds surely differs from that of the bulk material on which the Pourbaix diagrams are based. The fact that electrochemical oxide reduction is very irreversible would suggest that the oxide, once formed, will remain stable in the acid after the potential is returned to open circuit (in the absence of strong reducing agents like hydrogen gas). The same is even more true when the electrode is exposed to air or to the nearly neutral reaction mixtures. The point will be examined again in Chapter VII.

### III.3. Electrochemistry of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ and of $\text{I}^-/\text{I}_2(\text{I}_3^-)$ on Platinum.

a) The  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple has been investigated by a number of authors. Jahn and Vielstich<sup>32</sup> obtained values for the standard rate constant and transfer coefficient of  $0.05 \text{ cm s}^{-1}$  and 0.61, respectively in 1 M KCl at  $25^\circ\text{C}$ , using the RDE. Daum and Enke<sup>33</sup> have carried out a careful study using the current impulse technique, in 1 M KCl. The cathodic reaction is first order in ferricyanide and the anodic one also first order in ferrocyanide, in a concentration range of over 100-fold. On a reduced electrode (i.e., oxide-free) the standard rate constant is  $0.24 \text{ cm s}^{-1}$ , and  $0.028 \text{ cm s}^{-1}$  on an oxidised one. The transfer coefficient is close to 0.5. The activation energy of the exchange current density was  $3.49 \text{ Kcal mol}^{-1}$ , irrespective of the state of the surface. Daum and Enke have pointed out that their results indicate nothing other than a simple electron transfer step. In a later study Blaedel and Schieffer<sup>34</sup> using turbulent tubular electrodes have confirmed these results. Measurements of the reversible potential of this couple in solutions of varying concentration of potassium salts have led Hanania, et al.,<sup>35</sup> to conclude that there is a significant amount of ion pair formation between the cations in the solution and the ferr(i/o)cyanide species. This raises the question of identifying the species involved in charge transfer in the electrode kinetics, and in general in any reaction in which these species participate. Peter, et al.,<sup>36</sup> found that the cations influence the rate in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+, \text{Cs}^+$ . The activation energy of the electrochemical rate constants is independent of the concentration of the supporting electrolyte,

but the pre-exponential term in the Arrhenius equation varies linearly.\* They have, therefore, proposed that the activated complex is formed after one cation collides with an already cation-associated ferr(i/o)-cyanide molecule. These results were obtained on gold electrodes, but they are of obvious relevance to any electrode material at which this couple is studied. A complementary study on the effect of the anions of the supporting electrolyte has been done by Kulesza, Jedral and Galus<sup>37</sup> on platinum. At constant sodium salt concentration, the rate is increased in the order  $F^- < CNS^- < SO_4^{2-} < CH_3COO^- < ClO_4^- < PO_4^{3-} < NO_3^- < Cl^- < Br^-$ , but the increases are small and seem to be related to the increase in the formal potential of the couple and to the change in the potential of zero charge of the electrode. Thus, the anion effects do not appear to be specific to this couple.

It is convenient to point out that the standard rate constant for this couple is relatively large which makes it highly reversible. The study of its electrode kinetics is almost certainly bound to be complicated by mass transport if steady-state current voltage curves are used as a means of study.

Association with the cation may affect the limiting current density of ferr(i/o)cyanide due to an increase in the size of the electroactive species, which tends to reduce its diffusion coefficient according to the Stokes-Einstein equation:

$$D = kT/6\pi\eta r \quad (III-1)$$

where  $\eta$  is the viscosity of the solution and  $r$  is the radius of the hydrated ion pair. Müller and Sohr<sup>38</sup> obtained a straight line for plots

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\* with the cation concentration.

of  $D$  vs.  $1/r$  for the chloride salts of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ . The diffusion coefficients were obtained from the limiting current densities at a platinum RDE.

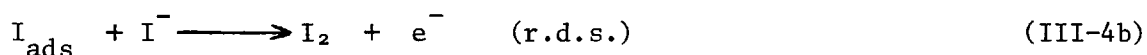
b) The kinetics of the  $\text{I}^-/\text{I}_3^-$  couple in  $\text{H}_2\text{SO}_4$  at platinum have been studied by Vetter<sup>39</sup> by the faradaic impedance method. By obtaining the concentration dependence of the anodic and cathodic current densities the following mechanism was proposed:



where step (III-2a) is rate determining. This mechanism gives rise to the observed concentration dependence of the current:

$$i = F\vec{k}_{\text{rds}} (K_1 K_2)^{\frac{1}{2}} [\text{I}_3^-]^{\frac{1}{2}} [\text{I}^-]^{-\frac{1}{2}} \exp(-\alpha fE) - F\overleftarrow{k}_{\text{rds}} [\text{I}^-] \exp[(1-\alpha)fE] \quad (\text{III-3})$$

where  $K_1$  is the equilibrium constant of step (2b) and  $K_2$  that of step (2c). This mechanism was confirmed by Newson and Riddiford by the RDE technique, who have also concluded that coverage by iodine atoms is insignificant.<sup>40</sup> Using the impedance method to determine the concentration dependence of the exchange current density, Dané, Janssen and Hoogland<sup>41</sup> have considered the sequence:



They concluded that (4b) is the r.d.s., and that the coverage by iodine is significant. The resulting rate law is given by:

$$i = F \bar{k} [I_3^-][I^-]^{-1} \exp(-\alpha fE) / [1 + K_{ads} [I^-] \exp(fE)] K - \\ - F \bar{k} [I^-] \exp[(1-\alpha)fE] / [1 + K^{-1} [I^-]^{-1} \exp(-fE)] \quad (III-5)$$

where  $K_{ads}$  is the ratio of the forward and backward rate constants of step (4a), and  $K$  is the equilibrium constant of (4c).

The electrodes were not prepared in the same way by all the authors. Vetter does not seem to have applied any particular pretreatment; Newson and Riddiford polished their RDE with  $Cr_2O_3$  prior to each run without subsequent conditioning, which rendered the surface probably oxide-free. Dané et al. state ambiguously that their electrode was subjected to alternate cathodic and anodic polarisation (and stored for two hours in solution of iodide and iodine). Barbasheva, et al.<sup>42</sup> and Povarov, et al.<sup>43</sup> who worked with an oxidised RDE obtained rate laws consistent with the mechanism of Dané et al.<sup>41</sup> They also agree on the presence of significant coverage by electrochemically active iodine. However, it is still necessary to reconcile these opinions on iodine coverage on oxidised platinum with the findings of Schwabe and Schwenke,<sup>44</sup> and of Hubbard, Osteryoung and Anson<sup>45</sup> that iodine and iodide do not seem to adsorb in significant amounts on oxidised platinum although they do so quite strongly on reduced platinum. Results on the isotopic exchange of iodide and iodine<sup>46</sup> point to the same conclusions.

Bejerano and Gileadi<sup>47</sup> have studied the formation of thick layers of iodine during the anodic oxidation of iodide. If the bulk concentration of iodide exceeds ca.  $5 \times 10^{-3}$  M, the iodine produced in the limiting current density region precipitates at the electrode surface because its concentration exceeds its solubility in the solution. The iodine film

hinders the transport of iodide and the limiting current falls to a lower, steady state value governed by the rate of dissolution of  $I_2$ , the transport of  $I_3^-$  and the transport of  $I^-$  across the film. The current is still proportional to  $\omega^{\frac{1}{2}}$  because the transport of iodide from the solution to the film is still controlled by mass transport.

#### III.4. Surface Films on Glassy Carbon.

Glassy carbon is an amorphous material obtained by calcination of organic material, mainly cellulose, which does not pass through a liquid or semi-liquid state.<sup>48a</sup> There are short range ordered regions of ribbon-like shapes with the graphite structure. These ribbons are randomly oriented and poorly stacked which leaves empty regions or pores, forming about 30% of the volume of glassy carbon. As a consequence its density is only about  $1.5 \text{ g cm}^{-3}$  compared with  $2.2 \text{ g cm}^{-3}$  for graphite.<sup>49</sup> Glassy carbon is an isotropic material with respect to several physical properties, in particular towards electrical conductivity, which is an advantage over graphite for electrochemical work. Its resistivity is about  $6 \times 10^{-3} \Omega \text{ cm}$ , higher than graphite ( $\sim 10^{-3} \Omega \text{ cm}$ ), and certainly much higher than that for metals ( $10^{-6} - 10^{-5} \Omega \text{ cm}$ ), which makes glassy carbon (and graphites in general) slightly semi-conducting. Indeed, the overlap between the conduction and valence bands in graphites is only about 0.6 eV.<sup>48b</sup> Therefore, one would expect smaller electrochemical rate constants on carbonaceous electrodes than on metals.<sup>48b</sup>

Hydrogen evolution is irreversible on glassy carbon, as on all carbonaceous materials, with  $6.8 \times 10^{-7} \text{ A cm}^{-2}$  exchange current density<sup>49</sup> (cf. ca.  $10^{-3} \text{ A cm}^{-2}$  on platinum<sup>50</sup>). Scarcity of adsorption sites from hydrogen atoms has been proposed to explain this.<sup>51</sup> On the anodic side,

oxygen evolution proceeds above the oxygen equilibrium potential with evolution of  $\text{CO}_2$ .<sup>48c</sup> Thus, glassy carbon does not become covered by oxide films in the anodic region. However, there is the possibility of creating chemical groups on the surface either by electrochemical or chemical treatment of the electrode. For example, Mamantov, et al.<sup>52</sup> report the existence of a reduction peak at  $\sim 0.35$  V (vs. SCE) in  $\text{H}_2\text{SO}_4$  on pyrolytic graphite upon application of a potential sweep. The peak height increases with an increase in the value of the potential at which the electrode is pre-anodised. Also, the cyclic voltammograms of graphite obtained by Majer, Veselý and Štulík<sup>53</sup> reveal an anodic wave with  $E_{p/2} \approx 0.9$  V (SCE), at pH 7.59. Taylor and Humffray<sup>54</sup> found that oxidising pre-treatment of their glassy carbon electrodes either with concentrated  $\text{H}_2\text{SO}_4$  or with chromic acid led to increased rate constants for the  $\text{Fe(II)/Fe(III)}$  and for the  $\text{Ce(III)/Ce(IV)}$  systems. The capacitance also rose from  $25 \mu\text{F cm}^{-2}$  for untreated electrodes to  $250 \mu\text{F cm}^{-2}$  for chromic acid-treated ones which pointed to an increase in the adsorbed charge or of charged groups at the surface. It seems that the presence of chemically active surface groups on carbonaceous materials is generally accepted<sup>48d</sup> although there is disagreement concerning their nature. Electrochemically, these groups are undoubtedly important. In molten salts they seem to be partly responsible for the currentless deposition of precious metals in solution in the melt<sup>55</sup> (a process which is probably under mixed potential control).

### III.5. Electrochemistry of $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ and $\text{I}^-/\text{I}_3^-$ on Glassy Carbon.

As with the previous section, evidence obtained on other carbonaceous materials will be considered too.

a) Taylor and Humffray<sup>54</sup> and Blaedel and Schieffer<sup>34</sup> have reported that the rate constant for the ferr(i/o)cyanide system is about 10 times lower on glassy carbon than on platinum. The former authors report cathodic and anodic transfer coefficients close to 0.5, while the latter often found  $\alpha_{\text{cath}} = 0.8$  and  $\alpha_{\text{an}} = 0.22$ . Blaedel and Schieffer attribute their results partly to adsorption of the electroactive species on their glassy carbon electrodes in accordance with the findings of other authors.<sup>56</sup> It should be pointed out, however, that in the analysis used Blaedel and Schieffer assume a first order dependence in the concentration of the electroactive species which was not found to be true on a graphite electrode by Sohr, Müller and Landsberg.<sup>56</sup> These authors reported that the order in ferricyanide for the reduction and in ferrocyanide for the oxidation was approximately 0.7. The anodic and cathodic transfer coefficient are both approximately equal to 0.2. The oxidation current of ferrocyanide also depends on the concentration of ferricyanide, which is the electrochemically inactive species. They have interpreted their results in terms of the formation of a complex between the oxidised and the reduced species, linked by a cation from the supporting electrolyte, which adsorbs on the electrode. The complex undergoes electron transfer more easily than either of the monomers. On graphite RDE (and also on the perovskite mixed oxide  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ ) Beley, Brenet and Chartier<sup>57</sup> found that preceding the charge transfer step there must be ion pair formation between a cation from the supporting electrolyte and a molecule either of ferro or ferricyanide, which subsequently adsorb on the electrode. Their conductimetric results also indicate that ferrocyanide forms ion pairs more easily, without

water molecules interposed between the partners; in the case of ferricyanide one water molecule separates them. However, they did not explore the possibility of complex formation. More recently, Müller<sup>58</sup> and Müller and Dietzsch<sup>59</sup> have re-interpreted their results by proposing that the one electron transfer occurs by two successive partial charge transfer steps, a mechanism that would be made possible by adsorption of the electroactive species. They have substantiated their claim experimentally by<sup>59</sup> showing that the exchange current density calculated from their mechanism agrees with the measured one on pyrolytic graphite over a  $10^4$ -fold range of the ratio  $[Ox]/[Red]$ . However, one would like to know whether this proposed mechanism is in agreement with the quantum properties of the electron or if it is consistent with transfer to an adsorbed complex.

b) Relatively little work has been carried out on the kinetics of the  $I^-/I_3^-$  couple on glassy carbon. There is some work on the overall electrode reaction in conditions of total mass transport control.<sup>60</sup> On flow-through graphite electrodes Wroblowa and Saunders<sup>61</sup> concluded that <sup>the</sup> mechanism proposed by Vetter on platinum<sup>49</sup> is also operative here (eqs. 2a-c), with low coverages by atomic iodine and transfer coefficients close to 0.5.

## CHAPTER FOUR

### TECHNIQUES AND INSTRUMENTATION

#### IV.1. The Rotating Disk Electrode (RDE).

##### a) The Ideal RDE.

In the present work the platinum and glassy carbon catalysts (used as electrodes too) have been fashioned as rotating disks, following the common practice in electrochemistry when mass transport limitations are present.

The theory of the RDE has been rigorously worked out by Levich<sup>62</sup> for a smooth disk of infinite radius rotating in an infinite volume of incompressible fluid, the disk arranged so that gravity acts perpendicularly to the disk, in steady state laminar flow. Figure 1 is a diagram of the ideal RDE, showing the velocity components  $V_y$ ,  $V_r$ , and  $V_\theta$  (perpendicular to the disk, in the direction of the disk radius, and perpendicular to the disk radius, respectively). Rotation causes the layers of fluid next to the disk to be dragged along and swept away along the radius. Since the fluid is incompressible (that is, unstretchable) mass moves in from the bulk towards the disk to replace what was swept away. The net effect of rotation is the sucking of fluid towards the disk and its throwing away along the radial coordinate in a swirling motion. Figure 2 shows the dimensionless velocity components as a function of the dimensionless distance from the disk surface,  $\gamma = (\omega/\nu)^{\frac{1}{2}}y$ . At  $\gamma = 3.6$  the  $y$  component reaches about 0.8 of its bulk value while the other two are nearly zero. Therefore, the distance  $\delta_p = 3.6(\nu/\omega)^{\frac{1}{2}}$  is defined

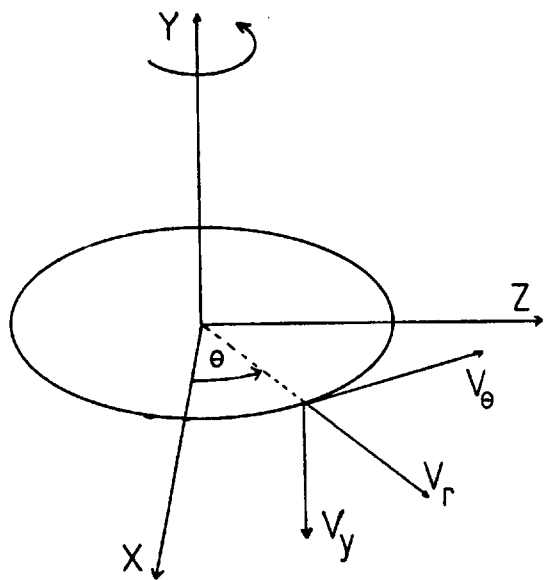


Figure IV-1

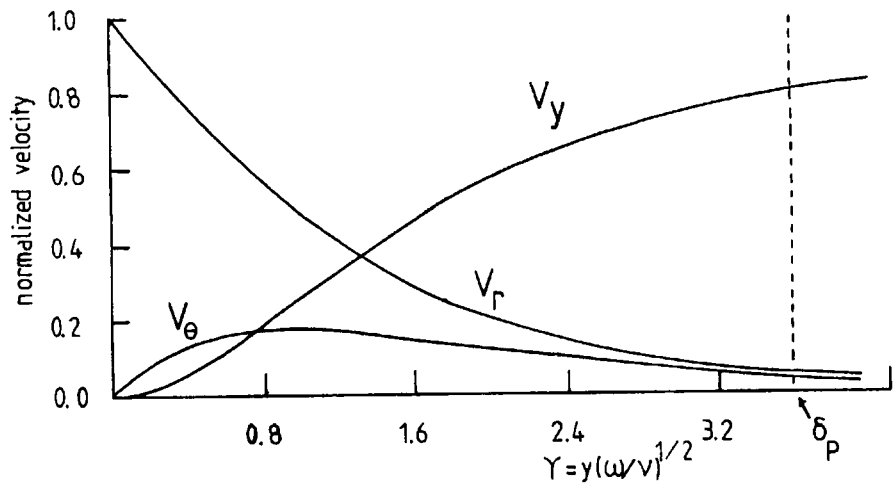


Figure IV-2

as the layer of liquid dragged by the disk, the Prandtl or momentum boundary layer.<sup>23</sup> If some of the material is consumed at the surface there will be a concentration difference between the bulk of the solution and the disk surface. However, Figure 2 suggests that a concentration gradient will only extend a short distance from the surface, inside  $\delta_p$ , due to mixing produced by considerable mass movements. Figure 3 shows the form of this gradient as a dotted line, and the equivalent Nernst diffusion layer of thickness  $\delta_N = 1.61 D_j^{\frac{1}{3}} \nu^{\frac{1}{6}} \omega^{-\frac{1}{2}}$ , through which the consumable species,  $j$ , may be considered to cross by diffusion alone. From this result the Levich equation (II-10) may be derived.

The ratio  $\delta_N/\delta_p = 0.42 D_j^{\frac{1}{3}} \nu^{-\frac{1}{3}}$  is independent of  $\omega$ . Its value is  $\sim 0.05$  if  $D_j \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , and  $\nu \sim 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ , which are typical values for aqueous solutions. This confirms that the Nernst diffusion layer is deep inside the momentum boundary layer.

Two points are worth noting. First, both  $\delta_p$  and  $\delta_N$  are independent of the radial distance (this is because  $V_Y$  is also independent of it). Thus, all of the disk surface is uniformly accessible to the reactants in the fluid, and the current density is uniform all over the disk. Secondly, the thickness of the diffusion layer,  $\delta_N$ , can be precisely and reproducibly controlled by the rotation speed of the disk. Also, once a steady state is established (which only takes less than a few seconds),  $\delta_N$  remains invariable with time. Abundant confirmation of Levich's theory exists in the literature.<sup>63</sup>

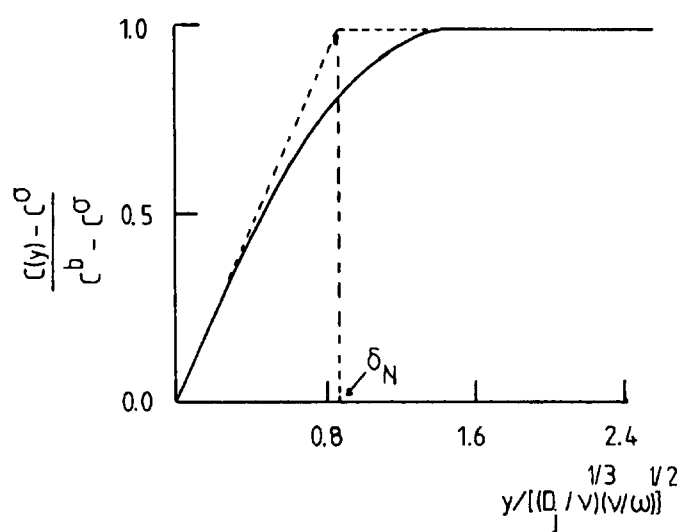


Figure IV-3

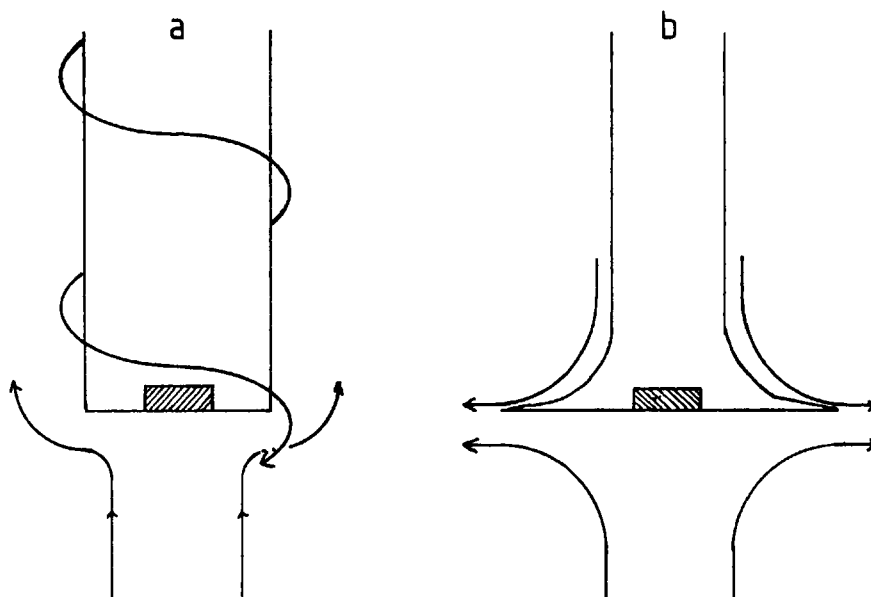


Figure IV-4

b) The Practical Rotating Disk Electrode.

In practice the RDE consists of polished disk of material embedded in an insulating mantle, as shown in Figure 4a and 4b. It is important to know how to design a RDE so that its behaviour is close to the Levich one.

One of the features of the Levich electrode is that mixing of the fluid on both sides of the disk is avoided by its being of infinite radius. This condition is best met<sup>23</sup> by mantle shapes as in Figure 4b, because mixing tends to occur in a horizontal plane away from the electroactive disk (cf. lines of flux in Figure 4). For this very reason the radius of the mantle should be large compared to the radius of the disk to allow the mantle to act as a "hydrodynamic insulator". Therefore, the "trumpet-shaped" form in Figure 4b was adopted in the present work.

Uniform accessibility of the surface is true only in an approximate sense. For a disk of finite radius, diffusion at the edge takes place not only from a distance perpendicular to the surface, but from the sides too. Therefore, the current density tends to be larger at the edge. The effect is minimised if  $\delta_N$  is much smaller than  $R$ , the radius of the disk, i.e.,

$$\delta_N/R \approx 0 \quad (\text{IV-1})$$

Another effect is connected with the solution having a finite resistance  $R_\Omega$ . There will be a potential drop between the RDE and the counter electrode, the equi-potential lines not being parallel to the surface (see Figure 5). In this situation the current distribution on the surface of the electroactive disk is<sup>64</sup>

$$i = 2vk/\pi(R^2-r^2)^{\frac{1}{2}} \quad (\text{IV-2})$$

## Primary Current Distribution

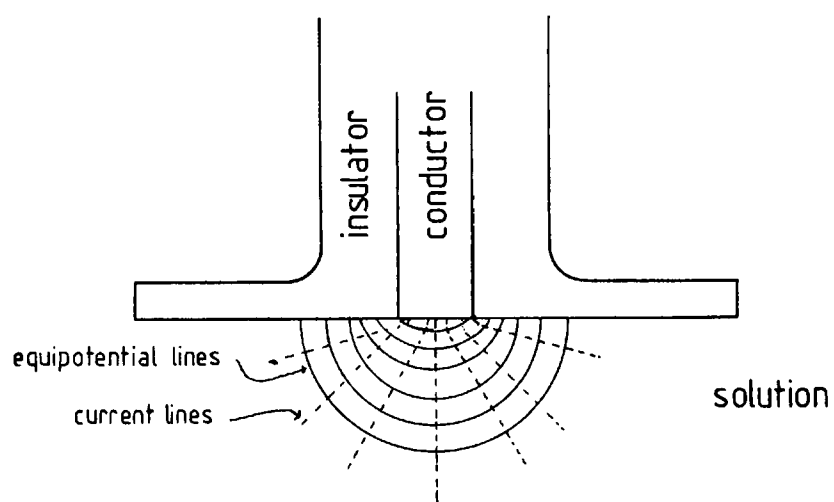


Figure IV-5

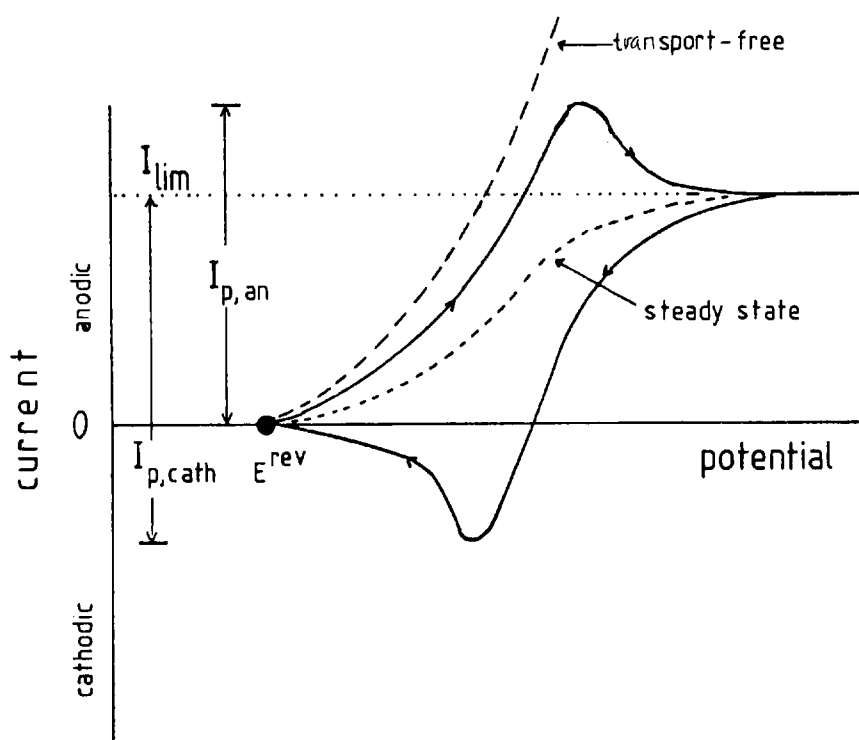


Figure IV-6

where  $v$  is the voltage difference between the RDE and the counter electrode,  $k$  is the conductivity of the solution, and  $r$  is the radial distance measured from the centre of the electrode. However, consideration of electrode kinetics produces a more uniform current distribution<sup>65</sup> if:

$$di/dE < 0.36 r k \quad (IV-3)$$

where  $di/dE$  is the slope of the  $i$ - $E$  curve. There is always uniform distribution at the limiting current since here  $di/dE = 0$ . In solutions of low conductivity or with small electrodes, one should avoid working near the half wave potential ( $E_{1/2}$ ) where  $di/dE$  is at its highest value.

It has been found that the flow changes from laminar to turbulent when the Reynolds number, defined for a rotating disk as  $Re = \omega R^2 / \nu$  reaches the value  $\sim 2 \times 10^5$ .<sup>63</sup> This sets an upper limit to the rotation speed  $\omega$ :

$$\omega_{\max} < \nu Re_{\text{crit.}} / r^2 \approx 2 \times 10^3 \text{ cm}^2 \text{ s}^{-1} / R^2 \quad (IV-4)$$

taking  $\nu$  as  $10^{-2} \text{ cm}^2 \text{ s}^{-1}$  for aqueous solutions. However, turbulence may start at values much lower than  $\omega_{\max}$  if the disk vibrates axially or laterally.

The lower rotation limit is dictated by the need to ensure that a natural convection does not become significant compared with forced convection. Authors,<sup>21,61</sup> use to express this condition as:

$$\delta_P / R \approx 0 \quad (IV-5)$$

It is not clear why this should be so. Indeed, for a Levich disk eq. (5) is true at all speeds, yet at low  $\omega$  values one would expect that convection

would affect the flow. Certainly, one must recognise the need to have a small  $\delta_p$  or  $\delta_N$ , i.e., more or less large  $\omega$  values, so that forced convection overshadows natural convection; but one would expect the corresponding condition to contain parameters characteristic of both transport processes.

The problem of mass transfer to an excentric disk electrode has been considered by Mohr and Newman.<sup>66</sup> It appears that excentricity is not important if the centre of the disk is off the centre of rotation by less than 64% of the radius length, which is a condition easily met by large electrodes. Smaller disks, say less than 1 mm in radius, are more prone to this abnormality since small absolute excentricities are easily of the same order of magnitude as the radius. It is certainly of no consequence for our large electrodes (> 2 cm radius).

c) Uses of the RDE.

The reasons why one would wish to use a RDE for electrochemical systems involving partial mass transport control are : (i) mass transport is rigorously described by the Levich theory; corrections due to non-ideality of practical disks can be worked out by more refined numerical calculations of the theory itself; (ii) introduction of mass transport into electrochemical equations is easy, and allows measurement of fast electrode processes, provided that the heterogeneous rate constant,  $k$ , is no larger than  $0.1D_j/\delta_N$ .<sup>67a</sup> (iii) The fact that the RDE is a flat disk embedded in a flat mantle allows it to be cleaned by polishing without changing the electrode geometry.

#### IV.2. Current-Voltage Curves.

The purpose of the recording of steady state  $i$ - $E$  curves in this work has been two-fold: to obtain the values of mixture current and potential in order to compare them with the corresponding catalytic values, and to try to obtain kinetic parameters of the couples to introduce into the corresponding theoretical rate expressions. Some cyclic voltammetry experiments have also been carried out to investigate (mainly qualitatively) the adsorption of reactants on the electrode. The basis of these techniques are explained here.

##### a) Steady State Recording.

This method simply consists of setting the potential of the electrode under study (working electrode, WE) at a fixed value against a reference electrode and noting the current when it has reached a constant steady state value. The entire  $i$ - $E$  curve is thus obtained point by point. If the electrode process is very reversible, and if a RDE is used, the steady state can be attained in a matter of seconds.

##### b) Potential Sweep Methods.

This technique exploits the time lag needed for the steady state to be reached by diffusion processes. When the potential of the electrode is scanned continuously<sup>67b</sup> the surface concentrations of the electroactive material adjust to a value dictated by the electrode kinetics. If the scan rate is fast enough the diffusion layer will not have time to adjust to its steady state value so that the rate of diffusion is larger than in the steady state. The current line in Figure 6 will be closer to the Butler-Volmer line, until it eventually overshoots the steady state limiting current.

However, as the scan progresses diffusion also progresses towards a steady state value, thus bringing down the current to its limiting value. If the scan is reversed at this point, the product (which is now present in large amounts at the surface) will begin to undergo the back reaction, bringing the current down until another peak is produced and the current finally takes the same value as at the beginning of the scan.

The technique is particularly useful for detecting reaction intermediates as they produce additional peaks in the voltammograms. Adsorptions and desorption peaks of electroactive species can be detected too. The main difference between them<sup>67c</sup> is that for reactions not involving adsorption,

$$i_p \propto v^{\frac{1}{2}} \quad (\text{IV-6})$$

and  $i_p \propto v \quad (\text{IV-7})$

for adsorbed reactants; where  $i_p$  is the peak current and  $v$  is the scan rate of the potential. For reversible, Nernstian, adsorptions it is also true that, at 25°C:

$$E_p - E_{p/2} = 90.6 \text{ mV}/n \quad (\text{IV-8})$$

where  $E_p$  is the peak potential and  $E_{p/2}$  is the potential for which  $i = i_p/2$ . The anodic and cathodic peaks should occur at the same values. For non-Nernstian reactions, the positions of the peaks become dependent on  $\ln v$ .

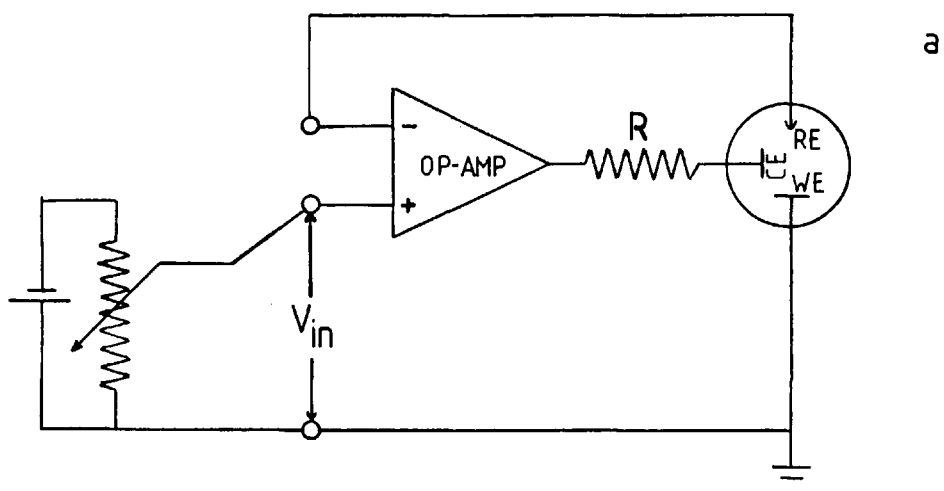
### IV.3. Electrochemical Instrumentation.

The basic modes of operation and desirable characteristics of the electrochemical equipment, including the electrochemical cell, are described in this section.

a) Potentiostat.

The potentiostat allows the potential of the WE to be kept constant against a reference electrode (RE).<sup>17d</sup> The current necessary to achieve this is passed between the WE and another auxiliary or counter electrode, (CE). The basic circuit of a potentiostat is shown in Figure 7a. Its basic element is the operational amplifier (labelled OP-AMP). It works by keeping the two inputs (labelled + and -) at the same potential. If they differ by an amount  $\Delta V$ , current flows from the output (apex opposite to input side) to restore  $\Delta V$  to zero. The input impedance is very large (infinite, for an ideal OP-AMP) so that all of the current flows between the output (CE) and earthed WE. The potential  $V_{in}$  fed to the + input is reproduced at the other input to which the RE is connected. From the connections it follows that the difference in potential between the WE and the RE is kept constant. The resistance  $R$  connected at the output allows measurement of the current through the voltage drop across it. The size of  $R$  has no influence upon the current because it depends only on the potential difference between the inputs. The high input resistance of the amplifier means that it draws negligible current (i.e., input bias current) from the cell both during operation and in standby.

For steady state work it is important that the input bias current (IBC) be of the order  $10^{-8}$  A or less, otherwise the WE and RE potential will be altered due to their intrinsic faradaic resistance. For the same reason any other measuring device like digital voltmeters (DVM) should have a very high input impedance. The maximum output voltage between WE and RE should be as high as possible, and so should the maximum output



$R$  = counting resistor

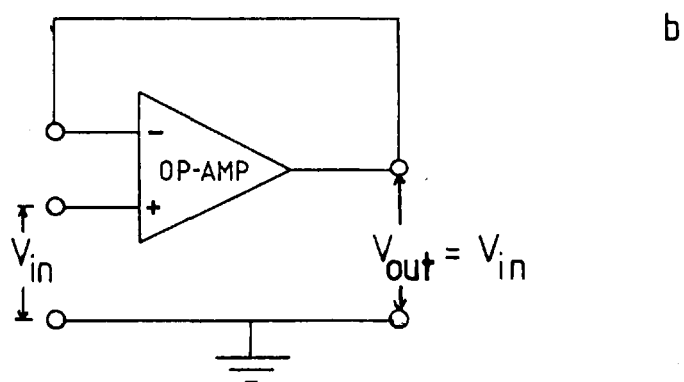


Figure IV-7

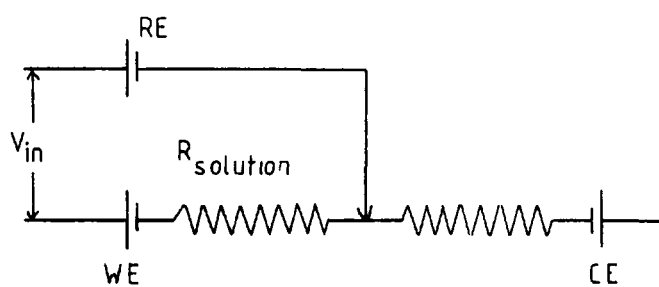


Figure IV-8

current. For non-steady-state work (in which  $V_{in}$  is replaced by , or fitted with, a time-varying source like a ramp generator for cyclic voltammetry, or a square-wave generator for pulse experiments), the potentiostat must be able to assume the programmed potential values at a rate at least as fast as the changes in the source output. This is measured by the rise time of the instrument.

Connection of low impedance recording devices to the inputs of the potentiostat should be made via a voltage follower (basic circuit in Figure 7b) which senses the measured voltage while at the same time it supplies the recorder with the input current it needs without altering the cell voltage.

b) The Uncompensated Solution Resistance.

Ideally, the reference electrode should be just outside the double layer of the WE. In practice the RE (or the tip of its Luggin capillary) has to be placed tenths of millimeters away.<sup>17e</sup> Figure 8 illustrates how the voltage difference controlled by the potentiostat includes a part due to the effective ohmic resistance  $R$  of the solution between the WE and the tip of the RE. Therefore:

$$V_{in} = E_{WE} - E_{RE} + IR \quad (IV-9)$$

where  $I$  is the net current. Or, in the more familiar overpotential notations:

$$\eta_{app} = \eta + IR \quad (IV-10)$$

Only a part  $\eta$  of the applied overvoltage is kinetically useful. The ohmic drop always causes  $\eta$  to be smaller than  $\eta_{app}$ , and the effect

is larger the larger the magnitude of  $I$ . The effects of the IR drop can be minimised by: (i) making the supporting electrolyte as concentrated as possible; (ii) placing the tip of the Luggin capillary as close as possible to the WE surface (but see next section); (iii) using low area electrodes, as this reduces the net current at a given overpotential. The effect on the steady state current-voltage curve of an irreversible couple is shown in Figure 9a for different values of  $R$ . A similar distortion pattern is found in cyclic voltammograms. When a sudden voltage step is applied to the WE, the effect of the ohmic drop is to cause a delay in the attainment of the new potential by the WE. This is illustrated in Figure 9b.<sup>67d</sup> In the absence of faradaic processes, the WE double layer can be regarded as a capacitor of fixed capacitance  $C$  in series with the solution resistance,  $R$ . Applying Kirchhoff's laws to the corresponding circuit (Figure 10), we have:

$$-V = IR + E_{WE} = Rdq/dt + q/C \quad (IV-10)$$

where  $V$  is the applied potential and  $q$  is the WE charge. This is a simple first order, constant coefficient, non-homogeneous differential equation. Its solution is,

$$E_{WE} = -V[1 - \exp(-t/RC)] \quad (IV-11)$$

$RC$  is the time constant of the circuit and allows quantitative assessment of the severity of the IR delay, if  $R$  and  $C$  are known or can be estimated. If the rate constant,  $k$ , of the electrode process studied can be estimated, then the condition

$$\tau \ll RC \ll 0.69/k \quad (IV-12)$$

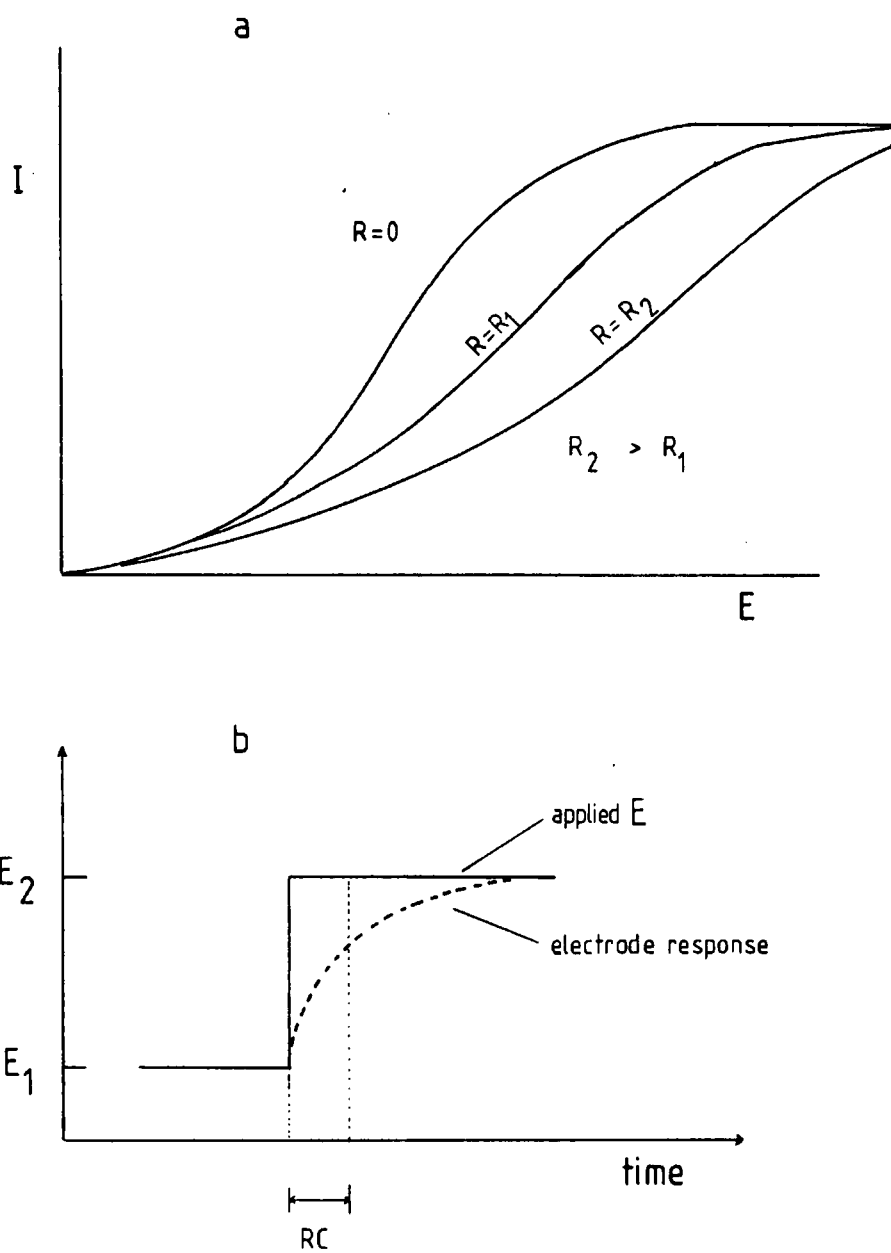


Figure IV-9

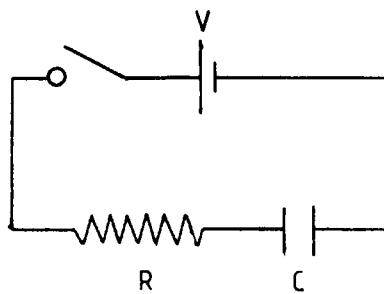


Figure IV-10

must be fulfilled (if  $k$  is a first order rate constant), where  $\tau$  is the rise time of the potentiostat, or the slewing rate multiplied by the total applied potential.

c) Cell Design.

Some general design factors common to all electrochemical cells are:

- 1) The reference electrode compartment must be fitted with a Luggin capillary whose tip should be positioned close to the WE surface. The distance from the WE should not be less than  $2\phi^{1/3}$  ( $\phi$  = outer diameter of capillary tip) as a screening effect of the electrode potential would be effected; larger distances produce larger IR drops, so this is an optimum distance. If the WE is a RDE the capillary must be placed vertically beneath the disk, pointing to the centre as this arrangement produces the least disturbance of the flow pattern.<sup>23</sup>
- 2) It is desirable in principle to have the three electrodes in separate compartments to avoid contamination of the WE with the reaction products of the CE and with the material of the RE. The inter-compartmental connections should be of low resistance so that the maximum output voltage of the potentiostat is not reached too soon. This is particularly important in experiments involving transients.
- 3) The CE should be positioned with respect to the WE so as to produce as uniform an electric field as possible. If this is not so, the current density will not be uniform, nor will the effective solution resistance. The CE should possess a large surface area compared with the WE.
- 4) In order to minimise the IR drop and the time constant of the cell, the actual surface area of the WE should be kept to a minimum in order to reduce the net current available and the overall capacitance of the electrode.

## CHAPTER FIVE

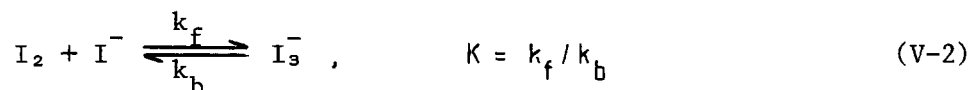
### THE REACTION BETWEEN FERRICYANIDE AND IODIDE IN SOLUTION.

#### V.1. Introduction.

The reaction between ferricyanide and iodide appears to have been first studied by Donnan and Le Rossignol<sup>68</sup> who found the reaction to be of second order in ferricyanide and of third order in iodide, at room temperature. Further research by Just<sup>69</sup> and by Wagner<sup>70</sup> has shown the initial rate to be rather of the form:

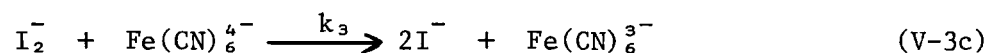
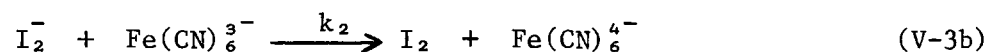
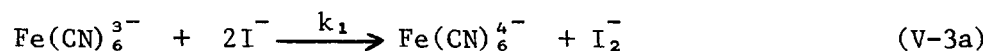
$$v_{\text{hom}} = k[\text{Feic}][\text{I}^-]^2 \quad (\text{V-1})$$

This was confirmed by Beckman and Sandved<sup>71</sup> who followed the reaction colorimetrically at 350 nm (where  $\text{I}_3^-$  absorbs strongly) instead of titrating the iodine produced with thiosulphate in the presence of starch as had been done by previous authors (the so-called Harcourt-Esson technique). It should be pointed out that the reaction between the iodine produced and iodide ions in solution is extremely fast<sup>72</sup>:



with  $k_f = (6.2 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_b = (8.5 \pm 1.0) \times 10^6 \text{ s}^{-1}$  at 25°C; therefore, the above techniques at least are not rate-limiting.

The reaction was found to be inhibited by ferrocyanide, and to explain this Just proposed the mechanism:



By assuming that all the forward steps occur at the same rate  $v_{\text{hom}}$ :

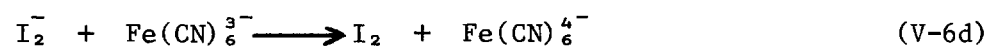
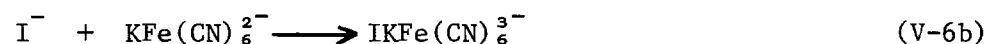
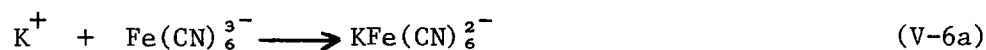
$$v_{\text{hom}} = k_1[\text{Feic}][\text{I}^-]^2/(1 + k_3[\text{Feoc}]/k_2[\text{Feic}]) \quad (\text{V-4})$$

which explains his results. This mechanism was criticised by Indelli and Guaraldi<sup>73</sup> because there was no evidence of the existence of the  $\text{I}_2^-$  ion. They proposed instead the formation of the eight ligand activated complex,  $\text{I}_2\text{Fe}(\text{CN})_6^{5-}$ , with release of an iodine atom and an iodine ion. In this case one should seek evidence for the existence of I atoms in solution.

Friedman and Anderson<sup>74</sup> seem to have been the first to study the effect of the concentration and nature of the supporting electrolyte. They found that  $\text{K}^+$  ion has a bigger effect on the rate than  $\text{Na}^+$  ion, chloride salts being more effective than nitrate ones. A systematic study has been carried out by Majid and Howlett.<sup>75</sup> Their main finding was that the initial rate can be expressed by:

$$v_{\text{hom}} = k^{\text{IV}}[\text{K}^+][\text{Feic}][\text{I}^-]^2 \quad (\text{V-5})$$

$k^{\text{IV}}$  appeared independent of ionic strength for variations in the supporting electrolyte ( $\text{KNO}_3$ ) between 0.193 and 0.372 M. They proposed the following mechanism:



with (6c) as the r.d.s., which gives rise to eq. (5). Notice that eq. (4) can be more conveniently expressed as:

$$v_0/v = 1 + k'[\text{Feoc}]/[\text{Feic}] \quad (\text{V-7})$$

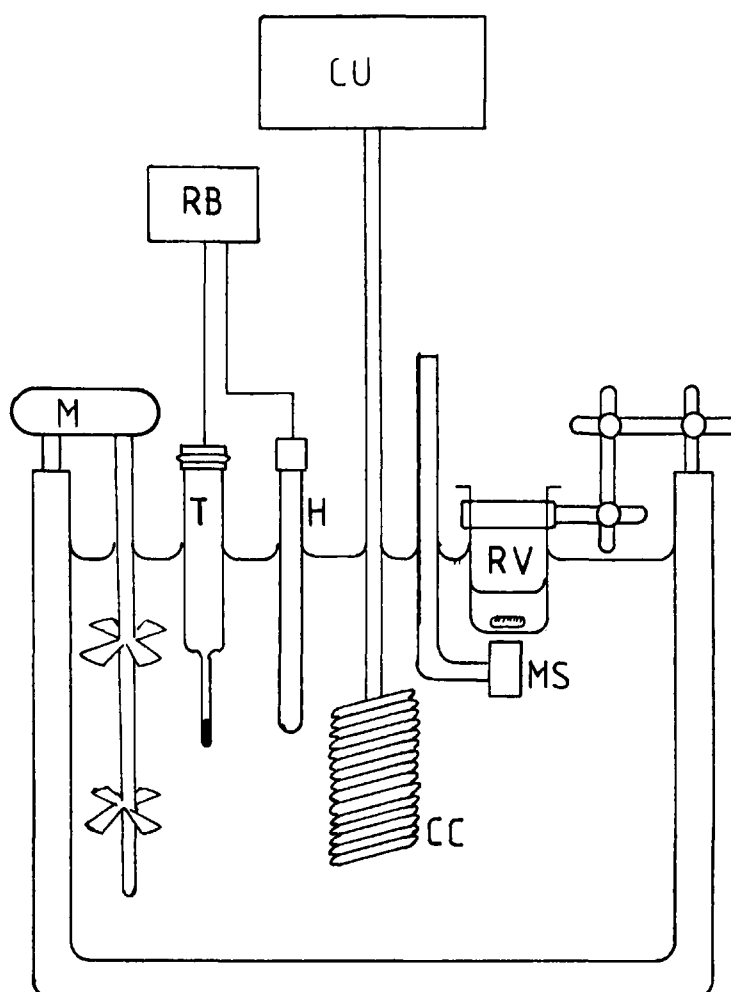
where  $v_0$  is the rate in the absence of ferrocyanide,  $v$  is given by the full eq. (4), and  $k'$  is the combination of the various constants accompanying the ratio  $[\text{Feoc}]/[\text{Feic}]$ .

## V.2. Experimental.

### a) Apparatus.

The basic experimental arrangement for the homogeneous runs is shown in Figure 1. The thermostat bath (38 cm depth x 50 cm x 38 cm) was fitted with side glass windows and lined inside with enamel-painted copper plates. The outer casing, of cemented asbestos sheet (Sindanyo), was hollow and filled with Vermiculite as insulation. The bath was provided with a motor and paddle stirrer, and filled with distilled water. Since most of the work had to be carried out well below room temperature, to reduce the contribution of the homogeneous rate, the thermostat was provided with a refrigerating unit (Townson and Mercer, Ltd., Croydon). Temperature control was achieved with an Ether control relay, type no. 213 B, fitted with a red rod heater (Electrothermal, 400 Watts) and connected to a contact thermometer (Jumo, D.B.P., Germany). The temperature of the bath, measured with a mercury thermometer graduated in  $0.01^{\circ}\text{C}$  divisions, could be controlled within  $\pm 0.02^{\circ}\text{C}$  of the intended value.

The reaction vessel was a straight walled 500 ml Quickfit glass vessel (FV500), with a flat lip around the upper edge which allowed it to be placed inside the bath supported by an iron ring fastened to a bar at the edge of the thermostat. The reaction mixture was stirred by a Teflon-covered magnetic bar driven by a submersible magnetic stirrer (Rank Brothers, Botolph Claydon). Absorbances were measured with a Unicam SP 1800 ultraviolet Spectrophotometer. Readings in the range of 0.001 to 2.00 could be made with accuracy ranging from 0.001 to 0.01, depending on the particular scale used. Quartz cells of 4 cm optical path length were used.



CC : cooling coil  
 CU : cooling unit  
 H : heater  
 M : motor  
 MS : magnetic stirrer  
 RB : relay box  
 RV : reaction vessel  
 T : thermoregulator

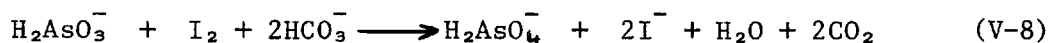
Figure V-1

b) Chemicals.

The chemicals were all of Anala<sup>R</sup> grade and were used without further purification:  $K_3Fe(CN)_6$ ,  $KNO_3$ ,  $KCl$ ,  $H_2SO_4$ ,  $NaOH$ , and iodine (resublimed) from BDH;  $K_4Fe(CN)_6 \cdot 3H_2O$ , soluble starch and  $As_2O_3$  from Hopkin and Williams Ltd.;  $KI$  from May and Baker. Solutions were prepared in distilled water; those to be used for kinetic runs contained already the supporting electrolyte (i.e.,  $KNO_3$ , or  $KCl$ ), and were equilibrated inside the thermostat before filling the graduated flasks up to the mark. The solution with the greatest volume, usually that of  $KI$ , was then passed through a Quickfit SF3A33 sintered glass filter to remove suspended solids, and stored in a clean stoppered Pyrex glass bottle.

c) Measurement of Extinction Coefficients.

The extinction coefficient of  $I_3^-$ , either in 1 M  $KNO_3$  or in 1 M  $KCl$ , was obtained from the slope of the plot of the absorbance vs. the concentration of diluted samples of a standardised iodine solution. The standardisation of the stock iodine solution was carried out with slightly basic  $As_2O_3$  solution according to the procedure cited in the literature,<sup>76</sup> the concentrations of  $I_2$  and  $As_2O_3$  being  $\sim 0.1$  M. The reaction is:



Aliquots of 20 ml of the  $As_2O_3$  were titrated with the iodine solution in a 25 ml burette (grade B) with an accuracy of 0.05 ml, but the actual volumes could be estimated to within 0.025 ml by eye. The titrations themselves were in the absence of  $KNO_3$  or of  $KCl$ . The stock solution was diluted 20-fold for  $\epsilon_{I_3^-}^{KNO_3}$  or 200 fold for  $\epsilon_{I_3^-}^{KCl}$  with 0.241 M  $KI$ . Samples were taken from this solution to prepare a series of dilutions whose  $[I_2]$  ranged from  $\sim 1 \times 10^{-6}$  to  $\sim 15 \times 10^{-6}$  M. These solutions

contained either 0.241 M KI, plus enough solid salt to give 1 M  $\text{KNO}_3$ , or 0.0167 M KI plus enough solid salt to reach 1 M  $\text{KCl}$ . The absorbances were obtained in 4 cm cells against a blank containing the background solution.

To measure the extinction coefficient of molecular iodine, about 50 ml of 1 M  $\text{KNO}_3$  were stirred overnight at room temperature with some crystals of iodine, and its absorbance read against 1 M  $\text{KNO}_3$ . The iodine concentration was obtained from the absorbance of a 1:21 dilution with 0.241 M KI in 1 M  $\text{KNO}_3$  and the previously determined  $\epsilon_{\text{I}_2}^{\text{KNO}_3}$ .

The extinction coefficient of ferricyanide was obtained from the absorbance of a  $2 \times 10^{-3}$  M solution in 1 M  $\text{KNO}_3$ , read vs. 1 M  $\text{KNO}_3$ .

d) Typical Homogeneous Run.

A typical homogeneous run is one started in the absence of added products, at (say)  $5^\circ\text{C}$ . First, 200 ml of the stock KI solution measured with a 100 ml volumetric pipette were placed in the reaction vessel, and stirring started. The reaction was initiated by adding 10 ml of  $\text{K}_3\text{Fe}(\text{CN})_6$ . Samples of 5 ml were taken at 10 minute intervals with pre-cooled volumetric pipettes (grade B) which had been kept inside a 250 ml cylinder almost completely submerged inside the thermostat bath. The samples were diluted with 10 ml of pre-cooled supporting electrolyte solution in order to quench the rate [according to eq. (1), a 3-fold dilution should produce a 27-fold decrease in the rate]. However, if the reaction was to be carried out close to or above room temperature, neither pipettes nor diluent were warmed. The spectrophotometer cell was rinsed with the diluted sample before filling it completely, and the absorbance read against a reference cell filled with a ferricyanide solution diluted so as to compensated roughly the background absorbance of the diluted sample at 350 nm.

If added iodine or ferrocyanide were to be present from the start, 200 ml of stock KI or ferricyanide solution respectively were first placed in the reaction vessel. A 4 cm<sup>2</sup> platinum electrode was immersed in the solution, which was connected by an agar bridge (0.6 g Agar in 20 ml supporting electrolyte) to a beaker containing supporting electrolyte solution and a 55 cm<sup>2</sup> platinum counter electrode. The electrodes were connected to the potentiostat (the latter arranged for galvanostatic operation), and a constant current passed for a fixed period of time, monitored by the voltage drop it produced across a decade resistance box (Croydon Instruments Ltd., 0.1%) connected to the potentiostat (Figure IV-7a). For example, if  $1.2 \times 10^{-5}$  M iodine had to be present in the final 210 ml of reaction mixture, 1.013 mA of current were passed for 8 minutes through the initial 200 ml of KI solution, under constant stirring; for this purpose the potentiostat had been set to give a drop of 405.3 mV across 400  $\Omega$  ( $\pm 0.1\%$ ) on the resistance box.

### V.3. Treatment of Kinetic Data.

Since the reaction was followed by the appearance of  $I_3^-$ , allowance must be made for its dissociation into  $I_2$  and  $I^-$ , for the change in the absorbance due to the appearance of  $Fe(CN)_6^{4-}$  and free  $I_2$ , and for the disappearance of  $Fe(CN)_6^{3-}$  and of  $I^-$ . With reference to Table 3, the total absorbance A of the diluted sample is given by Beer's law as:

$$A = \ell(\epsilon_{I_3^-}[I_3^-] + \epsilon_{I_2}[I_2] + \epsilon_{Feoc}[Feoc] + \epsilon_{Feic} \Delta[Feic]) \quad (V-9)$$

where  $\ell$  = optical path length, and  $\Delta[Feic]$  is the change in  $[Feic]$ . From the stoichiometry of the reaction and the expression for the equilibrium constant of reaction (2):

$$A = \ell[\epsilon_{I_3^-} + \epsilon_{I_2}/K[I^-] + 2(\epsilon_{Feoc} - \epsilon_{Feic})][I_3^-] \quad (V-10)$$

Values of K were obtained from the work of Katzin and Gebert<sup>77</sup> in 1 M HClO<sub>4</sub> and are given in the following table:

TABLE V-1.

|                           |       |       |       |
|---------------------------|-------|-------|-------|
| T/(°C) :                  | 20    | 25    | 30    |
| K/(mol ℓ <sup>-1</sup> ): | 877.2 | 740.7 | 699.3 |

The data are well represented by the equation (fitted by least squares):

$$K = 0.8763 \exp(2020.2/T) \quad (V-11)$$

with a correlation coefficient of 0.96 (T is the absolute temperature in °K). From eq. (11) the values of K at other temperatures were found to be:

TABLE V-2

|                           |      |      |     |
|---------------------------|------|------|-----|
| T/(°C) :                  | 5    | 10   | 15  |
| K/(mol ℓ <sup>-1</sup> ): | 1250 | 1100 | 972 |

[I<sup>-</sup>] varies between 0.01 and 0.1 M in the diluted sample; this and the values of the extinction coefficients in Table 3 cause  $\epsilon_{I_3^-}$  to be the only important contributor to the total absorbance.

The total iodine in the dilution  $[I_2]_{total}^{dil}$  is:

$$[I_2]_{total}^{dil} = [I_2] + [I_3^-] = (1 + 1/K[I^-])[I_3^-] = f[I_3^-] \quad (V-12)$$

where

$$f = 1 + 1/K[I^-] \quad (V-13)$$

Introducing eq. (12) into eq. (10), and neglecting the  $(\epsilon_{\text{Feoc}} - \epsilon_{\text{Feic}})$  term (see the next section):

|                                                                                                                                |                                                                  |        |
|--------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|--------|
| $[\text{I}_2]_{\text{TOTAL}}^{\text{RM}} = [\text{I}_2]_{\text{total}}^{\text{dil}}/b = A/b\epsilon_{\text{I}_2}^{\text{app}}$ | $\epsilon_{\text{I}_2}^{\text{app}} = \epsilon_{\text{I}_3}^-/f$ | (V-14) |
|--------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|--------|

where  $[\text{I}_2]_{\text{TOTAL}}^{\text{RM}}$  is the total iodine concentration in the reaction mixture,  $b$  is the dilution factor (volume of sample divided by total volume of dilution, usually 1/3), and  $\epsilon_{\text{I}_2}^{\text{app}}$  is defined as the apparent extinction coefficient of iodine. From eqs. (14) and (13) it follows that  $\epsilon_{\text{I}_2}^{\text{app}}$  depends on the temperature of the diluted sample and its iodide concentration. For each run where any of these conditions changed, a new value of  $f$  and hence of  $\epsilon_{\text{I}_2}^{\text{app}}$  had to be calculated. When precooled diluant was used, it was assumed that the temperature of the dilution at the moment of taking the absorbance reading was the same as that of the thermostat; if the diluant had been at room temperature, the final temperature was estimated from the formula:

|                         |        |
|-------------------------|--------|
| $T_f = bT_s + (1-b)T_d$ | (V-15) |
|-------------------------|--------|

where  $T_s$  is the temperature of the sample and  $T_d$  is the temperature of the diluant (equal to the room temperature, constantly monitored with a thermometer hung above the bench, both in  $^{\circ}\text{C}$ ). When deriving eq. (15) equal heat capacities for the diluant and for the reaction mixture were assumed. In the two cases it is also assumed that the dilution does not warm up appreciably during the 1-1.5 minutes handling before reading the absorbances.

#### V.4. Results and Discussion.

##### a) Extinction Coefficients.

The real extinction coefficients of reactants and products at 350 nm in 1 M KNO<sub>3</sub> are given in Table 3:

TABLE V-3. EXTINCTION COEFFICIENTS AT 350 nm IN 1 M KNO<sub>3</sub>.

| Species                           | $\epsilon_{I_3^-}$ 1 M KNO <sub>3</sub> /(mol <sup>-1</sup> 1 cm <sup>-1</sup> ) | Source    |
|-----------------------------------|----------------------------------------------------------------------------------|-----------|
| Fe(CN) <sub>6</sub> <sup>3-</sup> | 304 <sup>b</sup>                                                                 | p.w.      |
|                                   | 305                                                                              | ref. (78) |
|                                   | 318                                                                              | ref. (79) |
| Fe(CN) <sub>6</sub> <sup>4-</sup> | 175 <sup>b</sup>                                                                 | ref. (78) |
|                                   | 184                                                                              | ref. (79) |
| I <sup>-</sup>                    | 0 <sup>b</sup>                                                                   | ref. (78) |
|                                   | 0 <sup>b</sup>                                                                   | ref. (79) |
| I <sub>2</sub>                    | 600                                                                              | p.w.      |
|                                   | 170                                                                              | ref. (79) |
| I <sub>3</sub> <sup>-</sup> a     | 2.53 x 10 <sup>4</sup> b                                                         | p.w.      |
|                                   | 2.50 x 10 <sup>4</sup>                                                           | ref. (78) |
|                                   | 2.63 x 10 <sup>4</sup>                                                           | ref. (80) |
|                                   | 2.43 x 10 <sup>4</sup>                                                           | ref. (79) |

p.w. = present work; a = with an excess of I<sup>-</sup>;

b = value used in this work

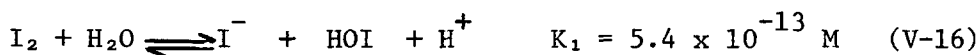
The measured  $\epsilon_{I_2}^{\text{app}}$  in 1 M KCl (5°C, [I<sup>-</sup>] = 0.0167 M) was  $(2.29 \pm 0.02) \times 10^4$ .

Under these conditions  $f = 1.048$ . Therefore, from eq. (14):

$$\epsilon_{I_3^-}^{1 \text{ M KCl}} = f \epsilon_{I_2}^{\text{app}, 1 \text{ M KCl}} = (2.40 \pm 0.02) \times 10^4 \text{ mol}^{-1} \text{ 1 cm}^{-1}$$

The values measured in this work agree with those determined by other authors.<sup>76-78</sup>

Our value for  $\epsilon_{I_2}$  was corrected for the absorbance of the  $I_3^-$  produced according to the following equilibria present in iodine solution<sup>79</sup>:



These equilibria are rapidly established.<sup>79</sup> The equilibrium constants quoted are at 25°C in water, except  $K_2$  which is in 1 M  $KNO_3$  (Table 1). The pH of a saturated  $I_2$  solution in 1 M  $KNO_3$  was 5.09, well below pH 6.72 of 1 M  $KNO_3$  alone. Using the equilibrium expressions for equilibria (16) to (19), together with the balances of matter

$$[H^+] = [H^+]_o + ([OH^-] - [OH^-]_o) + 2[OI^-] + [HOI] \quad (V-20)$$

$$2[I_2]_o = 2[I_2] + [I^-] + 3[I_3^-] + [HOI] + [OI^-] + [H_2OI^+] \quad (V-21)$$

and the electroneutrality expression

$$[H^+] + [H_2OI^+] = [OH^-] + [I^-] + [I_3^-] + [OI^-] \quad (V-22)$$

and the ion product of water

$$[H^+]_o[OH^-]_o = [H^+][OH^-] = K_W \quad (V-23)$$

(where  $[H^+]_o$  and  $[OH^-]_o$  are in the absence of iodine), one obtains for a saturated  $I_2$  solution at  $\sim 20^\circ\text{C}$

$$[I_3^-] = 3.4 \times 10^{-6} \text{ M}, [I^-] = 4.8 \times 10^{-6} \text{ M}, [H^+]_o = 5.1 \times 10^{-6} \text{ M} \quad (V-24)$$

The experimental solubility was  $9.64 \times 10^{-4} \text{ M}$  which agrees with  $1.053 \times 10^{-3} \text{ M}$  in 1 M  $HClO_4$  at the same temperature.<sup>77</sup> The resulting value of  $\epsilon_{I_2}$  of 600 in Table 3 allows for the contribution to the

absorbance by  $I_3^-$ . However, this may not be enough to obtain the true  $\epsilon_{I_2}$  as the following equilibrium is also present<sup>81,82a</sup>:



This contributes more  $I_3^-$  - forming iodide. The calculated pH for 1 M  $KNO_3$  ( $-\log[H^+]_0$ ) is 5.3, markedly different from the experimental value. This points to further reactions, besides reactions (16) and (25) that push the pH to acid values.

It is difficult to say whether Reynolds' extinction coefficient of 170 is closer to the "true" value than our result of 600, because no explicit conditions are mentioned although  $pH < 4.8$  is implied. If the pH is acid enough then all of the  $I^-$ -forming equilibria are repressed, including reaction (25). Luckily, however, the concentration of free iodine is so small in our reaction mixtures than even an  $\epsilon_{I_2}$  value as high as 600 would contribute less than 1% in the more dilute iodide solution to the total absorbance of the samples. Therefore, the actual value of  $\epsilon_{I_2}$  is immaterial.

#### b) Verification of the Value of K.

Because the values of K for our low temperatures had been obtained from extrapolation of previous work<sup>77</sup> in 1 M  $HClO_4$ , an attempt was made to verify these values. Two hundred ml of 0.050 M KI solution were electrolysed at 5°C, at 0.5 mA constant current in the manner described, except that the WE platinum RDE was used at 500 rpm. Samples of 5 ml were taken every 4 minutes and diluted with 10 ml of  $KNO_3$  solution at room temperature.  $T_f$  was 15°C.  $\epsilon_{I_2}^{app}$  was calculated from the change in absorbance between successive samples and from the number of coulombs passed:

$$\epsilon_{I_2}^{app} = 2F V_j (A_j - A_{j-1}) / I(t_j - t_{j-1}) \ell \quad (V-26)$$

where  $V_j$  is the volume of the electrolyte at the moment of taking the  $j$ th sample,  $I$  is the current and  $t_j - t_{j-1}$  is the time interval between successive samples. For eight samples, the results for  $T_f = 15^\circ\text{C}$ ,  $[\text{I}^-] = 0.0167 \text{ M}$  were:

TABLE V-4

| $C_{\text{KNO}_3} / \text{M}$ | $10^4 \epsilon_{\text{I}_2}^{\text{app}} / \text{mol}^{-1} \ell \text{ cm}^{-1}$ | $f = \epsilon_{\text{I}_3^-} / \epsilon_{\text{I}_2}^{\text{app}}$ | $K_{\text{calc}}^{15^\circ\text{C}} / \text{mol}^{-1} \ell$ |
|-------------------------------|----------------------------------------------------------------------------------|--------------------------------------------------------------------|-------------------------------------------------------------|
| 0.5                           | $2.39 \pm 0.06$                                                                  | $1.059 \pm 0.003$                                                  | $1015 \pm 52$                                               |
| 1.5                           | $2.39 \pm 0.12$                                                                  | $1.059 \pm 0.053$                                                  | $1015 \pm 910$                                              |

The  $K_{\text{calc}}$  values were obtained from eq. (13). They are in reasonable agreement with the value extrapolated from Katzin and Gebert's results in Table 2, considering the large uncertainties involved due to the  $f$  being close to unity, and the approximation incurred by using for conc.  $\text{KNO}_3$  values obtained in conc.  $\text{HClO}_4$ . Table 4 suggests that  $K$  does not vary much with  $[\text{KNO}_3]$ .

c) Homogeneous Rate Under Various Conditions.

The results are summarised in Tables 5-9. The rates are expressed as  $d[\text{I}_2]/dt$ . The effect of reactants in the absence of the products was measured as a test of the rate laws (5) and (7) and to obtain the rate constant under our experimental conditions. The bracketted numbers in the last column refer to the number of runs carried out.

TABLE V-5. EFFECT OF REACTANT AND SUPPORTING ELECTROLYTE  
CONCENTRATIONS ON HOMOGENEOUS RATE, AT 5°C.

| [KNO <sub>3</sub> ]/M | [KCl]/M | 10 <sup>3</sup> [Feic]/M | 10 <sup>3</sup> [KI]/M | 10 <sup>9</sup> v <sub>hom</sub> /mol l <sup>-1</sup> s <sup>-1</sup> |
|-----------------------|---------|--------------------------|------------------------|-----------------------------------------------------------------------|
| 0.5                   | 0       | 1.0                      | 50                     | 0.361 ± 0.006 (2)                                                     |
| 1.0                   | 0       | 1.0                      | 50                     | 0.65 ± 0.02 (4)                                                       |
|                       |         | 2.0                      |                        | 1.22 (1)                                                              |
|                       |         | 3.0                      |                        | 1.95 ± 0.20 (2)                                                       |
| 1.0                   | 0       | 1.0                      | 70.7                   | 1.20 ± 0.01 (2)                                                       |
| 0.95                  |         |                          | 100                    | 2.46 (1)                                                              |
| 0.85                  |         |                          | 200                    | 16.5 ± 0.02 (2)                                                       |
| 0.75                  |         |                          | 300                    | 41.8 ± 1.5 (2)                                                        |
| 1.5                   | 0       | 1.0                      | 50                     | 0.849 ± 0.11 (2)                                                      |
| 0                     | 1.0     | 1.0                      | 50                     | 1.12 ± 0.002 (2)                                                      |

From the data in Table V-5 it can be calculated that the order in [Feic] is 0.93 and in [I<sup>-</sup>] (below 0.1 M KI) 2.06. Figure 2 shows the dependence on [KNO<sub>3</sub>] which is close to first order below 1 M. This agrees with the rate law in eq. (5).

The third order rate constant  $k^{\text{III}}$  is  $2.50 \times 10^{-4} \text{ mol}^{-2} \text{ l}^2 \text{ s}^{-1}$  at 5°C in 1 M KNO<sub>3</sub>. In order to compare it with the value of  $7.08 \times 10^{-4} \text{ mol}^{-3} \text{ l}^3 \text{ s}^{-1}$  at 5°C for the fourth order rate constant,  $k^{\text{IV}}$ , reported by Majid and Howlett,<sup>75</sup> one must divide  $k^{\text{III}}$  by the free K<sup>+</sup> concentration, allowing for association between K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> (there is no need to consider the association between K<sup>+</sup> and Feic, since the concentration of the latter is so small).

The association constant  $K_{\text{ass}}$  is<sup>82b,c</sup>: 0.75 (18°C), 0.59 (25°C), 0.71 (25°C) and 0.56 (39°C), leading to  $K_{\text{ass}}^{5^\circ\text{C}} \approx 1.1 (\pm 0.1) \ell \text{ mol}^{-1}$  at zero ionic strength. Therefore, one must include the activity coefficients appropriate to the concentrations involved. The molar concentrations,  $C$  ( $\text{mol } \ell^{-1}$ ) were converted to molalities ( $\text{mol Kg}^{-1}$  of solvent) via the solution density,  $\rho$ , at 25°C<sup>83a</sup> according to the formula:

$$m = 1/(\rho/C-M) \quad (\text{V-27})$$

$M$  is the molecular weight of the solute. The corresponding stoichiometric activity coefficients,  $\gamma_{\pm}$  (25°C)<sup>84</sup> are listed in Table 6.

TABLE V-6.

| $[\text{KNO}_3]$<br>/mol $\ell^{-1}$ | $\rho^{25^\circ\text{C}}$<br>/g $\text{cm}^{-3}$ | $m$<br>/mol $\text{Kg}^{-1}$ | $\gamma_{\pm}^{(25^\circ\text{C})}$ | $\gamma_{\pm}^2$ |
|--------------------------------------|--------------------------------------------------|------------------------------|-------------------------------------|------------------|
| 0.5                                  | 1.0279                                           | 0.512                        | 0.545                               | 0.297            |
| 1.0                                  | 1.0580                                           | 1.045                        | 0.436                               | 0.190            |
| 1.5                                  | 1.088                                            | 1.603                        | 0.369                               | 0.136            |

If we take the  $\gamma_{\pm}$  at 25°C to be approximately applicable at 5°C, and remembering that  $\gamma_{\pm} = \alpha f_{\pm}$  ( $\alpha$  = degree of dissociation, and  $f_{\pm}$  = ionic activity coefficient), the following table is obtained:

TABLE V-7.

| $[\text{KNO}_3]$<br>/mol $\ell^{-1}$ | $\gamma_{\pm}^2 K_{\text{ass}}^{5^\circ\text{C}}$ | $\alpha$ | $[\text{K}^+]$<br>/mol $\ell^{-1}$ | $10^4 k^{\text{III}}$<br>/ $\text{M}^{-2} \text{s}^{-1}$ | $10^4 k^{\text{IV}}$<br>/ $\text{M}^{-3} \text{s}^{-1}$ |
|--------------------------------------|---------------------------------------------------|----------|------------------------------------|----------------------------------------------------------|---------------------------------------------------------|
| 0.5                                  | 0.327                                             | 0.817    | 0.458                              | 1.44                                                     | 3.14                                                    |
| 1.0                                  | 0.209                                             | 0.778    | 0.828                              | 2.57                                                     | 3.10                                                    |
| 1.5                                  | 0.150                                             | 0.765    | 1.198                              | 3.4                                                      | 2.84                                                    |

where the following expression has been used:

$$(1-\alpha)/\alpha(\alpha C + 0.05) = f_{\pm}^2 K_{\text{ass}} \quad (\text{V-28a})$$

or

$$\gamma_{\pm}^2 K_{\text{ass}} = (1-\alpha)/\alpha C + 0.05/\alpha \quad (\text{V-28b})$$

where 0.05 refers to the molar  $K^+$  contributed by the KI.

Thus, the mean value of  $k^{\text{IV}}$  at  $5^{\circ}\text{C}$  is  $3.03 \times 10^{-4} \text{ M}^{-3} \text{ s}^{-1}$ , compared with Majid and Howlett's value (their Table 2) of  $(1/2)(7.1) \times 10^{-4} = 3.55 \times 10^{-4}$  (their rate constants refer to Feoc formation, hence the 1/2 factor to convert them to iodine formation). However, the figures in Table 7 suggest that  $k^{\text{IV}}$  is not actually constant at the high ionic strengths employed in this work, and that at the lower  $[K^+]$  values used by Majid and Howlett our  $k^{\text{IV}}$  is probably  $> 3 \times 10^{-4}$ . At  $25^{\circ}\text{C}$   $k^{\text{IV}} = 8.7 \times 10^{-4} \text{ M}^{-3} \text{ s}^{-1}$  (using:  $k^{\text{III}}$  calculated from Table 5,  $K_{\text{ass}} = 0.65$ ,  $\gamma_{\pm}^2 K_{\text{ass}} = 0.1235$  for 1 M  $\text{KNO}_3$ ; hence  $\alpha = 0.870$ , and  $[K^+] = \alpha C + 0.05 = 0.92$ ). Majid and Howlett's is (from their Table 2)  $(1/2)(18.8) \times 10^{-4} = 9.4 \times 10^{-4}$ . Since their  $k^{\text{IV}}$  are higher at their lower ionic strengths, the disagreement is well within our uncertainty of  $\pm 4\%$  (Table 5).

Our rate extrapolated to  $0^{\circ}\text{C}$  is  $0.49 \times 10^{-9} \text{ M s}^{-1}$  [Table 8 and eq. (29)] agrees with Spiro and Griffin's<sup>4</sup>  $0.51 \times 10^{-9}$  in the same conditions.

TABLE V-8. EFFECT OF TEMPERATURE ON HOMOGENEOUS RATE,

$10^{-3} \text{ M Feic}$ ,  $5 \times 10^{-2} \text{ M KI}$ , 1 M  $\text{KNO}_3$ .

| $T/^{\circ}\text{C}$ | $10^9 v_{\text{hom}}/\text{mol l}^{-1} \text{ s}^{-1}$ | $10^9 v_{\text{hom}}[\text{calc. eq. (29)}]/\text{mol l}^{-1} \text{ s}^{-1}$ |
|----------------------|--------------------------------------------------------|-------------------------------------------------------------------------------|
| 5                    | $0.65 \pm 0.02$ (4)                                    | 0.66                                                                          |
| 10                   | $0.91 \pm 0.03$ (4)                                    | 0.89                                                                          |
| 15                   | $1.20 \pm 0.009$ (4)                                   | 1.18                                                                          |
| 20                   | $1.50 \pm 0.08$ (4)                                    | 1.55                                                                          |
| 25                   | $2.00 \pm 0.08$ (4)                                    | 2.02                                                                          |
| 30                   | $2.66 \pm 0.16$ (4)                                    | 2.61                                                                          |

TABLE V-9. EFFECT OF INITIAL PRODUCT CONCENTRATION ON THE  
HOMOGENEOUS RATE IN 1 M KNO<sub>3</sub>, 5 °C.

| $10^3[\text{Feic}]$<br>/M | $10^3[\text{Feoc}]$<br>/M | $10^3[\text{KI}]$<br>/M | $10^3[\text{I}_2]$<br>/M | $10^9 v_{\text{hom}}/\text{mol } \ell^{-1} \text{s}^{-1}$ |
|---------------------------|---------------------------|-------------------------|--------------------------|-----------------------------------------------------------|
| 1.0                       | 0.005                     | 50                      | 0                        | 0.62 (1)                                                  |
|                           | 0.010                     |                         |                          | 0.72 (1)                                                  |
|                           | 0.020                     |                         |                          | 0.65 (1)                                                  |
|                           | 0.050                     |                         |                          | $0.68 \pm 0.12$ (2)                                       |
|                           | 0.100                     |                         |                          | 0.57 (1)                                                  |
|                           | 0.500                     |                         |                          | 0.48 (1)                                                  |
|                           | 1.000                     |                         |                          | 0.25 (1)                                                  |
| 1.0                       | 0                         | 50                      | 0.012                    | 0.67 (1)                                                  |
|                           |                           |                         | 0.020                    | 0.69 (1)                                                  |
|                           |                           |                         | 0.040                    | 0.80 (1)                                                  |
|                           |                           |                         | 0.100                    | 0.58 (1)                                                  |
| 1.5                       | 0.4                       | 50                      | 0                        | 0.817 (1)                                                 |
| 2.0                       |                           |                         |                          | $1.09 \pm 0.1$ (2)                                        |
| 1.0                       | 0.4                       | 60                      | 0                        | $0.713 \pm 0.005$ (2)                                     |
|                           |                           | 70                      | 0                        | $1.054 \pm 0.011$ (2)                                     |
| 1.0                       | 0.010                     | 50                      | 0                        | $1.99 \pm 0.17$ (2)                                       |
|                           | 0.100                     |                         |                          | 1.95 (1)                                                  |
|                           | 1.000                     |                         |                          | 1.47 (1)                                                  |

The rate experiences a big boost when  $[\text{KI}] > 0.1 \text{ M}$ , although the reaction order, w.r.t.  $\text{I}^-$ , settles at  $\sim 1.8$ . It is difficult to explain this feature as Majid and Howlett did not observe such an effect under similar experimental conditions.

The effect of temperature is shown in Table 8. The data are well expressed by the Arrhenius expression,

$$k^{\text{III}}/\text{mol}^{-2} \ell^2 \text{s}^{-1} = 4.40 \times 10^3 \exp(-4625/T) \quad (\text{V-29})$$

with  $r = 0.997$ . The apparent activation energy  $E_a$  is  $9.19 \text{ Kcal mol}^{-1}$ , in fair agreement with Majid and Howlett's value of  $8.4 \text{ Kcal mol}^{-1}$ , and

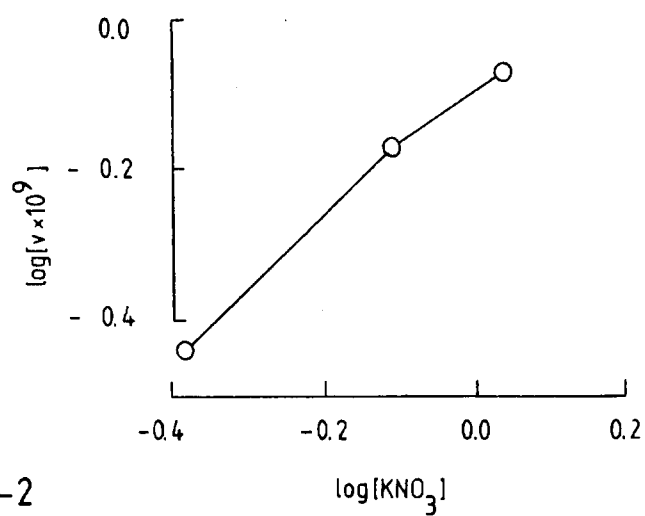


Figure V-2

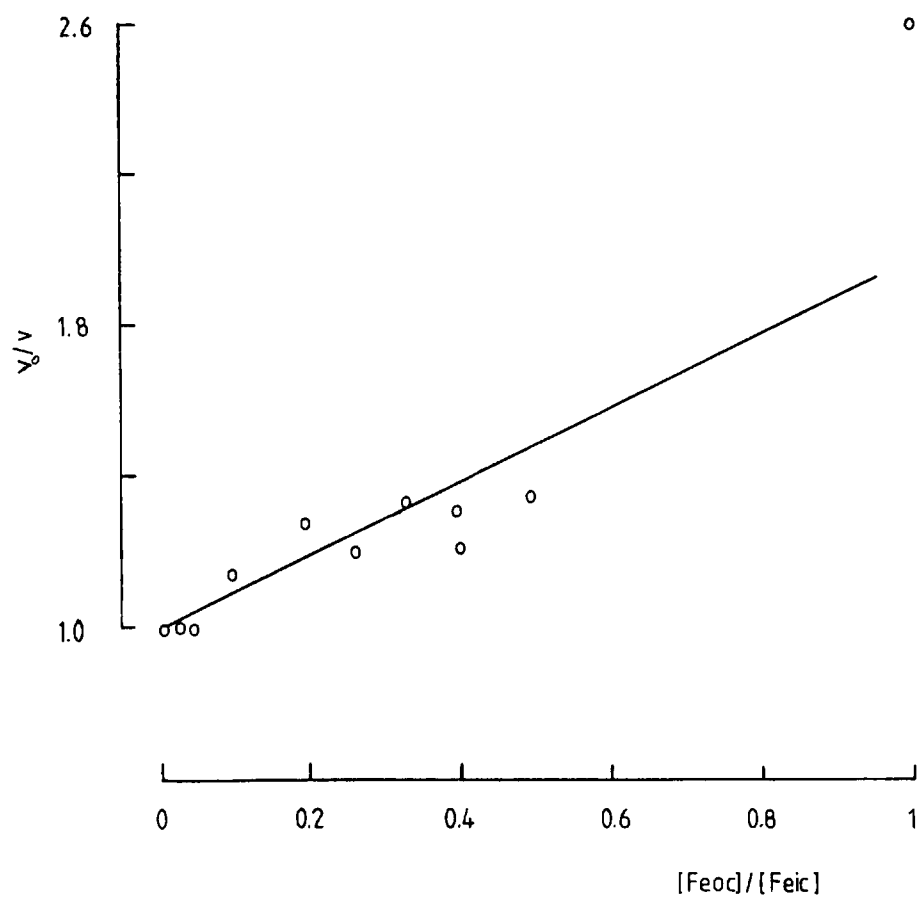


Figure V-3

Hussain's value of  $8.84 \text{ Kcal mol}^{-1}$ .<sup>85</sup> The former did not correct their data for the dissociation of  $\text{I}_3^-$ , which tends to produce smaller apparent activation energies according to:

$$E_a^{\text{app}} = E_a - \Delta H(1-1/f) \quad (\text{V-30})$$

where  $f$  is given by equation (13), and  $\Delta H$  is the enthalpy change of (2). However, the decrease is marginal (of the order of  $20\text{--}30 \text{ cal mol}^{-1}$  if  $K \approx 900 \text{ M}^{-1}$  and  $[\text{I}^-] \approx 0.2 \text{ M}$ , which fit typical Majid and Howlett's conditions).  $E_a$  contains too the temperature variations of the other association equilibria: between  $\text{K}^+$  and  $\text{NO}_3^-$  and  $\text{K}^+$  and  $\text{Feic}$ ; their contribution is bound to depend on the concentration of the ionic species concerned, through expressions like eq. (30). Thus, slight discrepancies between authors using different total ionic concentrations are not surprising.

Table 9 shows the effect of the products. It should be mentioned than values of  $[\text{Feoc}] > 10^{-3} \text{ M}$  are impractical because the rate becomes so small that it is difficult to measure. Also,  $[\text{I}_2] > 10^{-4} \text{ M}$  cannot be used because the large absorbances in both the sample and reference cells of the spectrophotometer cause the absorbance pointer to wobble markedly. Some of the data are plotted according to eq. (7) in Figure 3. The points are scattered and they do not seem to correlate well according to this plot. Conventional log-log plots were used instead. For  $[\text{Feoc}] \geq 5 \times 10^{-5} \text{ M}$ ,  $[\text{Feic}] = 10^{-3} \text{ M}$ ,  $[\text{I}^-] = 5 \times 10^{-2} \text{ M}$ ,  $[\text{KNO}_3] = 1 \text{ M}$ :

$$v_{\text{hom}}/\text{mol l}^{-1}\text{s}^{-1} \approx (1.23 \times 10^{-10}) \cdot [\text{Feoc}]^{-0.17} \quad (\text{V-31})$$

In the presence of increasing concentrations of  $\text{I}_2$  the rate seems to increase at first and then to decrease. The mean rate of the four runs at  $5^\circ\text{C}$  is, however, only  $0.68 \times 10^{-9} \text{ M s}^{-1}$ , very close to  $0.65 \times 10^{-9} \text{ M s}^{-1}$  in the absence of this product. It seems reasonable

to conclude that iodine has no significant effect on the initial rate, in agreement with the various mechanisms cited at the beginning of this chapter.

The concentration dependence on the reactants in the presence of  $4 \times 10^{-4}$  M Feoc were checked too. When  $[I^-] = 5 \times 10^{-2}$  M and  $[KNO_3] = 1$  M at  $5^\circ\text{C}$ :

$$v_{\text{hom}}/\text{mol l}^{-1} \text{ s}^{-1} = 5.47 \times 10^{-9} [\text{Feic}]^{1.0} \quad (\text{V-32})$$

In the presence of  $10^{-3}$  M Feic, the dependence on  $C_{I^-}$  is:

$$v_{\text{hom}}/\text{mol l}^{-1} \text{ s}^{-1} = 6.17 \times 10^{-7} [I^-]^{2.4} \quad (\text{V-33})$$

This increase in the order w.r.t. iodide in the presence of Feoc is not very significant, probably because of the lack of accuracy due to the small rate values.

Because of the way in which rate-concentration data have been expressed here in the presence of the products, the correlating equations have been used in the next chapters for interpolation purposes but never for extrapolations.

## CHAPTER SIX

### CATALYSIS ON PLATINUM (OXIDISED) :

#### STUDIES IN THE PRESENCE OF $\text{KNO}_3$

##### VI.1. Introduction.

The catalysis by platinum of reaction (I-1) has been studied by several authors.<sup>1,4,69,85</sup> Spiro and Griffin<sup>4</sup> were the first to show that catalysis proceeds by electron transfer through the metal, while Spiro and Ravnö<sup>1</sup> and Hussain<sup>85</sup> suggested diffusion-limited kinetics.

In this work the kinetics of the catalytic rate have been measured for the first time, as well as the effects of stirring in order to compare the experimental results with the theoretical predictions in Chapter 2.

The work has been carried out on a rotating platinum disk which allows precise control of the thickness of the diffusion layer by controlling the angular velocity of rotation (Chapter IV). The catalytic rate  $\nu'_{\text{cat}}$  is reported as moles of iodine per unit time.

##### VI.2. Materials and Methods.

The thermostat and experimental arrangement as well as the chemicals have been discussed in Chapter V.

###### a) Platinum Rotating Disk Electrode.

The platinum RDE used in kinetic and electrochemical experiments is depicted in Figure 1. It consisted of a mirror-polished circular platinum plate of  $\sim 1$  mm thickness and  $11.2 \text{ cm}^2$  geometric surface area,

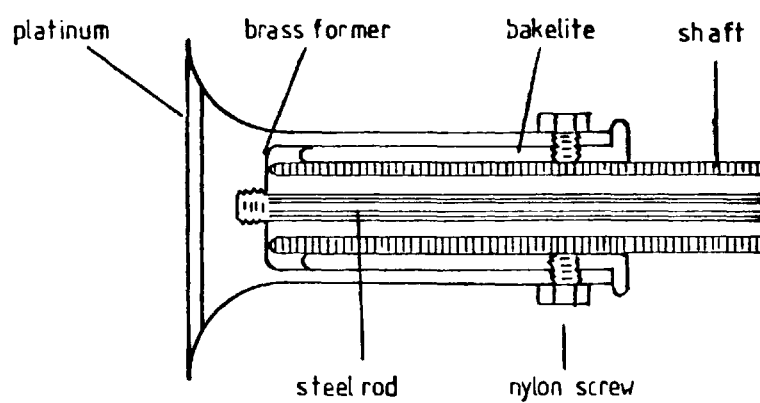


Figure VI-1

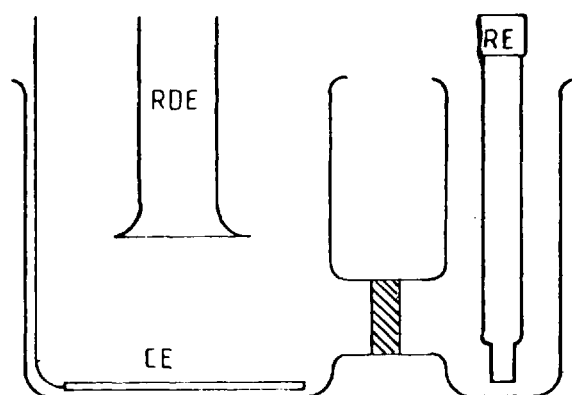


Figure VI-2

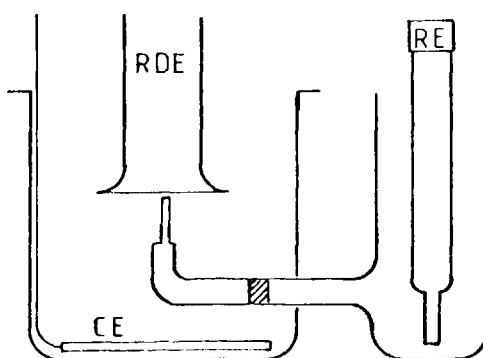


Figure VI-3

soldered onto a trumpet-shaped brass former. The electrode was fixed to the steel shaft of the rotating system by means of nylon screws. Direct contact between the shaft and the brass former was avoided by a bakelite cylinder interposed between them. The non-platinum parts of the electrode were covered with white radiator enamel (International), and baked on in an oven for 2 hours at 100°C. The coat had to be periodically removed with the enamel thinner as it tended to peel off around the edges of the disk. Electrical contact was made through a stainless steel rod running down the hollow shaft and screwed into the back of the disk. The top of the rod ended in a mercury-filled teflon cup into which a lead fitted with a platinum coiled wire was dipped. The rod was wrapped in 2702 P.V.C. adhesive tape (Rotunda Ltd., Denton, Manchester). When rotating, the edge of the disk oscillated horizontally  $\pm 0.3$  mm around a central position; a slight up and down movement at the edge could also be observed. This indicated that the disk was not perfectly horizontal and that it had a slight excentricity. The motor driving the disk was a motor generator type 126/54451 (Newton Brothers Ltd., Derby). The speed could be controlled within  $\pm 1\%$  of the fixed speed with a Motor Controller, type MC43 (Servomex Controls, Ltd.); it was checked with Stroboscopic disks permanently attached to the shaft, using ordinary neon lamps as a source or with a universal counter, number 835 (Racal Communications, Ltd., Bracknell, Berks.), attached to a Racal tachometer, type MA38. The maximum speed tolerated by the motor generator was 6000 rpm. In practice, however, funnelling and swirling of the solution around the disk limited the speed to 2000 rpm. Above this limit bubbles tended to be sucked in. The theoretical limit for the onset of turbulence for a critical Reynolds number of  $10^5$  [eq. (V-4)] is over 5000 rpm for a disk of our dimensions. It is possible that the lateral motion of the RDE contributed to this limitation of the speed.

Runs at 2000 rpm were carried out in vessels of 10 cm inner diameter instead of the ordinary 7.5 cm vessel because funnelling tended to decrease in this large vessel.

b) Pre-Conditioning.

Prior to catalytic or electrochemical experiments the electrode was electrochemically pre-conditioned to obtain an oxidised surface. This was done in 1 M  $\text{H}_2\text{SO}_4$  prepared in doubly distilled water (distilled the second time from an alkaline permanganate solution in an all glass still). Oxygen-free nitrogen was passed through the solution in the pre-conditioning cell, shown in Figure 2, for 10 minutes. The pre-conditioning was carried out at the same temperature as would be used in subsequent kinetic or catalytic work. The counter electrode was a 8.5 cm x 8.5 cm platinum foil placed at the bottom of the RDE compartment. The reference electrode was always an EIL calomel reference electrode, number 1320, 3.8 M  $\text{KCl}$ . However, at  $5^\circ\text{C}$  at which most of the work was carried out, some  $\text{KCl}$  precipitated; before using it at higher temperatures, enough solid  $\text{KCl}$  Aristar grade (BDH Chemicals Ltd.) was added to the electrode in order to keep it saturated. When not in use, it was stored in saturated  $\text{KCl}$  and placed inside the thermostat. All the potentials quoted are vs. this electrode, unless otherwise specified. To facilitate comparisons, a table of the potential of the saturated calomel electrode (SCE) vs. the standard hydrogen electrode (SHE), taken from the book by Ives and Janz,<sup>147</sup> is given in Table 1.

TABLE VI-1.

| T/ $^\circ\text{C}$ | 0      | 5                   | 10     | 15                  | 20     | 25                  | 30     |
|---------------------|--------|---------------------|--------|---------------------|--------|---------------------|--------|
| E/V                 | 0.2602 | 0.2572 <sup>a</sup> | 0.2541 | 0.2509 <sup>a</sup> | 0.2477 | 0.2444 <sup>a</sup> | 0.2411 |

<sup>a</sup>: interpolated value

The electrodes were connected to the terminals of the potentiostat (TR70/2A, Chemical Electronics Co., Durham); the potential between the RE and WE was monitored with a Hewlett Packard digital voltmeter model 3440A, with a high gain auto range unit, model 3443A. The current could be calculated from the voltage drop across a 100  $\Omega$  (5%) resistor placed across the counting resistor terminal of the potentiostat.

The pre-conditioning potential sequence applied is shown in Table 2, the electrolyte being de-oxygenated 1 M  $\text{H}_2\text{SO}_4$ .

TABLE VI-2

| E vs. SCE/V | Time   | $\omega$ /rpm |
|-------------|--------|---------------|
| 1.560       | 10 s   | 500           |
| 0.960       | 40 s   | 500           |
| -0.162      | 3 s    | 0             |
| 1.400       | 10 min | 0             |

The timing was checked with a chronometer (English Clock Systems) which permitted 1 second accuracy. It was occasionally checked with a Rone chronometer (0.2 s accuracy). These usually agreed within 0.5 s. The sequence is similar to Gilroy's<sup>86</sup> as recommended by Gilman<sup>87</sup>: at 1.560 V adsorbed organic impurities are supposed to be oxidised, and desorbed at 0.960 V; at -0.162 V the surface is rendered free of oxides, a process completed during the first 10 ms according to Gilman,<sup>87</sup> but does not lead to H-atom deposition; the growth of the oxide is achieved at 1.400 V, without (or with little) oxygen evolution. At this potential only a thin layer of superficial  $\alpha$ -oxide is formed.<sup>88</sup> It is a fast process, requiring a few tens of ms to complete a monolayer

of oxygen.<sup>86</sup> Rotation during the first two steps should help to carry away the oxidation products. During the last two steps the disk was kept motionless to diminish deposition of cations which might be present as impurities. The RDE was then removed from the cell, rinsed with doubly distilled water and spun at high speed in the air for a few seconds. It was left in the air while arrangements for the subsequent run were being carried out, usually 10 minutes.

The electrode was used as found at the beginning of this work. It was never repolished, although it was occasionally wiped with Kleenex paper to remove white specks that accumulated with time. Its performance, as measured by the rate of the catalytic reaction, remained remarkably constant during the course of this work (~ 3 years), after and before cleaning off the specks. By contrast, Hussain<sup>85</sup> reports that his platinum foil catalyst showed a marked decrease in performance with time which he attributes to organic growths on the catalyst surface as revealed by electron micrographs. His pre-treatment consisted in washing the catalyst with concentrated HCl; it was stored in acidified distilled water. The state of this surface is therefore unknown though it may well have been in a more reduced form. It would appear that the difference in sensitivity towards contamination probably rests on the pre-conditioning procedures.

Repeated oxidation and reduction of platinum leads to roughening of the surface, according to Biegler.<sup>89</sup> In our case, repeated pre-conditioning would then have led to increased catalytic rates. A balance between progressive contamination and progressive roughening might have been achieved, thus keeping the apparent catalyst performance unaltered.

c) Steady State Current-Voltage Curves.

Steady state current-voltage curves were carried out with the cell shown in Figure 3, the same solution being used in both compartments. Oxygen-free nitrogen was passed through the solution for about ten minutes before recording the curve, which was carried out with the TR70/2A potentiostat, capable of a minimum of 1  $\mu$ A. The current was monitored by the voltage drop across a 400  $\Omega$  (0.1%) resistor, type RBB1 (Croydon Precision Instruments Co.) connected to the counting resistor terminal of the potentiostat. The applied potentials were monitored within 0.1 mV with a Hewlett Packard digital voltmeter. Prior to the run, the solution was electrolysed with the aid of an auxiliary WE (see Section V.2, d) to obtain either 2  $\mu$ M ferrocyanide or 1  $\mu$ M  $I_3^-$ .

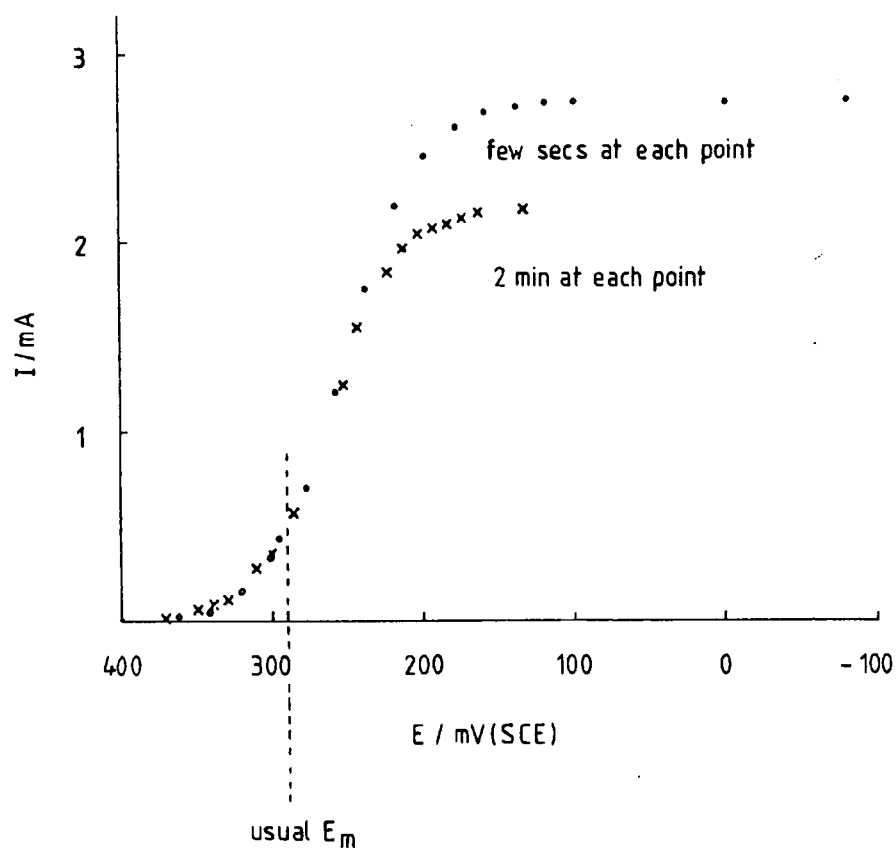
The solutions were prepared according to the same general procedure as used for the homogeneous runs. They were initially made up in doubly distilled water, but later ordinary distilled water was used since the same results were obtained.

The current became steady a few seconds after setting the potential between the RDE and RE, after which it decreased gradually by ca. 0.1% every minute or so, probably due to the accumulation of the product and the consumption of the reactant. The formal potential of the ferricyanide solutions tended to be 20-30 mV less positive after completing a curve, and that of the iodide solution 30-40 mV more positive; also, the absorbance at 421 nm of a ferricyanide solution indicated some 6% decrease in  $C_{Feic}$  which compared favourably with 6.9% calculated by Faraday's law from the currents at each potential and the estimated time spent at each (typically, less than 1 minute) which also indicates that not all of the product is reoxidised at the counter electrode.

Luckily, the curves were very reproducible, at least in the mixture potential region, and relatively independent of the period spent at each potential (see Figure 4). Irreproducibilities tended to show up at higher currents, and in this case probably contain IR drop errors due to uncertainty in the position of the Luggin capillary.

The limiting current densities  $L_j$  of ferr(i/o)cyanide, iodide and iodine as a function of  $C_j$  at a constant  $\omega = 500$  rpm at  $5^\circ\text{C}$  in 1 M  $\text{KNO}_3$ , were measured in separate runs with a view to determining the mass transport rate constants  $k_j$ . The only precautions worthwhile mentioning is that  $L_{\text{I}^-}$  was measured in the range of  $10^{-3} \text{ M} < [\text{I}^-] < 4 \times 10^{-3} \text{ M}$  in order to avoid formation of thick layers of solid iodine.<sup>47</sup> From previous experience, the approximate position of the current plateaus were known, so that the i-E curves were started at or very close to the  $L_j$  region, and E advanced in ca. 10 mV steps. The current readings were taken quickly. The whole run took no more than  $2\frac{1}{2} - 3$  minutes. The results are listed in Table 3. The  $k_j$  values were obtained from the slopes of the least squares fitting of the  $L_j$  vs.  $C_j$  data. Using the Levich equation, the resulting ratios  $D_{\text{Feoc}}/D_{\text{Feic}}$  and  $D_{\text{I}^-}/D_{\text{I}_3^-}$  are 0.868 and 1.71, respectively (at  $5^\circ\text{C}$  in 1 M  $\text{KNO}_3$ ). The corresponding values reported at  $25^\circ\text{C}$  are 0.71 for ferr(i/o)cyanide in 1 M  $\text{KCl}$ ,<sup>90</sup> and 2 in KI for iodine couple.<sup>23,91</sup>

From the Stokes-Einstein equation, eq. (III-1), values of  $D_j\eta/T$  were calculated using the values of  $k_j$  in Table 3<sup>92</sup> and  $A = 11.2 \text{ cm}^2$ . The values were well within the range of values reported in the literature.



0.001M Feic, 1M KNO<sub>3</sub>, 500rpm, 5°C

Figure VI-4

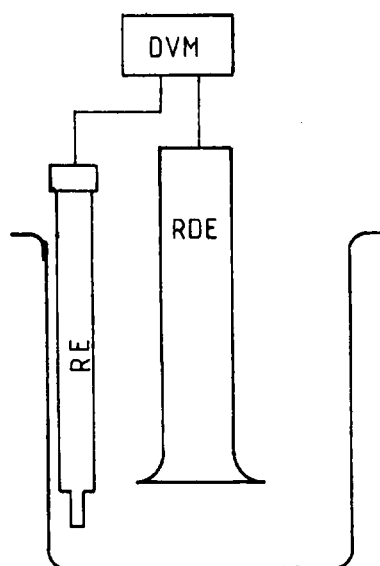


Figure VI-5

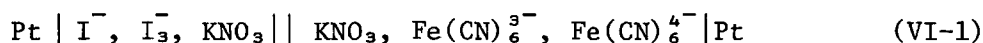
TABLE VI-3. LIMITING CURRENTS IN 1 M KNO<sub>3</sub>, 500 RPM, 5°C, ON 11.2 cm<sup>2</sup>  
PLATINUM RDE.

| (mol l <sup>-1</sup> )                |                    | 10 <sup>3</sup> Lj/A | k <sub>j</sub> /A M <sup>-1</sup> | Residual Current at<br>C <sub>j</sub> = 0 <sup>b</sup> (10 <sup>3</sup> A) |
|---------------------------------------|--------------------|----------------------|-----------------------------------|----------------------------------------------------------------------------|
| <u>10<sup>3</sup> [Feic]</u>          | 1.0                | 2.74                 | 2.665                             | 0.053                                                                      |
| (+ equimolar<br>Feoc)                 | 2.0                | 5.34                 |                                   |                                                                            |
|                                       | 3.0                | 8.07                 |                                   |                                                                            |
| <u>10<sup>3</sup> [Feoc]</u>          | 1.0                | 2.44                 | 2.425                             | 0.017                                                                      |
| (+ equimolar<br>Feic)                 | 2.0                | 4.87                 |                                   |                                                                            |
|                                       | 3.0                | 7.29                 |                                   |                                                                            |
| <u>10<sup>3</sup> [KI]</u>            | 1.04               | 4.98                 | 4.717                             | 0.059                                                                      |
| (no iodine<br>present)                | 1.07               | 5.08                 |                                   |                                                                            |
|                                       | 2.05               | 9.73                 |                                   |                                                                            |
|                                       | 3.34               | 15.8                 |                                   |                                                                            |
|                                       | 5.114 <sup>a</sup> | 23.8 <sup>a</sup>    |                                   |                                                                            |
|                                       | 7.879 <sup>a</sup> | 36.4 <sup>a</sup>    |                                   |                                                                            |
| <u>10<sup>3</sup> [I<sub>2</sub>]</u> | 0.4715             | 3.19                 | 6.588                             | 0.092                                                                      |
| (+ 0.1 M KI)                          | 0.9326             | 6.25                 |                                   |                                                                            |
|                                       | 1.399              | 9.30                 |                                   |                                                                            |

<sup>a</sup> Not considered for calculating  $k_I^-$ ; <sup>b</sup> Calculated from intercepts.

d) E.m.f. Measurements.

The e.m.f. of the cell



was measured at several temperatures. Each half cell was a 50 ml beaker filled with the corresponding solution, immersed in the thermostat. The bridge was an Agar gel (see Section V.2.d). The concentrations used were  $[\text{Feic}] = [\text{Feoc}] = 2 \times 10^{-3} \text{ M}$ ;  $[\text{I}^-] = [\text{I}_3^-]^{\frac{1}{3}} = 4 \times 10^{-2} \text{ M}$ ,  $[\text{KNO}_3]$  was 0.5, 1 or 1.5 M. The  $\text{I}_3^-$  was generated by passing 1.050 mA during 30 minutes through 150 ml of  $4 \times 10^{-2} \text{ KI}$  in 1 M  $\text{KNO}_3$  to give  $6.528 \times 10^{-5} \text{ M I}_2$  (net). The e.m.f. of each half cell was measured against a SCE always kept in the right hand side cell. The temperature was raised from  $5^\circ$  to  $30^\circ\text{C}$  in  $5^\circ\text{C}$  steps. Readings were taken when the e.m.f. did not appear to vary in a 15 minute period by more than 0.1 mV.

e) Catalytic Runs.

The basic arrangement is shown in Figure 5. The preparation of the solutions has been described in Section V.2.a. The preconditioned electrode was normally immersed in the KI solution, and so was the SCE. The solution was allowed to equilibrate thermally for 10 min while the disk rotated. The reaction was started by addition of the ferricyanide solution. The sampling procedure has already been discussed. Aliquots were taken every 4 minutes, 8 samples per run. The  $E_{\text{cat}}$  values were monitored with the DVM (Hewlett Packard). Addition of the products was done according to Section (V.2.d.).

f) Treatment of Kinetic Data.

The absorbances were given the same treatment as described in Section (V.3). Because of eq. (II-8)  $v_{\text{cat}}$  must change appreciably when the volume of the reaction mixture changes by 40 ml due to sampling.

Following the definitions of Section (II.2.a.), let us assume that  $v_{\text{hom}}$  and  $u_{\text{cat}}$  are constant. The concentration of  $I_3^-$  in each successive sample  $C_1, C_2, \dots$  of size  $v$  ml is then:

$$C_1 = C_0 + v_{\text{hom}} \Delta t_1 + \frac{Au_{\text{cat}}}{V_0} \Delta t_1 \quad (\text{VI-2a})$$

$$C_2 = C_1 + v_{\text{hom}} \Delta t_1 + \frac{Au_{\text{cat}}}{V_0 - v} \Delta t_2 \quad (\text{VI-2b})$$

and for the  $N$ -th sample:

$$C_N = C_{N-1} + v_{\text{hom}} \Delta t_N + \frac{Au_{\text{cat}}}{V_0 - (N-1)v} \Delta t_N \quad (\text{VI-3})$$

where  $\Delta t_j$  is the time interval  $t_j - t_{j-1}$  between sample  $j-1$  and  $j$ .

On addition, we have for the  $N$ -th sample:

$$C_N - v_{\text{hom}} t_N = C_0 + Au_{\text{cat}} S_N \quad (\text{VI-4})$$

where

$$S_N = \sum_{j=1}^N \Delta t_j / [V_0 - (j-1)v] \quad (\text{VI-5a})$$

$$t_N = \sum_{j=1}^N \Delta t_j, \quad t_0 = 0 \quad (\text{VI-5b})$$

Therefore a plot of  $C_N - v_{\text{hom}} t_N$  vs.  $S_N$  should produce a straight line from whose slope the initial catalytic rate  $v_{\text{cat}}$  can be calculated according to eq. (II-8). In practice, some of the resulting plots had slight downward curvatures, thus suggesting that  $u_{\text{cat}}$  decreased with time. The data were therefore fitted by least squares to a second degree polynomial (see Appendix 2) of the form:

$$C_N - v_{\text{hom}} t_N = C_0 + Au_{\text{cat}} S_N + a S_N^2 \quad (\text{VI-6})$$

The catalytic rate is reported as  $u'_{\text{cat}}$  in moles of iodine per second

( $u'_{\text{cat}} = Au_{\text{cat}}$ ).

### VI.3. Results and Discussion.

#### a) Comparison of Kinetic and Electrochemical Experiments.

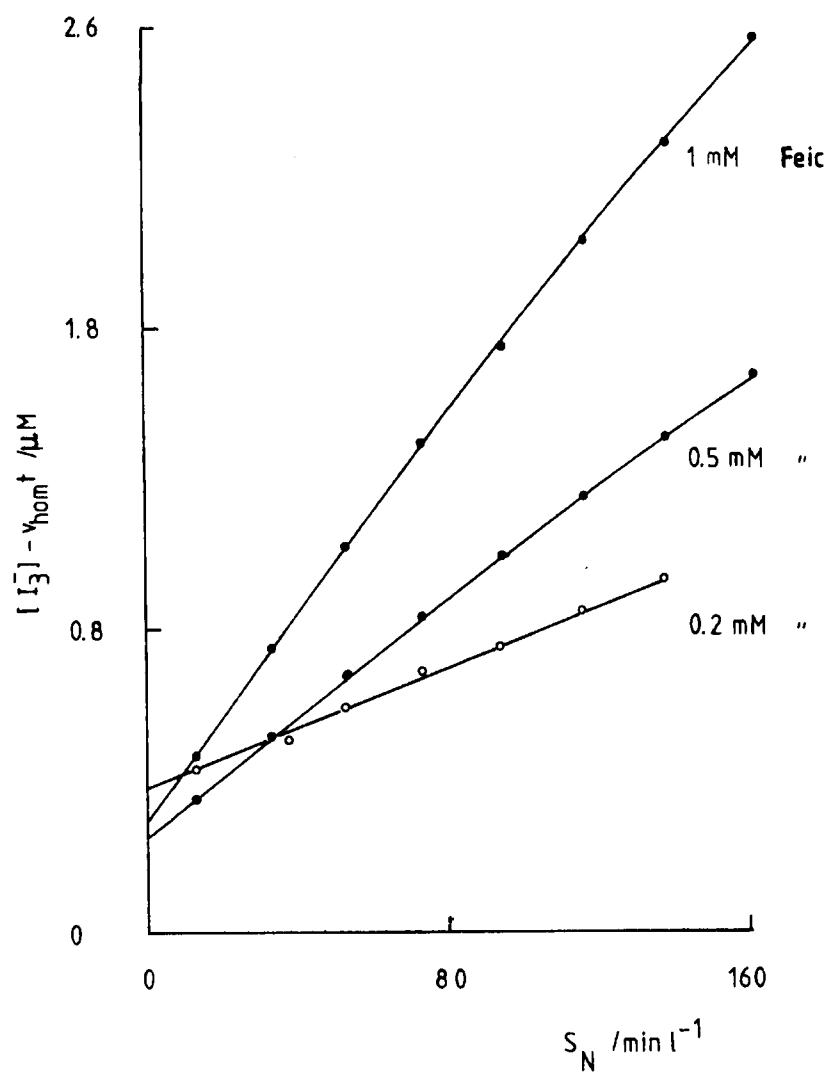
Figure 6 shows typical kinetic plots according to eq. (4). The lines usually do not cross the origin due to the uncertainty of the absorbance of the reference solution. This should not affect the slope at  $t = 0$ . Figure 7 shows typical I-E curves of ferricyanide and iodide. Their intercept denotes the mixture current and potential on the assumption of additivity. The value of the catalytic rate (in mA) at the catalyst potential  $E_{\text{cat}}$  obtained under the same experimental conditions is shown as a filled circle in Figure 7. It should coincide with the intersection point within experimental error if the electrochemical mechanism is followed. The closeness of the two points in many runs is taken as evidence in favour of the hypothesis, thus confirming earlier results by Spiro and Griffin.<sup>4</sup> The results of these comparative experiments are shown in Table 4. They prove that within experimental error the catalysis proceeds by electron transfer through the metal.

TABLE IV-4. KINETIC AND ELECTROCHEMICAL RUNS

$10^{-3}$  M Feic, 0.05 M KI, 1 M KNO<sub>3</sub>, 5°C

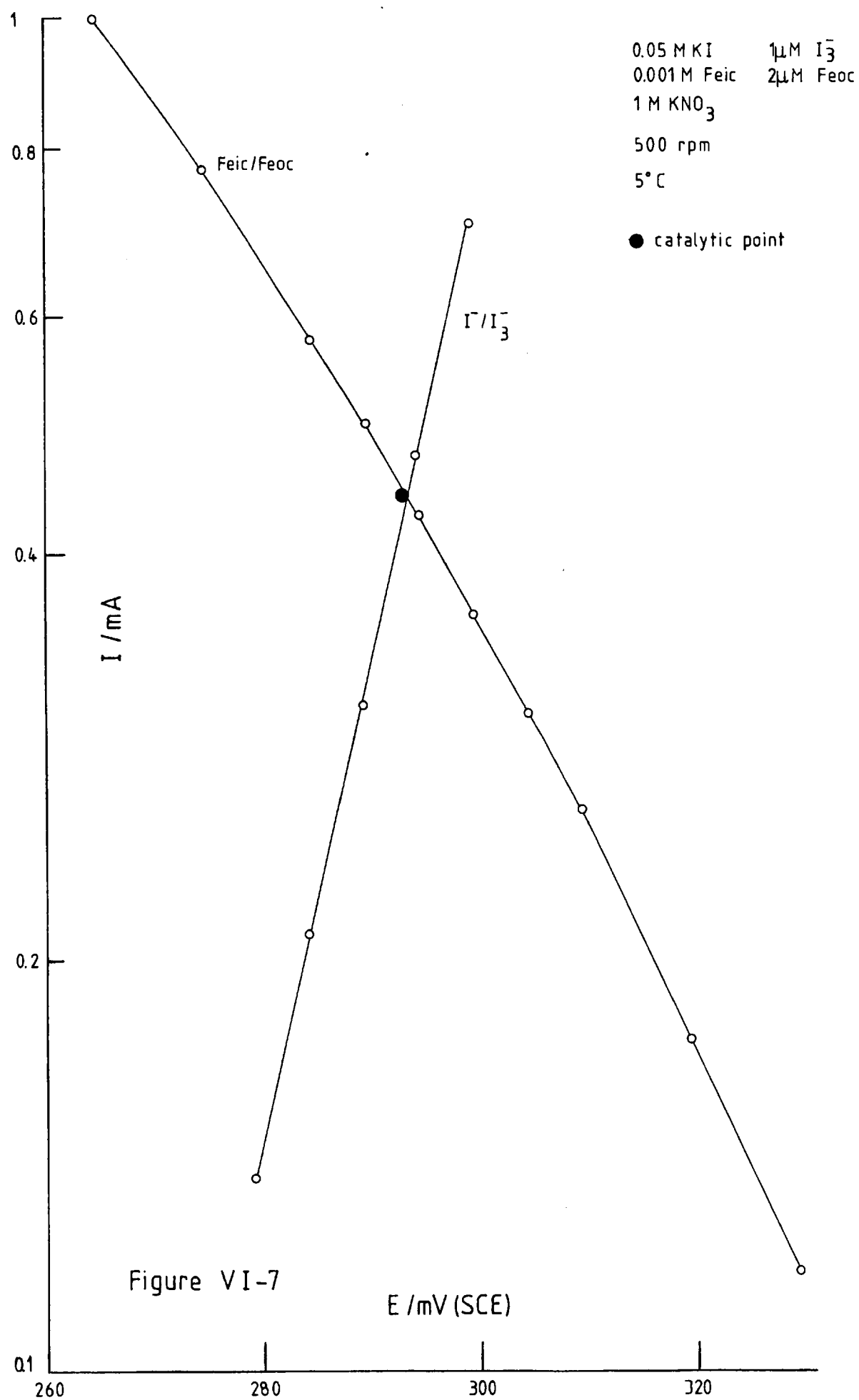
| $\omega$<br>/rpm | $10^9 u'_{\text{cat}}$<br>/mol s <sup>-1</sup> | $E_{\text{cat}}$<br>/mV | $10^9 i_m/2F$<br>/mol s <sup>-1</sup> | $E_m$<br>/mV      |
|------------------|------------------------------------------------|-------------------------|---------------------------------------|-------------------|
| 100              | $1.12 \pm 0.07$ (3)                            | $293 \pm 1$ (3)         | $1.17 \pm 0.01$ (2)                   | $293 \pm 0.5$ (2) |
| 500              | $2.48 \pm 0.03$ (5)                            | $295 \pm 1$ (5)         | $2.36 \pm 0.07$ (5)                   | $294 \pm 0.4$ (5) |

Number of runs are in brackets. Appended figures ( $\pm$ ) are standard deviations of the mean.



50 mM KI, 1 M  $\text{KNO}_3$ , 500 rpm, 5°C

Figure V I-6



During the kinetic runs the catalyst potential reached quite stable values almost immediately after completing addition of the ferricyanide solution; it fell by about 1 mV during the 30 minutes of reaction.

It was always very close to the final equilibrium potential.

The dependence of  $u'_{\text{cat}}$  on  $\omega$  is shown in the plot of  $1/u'_{\text{cat}}$  vs.  $\omega^{-\frac{1}{2}}$  (Figure 8) and Table 5. The line passes through the origin, which according to eq. (II-36) indicates that the reaction at the surface is very fast and therefore probably in equilibrium at the catalyst surface. This is borne out by the constancy of  $E_{\text{cat}}$  with  $\omega$ , according to eq. (II-30). It is worth checking the reversibility of the electrochemical couples.

TABLE VI-5. DEPENDENCE OF CATALYTIC RATE AND POTENTIAL ON  $\omega$

$10^{-3}$  M Feic,  $5 \times 10^{-2}$  M KI, 1 M KNO<sub>3</sub>, 5 °C.

| $\omega/\text{rpm}$ | $10^9 u'_{\text{cat}}/\text{mol s}^{-1}$ | $E_{\text{cat}}/\text{mV}$ |
|---------------------|------------------------------------------|----------------------------|
| 100                 | $1.12 \pm 0.07$ (3)                      | $293 \pm 1$ (3)            |
| 200                 | $1.56 \pm 0.05$ (2)                      | $293 \pm 0.5$ (2)          |
| 300                 | 2.06                                     | 293                        |
| 500                 | $2.48 \pm 0.03$ (5)                      | $295 \pm 0.1$ (5)          |
| 1000                | 3.74                                     | 293                        |
| 2000                | $5.42 \pm 0.3$ (2)                       | $292 \pm 0.1$ (2)          |

From eq. (II-30), assuming that  $[\text{Feoc}] = [\text{I}_3^-] = 0$  and that  $i/L_j \ll 1$  for Feic and  $\text{I}^-$ , it follows that the two  $i$ - $E$  curves are described by:

$$\frac{1}{i} = \frac{1}{L_{\text{Feic}}} + \frac{\exp [f(E-E_2^0)]}{k_{\text{Feoc}}[\text{Feic}]} \quad (\text{VI-7})$$

and

$$\frac{1}{i} = \frac{3}{L_{\text{I}^-}} + \frac{\exp[-2f(E-E_1^0)]}{k_{\text{I}_3^-}[\text{I}^-]^3} \quad (\text{VI-8})$$

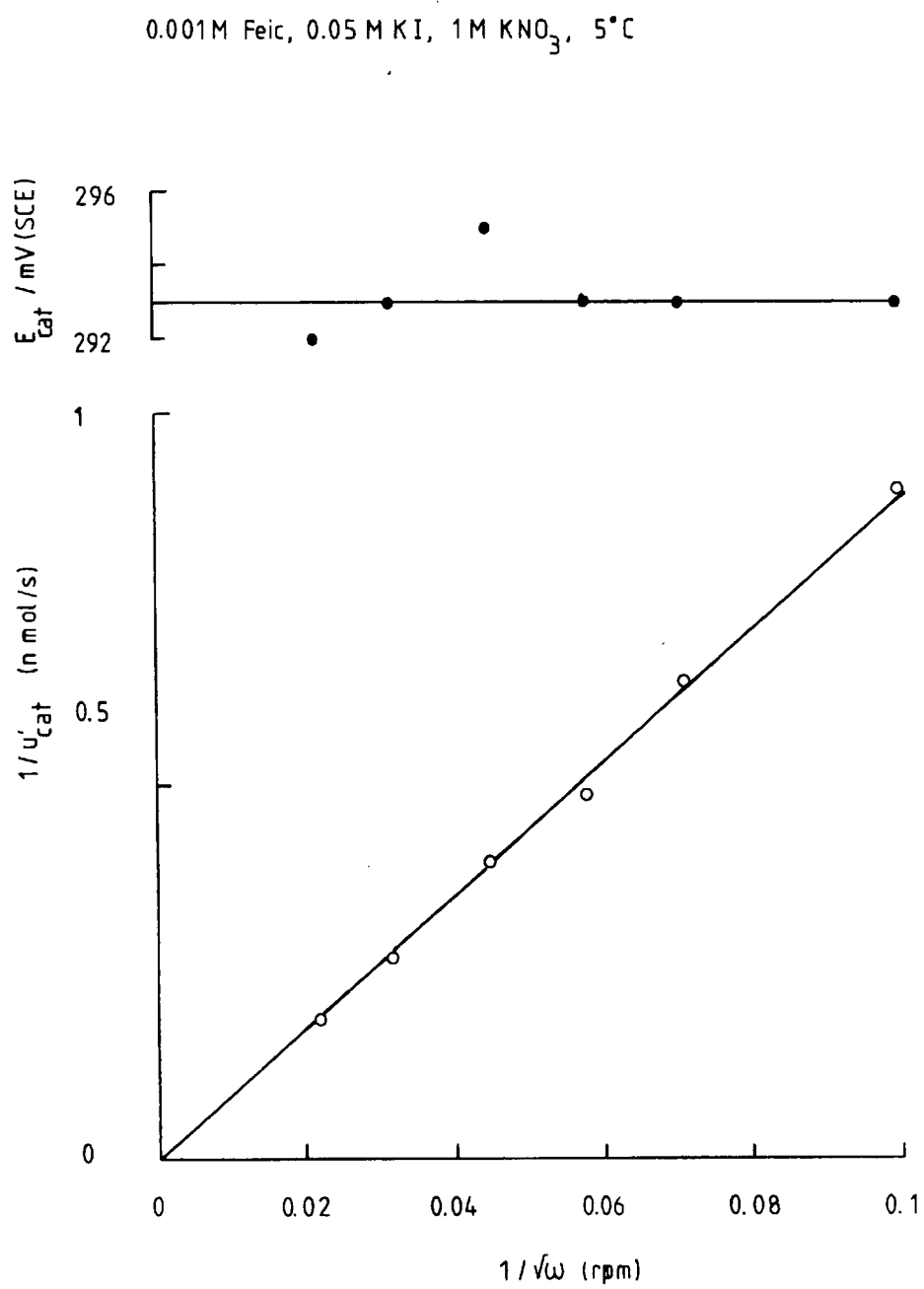


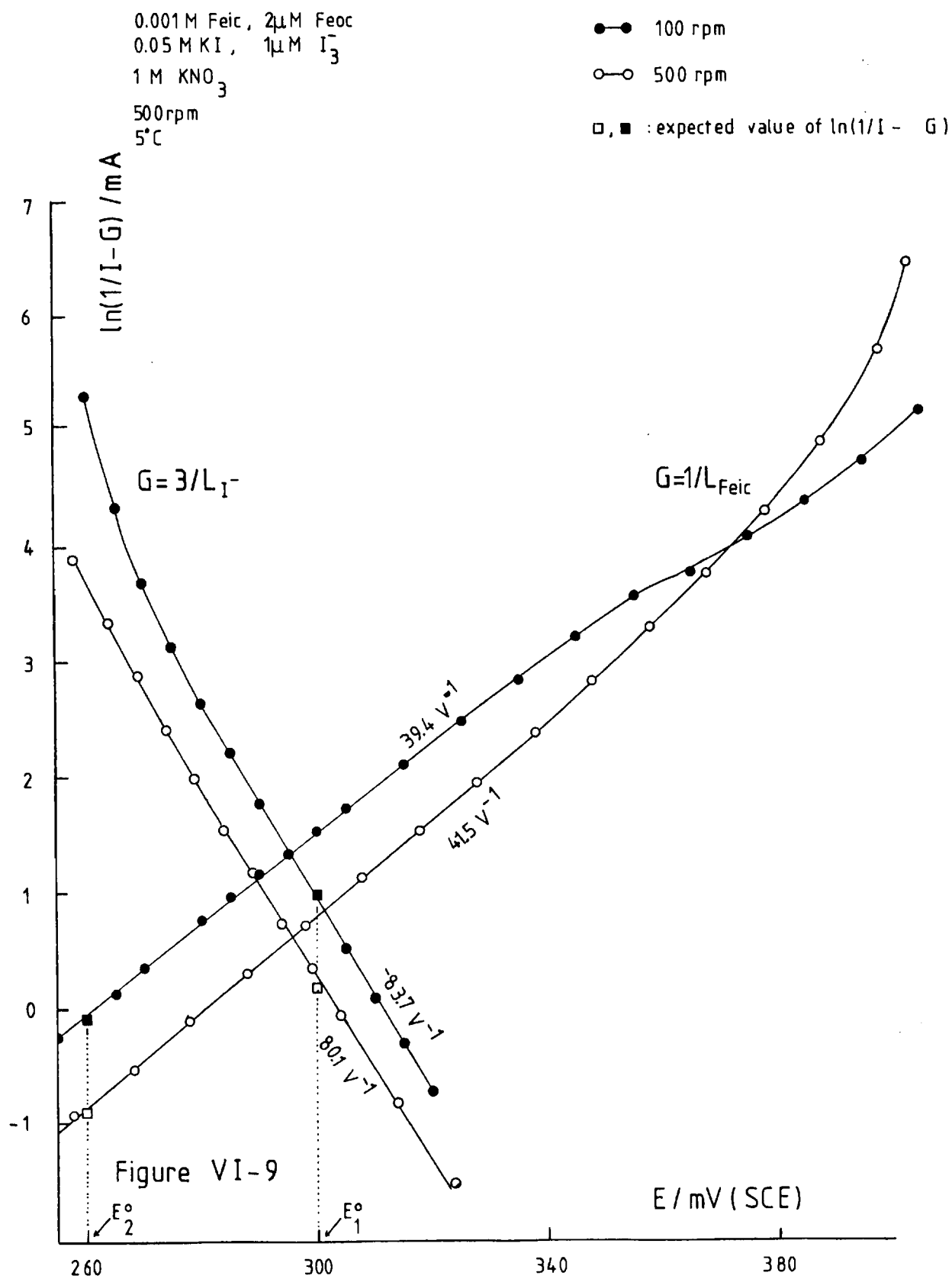
Figure VI-8

Therefore a plot of  $\ln(1/i - 1/L_{\text{Feic}})$  vs.  $E$  for the  $\text{Feic}/\text{Feoc}$  couple, and of  $\ln(1/i - 3/L_{\text{I}^-})$  vs.  $E$  for the  $\text{I}^-/\text{I}_3^-$  couple, should furnish straight lines, as shown in Figure 9 at 100 rpm and 500 rpm. The slopes are close to the expected  $41.7 \text{ V}^{-1}$  for  $\text{Feic}/\text{Feoc}$  and  $-83.4 \text{ V}^{-1}$  for  $\text{I}^-/\text{I}_3^-$ , and they pass very close to the calculated values  $-\ln(k_{\text{Feoc}}[\text{Feic}])$  and  $-\ln(k_{\text{I}_3^-}[\text{I}^-]^3)$  when  $E = E_j^\circ$ , which are shown as squares on the curves. Near the formal potentials there is a marked deviation from linearity, probably because the initial small amount of product cannot be neglected at these low currents. The mixture potential luckily lies well inside the unequivocal reversible region, and the catalytic rate may be described by the model in Section II.2.c. The magnitudes of the kinetic parameters to be expected in several situations are shown in Table 6, according to Table II-1.

TABLE VI-6. EXPECTED KINETIC PARAMETERS FOR THE CATALYSED REACTION  
I-1 UNDER TOTAL MASS TRANSPORT CONTROL.

| Condition                           | Reaction Order w.r.t.                             |              |                                                  |                | Calculated rate constant $\times 10^6$<br>(5°C, 500 rpm,<br>1 M $\text{KNO}_3$ ) |
|-------------------------------------|---------------------------------------------------|--------------|--------------------------------------------------|----------------|----------------------------------------------------------------------------------|
|                                     | <u>Reactants</u><br>$\text{Fe}(\text{CN})_6^{3-}$ | $\text{I}^-$ | <u>Products</u><br>$\text{Fe}(\text{CN})_6^{4-}$ | $\text{I}_3^-$ |                                                                                  |
| No added product                    | 2/3                                               | 1            | 0                                                | 0              | $5.70^a \text{ mol s}^{-1}$                                                      |
| Added $\text{Fe}(\text{CN})_6^{4-}$ | 2                                                 | 3            | -2                                               | 0              | $1.17 \text{ mol s}^{-1}$                                                        |
| Added $\text{I}_3^-$                | 1                                                 | 3/2          | 0                                                | -1/2           | $2.33 \text{ mol s}^{-1}$                                                        |

<sup>a</sup> From W (eq. II-36a).



b) Theoretical Calculation of Catalytic Rates.

The catalytic rate at 5°C, 500 rpm, and in 1 M KNO<sub>3</sub> was calculated from several concentrations of reactants and products, by solving eq. (II-31) for  $i_m$  and then converting to units of  $u'_{cat}$ ; the value of  $i_m$  was used to calculate  $E_m$ , or  $E_{cat}$ , from eq. (II-30b). The  $k_j$  used were those in Table 3; the  $E_j^0$ , those in Table 13. Solution of eq. (II-31) was accomplished numerically either by the Newton-Raphson method<sup>93</sup> or by successive partitioning of the interval to which the solution belonged (Appendix 3). Identical numerical results were obtained by both methods.

c) Effect of Reactant Concentration.

Table 7 summarises these effects on  $u'_{cat}$  and  $E_{cat}$ .

TABLE VI-7. EFFECT OF CHANGES IN THE REACTANT CONCENTRATION

1 M KNO<sub>3</sub>,  $\omega$  = 500 rpm, 5°C.

| $10^3$ [Feic]<br>/M | $10^3$ [KI]<br>/M | $10^9 u'_{cat}/\text{mol } \ell^{-1}$ |       | $E_{cat}/\text{mV}$ |       |
|---------------------|-------------------|---------------------------------------|-------|---------------------|-------|
|                     |                   | exp.                                  | calc. | exp.                | calc. |
| 0.2                 | 50                | 0.71                                  | 0.78  | 279                 | 280   |
| 0.5                 |                   | 1.45                                  | 1.52  | 286                 | 288   |
| 1.0                 |                   | 2.48                                  | 2.49  | 295                 | 294   |
| 2.0                 |                   | 3.72                                  | 4.05  | 299                 | 300   |
| 5.0                 |                   | 6.85                                  | 7.65  | 307                 | 307   |
| 1.0                 | 30                | 1.45                                  | 1.57  | 306                 | 307   |
|                     | 50                | 2.48                                  | 2.49  | 295                 | 294   |
|                     | 80                | 3.68                                  | 3.70  | 283                 | 282   |
|                     | 150               | 5.82                                  | 5.89  | 263                 | 265   |
|                     | 300               | 5.80                                  | 8.74  | 245                 | 244   |

The agreement between the experimental and the calculated value is good. The slightly larger calculated  $u'_{\text{cat}}$  values could indicate a certain amount of interference between the couples.

It is important to calculate the reaction orders in  $[\text{Feic}]$  and  $[\text{I}^-]$ . At  $10^{-3}$  M Feic and  $5 \times 10^{-2}$  M KI the ratio  $2F u'_{\text{cat}}/L_j$  is 0.18 for Feic and 0.002 for iodide. Thus, in eq. (II-36b) the  $L_{\text{I}^-}$  term may be neglected, but not the  $L_{\text{Feic}}$  term, and to obtain the reaction order the  $\ln(1/u'_{\text{cat}} - 4F/3L_{\text{Feic}})$  should be plotted vs.  $\ln C_j$ . From the resulting slopes the order w.r.t. Feic is  $0.66 \pm 0.02$ , and w.r.t.  $\text{I}^-$ ,  $1.02 \pm 0.01$ , in excellent agreement with expectations. Hussain too<sup>85</sup> found an order of 0.7 w.r.t. Feic and 1 w.r.t.  $\text{I}^-$ . The rate constant of  $5.24 \times 10^{-6}$  from the Feic plot, and of  $5.03 \times 10^{-6}$  from the  $\text{I}^-$  plot are somewhat lower than the predicted values in Table 6.

The dependence of  $E_{\text{cat}}$  on  $\ln C_j$  is shown in Figure 10. According to eqs. (II-41) the slopes should be -24.0 mV and +7.99 mV for  $\partial E_{\text{cat}}/\partial \ln[\text{I}^-]$  and  $\partial E_{\text{cat}}/\partial \ln[\text{Feic}]$ , respectively. The actual values of -23.2 mV and 8.25 mV agree reasonably well considering the approximations involved in these equations. At constant  $[\text{Feic}]$ , the ratio  $2F u'_{\text{cat}}/L_{\text{Feic}}$  becomes more favourable for  $u'_{\text{cat}}$  to be represented by eq. (II-41) at the lowest  $[\text{I}^-]$  values, while at constant  $[\text{I}^-]$  high  $[\text{Feic}]$  should be preferred. This is why the lines in Figure 10 are biased towards the experimental points more likely to meet this condition.

#### d) Effect of High $\text{Fe}(\text{CN})_6^{4-}$ Concentration.

High Feoc concentrations should have important effects on the kinetics, as summarised in Table 6. The approximations in the theory require that  $i_m$  or  $u'_{\text{cat}}$  be very small so that significant experimental uncertainties result. Disagreement between the expected and the experimental reaction orders may be a result of these uncertainties or of the fact that a value

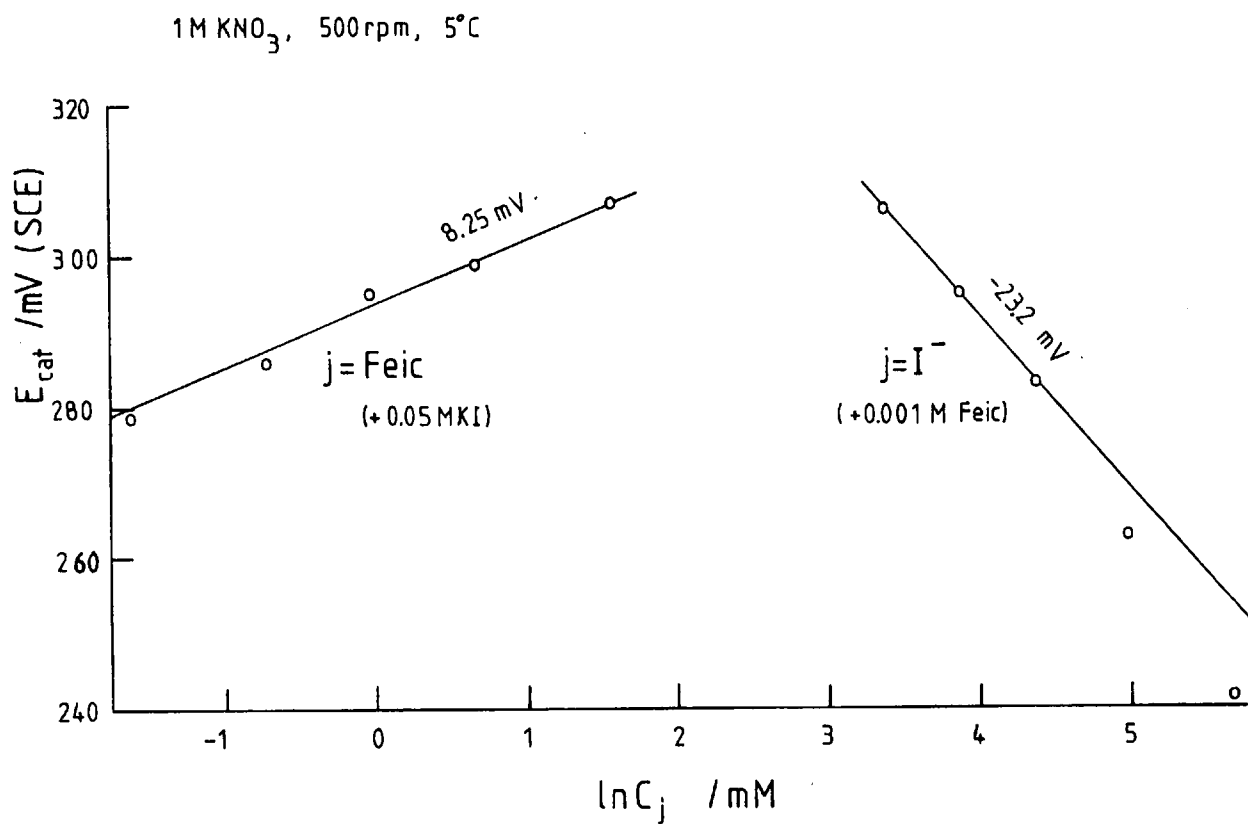


Figure VI-10

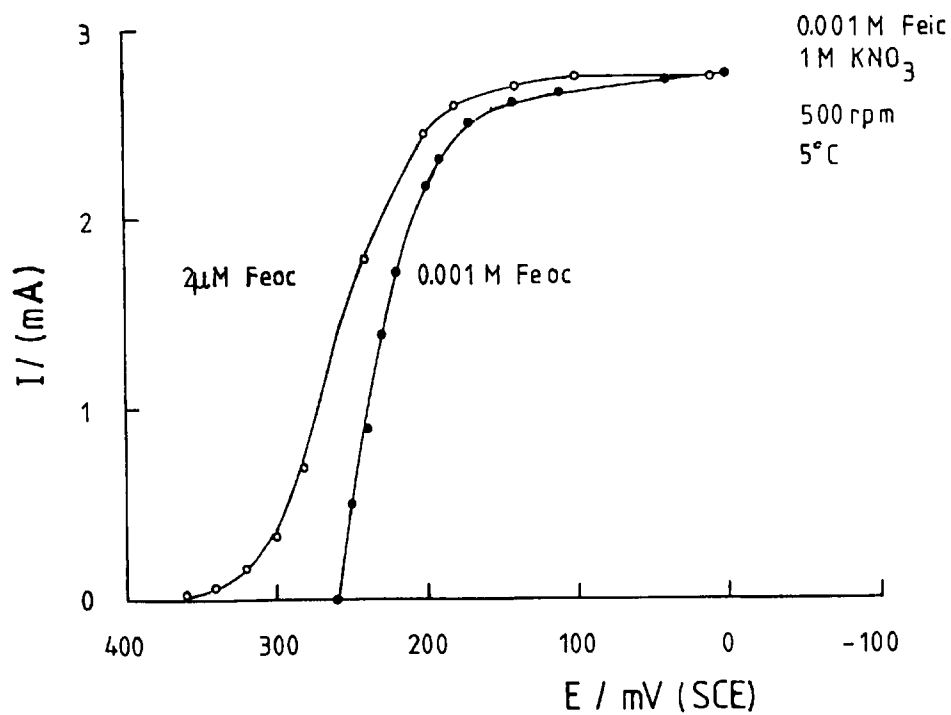


Figure VI-11

of  $u'_{\text{cat}}$  low enough has not been reached. Therefore numerical calculations of  $u'_{\text{cat}}$  are useful to check that the reaction follows the predicted behaviour. The results are in Table 8. The order in  $\text{Fe}(\text{CN})_6^{4-}$  appears

TABLE VI-8. EFFECT OF ADDED  $\text{Fe}(\text{CN})_6^{4-}$  ON CATALYTIC RATE

5°C, 500 rpm, 1 M  $\text{KNO}_3$ .

| Concentration $\times 10^3 / (\text{M})$ |              |                               | $u'_{\text{cat}} \times 10^9 / (\text{mol s}^{-1})$ |       | $E_{\text{cat}} / (\text{mV})$ |       | $E_2^{\text{rev}} / \text{mV}$ |
|------------------------------------------|--------------|-------------------------------|-----------------------------------------------------|-------|--------------------------------|-------|--------------------------------|
| $\text{Fe}(\text{CN})_6^{3-}$            | $\text{I}^-$ | $\text{Fe}(\text{CN})_6^{4-}$ | exp.                                                | calc. | exp.                           | calc. |                                |
| 0.5                                      | 50           | 0.4                           | 0.124                                               | 0.200 | 263                            | 264   | 265                            |
| 0.7                                      |              |                               | 0.248                                               | 0.361 | 270                            | 271   | 273                            |
| 1.0                                      |              |                               | 0.552                                               | 0.650 | 278                            | 278   | 282                            |
| 1.5                                      |              |                               | 1.00                                                | 1.19  | 285                            | 285   | 292                            |
| 2.0                                      |              |                               | 1.59                                                | 1.76  | 290                            | 290   | 298                            |
| 1.0                                      | 30           | 0.4                           | 0.109                                               | 0.179 | 280                            | 281   | 282                            |
|                                          | 32           |                               | 0.145                                               | 0.214 | 279                            | 280   |                                |
|                                          | 34           |                               | 0.267                                               | 0.252 | 280                            | 280   |                                |
|                                          | 37           |                               | 0.321                                               | 0.313 | 279                            | 280   |                                |
|                                          | 40           |                               | 0.338                                               | 0.382 | 280                            | 279   |                                |
|                                          | 50           |                               | 0.552                                               | 0.650 | 278                            | 278   |                                |
|                                          | 60           |                               | 0.876                                               | 0.962 | 277                            | 276   |                                |
|                                          | 70           |                               | 1.17                                                | 1.30  | 274                            | 274   |                                |
| 1.0                                      | 50           | 0.001                         | 2.39                                                | 2.48  | 294                            | 294   | 425                            |
|                                          |              | 0.01                          | 2.31                                                | 2.42  | 293                            | 294   | 370                            |
|                                          |              | 0.1                           | 1.71                                                | 1.82  | 290                            | 290   | 315                            |
|                                          |              | 0.2                           | 1.16                                                | 1.30  | 286                            | 286   | 286                            |
|                                          |              | 0.4                           | 0.552                                               | 0.651 | 278                            | 278   | 278                            |
|                                          |              | 0.6                           | 0.265                                               | 0.352 | 271                            | 270   | 270                            |
|                                          |              | 1.0                           | 0.046                                               | 0.140 | 259                            | 259   | 260                            |

to be  $\sim 1.8$  and that in  $I^- \sim 2.8$  over the concentration range studied. These values are certainly far away from the orders in the absence of products. The orders approach the predicted values of 2 and 3, respectively (Table 6). That they do not quite reach these values may be due to the ratios  $2F u'_{\text{cat}}/L_{\text{Feoc}}$  not being small enough and to the experimental uncertainty as  $u'_{\text{cat}}$  becomes smaller and smaller. The order in Feoc is  $\sim -2.5$ , in excess of the expected value of  $-2$ , again, probably because of experimental uncertainty. The order using the last two lines in Table 8 is  $-1.8$  in that concentration region. The feature of note in Table 8 is the generally good agreement between the experimental rates and potentials, and the calculated values, in these extreme conditions.

The reversible (formal) potential of the Feic/Feoc couple,  $E_2^{\text{rev}}$ , has been calculated from the Nernst equation and the  $E_j^0$  values in Section VI.3.g. Table 8 shows that as  $[\text{Feoc}]$  increases, the catalyst potential remains close to  $E_2^{\text{rev}}$  during the reaction, because the  $i$ - $E$  curve for this couple becomes much steeper, as shown in Figure 11, so that  $E_m$  must lie very close to  $E_2^{\text{rev}}$ .

#### e) Effect of High $I_2$ Concentration.

The concentration range that can be explored with  $I_2$  is limited because of the high optical absorbance in both the sample and reference cells due to the background  $I_3^-$ . This makes the spectrophotometer readings highly unstable because the small absorbance increase due to the  $I_3^-$  produced by the reaction depends on the small difference of two large quantities. The results are shown in Table 9. The agreement with theory is fair.

As explained in Chapter II, the effect of the products on the rate has a thermodynamic origin: the equilibrium at the catalyst surface is

TABLE VI-9. EFFECT OF HIGH ADDED IODINE CONCENTRATION

$10^{-3}$  M Feic, 1 M KNO<sub>3</sub>, 5°C, 500 rpm.

| $10^3$ [KI]<br>/M | $10^3$ [I <sub>2</sub> ]<br>/M | $10^9$ u' <sub>cat</sub> /mol s <sup>-1</sup> |       | E <sub>cat</sub> /mV |       | E <sub>i</sub> <sup>rev</sup> /mV<br>(calc.) |
|-------------------|--------------------------------|-----------------------------------------------|-------|----------------------|-------|----------------------------------------------|
|                   |                                | exp.                                          | calc. | exp.                 | calc. |                                              |
| 37                | 0.01                           | 1.62                                          | 1.90  | 303                  | 302   | 281                                          |
|                   | 0.03                           | 1.53                                          | 1.65  | 305                  | 305   | 294                                          |
|                   | 0.05                           | 1.09                                          | 1.52  | 306                  | 308   | 300                                          |
| 50                | 0.01                           | 2.39                                          | 2.40  | 294                  | 295   | 270                                          |
|                   | 0.03                           | 2.08                                          | 2.23  | 297                  | 297   | 283                                          |
|                   | 0.05                           | 1.96                                          | 2.09  | 298                  | 299   | 289                                          |

displaced towards the reactant side according to the principle of Le Chatelier, thereby reducing the concentration gradient across the diffusion layer. This decreases the rate-controlling fluxes of the various species.

f) Effect of [KNO<sub>3</sub>].

Changing the supporting electrolyte concentration affects several parameters. Among these are the viscosity and density of the solution; the diffusion coefficients depend on the ionic strength and on the viscosity [eq.(III-1)]; the formal potentials  $E_j^0$  depend on ionic strength too. The change in u'<sub>cat</sub> on [KNO<sub>3</sub>] is shown in Table 10, as well as the difference  $E_2^0 - E_1^0$ .

TABLE VI-10. EFFECT OF  $[\text{KNO}_3]$ . $10^{-3}$  M Feic, 0.05 M KI, 500 rpm, 5°C.

| $[\text{KNO}_3]$<br>/M | $10^9 u'_{\text{cat}}$<br>/mol s <sup>-1</sup> | $E_1^0$<br>/ V | $E_2^0$<br>/ V | $E_2^0 - E_1^0$ <sup>a</sup><br>/ V | $10^{-8} 2FW^{-1}K^{2/3}$<br>/mol s <sup>-1</sup> |
|------------------------|------------------------------------------------|----------------|----------------|-------------------------------------|---------------------------------------------------|
| 0.5                    | 1.84                                           | 0.2951         | 0.2430         | -0.0523                             | 1.16                                              |
| 1.0                    | 2.48                                           | 0.3000         | 0.2598         | -0.0404                             | 1.15                                              |
| 1.5                    | 2.79                                           | 0.2980         | 0.2638         | -0.0343                             | 1.19                                              |

<sup>a</sup> Directly measured difference.

The calculation in the last column is an attempt to correlate the value of  $u'_{\text{cat}}$  with the change in  $E_2^0 - E_1^0$  or its equivalent equilibrium constant,  $K$ , equal to  $\exp[2F(E_2^0 - E_1^0)/RT]$ . The quantity  $W^{-1}$  is, according to eq. (II-36b):

$$2F/W = 1/u'_{\text{cat}} - 4F/3L_{\text{Feic}} \quad (\text{VI-9})$$

Thus, by eq. (II-36a) the product  $W^{-1}K^{2/3}$  should remain constant if all of the change in  $u'_{\text{cat}}$  is due to changes in  $E_2^0 - E_1^0$ . The constancy of the figures in the last column ( $\pm 2\%$ ) supports this view, that variations in the equilibrium constant override all of the rheological variations when the concentration of the supporting electrolyte is changed.

The increase of  $u'_{\text{cat}}$  with increasing  $[\text{KNO}_3]$  was noted by Hussain<sup>85</sup> too, who attributed it to increased ion pairing between  $\text{K}^+$  and Feic that facilitates electron transfer at the catalyst to the  $\text{K}^+ - \text{Feic}$  complex. This is a basically correct interpretation. The changes in  $E_2^0$  towards more positive values support it.

g) Effect of Temperature.

This is shown in Table 11, which reveals that the rate decreases as the temperature is increased. From the Arrhenius plot an apparent activation energy of  $-4.05 \text{ Kcal mol}^{-1}$  is obtained by least squares (the homogeneous reaction has an activation energy of

TABLE VI-11. EFFECT OF TEMPERATURE ON THE CATALYTIC RATE  $10^{-3} \text{ M Feic}$ ,  
 $5 \times 10^{-2} \text{ M KI}$ ,  $1 \text{ M KNO}_3$ ,  $500 \text{ rpm}$ .

| $T/^{\circ}\text{C}$ | $u'_{\text{cat}} \times 10^9$<br>/mol s <sup>-1</sup> |
|----------------------|-------------------------------------------------------|
| 5                    | 2.48                                                  |
| 15                   | 1.86                                                  |
| 20                   | 1.73                                                  |
| 30                   | 1.35                                                  |

$+9.20 \text{ Kcal mol}^{-1}$  (Section IV.4.c)). This surprising negative value can be explained in terms of the total mass transport control model in Chapter II. In effect, from the definition of apparent activation energy:

$$E_a = -R \frac{\partial \ln u'_{\text{cat}}}{\partial (1/T)} = -R \frac{\partial \ln(k_{I_3}^{1/3} k_{\text{Feoc}}^{2/3})}{\partial (1/T)} - \frac{2F}{3} \frac{\partial [(E_2^{\circ} - E_1^{\circ})/T]}{\partial (1/T)} \quad (\text{VI-10})$$

where only the temperature-dependent terms have been included. From the definition of  $k_j$  in eq. (II-13):

$$k_{I_3}^{1/3} k_{\text{Feoc}}^{2/3} \propto D_{I_3}^{2/9} D_{\text{Feoc}}^{4/9} \nu^{-1/6} \quad (\text{VI-11})$$

where again temperature-independent terms have been left out. Since values of the diffusion coefficients are not available in  $1 \text{ M KNO}_3$ , it is convenient to introduce the Stokes-Einstein equation:

$$D = kT/6\pi\eta r \quad (\text{VI-12})$$

where  $r$  is the radius of the diffusing molecule. Although this equation is unlikely to hold quantitatively for the linear  $\text{I}_3^-$  ion, it is not unreasonable to assume that over a short temperature range  $D \propto T/\eta$ . Thus, eq. (10) becomes:

$$E_a = -R \frac{\partial \ln[\nu^{-1/6} (T/\eta)^{2/3}]}{\partial (1/T)} - \frac{2F}{3} \frac{\partial (E_2^0 - E_1^0)/T}{\partial (1/T)} \quad (\text{VI-13})$$

Thus the activation energy is composed of the activation energy for diffusion, expressed by the first differential term, and by the change in the standard enthalpy of the reaction,  $\Delta H^0$ . This follows from the Gibbs-Helmholtz equation, taking  $n = 1$ :

$$\Delta H^0 = \left( \frac{\partial (\Delta G^0/T)}{\partial (1/T)} \right)_P = -F \left( \frac{\partial (E_2^0 - E_1^0)/T}{\partial (1/T)} \right)_P \quad (\text{VI-14})$$

The transport term was evaluated from tabulated data. Viscosities of 101.1 g  $\text{KNO}_3$  in 1000 g  $\text{H}_2\text{O}$  (9.183% by weight) were obtained from Landolt-Bornstein.<sup>94</sup> The density of this solution was interpolated from the data of 8% and 10% solution from International Critical Tables.<sup>83a</sup> With these data, at  $10^\circ\text{C}$  a 9.183%  $\text{KNO}_3$  solution is  $\sim 0.965$  M, which is close to our experimental conditions. The resulting data are displayed in Table 12. From the corresponding Arrhenius plot an activation energy, of  $+ 3.63 \text{ Kcal mol}^{-1}$  is obtained.

TABLE VI-12. VARIATION OF  $\eta$  AND  $\rho$  WITH TEMPERATURE FOR 0.965 M  $\text{KNO}_3$ .

| $T$<br>/K | $\rho$<br>/g cm <sup>-3</sup> | $\eta$<br>/g cm <sup>-1</sup> s <sup>-1</sup> | $10^{-9} T^2 \eta \nu^{-1/2}$<br>/K <sup>2</sup> g <sup>-2</sup> cm <sup>3</sup> s <sup>3/2</sup> |
|-----------|-------------------------------|-----------------------------------------------|---------------------------------------------------------------------------------------------------|
| 273.15    | 1.0624                        | 0.01624                                       | 2.288                                                                                             |
| 283.15    | 1.0603                        | 0.01217                                       | 5.053                                                                                             |
| 303.15    | 1.0536                        | 0.007925                                      | 16.871                                                                                            |

The temperature variation of thermodynamic term is shown in Table 13. Figure 12 shows the corresponding plot of  $(E_2^0 - E_1^0)/T$  vs.  $1/T$ , from which it is possible to calculate its contribution to  $E_a$  as  $-7.72 \text{ Kcal mol}^{-1}$ .

TABLE VI-13. EFFECT OF TEMPERATURE ON e.m.f. s  $2 \times 10^{-3} \text{ M Feic}$ ,  
 $2 \times 10^{-3} \text{ M Feoc}$ ,  $4 \times 10^{-2} \text{ M KI}$ ,  $6.4 \times 10^{-7} \text{ M I}_3^-$ ,  $1 \text{ M KNO}_3$ .

| $T/^{\circ}\text{C}$ | $E_1^0/\text{V}$ | $E_2^0/\text{V}$ | e.m.f. <sup>a</sup> /V | e.m.f. <sup>b</sup> /V |
|----------------------|------------------|------------------|------------------------|------------------------|
| 5                    | 0.3000           | 0.2598           | -0.0404                | -0.0402                |
| 10                   | 0.3021           | 0.2514           | -0.0508                | -0.0507                |
| 15                   | 0.3031           | 0.2425           | -0.0606                | -0.0606                |
| 20                   | 0.3039           | 0.2333           | -0.0706                | -0.0706                |
| 25                   | 0.3043           | 0.2244           | -0.0800                | -0.0799                |
| 30                   | 0.3044           | 0.2156           | -0.0889                | -0.0888                |

<sup>a</sup> From direct measurement; <sup>b</sup> Calculated from  $E_2^0 - E_1^0$

Thus:

$E_a = -7.72 \text{ Kcal mol}^{-1} + 3.63 \text{ Kcal mol}^{-1} = -4.09 \text{ Kcal mol}^{-1}$   
 very close to the experimental value of  $-4.05 \text{ Kcal mol}^{-1}$ .

By inspection of the rate constant in the absence of products in Table II-1 and of the form of eq. (13), the apparent activation energy may be expressed as:

$$E_a = (v_{\text{ox}_1} E_d^{\text{ox}_1} + v_{\text{red}_2} E_d^{\text{red}_2})\phi + \phi\Delta H^0 \quad (\text{VI-15})$$

Assuming that the diffusion activation energies of  $\text{ox}_1$  and  $\text{red}_2$  are equal ( $=E_d$ ):

$$E_a = E_d + \phi\Delta H^0 \quad (\text{VI-16})$$

The energy diagram in Figure 13 represents the path of the reaction along the 'reaction coordinate'. The first step, bringing the reactants from the bulk of the solution to the catalytic surface, requires almost

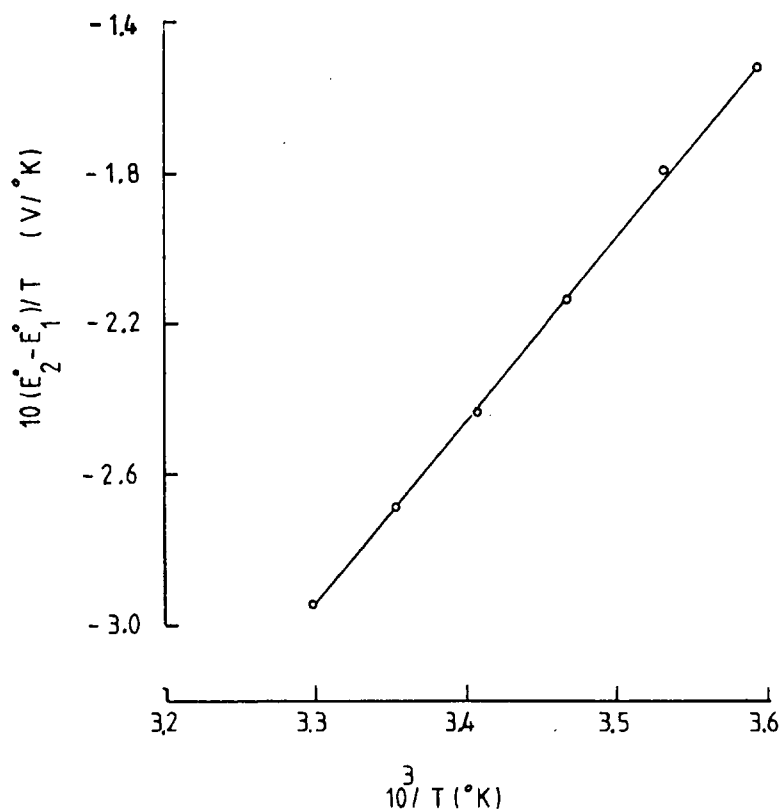


Figure VI-12

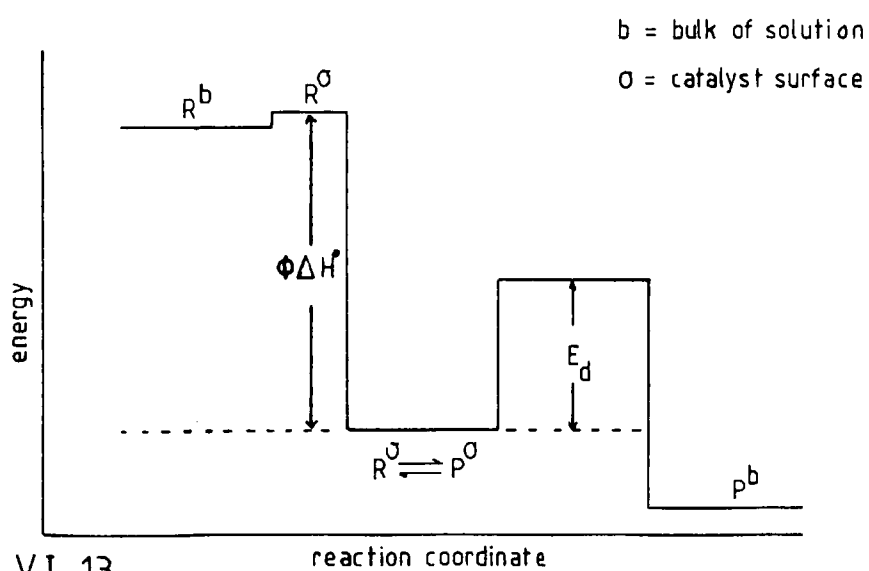
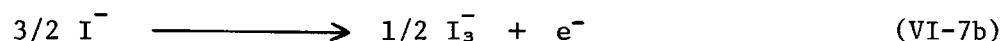
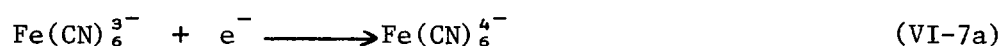


Figure VI-13

no energy expenditure, because of the assumption  $i_m/L_j \sim 0$  ( $j$  = reactants) which makes  $C_{\text{reactants}}^\sigma \approx C_{\text{reactants}}^{\text{bulk}}$ . At the surface the products are formed very quickly, liberating an amount  $\phi\Delta H^0$  calories on assuming equilibrium concentrations. Therefore, as far<sup>as</sup> the catalyst is concerned, the reaction rate is instantaneous. However, transport of products to the bulk phase does require energy, and since it involves the highest barrier in the sequence, controls the rate. Increasing the temperature shifts the equilibrium to the reactant side, and although it is easier now for the products to climb the diffusion barrier, there is less of them at the surface so that the overall balance is unfavourable to the rate.

#### VI.4. Conclusions.

The results in the previous section show that reaction (I-1) is in equilibrium at the surface of oxidised platinum, the reaction being controlled by the rate of mass transport across the diffusion layer. The fact that the partial electrochemical charge transfer reactions:



are also in equilibrium at the mixture potential is a strong indication that equilibrium of the overall reaction takes place by electron transfer between the reactants across the metal catalyst. The fact that neither of the participants of the reaction is adsorbed on oxidised platinum,<sup>33,44</sup> seems to rule out any mechanism other than charge transfer through the metal. Furthermore, this absence of adsorption renders more probable the assumption of undisturbed overlap of the  $i$ - $E$  curves. Therefore, each substance reacts according to their individual mechanisms of electron transfer.

The Feic/Feoc system has been studied on platinum<sup>32-34,38,95,96</sup> gold,<sup>34,36,37,97</sup> mercury and thallium-amalgam,<sup>98</sup> sodium-tungsten bronzes,<sup>99</sup> and on the soft metals bismuth, lead and cadmium.<sup>100</sup> Once mass transport-free data are obtained, the overall picture, especially on platinum and gold is that of a basically simple electron transfer. Tafel plots tend to be linear, giving anodic and cathodic transfer coefficients close to 0.5<sup>32-34</sup>; the reduction reaction is first order on [Feic], and the oxidation one is first order on [Feoc].<sup>32-34,36</sup> The differential capacitance of platinum<sup>33</sup> and gold<sup>97</sup> is independent of the concentration of the electroactive species, which rules out physical adsorption.<sup>17g</sup> There is no evidence that the primary coordination shell (the cyanide shell) is in any way altered during the reaction, a characteristic it shares with  $\text{MnO}_4^-/\text{MnO}_4^{2-}$ <sup>101</sup> and  $\text{Mo(CN)}_8^{3-}/\text{Mo(CN)}_8^{4-}$ <sup>102</sup> systems. In this respect, their electrodic behaviour is no different from that in the homogeneous electron exchange of these systems,<sup>103,104</sup> processes called "outer sphere reactions".<sup>105</sup>

Because of its large radius [ $3.51\text{\AA}$ ]<sup>106</sup> the centre of the hydrated Feic or Feoc anion does not coincide with the outer Helmholtz plane, OHP, which is the locus of the centres of the fully hydrated cations of the supporting electrolyte in contact with the electrode surface<sup>11d</sup> (the Stokes radius of the  $\text{K}^+$  ion is  $1.3\text{\AA}$ <sup>107</sup>). Thus, the centre of these anions is  $\sim 2\text{\AA}$  inside the diffuse double layer, as has been shown by Frumkin.<sup>98</sup>

Double layer effects play an important role in the reduction of Feic. Electrostatic repulsion between the negatively charged electrode and the highly charged anion (Frumkin effect, Chapter I), especially in dilute solutions of the base electrolyte, leads to a considerable drop in the current on bismuth, lead and cadmium electrodes at potentials more negative than the potential of zero charge ( $E_{\text{pzc}}$ ).<sup>98,100</sup> The magnitudes

of these effects follow the sequence  $\text{Bi} > \text{Pb} > \text{Cd}$ , in accord with the trend in the negativity of their  $E_{\text{pzc}}$ :  $\text{Bi} < \text{Pb} < \text{Cd}$ . The Frumkin effect must surely be a universal phenomenon, but its influence is often masked by other phenomena like H deposition and oxide formation especially on platinum.<sup>97</sup>

However, the authors in references 98 and 100, have not considered the possible effects of ion pair formation between the  $\text{Feic}/\text{Feoc}$  species and the cations from the base electrolyte,<sup>35</sup> which also shifts the standard reduction potential of the couple towards more positive values. It has been suggested,<sup>36</sup> that the enhanced kinetics are not so much due to more favourable  $E_j^0$ , but to a different mechanism by which the activated complex is formed by collision of a cation with the already formed ion pair. This explains the observed first order dependence of the current on the cation concentration. The activation energy itself is independent of the concentration of the supporting electrolyte.<sup>36</sup> The effect of the cation is not merely to reduce coulombic repulsion with the electrode, but to provide a new pathway for the electron transfer through a bridge between the electrode and the reacting anion. This process has been treated theoretically,<sup>108,109</sup> by an extension of current quantum theories of charge transfer,<sup>15,19,20</sup> and found to be more likely than direct non-bridged, electron transfer. A detailed study conducted on gold electrodes<sup>97</sup> has led to the conclusion that the reduction of  $\text{Feic}$  proceeds by the electron hopping first from the metal to the bridge, and then from here to the anion. Since this transfer is radiationless<sup>19</sup> its occurrence depends on equalisation of the electron energy levels of the ions by a favourable random fluctuation on the solvent polarisation around the ions, at which point the electron may tunnel between the degenerate energy levels in the activated complex.<sup>19</sup>

Theoretical treatment of these effects, including bridging by a cation, leads to the result that the experimental transfer coefficient  $\alpha_{\text{exp}}$  from Tafel plots corrected for every possible kind of extraneous effects is given by<sup>15</sup>:

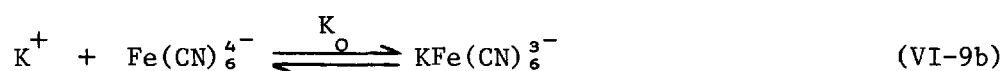
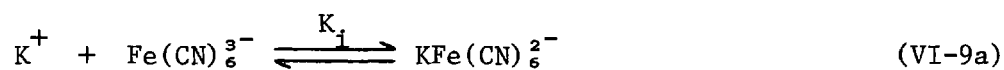
$$\alpha_{\text{exp}} = 0.5 + (E - E_j^{\text{rev}})F/2\lambda \quad (\text{VI-8})$$

where  $\lambda$  is the energy that would be required to change the solvent configuration from that of the reactants to that<sup>of</sup> the products, while keeping the reactant nuclei at their equilibrium positions. Its value has been estimated at  $\sim 1.2$  eV.<sup>106</sup> From the dependence of  $\alpha_{\text{exp}}$  on the potential, values of 0.45,<sup>97</sup> 0.31,<sup>110</sup> and 0.83<sup>36</sup> eV have been found. At low concentrations of supporting electrolyte the double layer effect of Frumkin would appear as well. The  $\text{I}^-/\text{I}_3^-$  system has not been studied to an extent comparable to Feic/Feoc. Mechanistic knowledge is still at a macroscopic stage and there is no agreement between the authors as to its course (cf. Chapter III). This is because the relatively complicated events of bond forming/breaking, and of charge transfer with possible adsorption of  $\text{I}^-$  or  $\text{I}_2$  on the electrode surface.

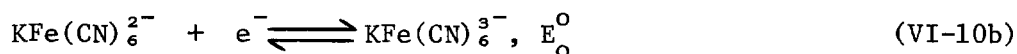
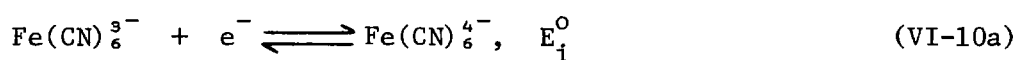
It has been reported that the exchange current density for iodide oxidation on previously oxidised platinum exhibits a 1/2 order dependence on the concentration of the  $\text{K}_2\text{SO}_4$  base electrolyte,<sup>111</sup> which again has been attributed to Frumkin effects. However, the analysis of the experimental data is based on the assumption of irreversible adsorption of iodide, which is unjustified as iodine species do not adsorb irreversibly on platinum.<sup>45</sup> Whatever the mechanisms of the Feic/Feoc and  $\text{I}^-/\text{I}_3^-$  charge transfers at the oxidised platinum surface, our evidence shows that they occur side by side in the mixed solution.

Rigorously speaking, however, one cannot deduce the mechanism of the reaction from the fact that equilibrium has been reached at the surface: for a given mass transport regime, the rate will be the same regardless of the mechanism (or mechanisms) leading to surface equilibrium. However, we have been able to show that the experimental ( $i_m$ ,  $E_m$ ) values coincide with the ( $2F u'_{cat}$ ,  $E_{cat}$ ) values, thus ruling out mechanisms other than electrochemical.

Another point concerns the species involved in the establishment of the formal potential and/or diffusion overpotential in the case of the Feic/Feic couple, since the cation-paired species must participate in the electron transfer too. Considering only association with one cation,  $K^+$  in this case, two equilibria are possible, with association constants,  $K_i$  and  $K_o$ :



Therefore, there are two simultaneous electrochemical equilibria:



These equilibria occur both in open circuit conditions (thus giving rise to the formal potentials of the couples) or in steady state current flow. In any case, only one potential is possible at the electrode. Then:

$$E = E_i^O + (1/f) \ln([Feic]/[Feoc]) \quad (VI-11a)$$

$$= E_o^O + (1/f) \ln([KFeic]/[KFeoc]) \quad (VI-11b)$$

where the  $E^O$  s are the standard equilibrium potentials of the couple concerned. The concentrations refer to those of the actual ionic

constituents. Either of eqs. (11) may be used to formulate the mixture potential in eq. (II-30b). From equilibria (9) it is found that

$$[\text{Feic}] = [\text{Feic}]_o / (1 + K_i [\text{K}^+]) \quad (\text{VI-12a})$$

$$[\text{Feoc}] = [\text{Feoc}]_o / (1 + K_o [\text{K}^+]) \quad (\text{VI-12b})$$

or that

$$[\text{KFeic}] = [\text{Feic}]_o / (1 + 1/K_i [\text{K}^+]) \quad (\text{VI-13a})$$

$$[\text{KFeoc}] = [\text{Feoc}]_o / (1 + 1/K_o [\text{K}^+]) \quad (\text{VI-13b})$$

The subindexed brackets refer to the overall Feic or Feoc concentration. Thus, whether one uses eq. (11a) in conjunction with eqs. (12) or eq. (11b) in conjunction with eqs. (13), the mixture potential depends on the overall concentration of Feic or Feoc.

## CHAPTER SEVEN

### CATALYSIS ON PLATINUM (REDUCED).

#### VII.1. Introduction.

The state of the electrode surface usually has noticeable consequences on electrode kinetics. Therefore it is important to examine this factor in an electrochemical catalytic mechanism.

The catalysis of reaction (I-1) on reduced (i.e., oxide-free) platinum is reported in this chapter.

#### VII.2. Experimental.

a) The chemicals and the experimental procedure were the same as in Chapters V and VI. All the experiments were carried out in doubly distilled water at 5°C. The catalytic runs were made either in the presence of 1 M KNO<sub>3</sub> or 1 M KCl.

#### b) Pre-Conditioning Procedures.

All the solutions employed were de-aerated with nitrogen. Once reduced (i.e., after step c in the following tables) the electrode was usually rinsed with doubly distilled water, spun in the air at high speed and left in it for ca. 10 minutes while the subsequent run was being prepared. The different procedures listed below were carried out in the sequence a, b, c, etc. In between the steps, the electrode was left on open circuit.

CAT (H<sub>2</sub>SO<sub>4</sub>)

| Step | Supporting Electrolyte             | E vs. SCE /V | Time | $\omega$ /rpm |
|------|------------------------------------|--------------|------|---------------|
| a    | 1 M H <sub>2</sub> SO <sub>4</sub> | 1.560        | 5 s  | 500           |
| b    | 1 M H <sub>2</sub> SO <sub>4</sub> | 0.960        | 40 s | 500           |
| c    | 1 M H <sub>2</sub> SO <sub>4</sub> | -0.162       | 3 s  | 0             |

CAT (KCl)

| Step | Supporting Electrolyte | E vs. SCE /V | Time    | $\omega$ /rpm |
|------|------------------------|--------------|---------|---------------|
| a    | 1 M KCl                | 1.560        | 5 s     | 500           |
| b    | 1 M KCl                | 0.960        | 40 s    | 500           |
| c    | 1 M KCl                | <-0.6        | ~ 3 min | 0             |

Step c in CAT (KCl) is similar to that used by Daum and Enke<sup>33</sup> in their study of the Feic/Feoc couple on platinum. Steps "a" and "b" were added in order to free the electrode of organic impurities. As this may cause dissolution of the metal,<sup>114</sup> the oxidation steps were later carried out in 1 M H<sub>2</sub>SO<sub>4</sub>, and the final reduction step in 1 M KCl (see following table).

CAT (H<sub>2</sub>SO<sub>4</sub>, KCl)

| Step | Supporting Electrolyte             | E vs. SCE /V | Time   | $\omega$ /rpm |
|------|------------------------------------|--------------|--------|---------------|
| a    | 1 M H <sub>2</sub> SO <sub>4</sub> | 1.560        | 5 s    | 500           |
| b    | 1 M H <sub>2</sub> SO <sub>4</sub> | 0.960        | 40 s   | 500           |
| c    | 1 M KCl                            | -0.600       | 15 min | 0             |

After step b in the CAT ( $\text{H}_2\text{SO}_4$ ,  $\text{KCl}$ ) procedure, the electrode was rinsed and spun in the air.

CAT ( $\text{H}_2\text{SO}_4$ ,  $\text{KCl}$ )/KI.

The CAT ( $\text{H}_2\text{SO}_4$ ,  $\text{KCl}$ ) procedure was first performed. Then enough solid KI was added to the 1 M  $\text{KCl}$  on open circuit to make a  $5 \times 10^{-2}$  M solution, while the electrode rotated at 500 rpm for 10 minutes.

CAT ( $\text{H}_2\text{SO}_4$ ,  $\text{KCl}$ )/KI/RM.

After the CAT ( $\text{H}_2\text{SO}_4$ ,  $\text{KCl}$ )/KI preparation the electrode was taken out, rinsed, and immersed for 10 min at 500 rpm in a reaction mixture containing  $10^{-3}$  M  $\text{Feic}$ ,  $5 \times 10^{-2}$  M KI and 1 M  $\text{KNO}_3$ , which had been prepared some 4 hours earlier.

c) Cyclic Voltammograms (CV).

Cyclic voltammograms were obtained by connecting a Chemical Electronics linear sweep generator LS1 to the external input of the Chemical Electronics TR70/2A potentiostat. The CVs were recorded on a Hewlett-Packard 7035B X-Y recorder. Its X-terminals were connected directly to the RE and WE terminals of the potentiostat; the Y-terminals (for current recording) were connected across a  $100 \Omega$  (5%) counting resistor (Figure IV-7a). The recorder settings were chosen so that its input resistance was larger than  $0.1 \text{ M } \Omega$  (the input resistance for each setting was listed in the instrument manual). This would have produced a maximum current drain of  $15 \mu\text{A}$  at the largest potential differences between WE and RE (1.5 V). Since the currents obtained are in the mA range, the error produced by this drain is not serious. The CVs reported here are interpreted mainly in a qualitative way.

### VII.3. Results and Discussion.

#### a) State of the Surface Following Pre-conditioning.

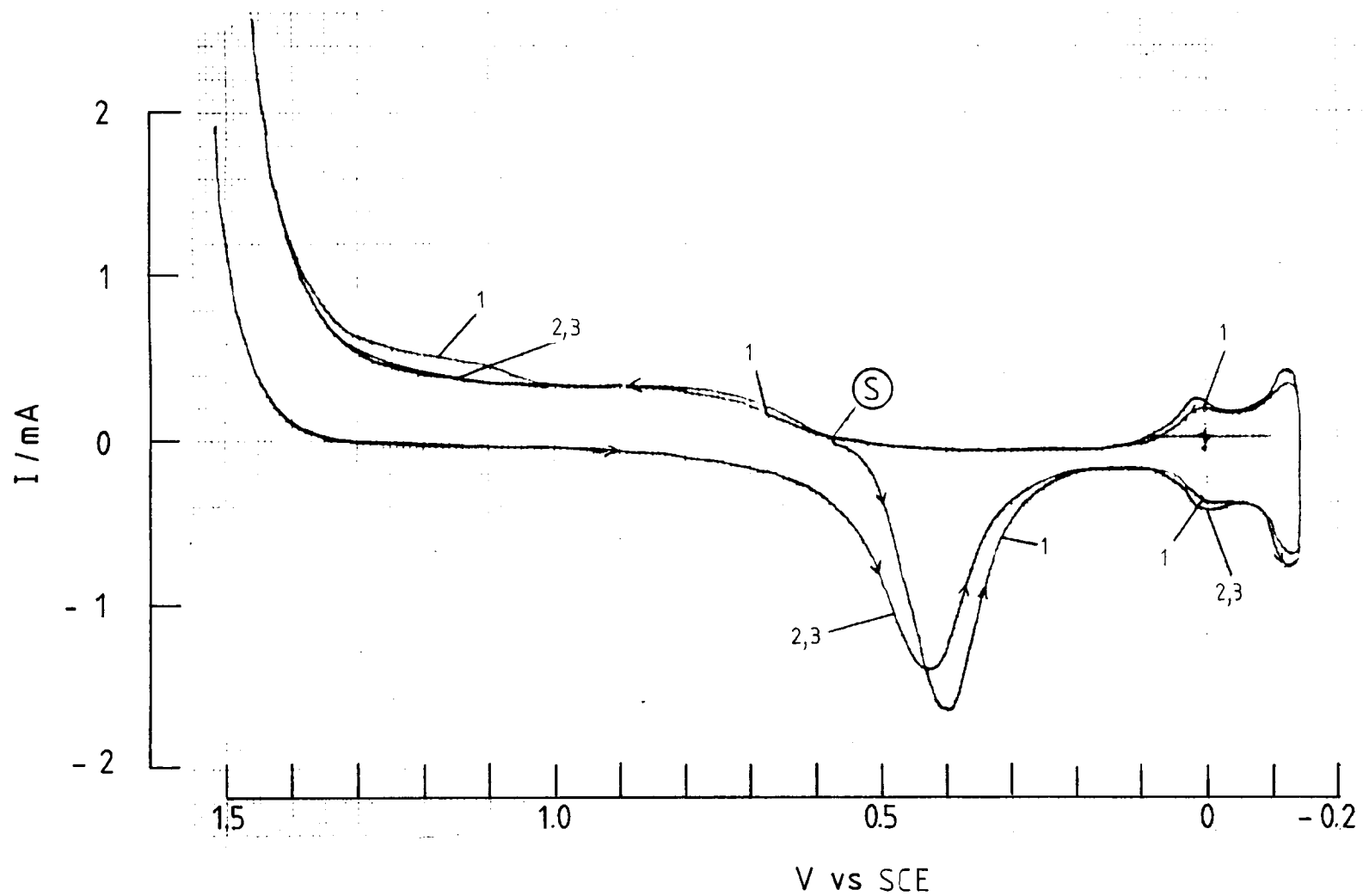
Figure 1 is a CV of the RDE in 1 M  $\text{H}_2\text{SO}_4$ ,  $\omega = 200$  rpm, at  $5^\circ\text{C}$ , at a sweep speed of  $28.5 \text{ mV s}^{-1}$ , between 1.560 V and -0.150 V. The electrode had been preoxidised according to the procedure outlined in Table VI-2, rinsed and immersed in a  $5 \times 10^{-2}$  M KI in 1 M  $\text{KCl}$  for 5 minutes, and rinsed again. The CV started in the cathodic direction (starting point marked "5") from OCV\*, and shows an oxide reduction peak at 0.4 V as would be expected from a pre-oxidised electrode (cf. Figure III-1). This peak shifts to 0.43 V in subsequent sweeps (marked "2" and "3") that reach the 1.560 V anodic limit. (Other features of the CV have been described in Chapter III, but our aim here is to show what happens to the oxide peak following pre-conditioning). Shifts in the oxide reduction peak towards more irreversible values (i.e., further away from the oxide formation region) as the positive limit of the sweep becomes more anodic have been attributed to re-arrangement of the oxide layer.<sup>29,112</sup> Progressive irreversibility with time at constant potential has been observed too,<sup>113</sup> and explained as strengthening of the oxide. Thus, the oxide formed according to Table VI-2 remains stable and attached to the surface in all the handlings preceding the catalytic run, and it is not altered either by contact with KI +  $\text{KCl}$  solutions.

Figure 2 shows the CV of the electrode preconditioned according to CAT ( $\text{H}_2\text{SO}_4$ ), rinsed, immersed in 1 M  $\text{KCl}$  without KI at OCV, and rinsed again. The conditions of the CV carried out in 1 M  $\text{H}_2\text{SO}_4$  are the same as in Figure 1. As expected, the first cathodic sweep lacks the oxide reduction peak at 0.4 V (although it reappears in subsequent sweeps at

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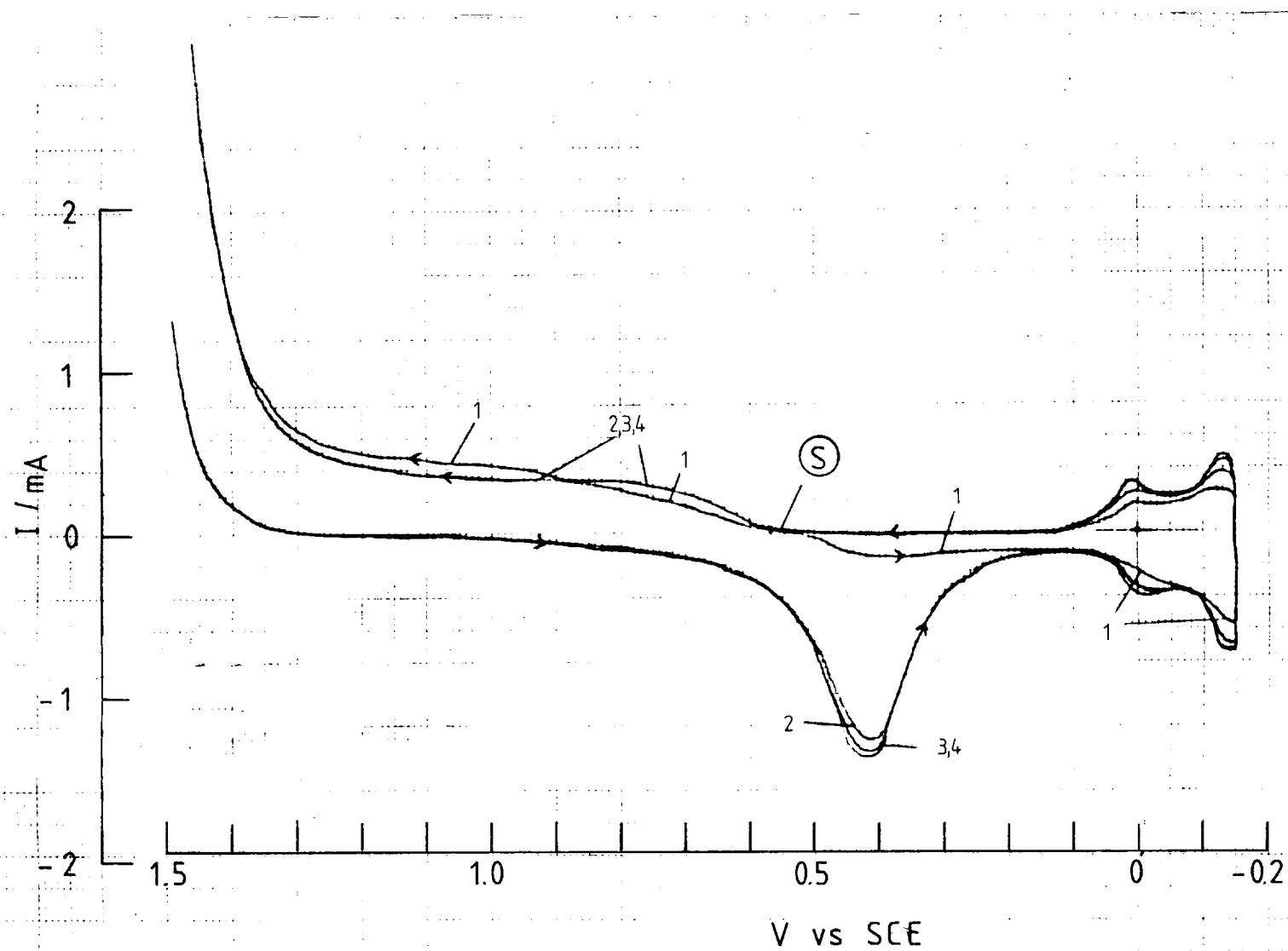
\* Open circuit voltage

Figure VII-1



Pt RDE, 200 rpm, 1 M  $\text{H}_2\text{SO}_4$ , 1.72 V / min, pretreated: AN ( $\text{H}_2\text{SO}_4$ ) / KCl + KI

Figure VII-2



Pt RDE, 200 rpm, 1 M  $\text{H}_2\text{SO}_4$ , 1.72 V/min, pretreated: CAT ( $\text{H}_2\text{SO}_4$ ) / KCl

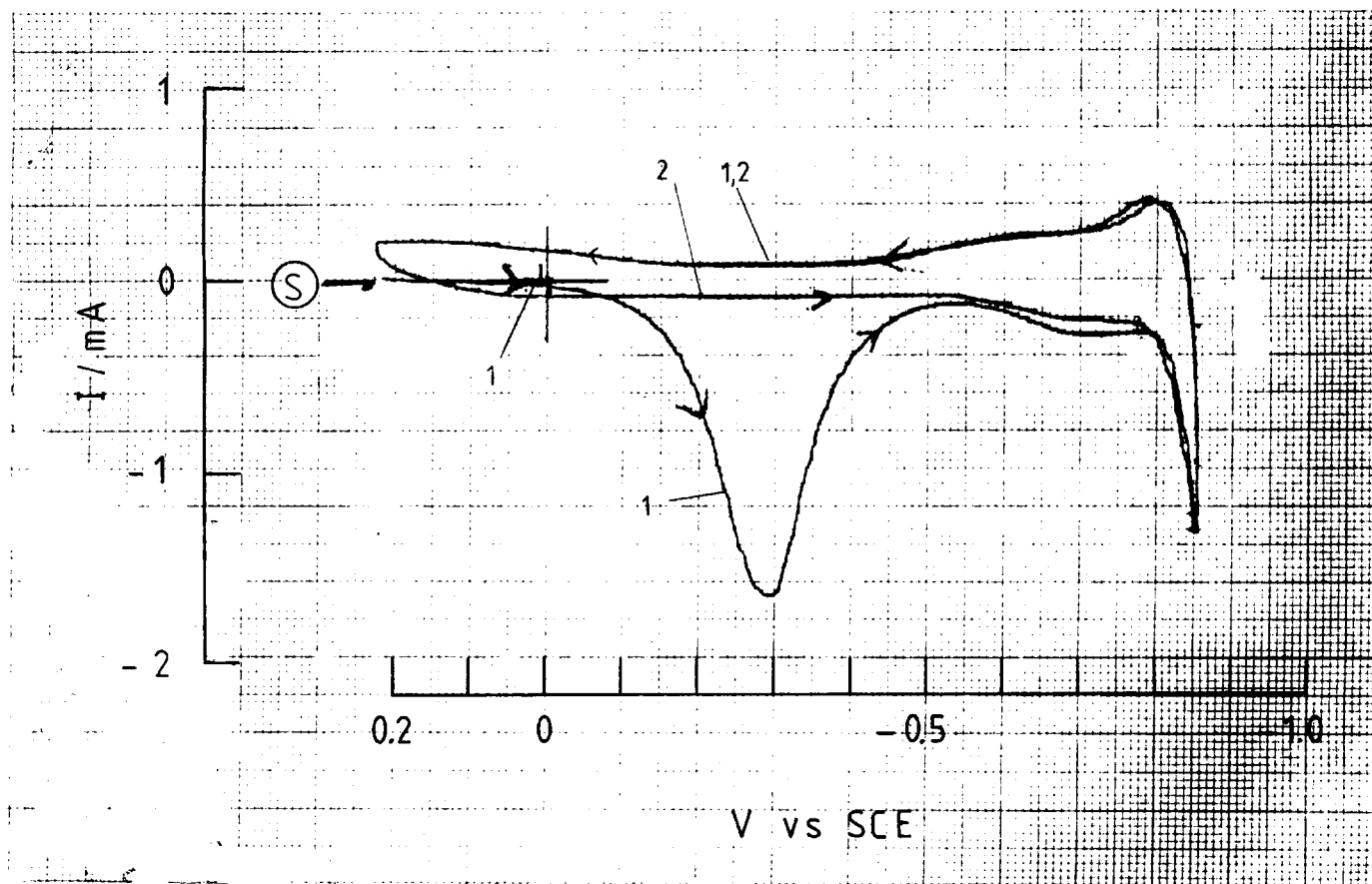
0.42 V); the horizontal trace appearing in its stead might be due to adsorbed atmospheric oxygen, reducible impurities from the KCl that remained adsorbed all through, ditto from the H<sub>2</sub>SO<sub>4</sub>, or the double layer charging current. In any case, this graph confirms the oxide-freeing result of the CAT (H<sub>2</sub>SO<sub>4</sub>) preconditioning.

Figure 3 shows the CV of the RDE in 1 M KCl oxidised according to Table VI-2 and rinsed before the CV. The CV was carried out at  $\omega = 0$  rpm, at  $31 \text{ mV s}^{-1}$ , between -0.850 and +0.210 V. The first cathodic sweep, started from OCV (marked "S") produces a large oxide reduction peak at -0.3 V, which disappears from the subsequent sweep since it was not allowed to reach oxide-forming potentials. The marked cathodic peak at -0.85 V is probably due to hydrogen evolution. The preceding H-adsorption/desorption peaks in the -0.6 to -0.8 V region are not as resolved as in H<sub>2</sub>SO<sub>4</sub> (Figures 1 and 2). Resolvability of this region is connected with the cleanliness of the solution.<sup>112</sup> This suggests that the 1 M KCl solution is a rather "dirty" one. The 0.7 V shift of the CV w.r.t. those obtained in H<sub>2</sub>SO<sub>4</sub> may be due to a combination of factors such as shift of the formal potentials of the oxide reduction and hydrogen evolution reactions due to change in pH ( $RT/F \ln 10^{-6} = -0.35 \text{ V}$ ), kinetic effects and possible blockage of the surface by adsorbed impurities. What Figure 3 shows clearly is that the oxide is reduced in 1 M KCl well before -0.600 V, the potential used in the pre-conditioning procedures for the reduction step.

#### b) Kinetic and Electrochemical Runs.

Table 1 shows the catalytic rates and the equivalent quantities obtained from the crossing points of the steady state current-voltage curves.

Figure VII-3



Pt RDE, 0rpm, 1 M KCl, 1.86 V/min, pretreated:  $\text{AN}(\text{H}_2\text{SO}_4)$ .

TABLE VII-1. CATALYTIC AND ELECTROCHEMICAL RUNS

 $10^{-3}$  M Feic,  $5 \times 10^{-2}$  M KI, 5°C, 500 rpm

 1 M KNO<sub>3</sub> (unless stated otherwise).

| Preconditioning                                         | $10^9 u'_{\text{cat}}$<br>/mol s <sup>-1</sup> | E <sub>cat</sub><br>/mV | i <sub>m</sub> /2F<br>/mol s <sup>-1</sup> | E <sub>m</sub><br>/mV |
|---------------------------------------------------------|------------------------------------------------|-------------------------|--------------------------------------------|-----------------------|
| CAT (H <sub>2</sub> SO <sub>4</sub> )                   | 1.83                                           | 291                     | 2.36                                       | 293                   |
| CAT (H <sub>2</sub> SO <sub>4</sub> )                   | 1.66 <sup>a</sup>                              | 290                     | 2.33 <sup>b</sup>                          | 292                   |
| CAT (H <sub>2</sub> SO <sub>4</sub> )                   | 1.47 <sup>a</sup>                              | 287                     | 2.33 <sup>c</sup>                          | 292 <sup>c</sup>      |
| CAT (KCl)                                               | 1.89                                           | 290                     |                                            |                       |
| CAT (H <sub>2</sub> SO <sub>4</sub> , KCl) <sup>d</sup> | 2.37                                           | 290                     | 2.82                                       | 293                   |
| CAT (H <sub>2</sub> SO <sub>4</sub> , KCl)/KI           | 1.35                                           | 287                     | 2.10                                       | 290                   |
| CAT (H <sub>2</sub> SO <sub>4</sub> , KCl)/KI/RM        | 0.76                                           | 280                     | 1.38                                       | 286                   |

<sup>a</sup> In the presence of  $2 \times 10^{-6}$  M Feoc and  $1.2 \times 10^{-7}$  M I<sub>2</sub>.

<sup>b</sup> i-E curve of I<sup>-</sup> in the presence of  $1.2 \times 10^{-7}$  M I<sub>2</sub>
<sup>c</sup> Duplicate of previous entry

<sup>d</sup> Kinetic and electrochemical runs in 1 M KCl. RDE not exposed to air after preconditioning.

These results are illustrated in Figures 4 and 5 where both the catalytic points (E<sub>cat</sub>, u'<sub>cat</sub> 2F) and the i-E curves are shown. They do not agree with each other, the catalytic rates being consistently lower than the "mixture current" rates. Moreover, the catalytic rates obtained with CAT (H<sub>2</sub>SO<sub>4</sub>) are clearly irreproducible.

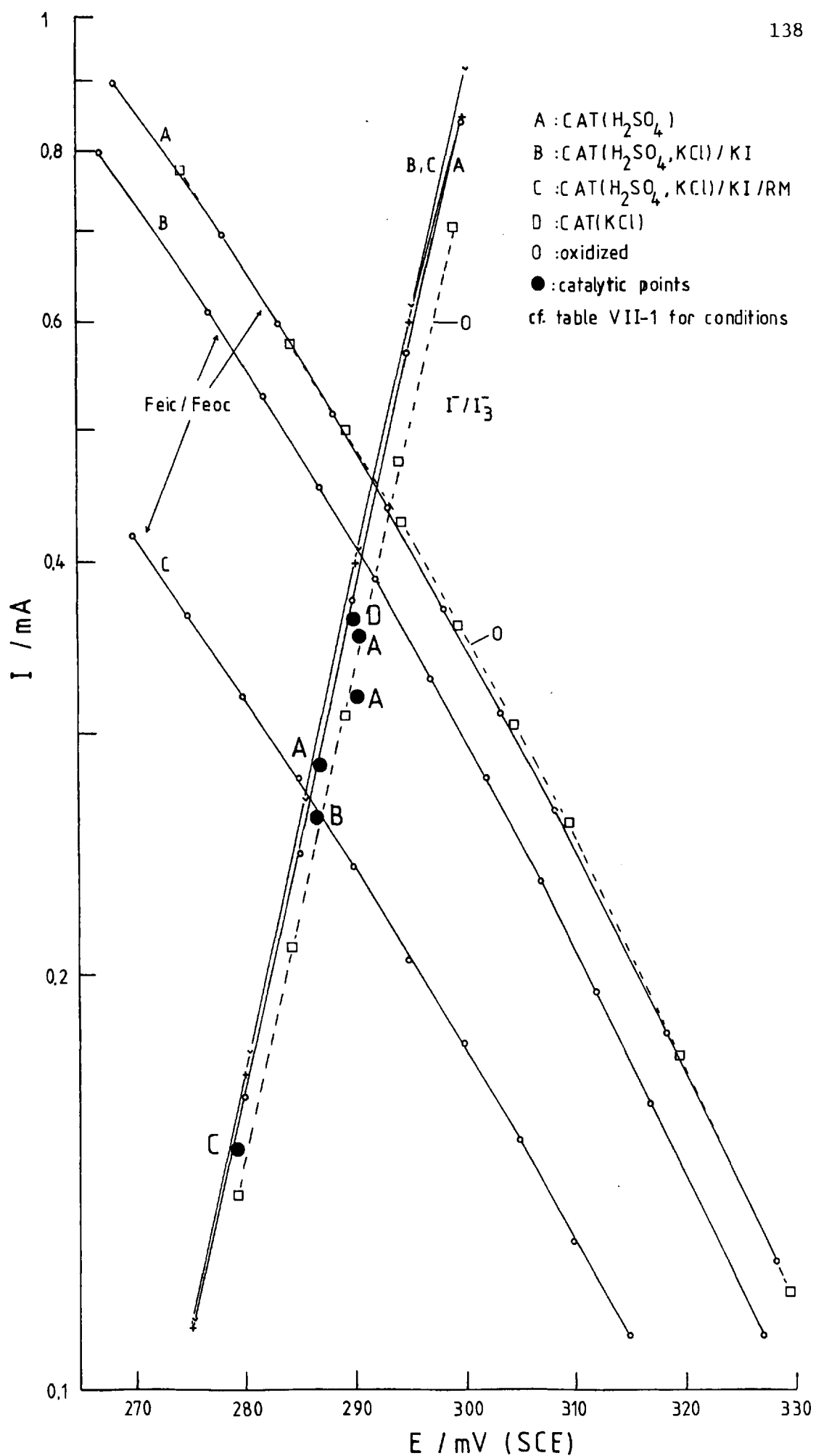
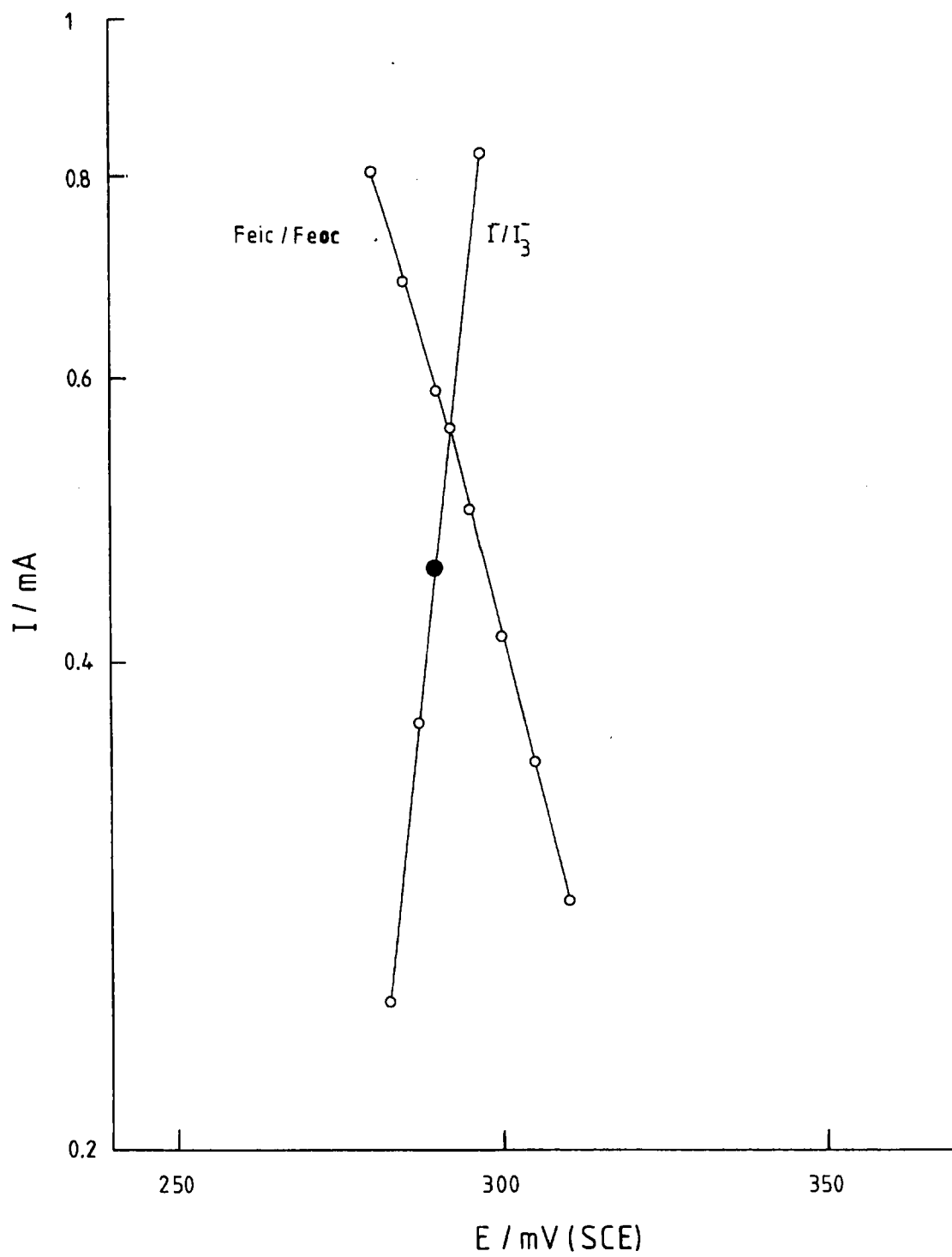


Figure VII-4

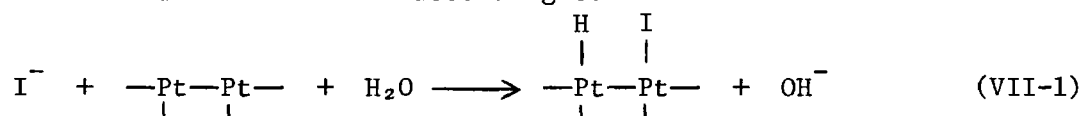


CAT( $\text{H}_2\text{SO}_4$ , KCl), 0.001 M Feic /  $2\mu\text{M}$  Feoc, 0.05 M KI /  $1\mu\text{M}$  I<sub>3</sub><sup>-</sup>, 1 M KCl, 500 rpm, 5°C

Figure VII-5

Oxygen adsorption as a cause for the discrepancy between catalytic and electrochemical runs was ruled out by carrying them out in 1 M KCl without removing the RDE from the preconditioning cell. Enough solid salts of reactants were added to the KCl to attain the desired final concentrations after preconditioning. Nitrogen was continuously passed. For this purpose, the calomel RE was placed inside the RDE compartment of the cell used (Figure VI-2) while the large platinum CE was rolled and squeezed inside the compartment normally occupied by the RE. The results are given in Table 1 and in Figure 5. The remaining preconditioning procedures, CAT (H<sub>2</sub>SO<sub>4</sub>, KCl)/KI and CAT (H<sub>2</sub>SO<sub>4</sub>, KCl)/KI/RM, were devised to test any effect of the reactants and products on the state of the surface just before the runs.

The disagreement between the two sets of experiments is probably a result of iodide and iodine adsorption which blocks the surface to the approach of Feic during the reaction although the latter still proceeds electrochemically. In effect, iodide adsorbs on reduced platinum as iodine<sup>45,115,116</sup> according to:



Iodine atoms cover  $1 \times 10^{-9} \text{ mol cm}^{-2}$ <sup>115,116</sup> compared with a surface concentration of platinum atoms of  $2 \times 10^{-9} \text{ mol cm}^{-2}$ .<sup>117</sup> Iodine in solution also adsorbs, covering  $2 \times 10^{-9} \text{ mol cm}^{-2}$ .<sup>45</sup> Adsorbed iodine is electrochemically inactive, but it allows reversible redox processes of soluble  $\text{I}^-/\text{I}_3^-$  and  $\text{Br}^-/\text{Br}_2$ .<sup>115</sup> It blocks the oxidation of impurities below ca. 0.3 V (SCE) in neutral aqueous solutions.<sup>117</sup> As shown in Figure 4, iodine adsorbed prior to the i-E curves inhibits the reduction of Feic but does not affect the oxidation of iodide. Ferricyanide reduction curves not involving previous contact with iodide-containing solutions are identical to those obtained on the oxidised electrode

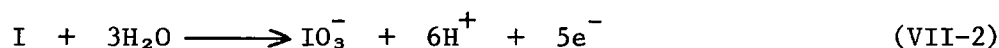
(dashed curves on Figure 4), at which the Feic/Feoc couple is in equilibrium. This also happens to the  $I^-$  oxidation curve. Therefore, the coincidence of the catalytic points with the iodide oxidation curve clearly shows that the reaction is still proceeding through the electrochemical mechanism. However, under these conditions the  $I^-/I_3^-$  couple remains in equilibrium during the reaction, while the Feic/Feoc couple is being interfered with by adsorbed iodine.

It is interesting to note that the catalytic rate is always lower than the corresponding rate from the i-E curves. This is because of further adsorption of iodine from the reaction mixture during the reaction. It is assumed that the H-co-adsorbed layer in eq. (1) formed during iodide-containing preconditionings is destroyed by aerial oxidation, because the electrode is exposed to air just before the reaction [except in the CAT ( $H_2SO_4$ ,  $KCl$ ) procedure]. This also explains why the CAT ( $H_2SO_4$ ,  $KCl$ )/KI/RM surface produces lower catalytic rates than the CAT ( $H_2SO_4$ ,  $KCl$ )/KI one. In other words, undisturbed overlap of the individual i-E curves does not hold true in the mixed solution on reduced platinum. The system investigated thus provides clear evidence of the failure in certain cases of the additivity hypothesis of Wagner and Traud.

#### c) Verification of Iodine Adsorption.

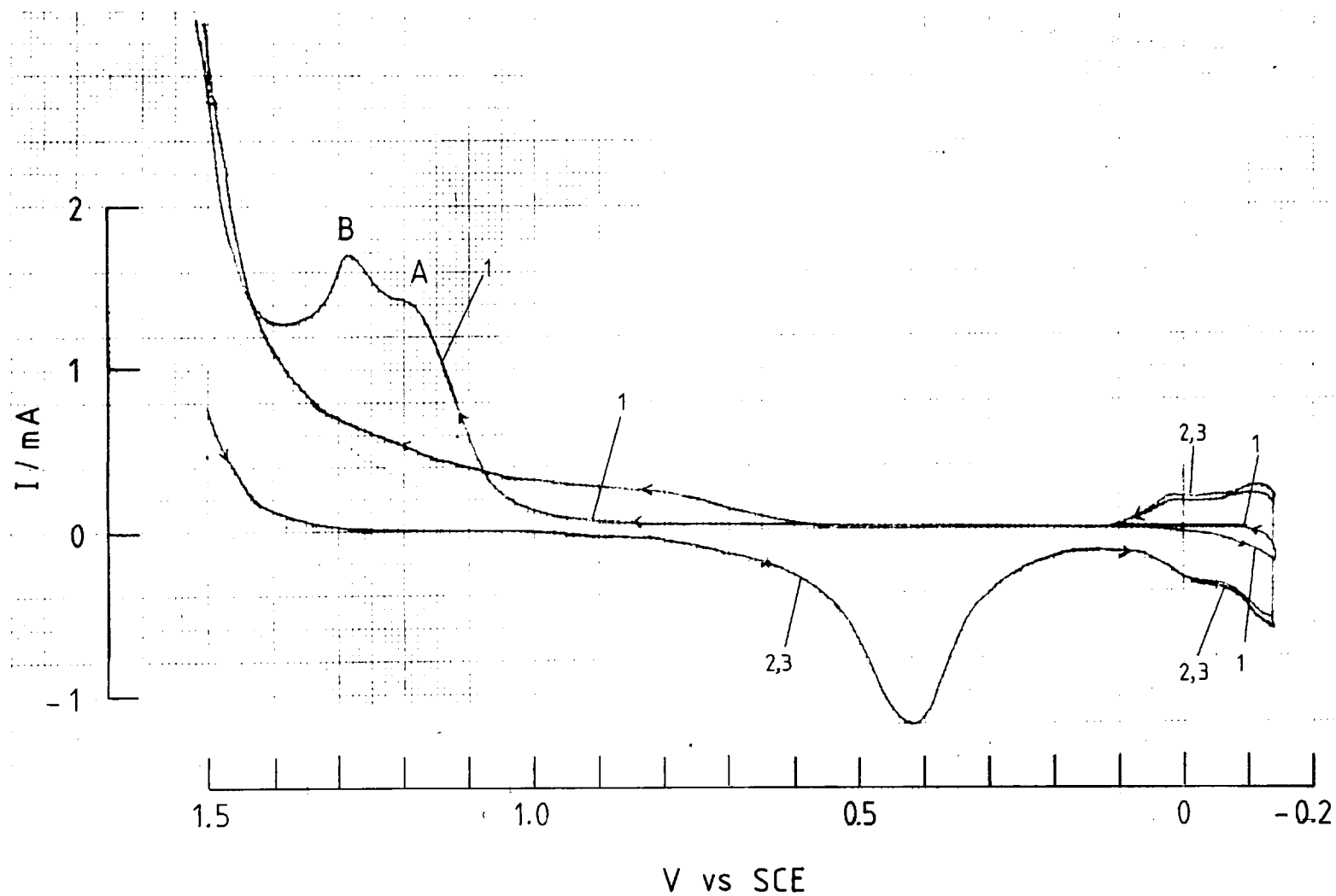
This was carried out by first subjecting the electrode either to oxidising preconditioning (Table VI-2) or to the reducing one according to CAT ( $H_2SO_4$ ). The electrode was rinsed and immersed at open circuit in a non-deaerated 1 M  $KCl$  solution containing also  $5 \times 10^{-2}$  M KI or saturated with iodine. It was then rinsed and a CV was performed at  $5^\circ C$  in 1 M  $H_2SO_4$ .

Figure 6 is a typical CV obtained when  $5 \times 10^{-2}$  KI was present during the immersion step. The absence of H-adsorption/desorption peaks in the first scan indicates the presence of adsorbed iodine which block the metal surface for hydrogen atoms.<sup>115,118</sup> Two anodic peaks (A and B) that appear at 1.2 V and 1.28 V (SCE) respectively are near the reported value of ca. 1.1 V (SCE) at ca. 25°C at which adsorbed iodine is oxidised to  $\text{IO}_3^-$ <sup>115,118</sup>.



A single peak is reported by these authors<sup>115,118</sup> who preadsorbed their iodine usually from  $\text{H}_2\text{SO}_4$  or  $\text{HClO}_4$  solutions. When iodine was preadsorbed in the presence of  $\text{KCl}$ , two peaks appear<sup>119</sup> at 1 and 1.1 V (Na-calomel electrode) respectively. The latter appears where these and other<sup>115-118</sup> authors have reported iodine oxidation [eq. (2)];  $\text{Cl}^-$  ion alone adsorbed only provokes inhibition of monolayer oxide formation at 1.05 V (SHE) without apparently suffering faradaic reactions up to 1.4 V (SHE)<sup>25</sup> (See Figure 2). Thus, peak B is probably due to adsorbed iodine oxidation. The nature of peak A is unclear. Identical results are obtained if the sweep is started in the anodic direction. In Figure 6, once the surface material has been oxidised, subsequent sweeps (marked "2" and "3") are similar to that in Figure 1. The combined charge enclosed by the two peaks (obtained by weighing the cut-out traces, having estimated the base line by eye) is  $11 \pm 2$  mC, from six independent CVs, which gives an apparent coverage of  $2 \times 10^{-9}$  mol  $\text{cm}^{-2}$ , assuming that all of the charge is due to reaction (2), and taking the real area of the electrode as 11.2  $\text{cm}^2$ . If iodine is present

Figure VII-6



Pt RDE, 200rpm, 1 M  $\text{H}_2\text{SO}_4$ , 1.72 V/min, pretreated: CAT ( $\text{H}_2\text{SO}_4$ ) / KCl + KI

instead of iodide during the immersion step, the peak currents are 1.4 and 2.2 mA for A and B, respectively (their usual height is ca. 1.7 mA each, measured from the estimated base line). The total charge remains close to 11 mC. Exposure to 0.1 M  $\text{KIO}_3$  in 1 M  $\text{H}_2\text{SO}_4$  (60 min.) or to  $10^{-3}$  M  $\text{Feic}$  (30 min) after the immersion step (and rinsing), and prior to the CV (and rinsing), also produced a "shift" of charge from peak A to peak B (the relative value of the peak current was very similar to the  $\text{I}_2$  case), while the total charge was close to 11 mC.

These results are difficult to explain because of the mainly qualitative approach of these experiments. The salts used were of AnalaR grade which is not suitable for experiments involving adsorption. The use of  $\text{KCl}$  as a base electrolyte is not convenient because of simultaneous adsorption of  $\text{Cl}^-$  and  $\text{I}^-$  ions, which further complicates the interpretation of the results. At least it seems clear by comparison of CVs in Figure 6 and 2 that iodide (as iodine) adsorbs on a reduced platinum electrode.

#### VII.4. Conclusions.

The catalytic rate on reduced platinum, under a variety of pre-conditioning procedures, proceeds by electron transfer through the catalyst. The mechanism is of a mixed type not considered in Chapter II, by which the  $\text{I}^-/\text{I}_3^-$  is totally mass transport controlled during the reaction, while the  $\text{Feic}/\text{Feoc}$  is not, because adsorbed iodine blocks the catalyst to this couple. The  $i$ -E curves are thus not additive, failing to comply with Wagner and Traud's hypothesis.

Quantitative study of this system requires knowledge of the electrode kinetics of both couples on the covered electrode. Adsorption of iodine would be expected to cause major differences to the  $I^-/I_3^-$  couple between reduced and oxidised electrodes. The effects are not observable because the rate constants are large enough in both cases for the system to remain at equilibrium. Some studies on this theme are described in Chapter III. The precise rôle of the irreversibly adsorbed iodine (adsorbability towards  $I^-$  or  $I_3^-$  or  $I_2$ , and towards cations, structure, bonding to the metal, effect on the potential profile across the double layer, electrical conductivity, etc.) is worth studying, particularly because of its impressive effects on Feic reduction. Irreversibly adsorbed iodine affects the oxidation of Pt(II) and Sb(III) complexes<sup>115,119-121</sup> which has been ascribed to desorption of less tightly bound anions, thus making the potential at the outer Helmholtz plane less negative.<sup>115</sup> This would explain the enhancement in the oxidation of negatively charged platinum complexes and Sb(III) complexes, and the lack of effect on neutral complexes.<sup>115,119</sup> Ferricyanide is a negatively charged reactant and one would expect its reduction to be enhanced by iodine-induced double layer effects. The fact that just the opposite happens indicates that some other factors are at play. The extent to which cations (i.e.,  $K^+$ ) can act as a bridge between the iodine layer and the  $K^+Feic$  ion pairs might be one of these (Section VI.4).

## CHAPTER EIGHT

### CATALYSIS ON PLATINUM (OXIDISED):

#### STUDIES IN THE PRESENCE OF KCl

##### VIII.1. Introduction.

This chapter is devoted to the effect of a different supporting electrolyte, KCl, on the catalytic rate on oxidised platinum. Considering that the couples involved in reaction (I-1) are in equilibrium at the oxidised platinum surface in 1 M KNO<sub>3</sub> (Chapter VI), it is almost certain that they will continue to be so in KCl, and thus the effects of the latter on the rate are bound to be modest.

##### VIII.2. Experimental.

a) The source of the chemicals has been mentioned in Chapter V. The supporting electrolyte during the catalytic runs was 1 M KCl. The runs and the i-E curves were carried out according to the procedure described in Chapter VI. Oxidation of the platinum RDE was accomplished according to Table VI-2. All experiments were carried out in doubly distilled water.

##### b) Electrolyses.

Electrolyses at constant current (typically, at 0.5 mA, 5°C, on 0.250 g of 0.05 M KI, plus supporting electrolyte, for 30-60 minutes, while the RDE was at 500 rpm) were carried out with the arrangement described in Chapter V. They were intended to study the  $I^-/I_3^-$  couple;

therefore the platinum RDE duly preoxidised was used. Electrolyses at constant potential [293.0 mV (SCE)] of 0.05 M KI solution either in 1 M KCl or in 1 M KNO<sub>3</sub>, at 5°C, 500 rpm, were carried out in the three-compartment cell in Figure 1. The solution composition was the same in all compartments, but the WE one contained exactly 0.250 ℓ of solution.

During both constant current and constant potential electrolyses, the formation of iodine was followed spectrophotometrically at 350 nm, from 1:3 dilutions with supporting electrolyte of 5 ml samples withdrawn every 4 minutes from the WE compartment.

c) Chemical Analysis of Solutions After Electrolysis.

After electrolysis at constant current, the solution was treated with sulphuric acid, after extraction of the iodine formed in the electrolysis, to try to detect oxidising compounds such as IO<sup>-</sup> or IO<sub>3</sub><sup>-</sup> that might have been formed.

About 100 ml of the electrolysed solution were shaken in a separating funnel with seven 15 ml portions of CCl<sub>4</sub> in order to extract the iodine formed. The absorbance at 350 nm of samples of the aqueous extract, diluted 1:3 with the supporting electrolyte ranged from 0.004 to 0.078, compared with 1.1 of similar dilutions of the unextracted solution.

Nitrogen was passed through the aqueous extract for 10 minutes to evaporate the CCl<sub>4</sub>. Then 1 ml of 1 M H<sub>2</sub>SO<sub>4</sub> was added to 10 ml of extract, and the absorbance at 350 nm read. This reading had to be corrected for the absorbance of the residual tri-iodide, taking into account the dilution factors. The resulting absorbance ranged from

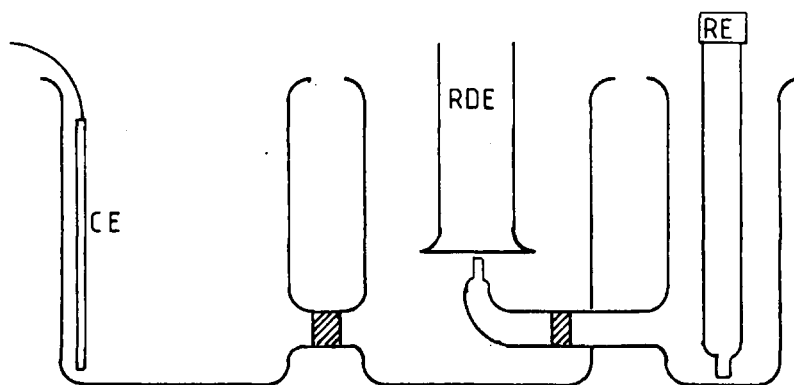
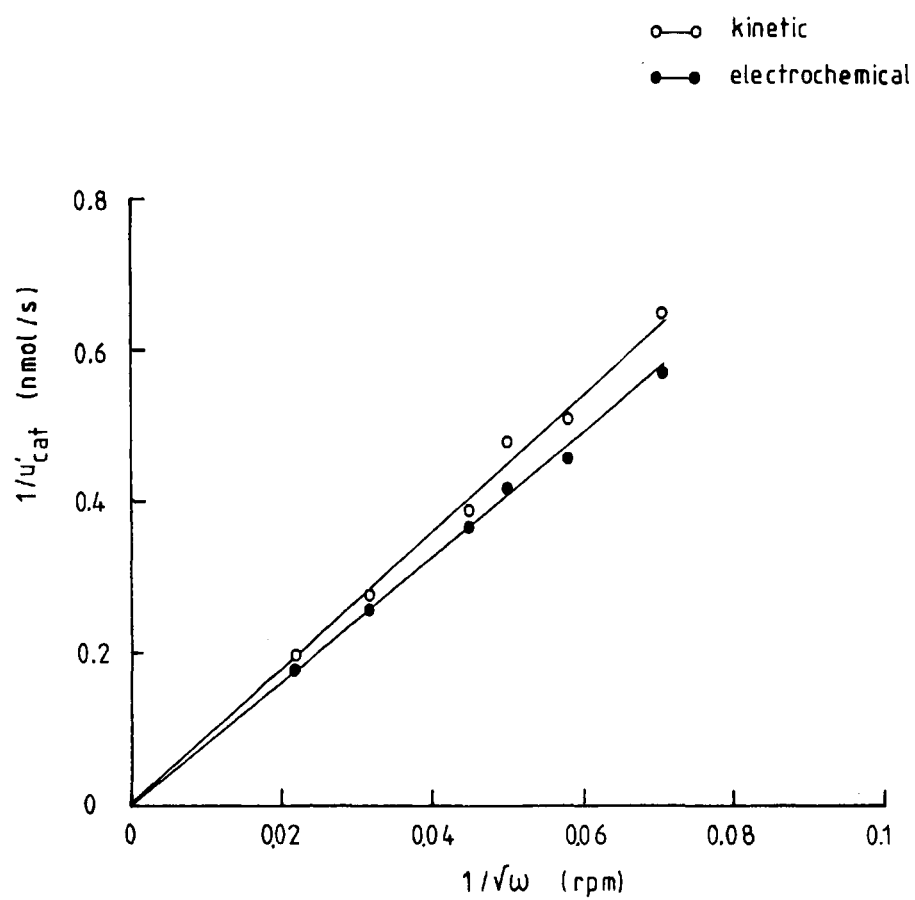


Figure VIII-1



0.001 M Feic, 0.05 M KI, 1 M KCl, 5°C

Figure VIII-2

0.048 to 0.214. A control test was made on a 0.05 M KI + 1 M KCl solution that had not been electrolysed. No significant increase in the absorbance was produced upon mixing with the acid.

d) Treatment of Electrolyses Data.

In order to compare the total number of moles of iodine (as coulombs) present in the solution at any time  $t_j$ ,  $Q_A(t_j)$ , ( $j$  = number of sample) obtained from the absorbance,  $A_j$ , of diluted samples, with the charge passed by the current and that still remains in the solution,  $Q_C(t_j)$ , allowance must be made for the "withdrawal" of charge due to the preceding  $j-1$  aliquots of size,  $v$ .  $Q_A(t_j)$  is simply given by:

$$Q_A(t_j) = 2FA_j(V_0 - (j-1)v)/b \cdot \ell \cdot \epsilon_{I_2}^{app} \quad (\text{VIII-1})$$

The subindex, A, indicates that the calculation is based on absorbance readings. Now, let  $\Delta Q_j$ , the charge passed by the current,  $I$ , during the time interval  $t_j - t_{j-1}$  between two successive samples,  $j-1$  and  $j$ , be defined by:

$$\Delta Q_j = \int_{t_{j-1}}^{t_j} I \, dt \quad (\text{VIII-2})$$

The relation between  $Q_C(t_j)$  and  $Q_C(t_{j-1})$  is then:

$$Q_C(t_j) = \Delta Q_j + F_{j-1} Q_C(t_{j-1}) \quad (\text{VIII-3})$$

The subindex C, indicates that  $Q$  is based on the current passed.  $F_{j-1}$  is defined as:

$$F_{j-1} = 1 - v/[V_0 - (j-1)v] \quad (\text{VIII-4})$$

It represents the fraction of  $Q_C(t_{j-1})$  retained in the remaining solution volume after removal of the  $j$ -th sample. Application of eq. (2) to successive values of  $Q_C(t_j)$  gives:

$$Q_C(t_j) = \Delta Q_j + (F_{j-1})\Delta Q_{j-1} + (F_{j-1} F_{j-2})\Delta Q_{j-2} + \dots + (F_{j-1} \dots F_1)\Delta Q_1 \quad (\text{VIII-5})$$

Since the  $F_j$  are always less than unity,  $Q_C$  at the end of the electrolysis will be always smaller than the corresponding value obtained by integration of the current alone (from  $t = 0$  to  $t = t_j$ ) if samples have been taken. It is important to observe that the analysis of  $Q_C$  is not based on any mechanistic or stoichiometric assumption. It applies to any system other than  $I^-/I_2$ . The main requirement is that the current be known as a function of time in order to obtain the  $\Delta Q_j$ s in eq. (2). If all of the current is used to convert  $I^-$  into  $I_2$  or  $I_3^-$ , then  $Q_A(t_j) = Q_C(t_j)$ . If substances other than  $I_2$  are formed, then  $Q_A(t_j) < Q_C(t_j)$ , provided that they do not absorb at 350 nm. For the special case in which only one unknown substance is formed in quantity of  $m_x$  mols, the number of equivalents,  $n$ , may be calculated as:

$$n = (Q_C - Q_A) / Fm_x \quad (\text{VIII-6})$$

### VIII.3. Results and Discussion.

#### a) Preliminary Results.

The catalytic rates at 5°C at several rotation speeds from kinetic runs and from the mixture current of  $i$ -E curves of the reactants are summarised in Table 1. The fact that the plots of  $1/u'_{cat}$  and of  $2F/i_m$  vs.  $\omega^{-\frac{1}{2}}$  in Figure 2 give straightlines which in each case pass very close to the origin, and the independence of  $E_{cat}$  and  $E_m$  on  $\omega$ , indicate that the reaction is completely mass-transport controlled and is therefore in equilibrium at the surface as with  $KNO_3$  (Chapters II and VI).

TABLE VIII.1. CATALYTIC RATE FROM KINETIC AND ELECTROCHEMICAL EXPERIMENTS

ON OXIDISED PLATINUM<sup>a</sup>  $10^{-3}$  M Feic, 0.05 MKI, 1 M KCl, 5°C.

| $\omega/\text{rpm}$ | $10^9 \frac{i_{\text{cat}}}{\text{mol s}^{-1}}$ | $E_{\text{cat}}/\text{mV}$ | $10^9 \frac{i_{\text{m}}/2F}{\text{mol s}^{-1}}$ | $E_{\text{m}}/\text{mV}$ |
|---------------------|-------------------------------------------------|----------------------------|--------------------------------------------------|--------------------------|
| 200                 | $1.53 \pm 0.15$ (2)                             | 293 (1)                    | $1.76 \pm 0.03$ (2)                              | $293 \pm 1$ (2)          |
| 300                 | 1.97 (1)                                        |                            | $2.17 \pm 0.02$ (2)                              | $293 \pm 0.5$ (2)        |
| 400                 | $2.09 \pm 0.21$ (2)                             | $293 \pm 0$ (2)            | $2.41 \pm 0.07$ (2)                              | $294 \pm 1$ (2)          |
| 500                 | $2.56 \pm 0.08$ (3)                             | $294 \pm 0.5$ (2)          | $2.74 \pm 0.07$ (6)                              | $293 \pm 1$ (6)          |
| 1000                | 3.61 (1)                                        | 293 (1)                    | $3.90 \pm 0.01$ (2)                              | $293 \pm 1$ (2)          |
| 2000                | 5.08 (1)                                        | 292 (1)                    | $5.47 \pm 0.22$ (2)                              | $293 \pm 0.6$ (2)        |

<sup>a</sup> Numbers in parentheses indicate number of runs. Appended  $\pm$  figures are the standard deviations.

The plots of  $i$ - $E$  data for each reactant according to eq. (I-43) (allowing for the presence of 4  $\mu\text{M}$  Feoc in the Feic curve, and of 2  $\mu\text{M}$   $\text{I}_2$  in the  $\text{I}^-$  curve) give straight lines (Figure 3). The  $L_j$ s were calculated using the  $k_j$ s previously obtained in 1 M  $\text{KNO}_3$  (Table VI-3), although they are likely to differ in 1 M KCl because  $k_j$  depends on the viscosity and density of the solution which depend on the nature of the electrolyte. The  $D_j$ s depend too on this factor. The expected slopes are  $83.5 \text{ V}^{-1}$  for  $\text{I}^-/\text{I}_3^-$  and  $41.7 \text{ V}^{-1}$  for Feic/Feoc. The observed slopes, marked on the figure are close to the expected ones, except for  $\text{I}^-/\text{I}_3^-$  at 2000 rpm, which indicates a deviation from the reversible behaviour. The expected value at  $E = E_j^0$  is marked as a heavy dot. The agreement is fair considering that they too are likely to be different in 1 M KCl. The currents due to Feic or to  $\text{I}^-$  at

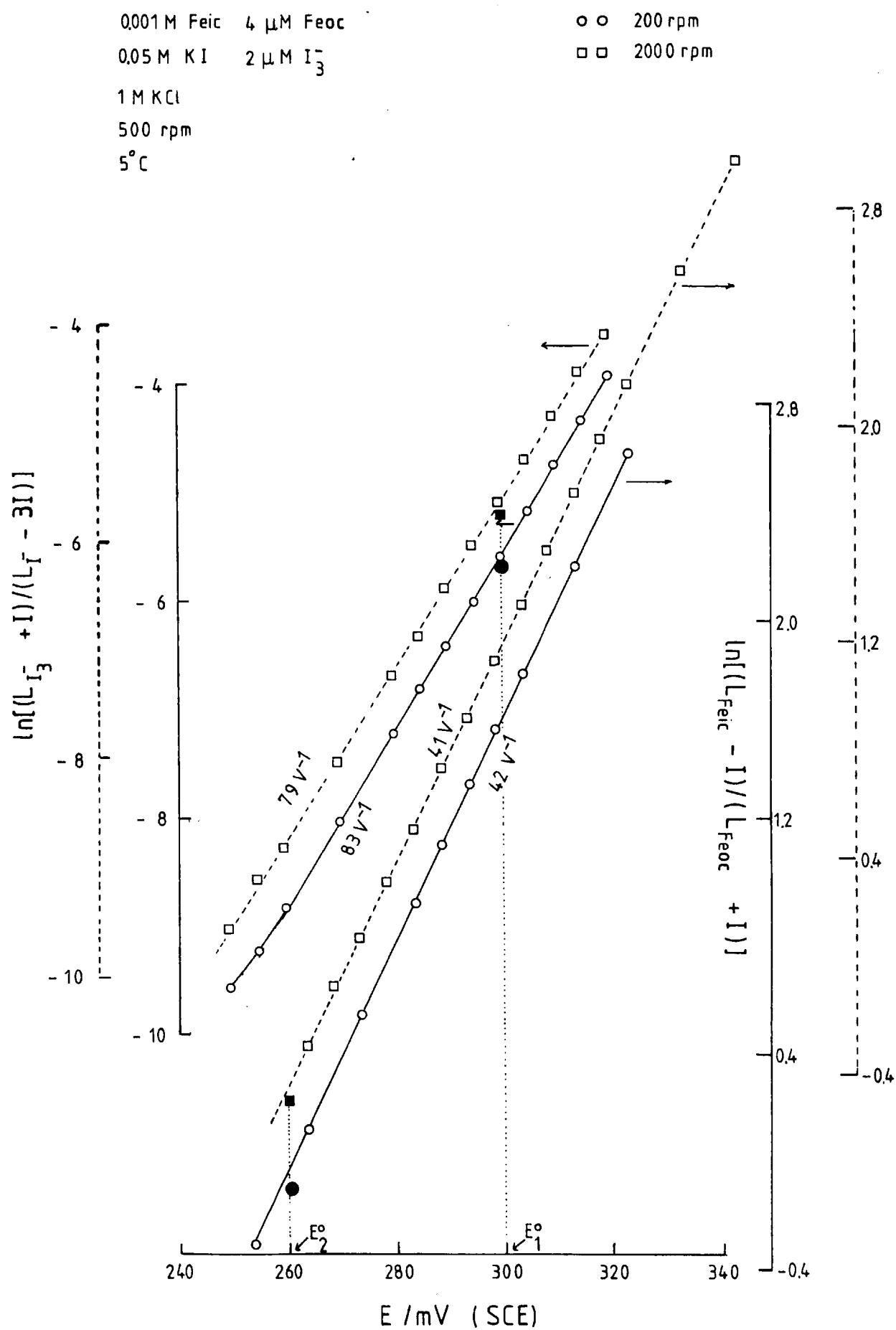


Figure VIII - 3

500 rpm are consistently 15% higher in 1 M  $\text{KCl}$  than in 1 M  $\text{KNO}_3$  at the same potential, all other conditions being the same ( $10^{-3}$  M  $\text{Feic}$  or 0.05 M  $\text{KI}$ ,  $5^\circ\text{C}$ ), probably reflecting the different  $E_j^\circ$  s and rheological values.

Although  $E_{\text{cat}}$  and  $E_m$  agree within 1 mV, the catalytic rates are always lower than the ones of i-E origin. The mean value of the difference (which appears to be independent of  $\omega$ ) is  $2.7 \times 10^{-10} \text{ mol s}^{-1}$ , outside the experimental uncertainty. The catalytic points ( $E_{\text{cat}}, 2\text{Fu}'_{\text{cat}}$ ) are shown in Figure 4 together with the sections of the appropriate i-E curves. The catalytic points do not lie close to any of the curves in a regular way (but tend to be close to the  $\text{I}^-/\text{I}_3^-$  curves, except at 500 rpm, where they are closer to the  $\text{Feic}/\text{Feoc}$  curve). Any such tendency is probably smothered by the experimental uncertainty in the catalytic and in the electrochemical data because the departures from the intersections are not large enough, unlike the situation encountered with reduced platinum (Chapter VII).

Initial efforts to find a reason for this discrepancy were directed towards finding some faulty points of technique. It was possible for example, that in  $\text{KCl}$  solution products from the counter electrode might have reached the RDE and affected the current since both electrodes were in the same compartment (Figure VI-3). To test this, i-E curves were carried out in a three-compartment cell (Figure 1) in which glass frits separated neighbouring compartments. No difference was observed in the curves obtained in this cell. Also, a catalytic run was carried out in the large compartment of the two compartment cell (Figure VI-3) (the RE compartment contained ca. 0.05 M  $\text{KI}$  in 1 M  $\text{KCl}$ ) at 500 rpm, but no difference was found with respect to the ordinary single

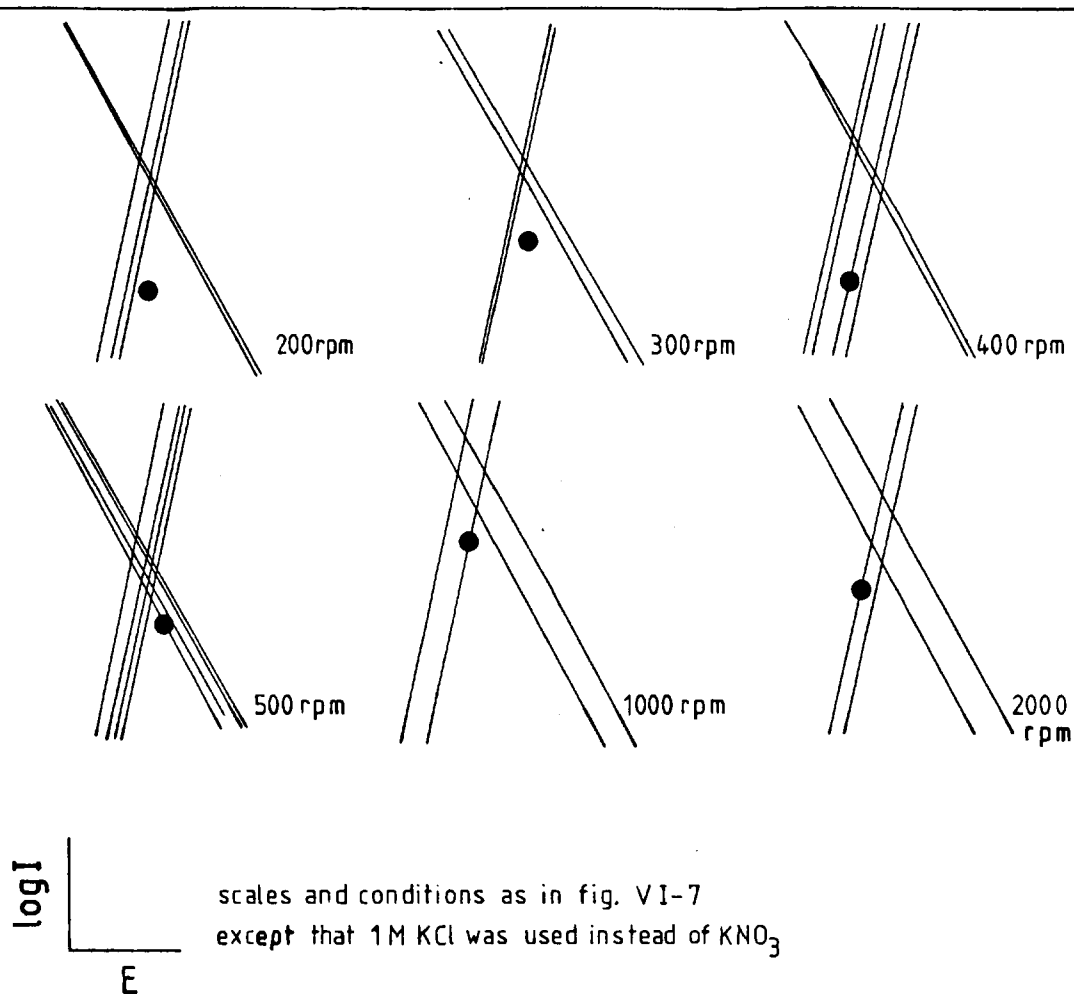
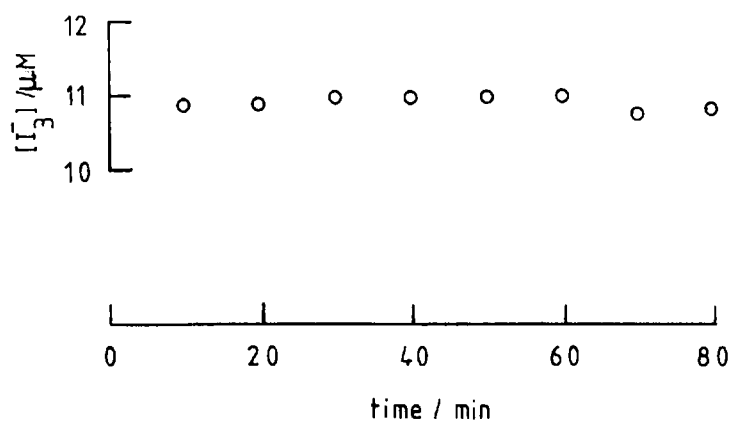


Figure VIII-4



1M KCl, 500 rpm, 5°C

Figure VIII-5

compartment reaction vessel. The dilution factor,  $b$ , in eq. (V-15) was checked by weighing 3 samples of 10 ml 1 M KCl at room temperature (measured with a grade B 10 ml volumetric pipette), and their increase in weight due to a further 5 ml aliquot (grade B 5 ml volumetric pipette). It was found that  $b$  was equal to 1/3 within 1 part in  $10^4$ . Loss of iodine to the air from the reaction mixture was tested by periodically sampling a solution of 0.0424 M KI, ca.  $12 \times 10^{-6}$  M  $I_2$ , 1.04 M KCl, at  $5^\circ\text{C}$ , and stirred with the RDE at 500 rpm. According to Figure 5, no significant amounts of iodine were lost to the air in a 80 minute period.

The background currents of 1 M KCl at 500 rpm,  $5^\circ\text{C}$ , in the absence of Feic and  $I^-$  are shown in Figure 6, together with the  $i$ -E curves of Feic and  $I^-$ . The background contribution around the mixture potential (293 mV) is negligible, even if the KCl solution had not been purged of oxygen. The  $i$ -E curves of Feic/Feoc and  $I^-/I_2$  had been obtained with purged solutions.

As a test for the presence of irreversibly adsorbed iodine, the  $i$ -E curve of Feic/Feoc was obtained at  $5^\circ\text{C}$ , 500 rpm, 1 M KCl, on a pre-oxidised electrode which had been put in contact with 0.05 M KI in 1 M KCl after preconditioning but before the  $i$ -E curve (thoroughly rinsed between stages). This was indistinguishable from the ones obtained with the electrode subject to the usual oxidising pre-treatment.

Thus, the above tests indicate that the experimental technique itself is not responsible for the discrepancy between catalytic and electrochemical experiments. It may be due to the appearance of small amounts of new products caused by the presence of large amounts of chloride ions, and born through the electrochemical mechanism. It is

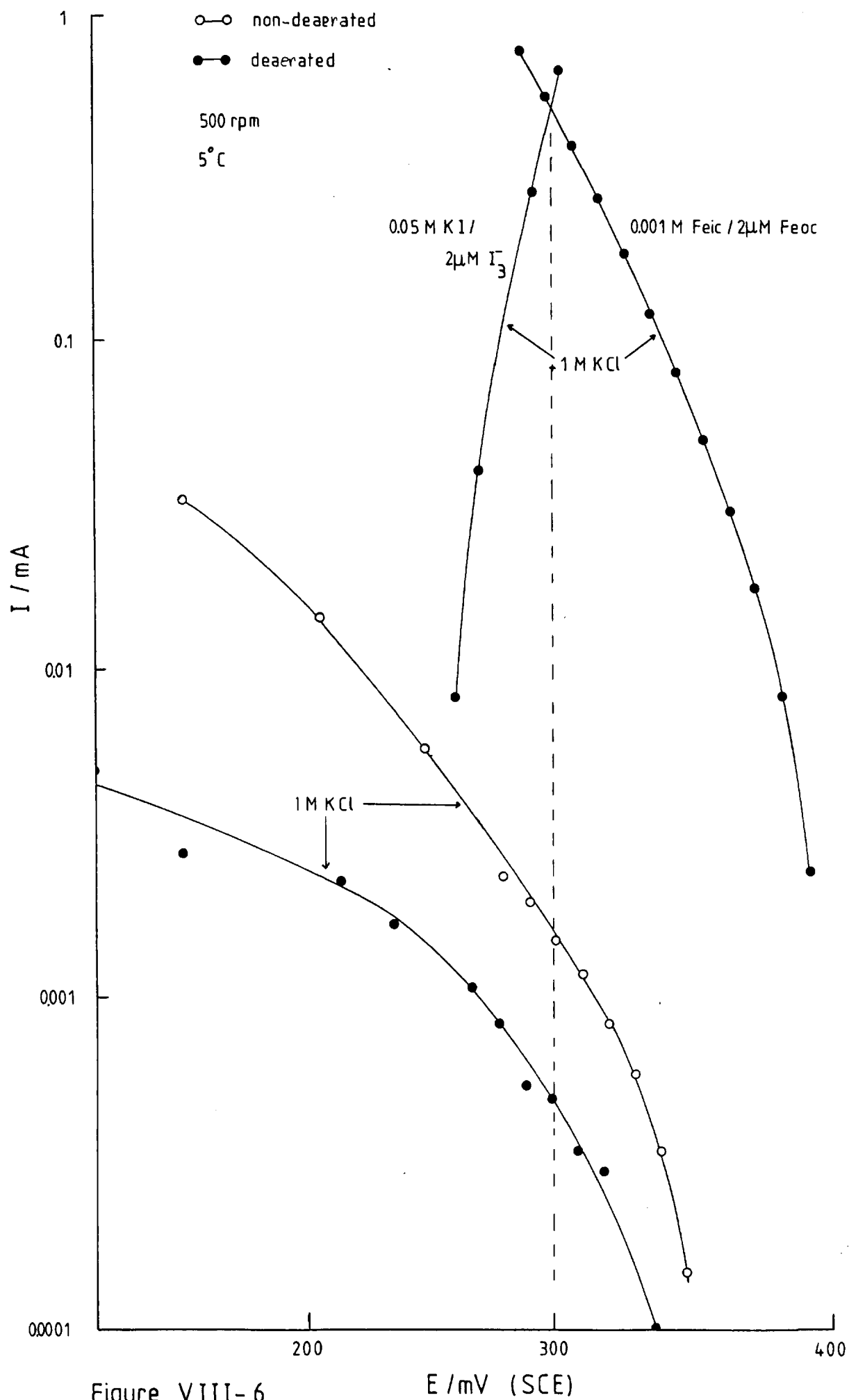


Figure VIII-6

TABLE VIII-2.

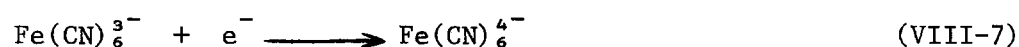
| couple                                  | $E^{\circ a}$<br>/V(SHE) | E (pH 6)<br>/V (SHE) |
|-----------------------------------------|--------------------------|----------------------|
| $I_2(s) + 2e^- = 2I^-$                  | 0.536                    | 0.536                |
| $I_2(aq) + 2e^- = 2I^-$                 | 0.621                    | 0.621                |
| $I_3^- + 2e^- = 3I^-$                   | 0.536                    | 0.536                |
| $HIO + H^+ + 2e^- = I^- + H_2O$         | 0.987                    | 0.964                |
| $2HIO + 2H^+ + 2e^- = I_2 + 2H_2O$      | 1.354                    | 1.308                |
| $IO^- + 2H^+ + 2e^- = I^- + H_2O$       | 1.313                    | 1.267                |
| $IO^- + H_2O + 2e^- = I^- + 2OH^-$      | 0.49                     | 0.49                 |
| $2ICl^- + 2e^- = 2I^- + 2Cl^-$          | 1.19                     | 1.19                 |
| $2ICl_2^- + 2e^- = I_2 + 4Cl^-$         | 1.06                     | 1.06                 |
| $HIO_3 + 5H^+ + 6e^- = I^- + 3H_2O$     | 1.077                    | 1.039                |
| $2HIO_3 + 10H^+ + 10e^- = I_2 + 6H_2O$  | 1.169                    | 1.123                |
| $IO_3^- + 6H^+ + 6e^- = I^- + 3H_2O$    | 1.085                    | 1.039                |
| $IO_3^- + 3H_2O + 6e^- = I^- + 6OH^-$   | 0.26                     | 0.26                 |
| $2IO_3^- + 12H^+ + 10e^- = I_2 + 6H_2O$ | 1.195                    | 1.140                |
| $HIO_4 + H^+ + 2e^- = IO_3^- + H_2O$    | 1.603                    | 1.58                 |
| $HIO_4 + 2H^+ + 2e^- = HIO_3 + H_2O$    | 1.626                    | 1.580                |
| $IO_4^- + 2H^+ + 2e^- = IO_3^- + H_2O$  | 1.653                    | 1.607                |
| $H_5IO_6 + H^+ + 2e^- = IO_3^- + 3H_2O$ | 1.6                      | 1.58                 |
| $HClO + H^+ + 2e^- = Cl^- + H_2O$       | 1.50                     | 1.48                 |
| $ClO^- + H_2O + 2e^- = Cl^- + 2OH^-$    | 0.89                     | 0.89                 |
| $ClO_3^- + 6H^+ + 6e^- = Cl^- + 3H_2O$  | 1.45                     | 1.40                 |
| $ClO_4^- + 8H^+ + 8e^- = Cl^- + 4H_2O$  | 1.35                     | 1.30                 |

<sup>a</sup> Source of data, reference 123, 25°C.

possible too that iodide is oxidised to products other than iodine, although this is not borne out by the results in  $\text{KNO}_3$  (Chapter VI). Reaction between iodine and some impurity in the  $\text{KCl}$  is another possibility. Table 2 lists some electrochemical equilibria in which iodine and chlorine species are involved. It must be considered too that the good agreement between  $E_{\text{cat}}$  and  $E_{\text{m}}$  points to homogeneous removal of iodine rather than to participation of another electrochemical process at the catalyst. It should be said too that it is highly unlikely that a mere change in the nature of the supporting electrolyte (especially to  $\text{KCl}$ , electrochemically inert in the potential range studied here) can bring about a change of mechanism at the catalyst surface, or participate itself in the reaction.

b) Experiments on the Oxidation of Iodide.

It is unlikely that the reduction of  $\text{Feic}$  gives anything other than  $\text{Feoc}$ . Indeed, electrochemical studies in  $\text{KCl}$ <sup>32,33,36</sup> have consistently supported the occurrence of the simple overall reaction:



Iodide and iodine, however, may in principle participate in a variety of electrochemical reactions, many of which are listed in Table 2. Some experimental work was therefore carried out to try to confirm the existence of a product of the oxidation of iodide different from  $\text{I}_2$ ,  $\text{I}_3^-$ , and  $\text{I}_2\text{Cl}^-$ , and to try to identify it. It is worth mentioning here that the formation of complexes between iodine and chloride ions is already considered in the apparent extinction coefficient of  $\text{I}_2$  in 1 M  $\text{KCl}$  solution, because of the way in which it was measured (Chapter V).

Figure 7 shows the variation with time of the current when a KI + KCl solution is electrolysed at a constant potential of 293.0 mV, which is close to  $E_{\text{cat}}$  both in KCl and in  $\text{KNO}_3$  (oxidised platinum, Chapter VI). The  $\text{KNO}_3$  experiment was carried out as a control. The fall in current is due to the accumulation of the main product  $\text{I}_3^-$ , which drives  $E_1^{\text{rev}}$  towards more positive values and decreases the diffusion overpotential according to eq. (I-47). Decrease in the  $\text{I}^-$  concentration is insignificant, and makes no impact on the current. To describe the temporal variation of the current, eq. (II-30a) can be integrated w.r.t.  $[\text{I}_3^-]$ . Noting that:

$$i = 2FV \, d[\text{I}_3^-]/dt \quad (\text{VIII-8})$$

and introducing it into (II-30a),  $[\text{I}_3^-]$  is:

$$[\text{I}_3^-] = \theta [1 - \exp(-t/(2FV(1/k_{\text{I}_3^-} + 3\theta/L_{\text{I}^-})))] \quad (\text{VIII-9})$$

$$\text{where } \theta = [\text{I}^-]^3 \exp[2f(E - E_1^0)] \quad (\text{VIII-10})$$

The current is obtained from eq. (8) as:

$$i = i_0 \exp(-i_0 t / 2FV\theta) \quad (\text{VIII-11})$$

where  $i_0$  is the current at  $t = 0$ :

$$i_0 = \theta / (1/k_{\text{I}_3^-} + 3\theta/L_{\text{I}^-}) \quad (\text{VIII-12})$$

The plots in Figure 7 were not corrected for the gradual decrease in the volume of the solution. Both give straight lines, in agreement with eq. (11). The slope is around  $-1.3 \times 10^{-4} \text{ s}^{-1}$ , close to a calculated one of  $-1.36 \times 10^{-4} \text{ s}^{-1}$  for an initial volume of 0.250 l. The intercept at  $t = 0$  is 505  $\mu\text{A}$  in 1 M  $\text{KNO}_3$ , which is 9% higher than the 462  $\mu\text{A}$  calculated from eq. (12), but it is not clear why. The

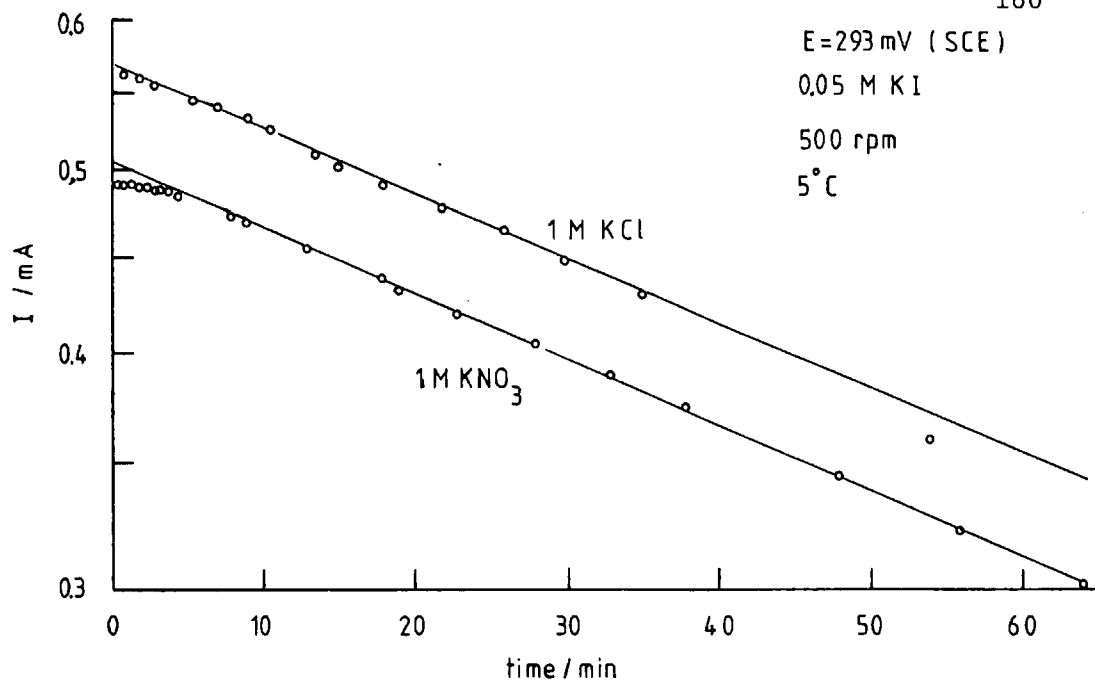


Figure VIII - 7

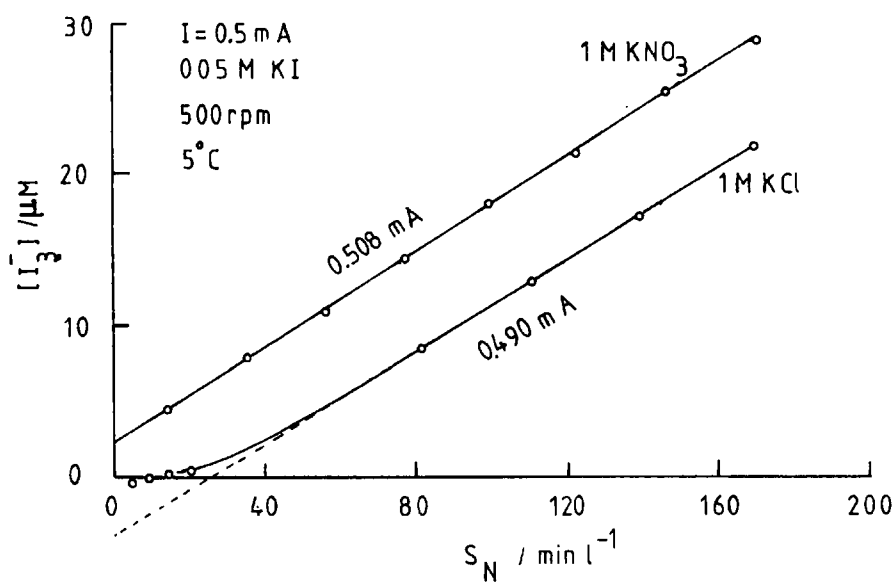


Figure VIII - 8

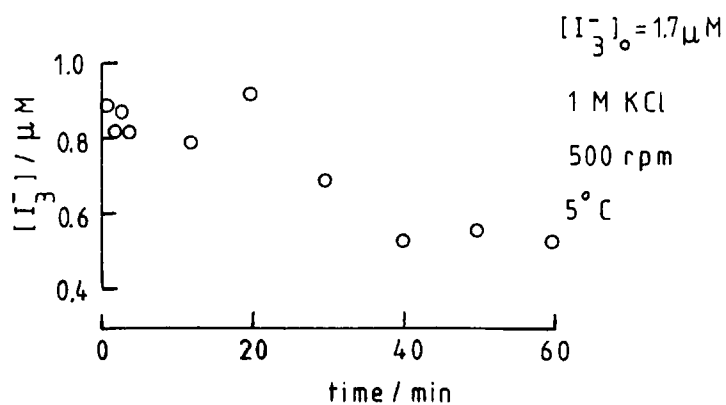


Figure VIII-9

current in  $\text{KCl}$  is 13% higher at any one time than in  $\text{KNO}_3$ , in accordance with the relative magnitude of the current observed in the  $i$ - $E$  curves (see previous section).

Comparison of the iodine produced during each of the time intervals between successive samples (as coulombs) and the electrical charge simultaneously passed during the same time interval, is shown in Table 3. Account has been taken of the decrease in the solution volume to calculate the "total charge remaining in the solution", according to eqs. (2)-(5). In  $\text{KCl}$  9.6% of the charge passed by the current fails to form iodine (or tri-iodide), while in  $\text{KNO}_3$  only 2.6% of iodine is "missing". If the first  $\Delta t$  is excluded (i.e., from  $t = 0$  to  $t = 3$  or 5 minutes) in order to avoid the uncertainty in the absorbance at  $t = 0$ , the missing iodine in the remaining total charge passed is 8.5% in  $\text{KCl}$  and 0.5% in  $\text{KNO}_3$ . This confirms the suspicion that iodide produces species other than  $\text{I}_2$  in the presence of  $\text{KCl}$ . It is interesting to note that the amount of iodine produced in successive time intervals in  $\text{KCl}$ , becomes closer and closer to the charge passed, thus suggesting a cessation of the parasite reaction which in turn suggests that it soon reaches equilibrium at that potential. However, these results do not disprove homogeneous scavenging of  $\text{I}_2$ .

Electrolyses at constant 0.500 mA of current were also carried out. Figure 8 shows the  $[\text{I}_2]$  vs.  $S_N$  [see eq. (VI-4)] obtained in 1 M  $\text{KNO}_3$  and in 1 M  $\text{KCl}$ . The slope furnishes a value of 0.508 mA in  $\text{KNO}_3$ , and of 0.490 mA in  $\text{KCl}$ , which are ca.  $\pm 2\%$  about the correct value. However, in  $\text{KCl}$  there is an initial 4-6 minute period during which the slope is much lower. If the electrode is withdrawn from the solution, pre-conditioned again according to Table VI-2, and the electrolysis continued in the same solution, the induction period disappears, and the slope

TABLE VIII-3. ELECTROLYSIS AT CONSTANT POTENTIAL: 293 mV (SCE),  
0.05 M KI<sup>-</sup>, 500 rpm, 5°C, V<sub>o</sub> = 0.250 ℓ, v = 0.005 ℓ.

| Time<br>/min | Coulombs Passed (During Δt <sub>j</sub> ) of      |        |           |        |
|--------------|---------------------------------------------------|--------|-----------|--------|
|              | (1 M KNO <sub>3</sub> )                           |        | (1 M KCl) |        |
|              | Iodine                                            | Charge | Iodine    | Charge |
| 3            |                                                   |        | 0.083     | 0.101  |
| 5            | 0.123                                             | 0.148  |           |        |
| 7            |                                                   |        | 0.102     | 0.131  |
| 10           | 0.146                                             | 0.143  |           |        |
| 11           |                                                   |        | 0.111     | 0.127  |
| 15           | 0.140                                             | 0.138  | 0.118     | 0.123  |
| 19           |                                                   |        | 0.116     | 0.120  |
| 20           | 0.126                                             | 0.133  |           |        |
| 23           |                                                   |        | 0.097     | 0.116  |
| 25           | 0.133                                             | 0.127  |           |        |
| 27           |                                                   |        | 0.116     | 0.112  |
| 30           | 0.121                                             | 0.122  |           |        |
| 31           |                                                   |        | 0.102     | 0.108  |
| 35           | 0.094                                             | 0.117  |           |        |
| 40           | 0.127                                             | 0.112  |           |        |
|              | Total charge remaining in solution <sup>a</sup> : |        |           |        |
|              | 0.933                                             | 0.958  | 0.784     | 0.867  |

<sup>a</sup> Including first time interval

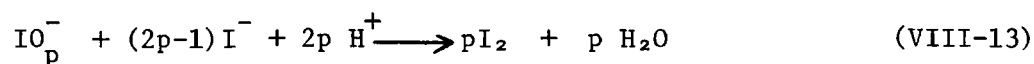
continues to be equivalent to 0.490 mA. This proves that the parasite reaction does not involve reaction with the platinum oxide, nor that iodine was being retained on the surface. The latter explanation for the induction period is unlikely for another reason. According to Table 3, the apparent deficit in iodine formation is 0.083 C of charge, equivalent to  $8.6 \times 10^{-7}$  mol of iodine atoms or  $7 \times 10^{-8}$  mol cm<sup>-2</sup> which is 35 times higher than the monolayer coverage of  $2 \times 10^{-9}$  mol cm<sup>-2</sup>.<sup>45</sup> Formation of layers of solid iodine do occur if [I<sup>-</sup>] > ca.

$7 \times 10^{-3} \text{ M}$ ,<sup>47,122</sup> but only if  $i = i_{\text{I}^-}$  because in this condition  $[\text{I}^-]^0 = 0$  and the iodine formed at the surface of the electrode must precipitate because its solubility is reached. In the 0.05 M KI used,  $i_{\text{I}^-} = 236 \text{ mA}$  which is several hundred times greater than the current employed.

In another test for adsorption, a 0.05 M KI + 1 M KCl solution was electrolysed for 55 minutes at 293.0 mV, at  $50^\circ\text{C}$ ,  $\omega = 500 \text{ rpm}$ , and the electrode withdrawn without switching to open circuit, spun in air and rinsed with water. The absorbance of 10 ml of a 0.1 M KI solution at the end of 5 minutes in contact with the electrode was 0.004, in a 4 cm cell. Had the missing iodine been adsorbed on the electrode surface, and desorbed into the KI solution to form  $\text{I}_3^-$ , the optical absorbance would have been around 4.

Experiments were now carried out to try to detect the formation of other oxidised iodine species such as  $\text{IO}^-$  or  $\text{IO}_3^-$ , according to the procedure outlined in Section VIII.2.c. During most of these runs, the production of  $\text{I}_2$  was followed spectrophotometrically at 350 nm, and the corrections in eq. (2)-(5) had to be applied. But continuous sampling is not essential. Only one sample at the end of the electrolysis suffices to establish the  $[\text{I}_2]$ .

If it is assumed that species of the general formula  $\text{IO}_p^-$  are produced, treatment of the extracted solution (which still contains 0.05 M KI) with acid, should produce iodine, according to:



If it is also assumed that the reaction is quantitative, then the amount of iodine produced by the acid is  $p$  times the amount of  $\text{IO}_p^-$  produced during electrolysis. They need not be restricted to  $\text{IO}_p^-$ , but it is a possibility worth investigating. The results are shown in Table 4.

The first column shows the electrolysis time at constant current. The fifth column represents the mols of iodine  $m_{I_2}$  produced in the extracted solution by addition of acid. This and the previous two columns refer to amounts in the volume of solution that remained at the end of the electrolysis (usually 0.210  $\ell$  if continuous sampling had been carried out during electrolysis; 0.250  $\ell$  if not, as in the second entry). The number of equivalents were calculated according to eq. (6), taking  $p = 1$  in eq. (13). It is important to realise that the actual number of coulombs employed in the electrolysis, given by  $It$  ( $t$  = electrolysis time), need not be equal to the charge values in the third or the fourth column, because some of it has been removed in the samples (see also Section VIII.2.d.), except in the run (second entry), for which it is actually equal to the charge remaining in the solution because only one sample was taken at the end of the electrolysis.

TABLE VIII-4. COULOMETRIC AND CHEMICAL ANALYSES. 0.500 mA, 0.05 M KI, 500 rpm, 5°C, 1 M KCl,  $V_0 = 0.250\ell$ .

| Electrolysis<br>time<br>/min | Volume<br>remaining<br>/ $\ell$ | Total Charge Remaining<br>in solution/Coulombs |         | $10^7 m_{I_2}^e$<br>/mol | Number of<br>equivalents <sup>b</sup> |
|------------------------------|---------------------------------|------------------------------------------------|---------|--------------------------|---------------------------------------|
|                              |                                 | $Q_A^c$                                        | $Q_C^d$ |                          |                                       |
| 45                           | 0.210                           | 1.233                                          | 1.316   | 2.9                      | 2.8                                   |
| 48 <sup>a</sup>              | 0.250 <sup>a</sup>              | 1.374                                          | 1.440   | 0.76                     | 9.0                                   |
| 60                           | 0.210                           | 1.572                                          | 1.715   | 2.7                      | 6.0                                   |
| 30                           | 0.210                           | 0.774                                          | 0.849   | 5.8                      | 6.4                                   |

<sup>a</sup> No samples taken during electrolysis;

<sup>b</sup> Assuming that  $m_{I_2} = m_x$  [cf. eq. (6)];

<sup>c</sup> Calculated from eq. (1);

<sup>d</sup> Calculated from eq. (5);

<sup>e</sup> Calculated from the  $I_2$  released by the acid on the basis of "volume remaining".

The results listed in Table 4 are quite irreproducible due to the very small quantities of iodine (in the form of tri-iodide) produced. The mean number of equivalents is  $6 \pm 2.5$  which leaves ample room for choice among the several reactions listed in Table 2. There is also the problem that more than one adventitious product might have formed. Our experimental approach cannot tell this. A further point is that if electrolysis is started in the presence of ca. 6  $\mu\text{M}$  iodine, the induction period disappears, and the rate of production of iodine remains at 0.490 mA during the electrolysis.

In a more carefully controlled experiment, 1.73  $\mu\text{M}$   $\text{I}_2$  were added to the  $\text{KI} + \text{KCl}$  solution and stirred at open circuit at 500 rpm, at  $5^\circ\text{C}$ . The concentration of iodine fell slightly with time (Figure 9) over a 60 minute period. However, during the time elapsed between introducing the RDE, switching on rotation, plus about 10 minutes to attain thermal equilibrium with the bath, the concentration fell to 0.85  $\mu\text{M}$ , which decrease would have accounted for 0.043 C of missing iodine. This is considerable (Table 4). This amount would surely increase as more iodine is added to the solution because of a shift towards the product side (unfortunately, no run was made without the RDE, so one cannot be sure that this is due to catalysis by the platinum). Notice that a further 0.030 C over 50 minutes is accounted for by the 0.01 mA difference between the applied 0.500 mA and the 0.490 mA production rate of iodine. Since this difference is only 2%, it may well be due to a corresponding error in the value of  $\epsilon_{\text{I}_2}^{\text{app}}$ , used in these calculations.

So it looks like an impurity in the  $\text{KCl}$  was reacting with  $\text{I}_2$  produced by the  $\text{Feic} + \text{I}^-$  reaction.

#### VIII.4. Conclusions.

From the results in Table 1 and Figure 2, it is clear that the catalytic rate is in equilibrium at the catalyst surface; since the isolated electrochemical couples are also in equilibrium at potentials around the  $E_{\text{cat}}$  value, the inescapable conclusion is that in  $\text{KCl}$  too the reaction at oxidised platinum proceeds by the electrochemical mechanism in the presence of  $\text{KCl}$ . However, this involves the assumption of undisturbed overlap of the individual  $i$ - $E$  curves in the mixed system, which is not supported by the discrepancy between the  $u'_{\text{cat}}$  and  $i_m/2F$  values. Alternatively, one could assume disturbed overlap, but evidence of the latter is still wanting. No evidence was detected of interference by iodide or iodine which might be irreversibly adsorbed on the electrode on the reduction of  $\text{Feic}$ , but this does not rule out interference by reversibly adsorbed species. It does not appear likely that the  $\text{Feic}/\text{Feoc}$  couple could interfere with  $\text{I}^-$  oxidation. But then, this situation would be similar to the one encountered on reduced platinum (Chapter VII), in which  $(E_{\text{cat}}, 2F u'_{\text{cat}})$  differs from  $(E_m, i_m/2F)$  but remains on the  $\text{I}^-/\text{I}_3^-$  curve. This has not been observed here, but rather an intermediate situation in which  $E_{\text{cat}} = E_m$ , which suggests that the reaction between  $\text{I}^-$  and  $\text{Feic}$  gives off iodine products other than  $\text{I}_3^-$ ,  $\text{I}_2$ , or  $\text{I}_2\text{Cl}^-$ .

The electrolyses at constant current suggest formation of extra iodine species. But they cannot tell whether they are of electrochemical origin or formed by homogeneous reaction of iodine with some impurity in the  $\text{KCl}$  (the amounts involved are in the  $\mu\text{M}$  region). Failure of Lambert-Beer's law at these low concentrations is possible too. Chemical analyses of the electrolysed solution suggest the formation of some oxidised form of iodine species.

The average value of the difference  $i_m/2F-u'_{\text{cat}}$  is  $2.7 \times 10^{-10}$  mol s<sup>-1</sup> of iodine, or 0.094 C over 30 minutes period; this is not far from the difference  $Q_C - Q_A = 0.075$  C from the last entry in Table 4, which is a constant current electrolysis (0.5 mA is close to the production rate of iodine during the catalytic run at 500 rpm; see Table 1, 4th entry).

Therefore, it seems that most of the discrepancy between catalytic and electrochemical data may be ascribed to events connected to the  $I^-/I_3^-$  couple, therefore to the fact that the reaction is followed by the appearance of tri-iodide.

## CHAPTER NINE

### CATALYSIS ON GLASSY CARBON

#### IX.1. Introduction.

It is known that carbons catalyse the reaction between ferricyanide and iodide<sup>124</sup> as well as several other redox reactions. However, the electrochemical rate constants for ferricyanide reduction and for the oxidation of iodide are considerably lower on carbonaceous electrodes like graphite and glassy carbon than on platinum.<sup>34,54</sup> It therefore seemed likely that the catalysis by carbon, unlike that by platinum, will not be completely mass transport controlled. The kinetics of reaction (I-1) were accordingly studied on a carbon surface in order to test that part of the theory of redox catalysis in Chapter II, which deals with irreversible or partly reversible charge transfer.

Glassy carbon was chosen for these studies because some information concerning the  $\text{Feic}/\text{Feoc}$  and  $\text{I}^-/\text{I}_3^-$  couples was available on this material.<sup>34,52</sup> Also, being harder than graphite, the surface of glassy carbon is less prone to physical damage; if necessary, it can be polished without great loss of material, which is an important consideration if it must be done repeatedly. As mentioned in Chapter III, it is an isotropic material (macroscopically), unlike graphite or pyrolytic graphite, whose electrical conductivity depends on the direction chosen for its measurement, i.e., along or across the stacked planes.

## IX.2. Experimental.

### a) The Glassy Carbon RDE.

The electrode in Figure 1 was made of a D82-2 glassy carbon disk (Vitrecarb, USA), 0.32 cm thick and polished on one side. Because it possessed an irregular radius that gave it a slightly elliptical shape, its circumference had to be smoothed so that its final diameter was 4.30 cm, instead of the original 5.1 cm, giving an apparent surface area of 14.5 cm<sup>2</sup>. The non-polished side was glued to a stainless steel former with conducting Araldite and both were squeezed inside a niche of the same dimensions in a rod of heated vitrathene. The other end of the rod had been hollowed and a thread carved in its inner wall in order to be fastened to the complementary thread of the stainless steel holder. The vitrathene was subsequently machined to a trumpet shape around the disc. Care was taken not to scratch or touch the polished surface during construction. As with the platinum RDE, the holder was provided with a bakelite lining and nylon screws to avoid electrical contact with the shaft of the rotation system, although the holder itself is not in contact with the back of the electrode. Electrical contact to the carbon was provided in exactly the same way as with the platinum RDE (Chapter VI). The holder was painted with white radiator enamel (International) and left to dry in the air without baking it in the oven, although the construction was such that no metal part ever came into contact with the electrolyte solution. There was no actual need to paint the vitrathene as it is an inert polymer, but before being used for the first time it was rubbed with Kleenex soaked in acetone, and left in distilled water for several days. As with the platinum RDE, the disk oscillated horizontally about  $\pm 0.5$  mm around

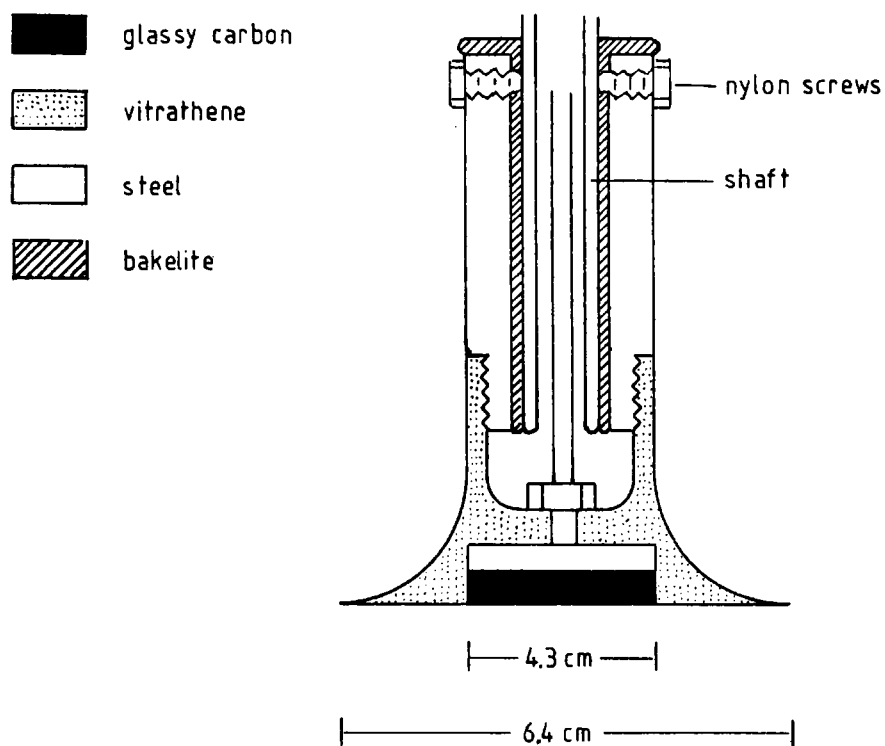


Figure IX-1

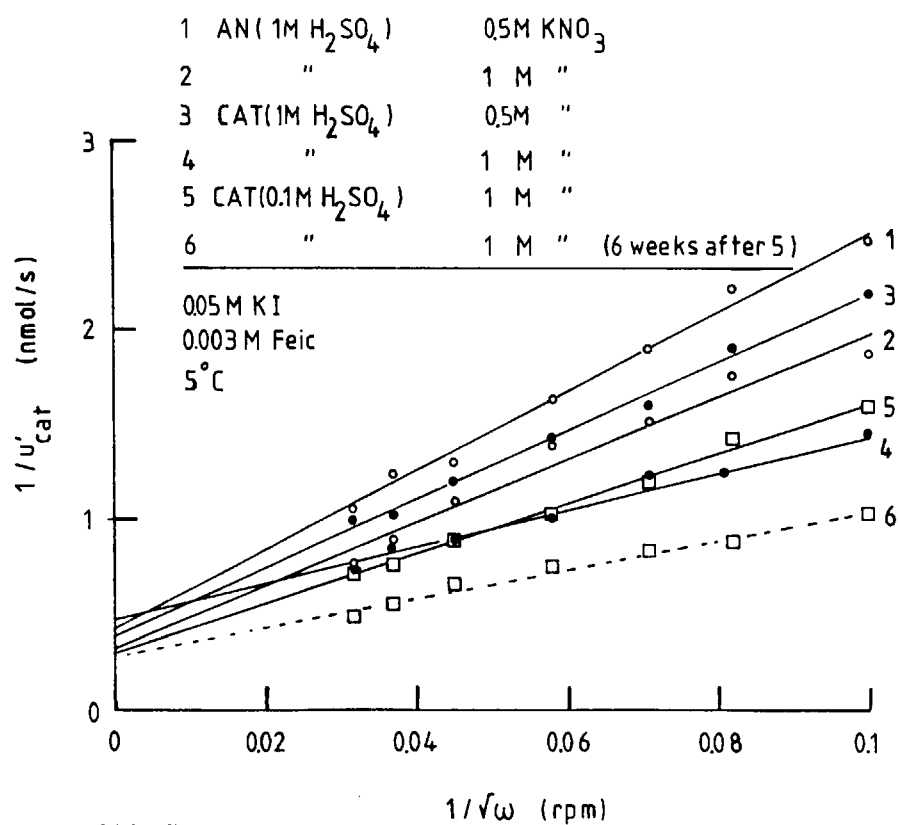


Figure IX-2

a central position; some vertical displacement of the edge could be described distinctly and seemed larger than for the platinum electrode. The maximum working speed was correspondingly lower: 1000 rpm, although  $\omega_{\max}$  from eq. (IV-4) is  $\sim 1800$  rpm (taking  $R = 3.2$  cm, from the centre of the electrode to the edge of the mantle). The vessel used for the catalytic runs was 10 cm in diameter, which probably induced enhanced stirring because the edge of this bigger electrode was closer to the wall of the vessel.

A major flaw of this electrode was that electrolyte crept at the carbon disk/mantle contact line. The gap was not apparent to the naked eye. It was only noticed when, after thoroughly cleaning the electrode of a pink teecepol slurry, more of it appeared at the edges upon pressing the edge of the mantle. It must be assumed that the liquid reached the steel former. Thus, all the earlier work with this disk was vitiated by this flaw. Once it was found, the electrode was left overnight in distilled water to leach out the electrolyte and remaining slurry from the cleft, dried in vacuum at room temperature, and the cleft covered with yellow Humbrol enamel which sets at room temperature. It was applied with the moistened tip of a needle to avoid excessive spread of the paint. It was frequently renewed as it tended to wear off after several polishings.

The manufacturers specify  $30-80 \times 10^{-4} \Omega \text{ cm}$  as the electrical resistivity for their glassy carbon, which leads to a total resistance of about  $1 \times 10^{-4} \Omega$  across a disk of our dimensions; this is very small as 1 A would be required to produce  $10^{-4}$  V drop across the electrode. Typical currents in this work are in the mA range. The Araldite (RS, silver loaded) used to glue the electrode to the stainless steel former was of  $500 \mu\Omega \text{ cm}$  specific resistance. Assuming a thickness of 0.01 cm, the hardened glue contributed only  $\sim 10^{-7} \Omega$ , across the  $14.5 \text{ cm}^2$  disk area.

b) Chemicals, Experimental Arrangement and Catalytic Runs.

The chemicals are described in Chapter V; the experimental arrangement in Chapters V and VI. The potassium nitrate (AnalaR, BDH) was recrystallised from distilled water (800 g  $\text{KNO}_3$  + 1  $\ell$   $\text{H}_2\text{O}$ , heated to  $70^\circ\text{C}$  and filtered while hot through porosity 3 Quickfit sintered glass filter; filtrate cooled to  $5^\circ\text{C}$ , crystals collected in the Quickfit filter and washed with chilled distilled water; the recovery was about 70%). Aristar grade KI (BDH) was used. All runs were carried out in distilled water. The supporting electrolyte was always  $\text{KNO}_3$ .

The volume of solution in the catalytic rates was 0.310  $\ell$ , because the larger electrode required the large 10 cm diameter Quickfit FV1500 vessel. With that volume of reaction mixture the electrode could be kept about 1 cm below the surface of the solution, and about 2 cm above the bottom of the reaction vessel.

Sampling was performed as described in Chapters V and VI, except when high concentrations of iodine or ferricyanide were initially present: for runs in the presence of  $10^{-4}$  M  $\text{I}_2$ , 2 ml samples were diluted with 20 ml of 1 M  $\text{KNO}_3$ ; with  $5 \times 10^{-5}$  M  $\text{I}_2$  or  $5 \times 10^{-3}$  M  $\text{Feic}$ , 5 ml samples were diluted with 20 ml. In all runs, 10 samples were taken one every 3 minutes, beginning at one minute after the start of the reaction.

Except for  $u'_{\text{cat}}$  values at a single rotation speed, all the errors quoted for parameters calculated by least squares fitting of data are the standard deviations of the fitting itself, as defined in Appendix 4.

c) Pre-Conditioning Procedures.

Several pre-conditioning procedures were tried until the catalytic rate became reasonably reproducible. As in other chapters, the acronyms CAT or AN indicate a final negative or positive potential (SCE),

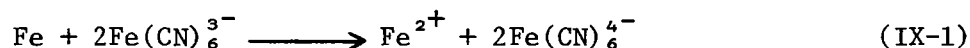
respectively, in the sequence. The words in parentheses refer to the solution (prepared in doubly distilled water), in which the preconditioning was carried out. It was made at the temperature of the subsequent catalytic run. After pretreatment, the electrode was withdrawn from the cell and spun at high speed in the air while being rinsed with distilled water. It is more convenient to discuss the preconditioning in connection with the results obtained, and it is therefore deferred to the results section.

The preconditioning cell itself had three compartments (Figure VIII-1) separated by porosity 3 glass frits, so that the platinum CE could be kept separated from the WE to avoid possible contamination of the latter with platinum, which may affect the catalytic properties of the glassy carbon.<sup>126</sup> Nitrogen was always passed for 10-15 min through the WE solution before each preconditioning.

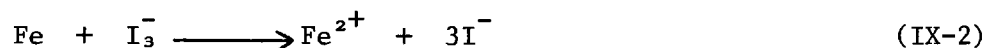
### IX.3. Results and Discussion.

A brief review will first be given of the results obtained for several preconditioning procedures that were tried. They are vitiated in some way by solution creeping at the carbon/mantle cleft, as mentioned in the previous section. Probable effects are: corrosion of the steel former, especially during preconditioning in  $\text{H}_2\text{SO}_4$  solution at anodic potentials, diffusion along the cleft of the corrosion products and deposition on the carbon outer surface upon application of cathodic potentials ( $-0.700$  V or  $-0.500$  V (SCE) in some procedures). Here, hydrogen evolution inside the gap is possible. Indeed, on occasions after application of a cathodic potential, the open circuit voltage (OCV) took about 20 minutes to reach  $+0.2$  V (SCE), which seems reasonable if hydrogen dissolved in the gap solution slowly diffuses away towards

the bulk of the solution. During the catalytic run, participation of the Fe/Fe(II) couple at the steel former is conceivable, with electron transfer taking place across the steel/Araldite/carbon highly conductive phases. Several interfering redox reactions are possible:



followed by precipitation of  $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ , and



The  $E^\circ$  value for the  $\text{Fe}^{2+}/\text{Fe}$  couple is  $-0.409 \text{ V (SHE)}$ ,<sup>126</sup> which makes these reactions likely.<sup>5</sup> Although the  $\text{Fe}^{2+}$  would be essentially confined to the gap, it is difficult to estimate the magnitude of these effects.

a) Preliminary Results.

Tables 1 and 2 define the AN (1 M  $\text{H}_2\text{SO}_4$ ) and CAT (1 M  $\text{H}_2\text{SO}_4$ ) pre-conditioning procedures employed. The period at open circuit (OC) was provided to allow the electrode to reach  $0.20 \text{ V (SCE)}$ , an arbitrary selected value.

TABLE IX.1 AN (1 M  $\text{H}_2\text{SO}_4$ ) Procedure.

| Potential/<br>V (SCE) | Time   | $\omega/\text{rpm}$ |
|-----------------------|--------|---------------------|
| 1.000                 | 60 s   | 100                 |
| -0.700                | 15 s   | 0                   |
| 1.000                 | 10 min | 100                 |

TABLE IX.2 CAT (1 M H<sub>2</sub>SO<sub>4</sub>) Procedure.

| Potential/<br>V (SCE) | Time      | $\omega$ /rpm |
|-----------------------|-----------|---------------|
| 1.560                 | 2 s       | 100           |
| 1.000                 | 60 s      | 100           |
| -0.700                | 15 s      | 0             |
| OC                    | 10-20 min | 100           |

Figure 2 shows a  $1/u'_{\text{cat}}$  vs.  $1/\omega^{\frac{1}{2}}$  plot for 0.5 and 1 M KNO<sub>3</sub> for both types of preconditionings. Figure 3 shows how  $E_{\text{cat}}$  varied with time under these conditions. The values of  $E_{\text{cat}}$  at 10 minutes were arbitrarily chosen as representative of the run, and these are plotted vs.  $\omega$  in Figure 4.

The non-zero intercepts in Figure 2 show clearly that the reaction is not at equilibrium at the surface of glassy carbon. Moreover, the  $E_{\text{cat}}$  value at 10 min appear to vary with  $\omega$ , although they do not follow any obvious trend. The results show also that the type of preconditioning has a marked effect on the rate and on  $E_{\text{cat}}$ . This suggests that chemical groups on the glassy carbon surface formed during the preconditioning participate in the reaction, either in the electron transfer act (assuming that the reaction proceeds by the electrochemical mechanism) or on the adsorbability of the species involved, or both. Since both reactants are negatively charged, the rate must be very sensitive to the charge of the surface groups. Predominance of positively charged groups would tend to increase the rate, while the opposite would happen with negatively charged ones. Marked increases in the rate were produced

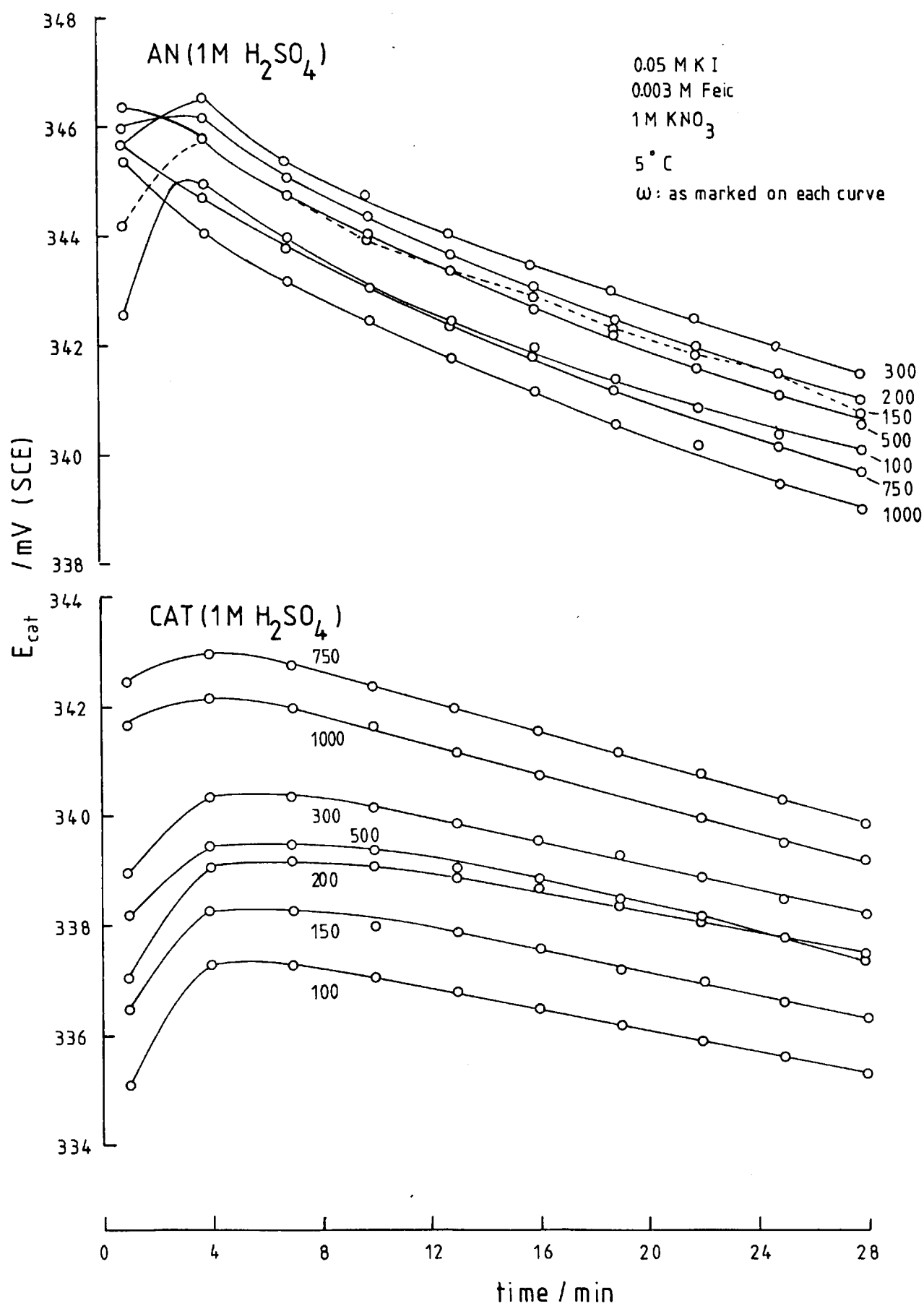


Figure IX-3

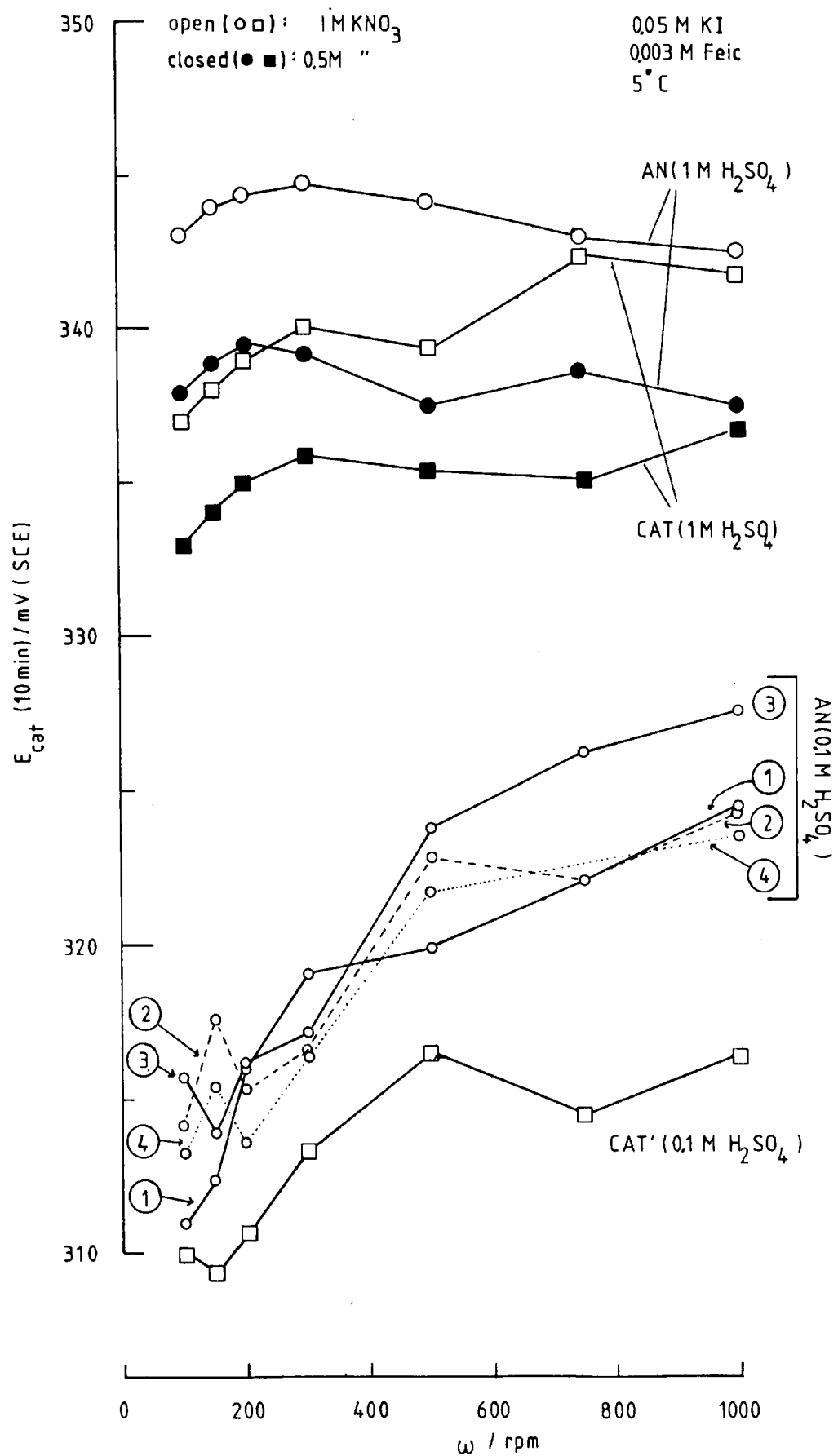


Figure IX-4

when  $[\text{KNO}_3]$  was doubled. As shown in Chapter VI, the difference between the standard equilibrium potentials  $E_2^0 - E_1^0$  becomes less negative as  $[\text{KNO}_3]$  increases (Table VI-10), which favours the catalytic rate according to eqs. (II-17) and (II-22). The actual magnitude of this effect depends on the term  $\alpha_2 Z_2 r_1$  in the exponential of eq. (II-17).

It is not clear why the line in Figure 2 corresponding to the CAT (1 M  $\text{H}_2\text{SO}_4$ ), 1 M  $\text{KNO}_3$ , crosses all of the other lines and gives a larger intercept. It will be seen later than even with preconditioning procedures in which the conditions were more carefully controlled, aberrant plots were occasionally obtained. The intercepts and slopes of the lines in Figure 2 are listed in Table 3.

TABLE IX.3 Dependence of  $u'_{\text{cat}}$  on  $\omega$  [equation (II-24)],  $5 \times 10^{-2}$  M KI,  $3 \times 10^{-3}$  M  $\text{Feic}$ ,  $5^\circ\text{C}$ .

| $[\text{KNO}_3]$                                                              | AN (1 M $\text{H}_2\text{SO}_4$ ) |       | CAT (1 M $\text{H}_2\text{SO}_4$ ) |       |
|-------------------------------------------------------------------------------|-----------------------------------|-------|------------------------------------|-------|
|                                                                               | 0.5 M                             | 1.0 M | 0.5 M                              | 1.0 M |
| $10^9 u'_{\text{cat}} / \text{mol s}^{-1}$                                    | 2.39                              | 3.09  | 2.63                               | 2.12  |
| $10^{-9} b^{(*)} / \text{mol}^{-1} \text{s} \quad (\text{rpm})^{\frac{1}{2}}$ | 21.1                              | 16.7  | 18.3                               | 9.91  |

$$(*): b = d(1/u'_{\text{cat}}) / d(\omega^{-\frac{1}{2}})$$

At this stage the CAT preconditioning was modified: it was carried out in 0.1 M  $\text{H}_2\text{SO}_4$  instead and the potential programme is set out in Table 4. The OCV at the end was only ca. 0.03 V (SCE) compared with 0.20 V in Table 2.

TABLE IX.4 CAT (0.1 M H<sub>2</sub>SO<sub>4</sub>) Procedure.

| Potential/<br>V (SCE) | Time      | $\omega$ /rpm |
|-----------------------|-----------|---------------|
| 1.560                 | 2 s       | 100           |
| 1.000                 | 60 s      | 100           |
| -0.500                | 5 min     | 0             |
| OC                    | 10-20 min | 100           |

The catalytic rates obtained for several values of  $\omega$  in 1 M KNO<sub>3</sub> are shown in Figure 2, and the corresponding line 5 is seen to agree with the general trend of the other lines obtained with reduced electrodes. However, a set of runs carried out some 6 weeks later under the same conditions and with the same modified CAT (0.1 M H<sub>2</sub>SO<sub>4</sub>) gave much larger rates, plotted as line 6 in Figure 2. Increased rates after prolonged periods of idleness were a recurrent feature in these early experiments. The initial lower rates were never reproduced. This trend almost certainly affects all of the results presented so far. By this time the glassy carbon disk had lost some of its initial glossyness. Examination with a magnifying lens revealed an irregular surface, formed of very tiny lumps, probably a result of burning of the electrode at 1.560 V (SCE) during preconditioning, and aerial oxidation. The most obvious effect would be an increase in the surface rugosity which would increase the real area available for the reaction. These two phenomena could have also progressively eliminated impurities accumulated at the surface during construction of the rotating disk. Thus, reproducibility of the state of the surface cannot be achieved

by electrochemical preconditioning alone, in the case of glassy carbon. Polishing of the electrode with grinding powder prior to electrochemical treatment was therefore tried.

b) The correct polishing procedure was achieved by trial and error. Initial trials involved rotating the disk in its shaft at ca. 100 rpm, while hand-pressing on it with moderate strength a moistened cotton wool ball (Booths Ltd., B.P. quality) sprinkled with some 0.3  $\mu\text{m}$  teecepol polishing powder (Abrafract Ltd., Sheffield). The ball was made to go back and forth on the electrode over about 1 hour. This treatment did not eliminate the tarnish on the surface. Examination with the magnifying glass did not reveal any change in the appearance, although the cotton had acquired a very dark tonality because of material scratched from the carbon surface.

At this stage, creeping of the electrolyte into the carbon/mantle gap was realised, and the flaw was rectified as described in Section 2a. More drastic polishing conditions were also employed. The electrode was rotated at 1000 rpm, and the cotton ball with the teecepol slurry was pressed hard against the electrode in a back and forth movement for another hour. This unfortunately produced concentric grooves on the electrode, visible to the naked eye, and some very visible scratches. The grooves and the tarnish, but not the scratches, disappeared upon polishing for 1 hour with 25  $\mu\text{m}$  alumina powder (Banner Scientific Ltd., Coventry) in the initial more moderate manner. Polishing the electrode while it rotated on its shaft was not very convenient. Thus, the final polishing procedure performed before every run was as follows. The RDE was taken out of the shaft, thoroughly rinsed with distilled water, placed face upwards on the bench, sprinkled with teecepol and rubbed

with a moistened cotton ball, as evenly as possible. Preferential polishing in a direction or in a given area was minimised by frequently turning the electrode, and by trying to vary the movement patterns of the hand. The electrochemical treatment described in Table 5 or in Table 6 always followed. In future reference to them, no explicit mention of prior polishing will be made, but it must be understood that it was carried out.

TABLE IX.5 CAT' (0.1 M H<sub>2</sub>SO<sub>4</sub>) Procedure.

| Potential/<br>V (SCE) | Time   | $\omega$ /rpm |
|-----------------------|--------|---------------|
| 1.000                 | 1 min  | 100           |
| -0.500                | 2 min  | 0             |
| OC                    | 10 min | 100           |

TABLE IX.6 AN (0.1 M H<sub>2</sub>SO<sub>4</sub>) Procedure.

| Potential/<br>V (SCE) | Time   | $\omega$ /rpm |
|-----------------------|--------|---------------|
| 1.000                 | 1 min  | 100           |
| OC                    | 10 min | 0             |

The OCV was ca. 0.20 V at the end of CAT', and ca. 0.45 V at the end of AN (0.1 M H<sub>2</sub>SO<sub>4</sub>).

c) Long Term Performance with AN (0.1 M H<sub>2</sub>SO<sub>4</sub>) Pretreatment.

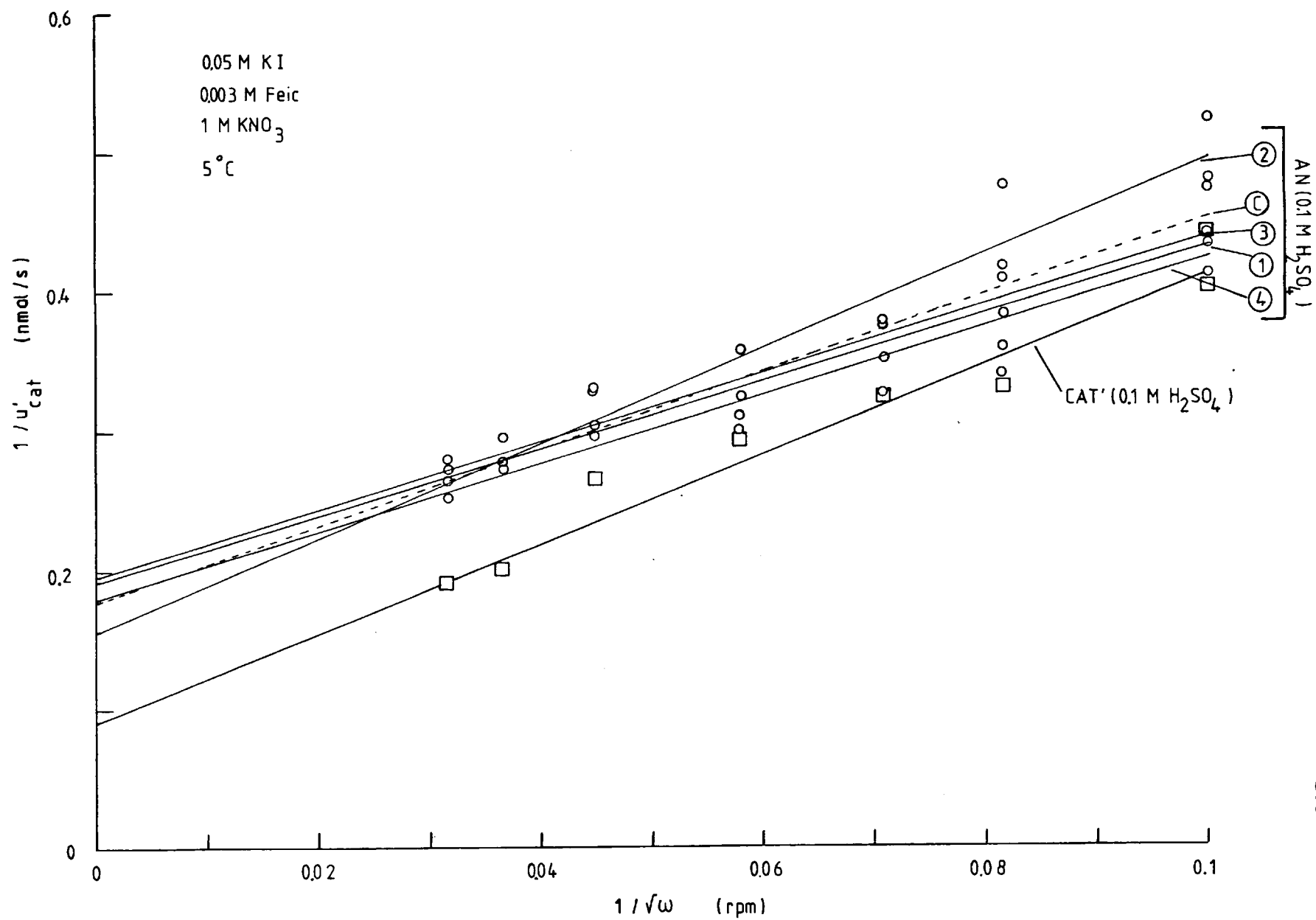
Most of the work described in the remaining part of this Chapter was carried out with this pretreatment over a period of ca. 17 weeks. The performance of the glassy carbon rotating disk catalyst, judged from the value of  $u'_{\text{cat}}$  at 5°C, with  $5 \times 10^{-2}$  M KI,  $3 \times 10^{-3}$  M Feic, and 1 M KNO<sub>3</sub> at several  $\omega$  values, was periodically tested. The  $1/u'_{\text{cat}}$  vs.  $1/\omega^2$  plots obtained are shown in Figure 5. The curves are marked 1 to 4 in the order in which they were obtained. Line C was obtained with the collected data of all the other curves. Table 7 gives the least squares parameters of each line, as well as the time elapsed since beginning the runs with the polished catalyst and the cumulative number of runs, in all sorts of conditions.

TABLE IX.7 LONG TERM PERFORMANCE OF GLASSY CARBON CATALYST  
AN (0.1 M H<sub>2</sub>SO<sub>4</sub>), 0.05 M KI, 0.003 M Feic, 1 M KNO<sub>3</sub>, 5°C.

| Curve Number<br>(w.r.t. Fig. 5)                                        | 1         | 2         | 3         | 4         | C         |
|------------------------------------------------------------------------|-----------|-----------|-----------|-----------|-----------|
| $10^9 u'_{\text{cat}} / \text{mol s}^{-1}$                             | 5.21±0.39 | 6.43±1.1  | 5.13±0.77 | 5.59±0.74 | 5.62±0.92 |
| $10^{-9} b^{(*)} / \text{mol}^{-1} \text{s}(\text{rpm})^{\frac{1}{2}}$ | 2.41±0.22 | 3.40±0.39 | 2.44±0.45 | 2.46±0.34 | 2.75±0.41 |
| <u>Accumulated</u>                                                     |           |           |           |           |           |
| Time/weeks                                                             | 1         | 3         | 12        | 17        | -         |
| Number of runs                                                         | 8         | 38        | 96        | 110       | -         |

(\*):  $b = d(1/u'_{\text{cat}}) / d(\omega^{-\frac{1}{2}})$

Figure IX-5



In spite of the long times involved in between, the plots show no apparent trend towards increasing rates.

The value of  $E_{cat}$  at 10 minutes for the AN (0.1 M  $H_2SO_4$ ) is shown in Figure 4 as a function of  $\omega$ . The curves "1" to "4" correspond to the respective "1" to "4" curves in Figure 5. No long term trends are observed in this case either. These results and those in Figure 5 must surely be due to the polishing of the catalyst which produces a fresh surface every time, scratching off any irreversibly adsorbed chemicals and impurities and obliterating any roughening due to electrochemical preconditioning or to aerial oxidation of the carbon. Thus, it is reasonable to assume that the curves will be reproducible in the long term whatever the electrochemical treatment following polishing.

However, the values of  $u'_{cat}$  at fixed  $\omega$  show considerable scatter (Figure 5 and Table 8), perhaps because of traces of grease from the fingers and from the cotton.

TABLE IX.8 CATALYTIC RATE AS A FUNCTION OF  $\omega$ . AN (0.1 M  $H_2SO_4$ )  
0.05 M KI, 0.003 M  $FeCl_3$ , 1 M  $KNO_3$ , 5°C.

| $\omega$ /rpm                 | 100          | 150          | 200  | 300  | 500  | 750  | 1000 |
|-------------------------------|--------------|--------------|------|------|------|------|------|
| $10^9 u'_{cat}/mol\ s^{-1}$ : |              |              |      |      |      |      |      |
| Curve 1                       | 2.27<br>2.31 | 2.77<br>2.60 | 2.67 | 2.81 | 3.38 | 3.63 | 3.80 |
| Curve 2                       | 1.91<br>2.12 | 2.10<br>2.46 | 2.65 | 3.09 | 3.02 | 3.68 | 3.68 |
| Curve 3                       | 2.08         | 2.77         | 2.84 | 3.34 | 3.05 | 3.38 | 3.57 |
| Curve 4                       | 2.42         | 2.39         | 3.07 | 3.23 | 3.28 |      | 3.97 |
| Mean                          | 2.2          | 2.5          | 2.8  | 3.1  | 3.2  | 3.6  | 3.8  |
| $\pm \sigma$                  | 0.2          | 0.3          | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  |

It is interesting to compare the values in Table 8 obtained with the AN (0.1 M H<sub>2</sub>SO<sub>4</sub>) with those in Figure 2 [AN (1 M H<sub>2</sub>SO<sub>4</sub>), 1 M KNO<sub>3</sub>]. The latter procedure gave catalytic rates 3-4 times lower than the former. Since the electrochemical treatment was very similar, the increased rates with AN (0.1 M H<sub>2</sub>SO<sub>4</sub>) must be mainly due to the polishing of the catalyst: roughening of the electrode and/or removal of adsorbed films of impurities. In the absence of measurements of the real surface area, changes in the latter remain conjectural. However, if this were the only factor,  $E_{cat}$  should have remained unchanged when passing from AN (1 M H<sub>2</sub>SO<sub>4</sub>) to AN (0.1 M H<sub>2</sub>SO<sub>4</sub>). In fact,  $E_{cat}$  during runs with the latter was considerably less anodic (Figure 4). Moreover, the product  $b u'_{cat}^{\infty}$  should be independent of the magnitude of the real surface area: it is ca. 52 (rpm) <sup>$\frac{1}{2}$</sup>  for the AN (1 M H<sub>2</sub>SO<sub>4</sub>) data (in 1 M KNO<sub>3</sub>), and ca. 15 (rpm) <sup>$\frac{1}{2}$</sup>  for curve C for the AN (0.1 M H<sub>2</sub>SO<sub>4</sub>) data. The difference in values is due to changes in the various kinetic parameters in  $u'_{cat}^{\infty}$  and in  $b$ . The transport parameters  $\sigma_j$  are not affected by the state of the surface. This interpretation is independent of the actual mechanism of the catalysis. Assuming momentarily that the electrochemical mechanism holds, then the increased catalytic rates and less positive catalyst potentials would indicate that the AN (0.1 M H<sub>2</sub>SO<sub>4</sub>) procedure enhances the electrode kinetics of the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> couple over those of the Feic/Feoc couple.

d) Comparison Between Oxidised and Reduced Catalyst.

Figure 5 also shows  $1/u'_{cat}$  vs.  $1/\omega^{\frac{1}{2}}$  for reduced [CAT' (0.1 M H<sub>2</sub>SO<sub>4</sub>)] glassy carbon. Comparisons should be made with curve C. The actual values for the reduced catalyst are in Table 9. The least squares fitting

produces  $u'_{\text{cat}}{}^{\infty} = (11 \pm 2) \times 10^{-9} \text{ mol s}^{-1}$ , and  $b = (3.21 \pm 0.30) \times 10^9 \text{ mol}^{-1} \text{ s (rpm)}^{\frac{1}{2}}$ , which gives  $u'_{\text{cat}}{}^{\infty} b = 34 \text{ (rpm)}^{\frac{1}{2}}$ . The variation of  $E_{\text{cat}}$  at 10 minutes with  $\omega$  is shown in Figure 4.

TABLE IX.9 CATALYTIC RATE AS A FUNCTION OF  $\omega$ .  $5 \times 10^{-2} \text{ M KI}$ ,  
 $3 \times 10^{-3} \text{ M Feic}$ ,  $1 \text{ M KNO}_3$ ,  $5^\circ\text{C}$ , REDUCED CATALYST  
[CAT' ( $0.1 \text{ M H}_2\text{SO}_4$ )].

| $\omega/\text{rpm}$                      | 100  | 150  | 200  | 300  | 500  | 750  | 1000 |
|------------------------------------------|------|------|------|------|------|------|------|
| $10^9 u'_{\text{cat}}/\text{mol s}^{-1}$ | 2.27 | 3.00 | 3.17 | 3.47 | 3.80 | 5.00 | 5.29 |
|                                          | 2.48 |      |      |      |      |      |      |

Qualitatively, these results vindicate those obtained earlier without polishing the catalyst (Section IX.3.a.). The rates with the reduced catalyst are larger, and  $E_{\text{cat}}$  less positive than with oxidised surfaces. This agreement suggests that the CAT' results are not uncharacteristic despite the relatively few runs carried out and the scatter of the points.

The variation of  $E_{\text{cat}}$  with time is shown in Figure 6. The difference in behaviour is striking:  $E_{\text{cat}}$  for oxidised catalyst decreases with time while it increases for the reduced catalyst. From the values of  $E_j^0$  in Table VI-13, it is possible to calculate the equilibrium constant at  $5^\circ\text{C}$  for reaction (I-1) as 0.03432, and the equilibrium concentration of total iodine is  $1.921 \times 10^{-4} \text{ M}$ , for the initial conditions of  $5 \times 10^{-2} \text{ M KI}$  and  $3 \times 10^{-3} \text{ M Feic}$  in  $1 \text{ M KNO}_3$ ; this furnishes 305.7 mV (SCE) for the equilibrium potential of the mixture,  $\hat{E}$  (i.e.,  $E_{\text{cat}}$  at infinite time), upon application of eqs. (II-30). Therefore, one would expect  $E_{\text{cat}}$  to change with time from its initial value towards  $\hat{E}$ . In

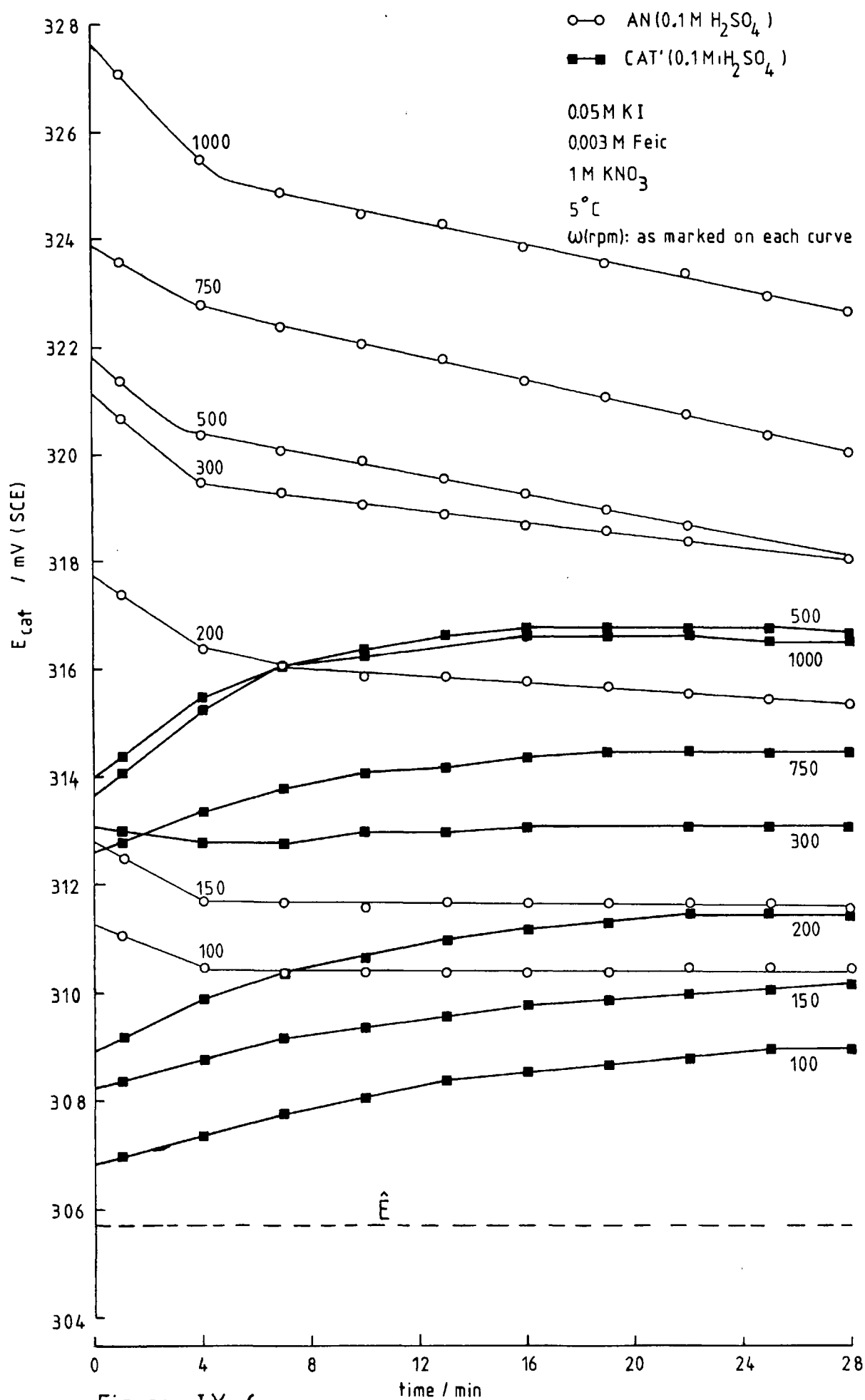


Figure IX-6

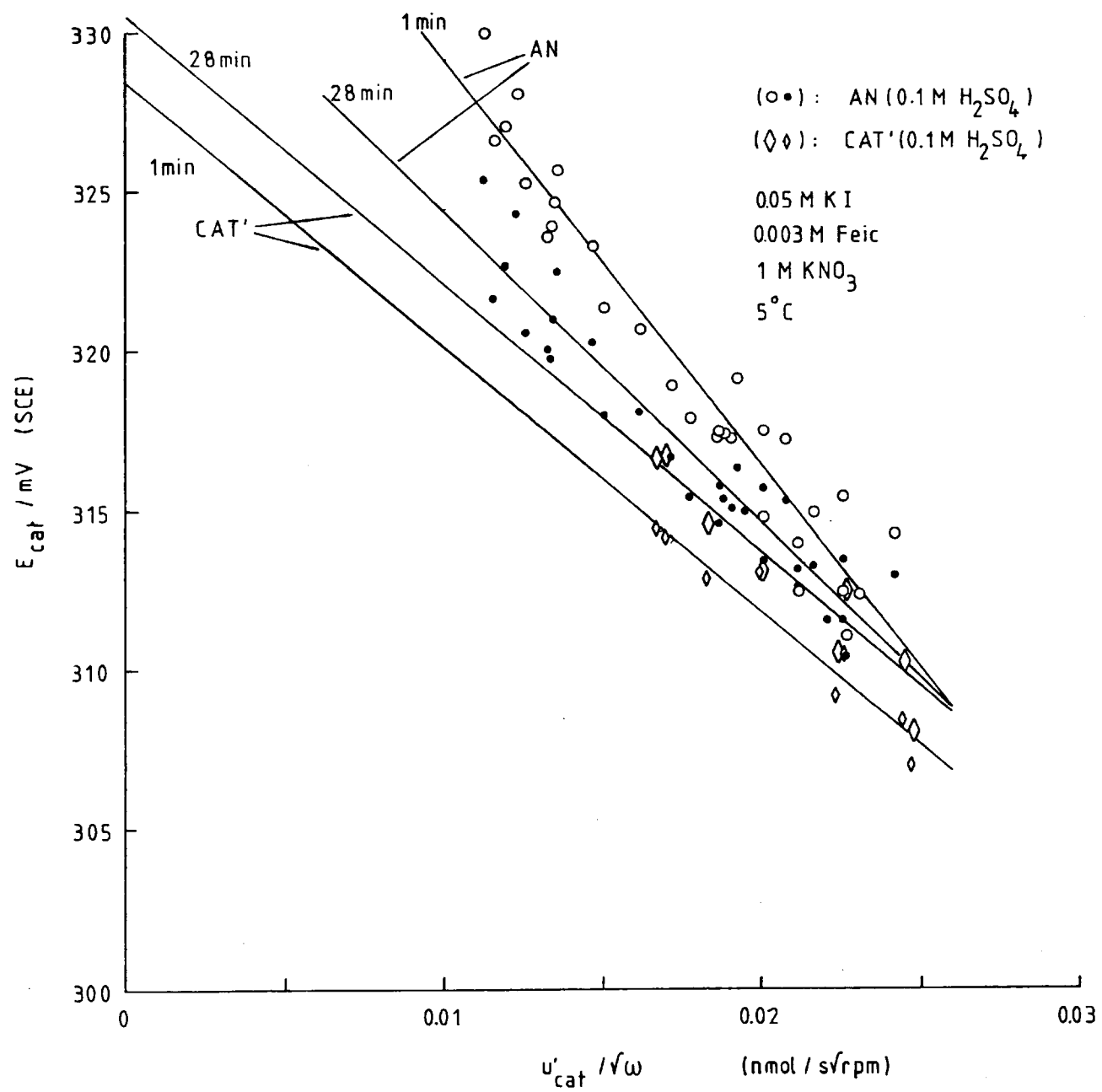
the case of the reduced catalyst, the initial potential is close to the equilibrium potential  $\hat{E}$  in agreement with its fast catalytic rate. The subsequent increase in  $E_{cat}$  for the reduced catalyst is difficult to explain, and may suggest that surface groups participate very actively in the electron transfer process. Another characteristic of cathodically pretreated disks is that  $E_{cat}$  at a given time varies somewhat erratically with  $\omega$ . By contrast, for the oxidised electrode,  $E_{cat}$  decreases with time, faster at faster  $\omega$  values. (That the initial fast decreasing part is not due to slow homogenisation of the reactants solutions is shown by the fact that it is present even at the faster rotation speeds).

Equation (II-26), based on the electrochemical model, can be re-written in the form

$$E_{cat} = E_{cat}^{\infty}(t) + a(t) u'_{cat} / \omega^{\frac{1}{2}} \quad (IX-1)$$

This takes into account the fact that  $E_{cat}$  and  $a$  vary with time due to the constant formation of the products.  $u'_{cat}$  too depends on time, but since the initial values are available for every  $\omega$ , they will be the ones used in eq. (1). Thus,  $E_{cat}$  was plotted against  $u'_{cat} / \omega^{\frac{1}{2}}$  according to this equation, one plot for each time,  $t$ , at which an  $E_{cat}$  reading had been made during the catalytic run, and fitted by least squares. Two such plots at  $t = 1$  minute and 28 minutes are shown in Figure 7 obtained with the oxidised catalyst and with the reduced catalyst. These are straight lines in the case of the former, but for the reduced one the points are too scattered for linearity to be assured. The  $E_{cat}^{\infty}(t)$  and  $a(t)$  values obtained were then plotted vs. time and extrapolated to  $t = 0$  to obtain the initial values to which the equation refers. The lines are shown in Figure 8 for a variety of experimental conditions. The extrapolated values and slopes are listed in Table 10, together with data reported earlier for  $u'_{cat}$  itself in Tables 7 and 9.

Figure IX-7



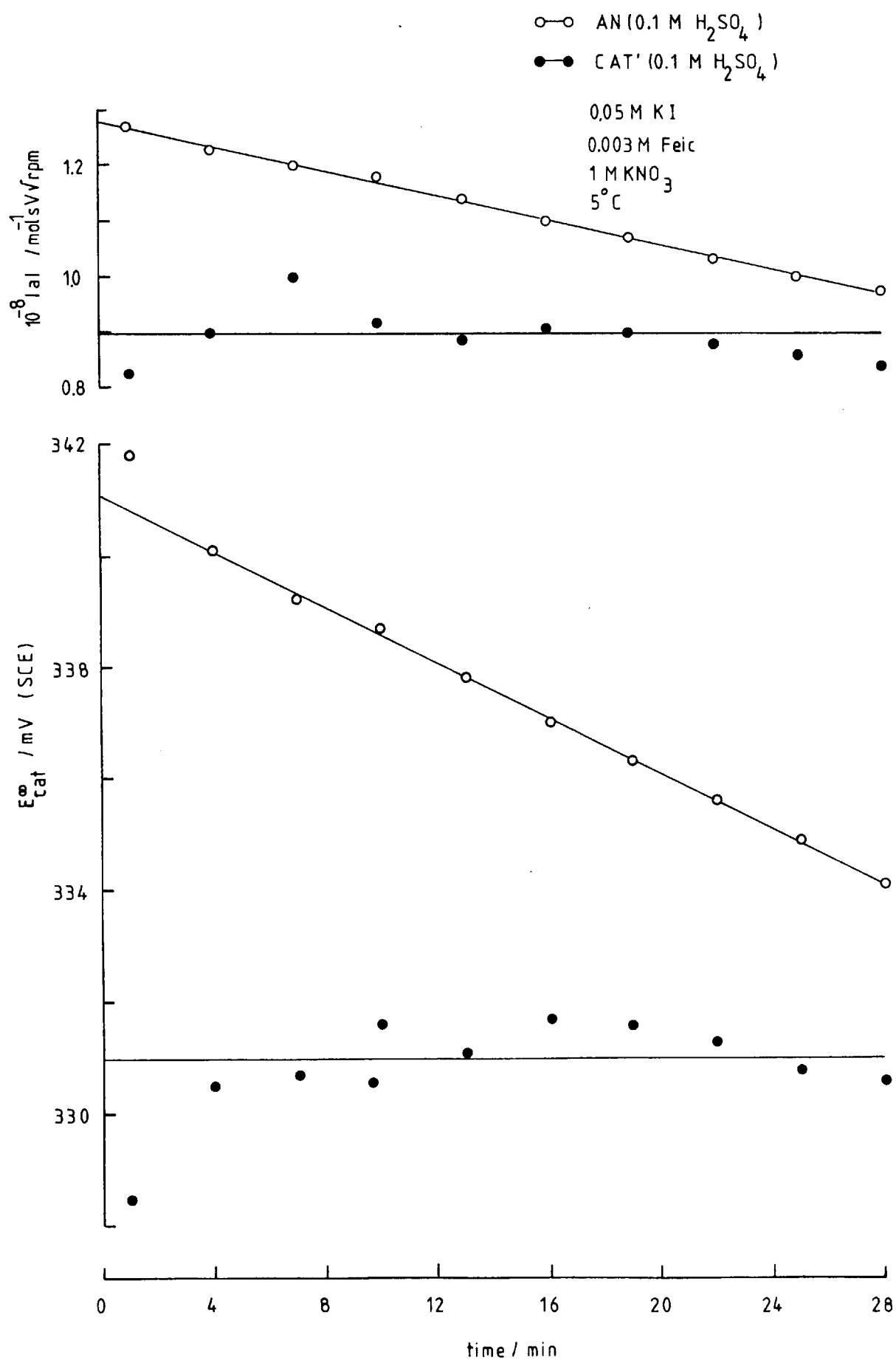


Figure IX-8

TABLE IX.10 KINETIC PARAMETERS AT  $\omega = \infty$ . 0.05 M KI, 0.003 M Feic,  
1 M KNO<sub>3</sub>, 5°C.

|                                                                     | AN (0.1 M H <sub>2</sub> SO <sub>4</sub> ) | CAT' (0.1 M H <sub>2</sub> SO <sub>4</sub> ) |
|---------------------------------------------------------------------|--------------------------------------------|----------------------------------------------|
| $10^9 u'_{\text{cat}}/\text{mol s}^{-1}$                            | $5.6 \pm 0.9$                              | $11 \pm 2$                                   |
| $E_{\text{cat}}^\infty/\text{mV (SCE)}$                             | $341 \pm 1$                                | $331 \pm 1$                                  |
| $10^{-9} b/\text{mol}^{-1} \text{ s (rpm)}^{\frac{1}{2}}$           | $2.8 \pm 0.4$                              | $3.2 \pm 0.3$                                |
| $10^{-8} a/\text{mol}^{-1} \text{ s (rpm)}^{\frac{1}{2}} \text{ V}$ | $-1.3 \pm 0.1$                             | $-0.90 \pm 0.03$                             |

TABLE IX.11 DEPENDENCE OF THE CATALYTIC RATE ON REACTANT CONCENTRATION.  
AN (0.1 M H<sub>2</sub>SO<sub>4</sub>) PRECONDITIONING, 1 M KNO<sub>3</sub>, 5°C.

| $\omega/\text{rpm}$           | 100                                                              | 150  | 200  | 300  | 500  | 750  | 1000 |
|-------------------------------|------------------------------------------------------------------|------|------|------|------|------|------|
| $10^3 [\text{Feic}]/\text{M}$ | $10^9 u'_{\text{cat}}/\text{mol s}^{-1} (+0.05 \text{ M KI})$    |      |      |      |      |      |      |
| 1.0                           | 0.945                                                            | 1.26 | 1.14 | 1.44 | 1.55 | 1.72 | 1.79 |
| 2.0                           | 1.91                                                             | 1.99 | 2.18 | 2.01 | 2.39 | 2.81 | 2.75 |
| 3.0                           | 2.2                                                              | 2.5  | 2.8  | 3.1  | 3.2  | 3.6  | 3.8  |
| 5.0                           | 2.58                                                             | 2.98 | 3.49 | 3.51 | 4.20 | 4.22 | 4.77 |
| $10^3 [\text{KI}]/\text{M}$   | $10^9 u'_{\text{cat}}/\text{mol s}^{-1} (+0.003 \text{ M Feic})$ |      |      |      |      |      |      |
| 30                            | 1.47                                                             | 1.65 | 1.70 | 2.18 | 2.16 | 2.35 | 2.75 |
| 50                            | 2.2                                                              | 2.5  | 2.8  | 3.1  | 3.2  | 3.6  | 3.8  |
| 100 <sup>a</sup>              | 3.34                                                             | 3.55 | 3.53 | 4.16 | 4.14 | 5.25 | 5.08 |
| 200 <sup>a</sup>              | 4.75                                                             | 5.88 | 6.09 | 5.84 | 6.20 | 7.14 | 8.21 |

<sup>a</sup> [KNO<sub>3</sub>] adjusted to give  $[\text{K}^+] \approx 1.05 \text{ M}$

TABLE IX.12 DEPENDENCE OF KINETIC PARAMETERS ON THE REACTANT CONCENTRATION  
1 M KNO<sub>3</sub>, 5°C.

| $10^3 [\text{Feic}]$<br>/M | $10^3 [\text{I}^-]$<br>/M | $10^9 u'_{\text{cat}}{}^\infty$<br>/mol s <sup>-1</sup> | $E_{\text{cat}}^\infty$ (SCE)<br>/mV | $10^{-9} b$<br>/mol <sup>-1</sup> s<br>(rpm) <sup><math>\frac{1}{2}</math></sup> | $10^{-8} a / \text{mol}^{-1}$<br>(rpm) <sup><math>\frac{1}{2}</math></sup> V |
|----------------------------|---------------------------|---------------------------------------------------------|--------------------------------------|----------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| 1                          | 50                        | $3.0 \pm 0.6$                                           | $333 \pm 1$                          | $6.8 \pm 0.7$                                                                    | $-2.86 \pm 0.03$                                                             |
| 2                          |                           | $3.4 \pm 0.3$                                           | $338 \pm 1$                          | $2.4 \pm 0.6$                                                                    | $-1.74 \pm 0.03$                                                             |
| 3                          |                           | $5.6 \pm 0.9$                                           | $341 \pm 1$                          | $2.8 \pm 0.4$                                                                    | $-1.3 \pm 0.1$                                                               |
| 5                          |                           | $7.4 \pm 0.6$                                           | $345 \pm 1$                          | $2.4 \pm 0.2$                                                                    | $-1.06 \pm 0.02$                                                             |
| 3                          | 30                        | $4.1 \pm 0.4$                                           | $349 \pm 1$                          | $4.4 \pm 0.5$                                                                    | $-1.82 \pm 0.03$                                                             |
|                            | 50                        | $5.6 \pm 0.9$                                           | $341 \pm 1$                          | $2.8 \pm 0.4$                                                                    | $-1.3 \pm 0.1$                                                               |
|                            | 100                       | $6.7 \pm 0.6$                                           | $330 \pm 1$                          | $1.6 \pm 0.3$                                                                    | $-0.89 \pm 0.03$                                                             |
|                            | 200                       | $9.8 \pm 1$                                             | $318 \pm 1$                          | $1.0 \pm 0.2$                                                                    | $-0.65 \pm 0.03$                                                             |

In the absence of electrochemical data and of knowledge of the changes that may happen to glassy carbon surfaces following electrochemical treatment, it is not possible to point out the reason for the increased catalytic rates and decreased potential on the reduced catalyst. The differences are certainly outside the experimental uncertainty. The results indicate that the reducing treatment increases the reversibility of the  $\text{I}^-/\text{I}_3^-$  couple relative to the Feic/Feoc couple.

In order to minimise the error due to long extrapolation when  $u'_{\text{cat}}{}^\infty$  is obtained from  $1/u'_{\text{cat}}$  vs.  $1/\omega^{\frac{1}{2}}$  plots, it is best to work under conditions that give the smallest  $b u'_{\text{cat}}{}^\infty$ . Since this is  $15 (\text{rpm})^{\frac{1}{2}}$  for the oxidised disk and  $34 (\text{rpm})^{\frac{1}{2}}$  for the reduced one, the oxidising procedure AN (0.1 M H<sub>2</sub>SO<sub>4</sub>) was chosen to carry out the remainder of the work. Another reason for this choice was the curious time-dependence of  $E_{\text{cat}}$  observed for the reduced disk.

e) Dependence of the Catalytic Rate on the Reactant Concentration for Disks Preconditioned by Polishing and AN (0.1 M H<sub>2</sub>SO<sub>4</sub>).

The results are summarised in Tables 11 and 12. By plotting  $\ln u'_{\text{cat}}^{\infty}$  vs.  $\ln C_j$ , the reaction orders were found to be  $0.6 \pm 0.2$  in [Feic] and  $0.43 \pm 0.01$  in [I<sup>-</sup>]. The uncertainty in the rates is ca.  $\pm 10\%$  ( $\pm 0.1$ ). Thus, if this is added to the quoted uncertainties from the least squares fittings, the probably more realistic figures are  $0.6 \pm 0.3$  in [Feic] and  $0.4 \pm 0.1$  in [I<sup>-</sup>]. Such large uncertainties in these crucial kinetic parameters much reduce the value of modelistic interpretation of the data. However, attempts to verify the electrochemical model may at least indicate if the values being obtained are of the correct order of magnitude.

Assuming that the mechanism for I<sup>-</sup> oxidation at glassy carbon in the presence of Feic is that described by Wroblowa and Saunders<sup>61</sup> on graphite for which  $\alpha = 0.5$ ,  $Z = 1$  and  $W_{\text{I}^-} = 1$ , and that the reaction of Feic follows the path proposed by Sohr, Müller and Landsberg<sup>56</sup> on graphite for which  $\alpha = 0.2$ ,  $Z = 1$  and  $W_{\text{Feic}} = 0.7$ , then  $r_1$  and  $r_2$  may be calculated according to eqs. (II-18) to be 0.71 and 0.29, respectively. According to eq. (II-17), the catalytic reaction orders  $r_1 W_{\text{Feic}}$  in [Feic], and  $r_2 W_{\text{I}^-}$  in [I<sup>-</sup>] would then be, respectively, 0.50 and 0.29. This is not inconsistent with the experimental values, considering the large errors in the  $u'_{\text{cat}}^{\infty}$  values.

It is possible to show from eqs. (II-56) that, on assuming Tafel region behaviour for the couples:

$$E_{\text{cat}}^{\infty} = (r_2 / \alpha_2 Z_2 f) \ln(\vec{k}_2 / \vec{k}_1) + (r_2 W_{\text{Feic}} / \alpha_2 Z_2 f) \ln[\text{Feic}] - (r_2 W_{\text{I}^-} / \alpha_2 Z_2 f) \ln[\text{I}^-] \quad (\text{IX-2})$$

Figure 9 shows plots of  $E_{\text{cat}}^{\infty}$  vs.  $\ln [\text{Feic}]$ , and vs.  $\ln [\text{I}^-]$ . The slopes are  $(7 \pm 1) \times 10^{-3}$  V and  $(1.6 \pm 0.1) \times 10^{-2}$  V, respectively.

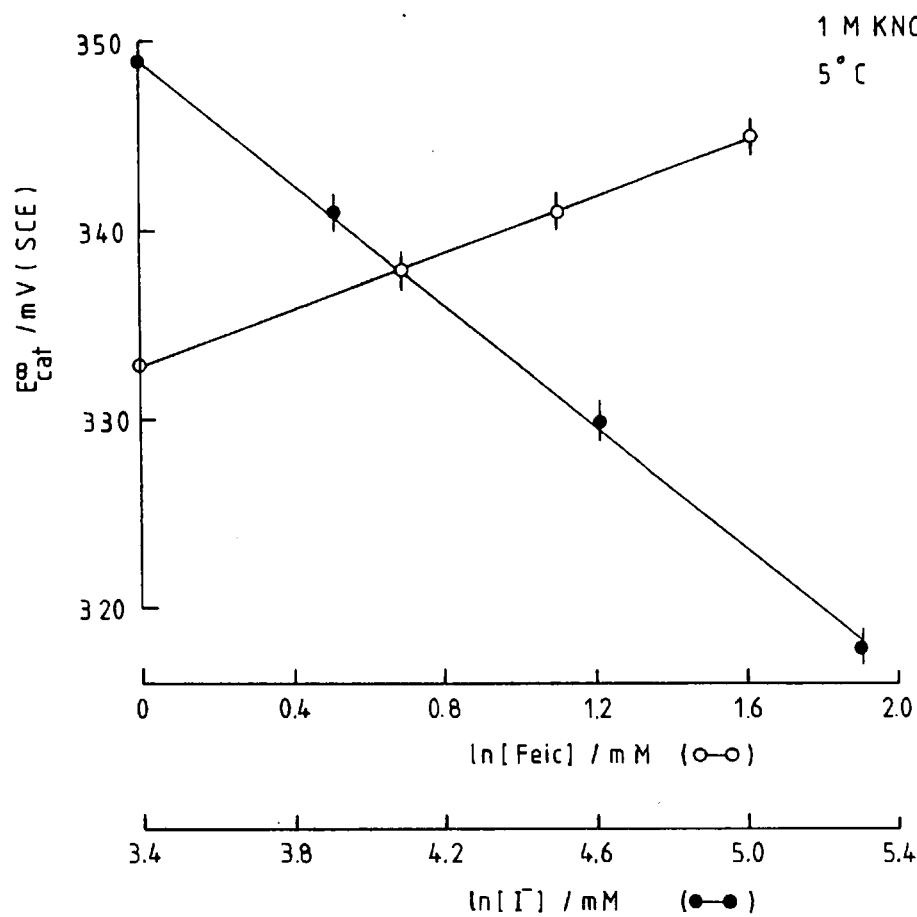


Figure IX-9

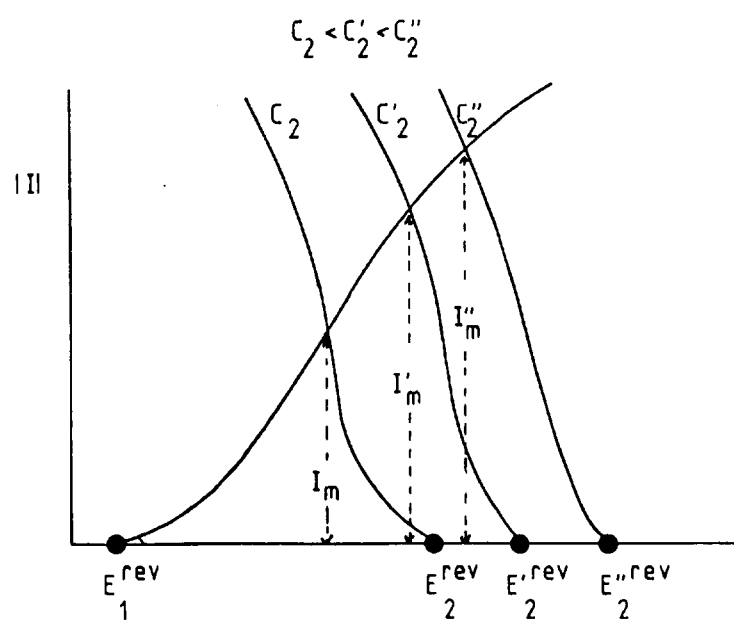


Figure IX-10

The calculated slopes using the parameters from the literature work cited above<sup>56,61</sup> are  $2.4 \times 10^{-2}$  V and  $3.4 \times 10^{-2}$  V, for Feic and  $I^-$ , respectively, in considerable disagreement with the experimental data, although the orders of magnitude are the same.

The disagreement does not disprove the electrochemical model, because the kinetics of electron transfer are likely to be complicated by the simultaneous presence of the two couples, specially if both Feic and  $I^-$  are adsorbed.<sup>56,61</sup> One must not discard the possibility of adsorption of iodide on glassy carbon, even if it has not been found to be the case on graphite.<sup>61</sup>

In order to gain some insight into the kinetics of the Feic/Feoc and  $I^-/I_3^-$  couples, the following calculations have been carried out on the basis of the electrochemical model. The results offer some guidance as to what to expect from electrochemical studies. Figure 10 shows schematic  $i$ - $E$  curves. If the concentration of one of the reactants, say  $I^-$ , is kept constant, the crossing points of the curves describe the  $i$ - $E$  curves of the  $I^-/I_3^-$  couple as the concentration of the other reactant, Feic, is varied. Thus, according to eqs. (II-56), by plotting  $\ln(2F u'_{cat}{}^\infty)$  vs.  $E_{cat}^\infty$  either at constant  $[I^-]$  or at constant  $[Feic]$ , one obtains the corresponding symmetry factors  $(1-\alpha_1)Z_1$  and  $\alpha_2Z_2$ . This is illustrated in Figure 11. Moreover, eqs. (II-56) may be rearranged as:

$$\ln(2F u'_{cat}{}^\infty) - (1-\alpha_1)Z_1 f E_{cat}^\infty = \ln(\vec{Fk}_1) + W_I - \ln[I^-] \quad (IX-3a)$$

$$\ln(2F u'_{cat}{}^\infty) + \alpha_2 Z_2 f E_{cat}^\infty = \ln(\vec{Fk}_2) + W_{Feic} \ln[Feic] \quad (IX-3b)$$

Therefore, by plotting the left hand side of eqs. (3) vs. the  $\ln$  of the corresponding concentration, the electrochemical reaction orders  $W_j$  are

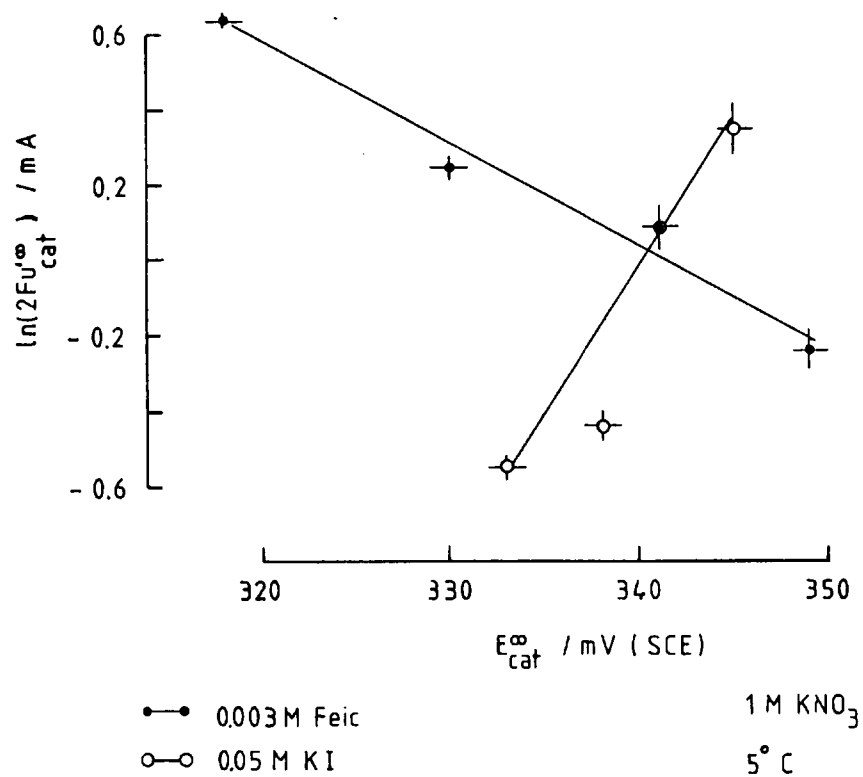


Figure IX-11

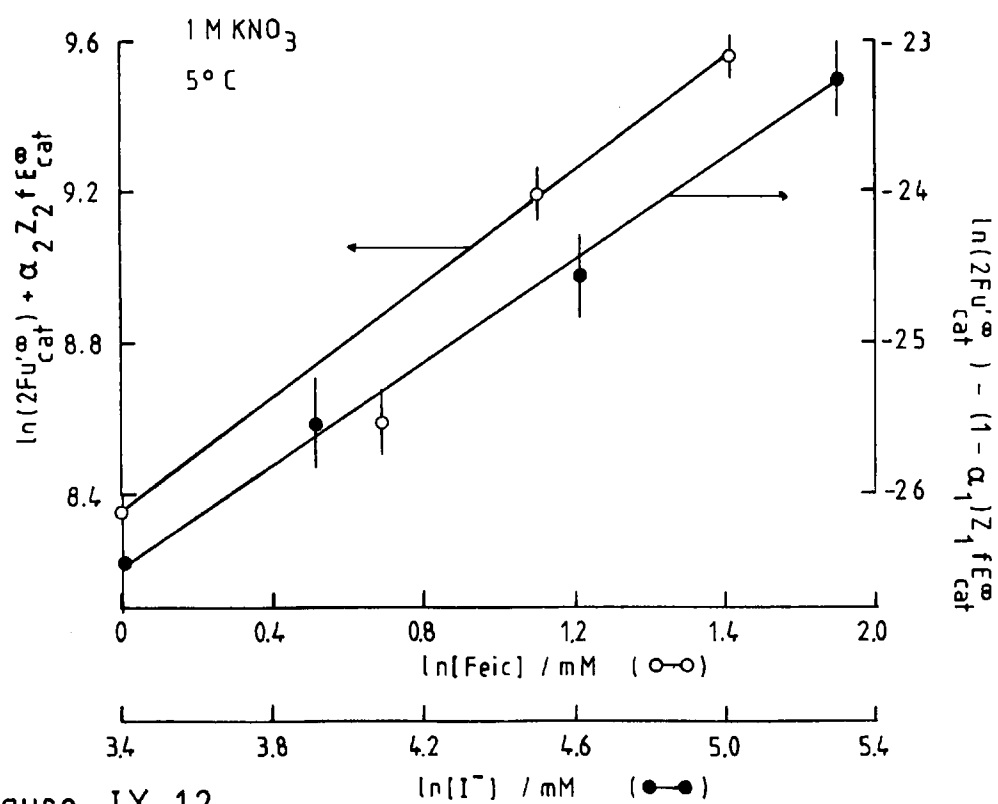


Figure IX-12

obtained. Such plots, based on the results in Table 12, are drawn in Figure 12. The results from Figures 11 and 12 may be summarised as:

$$(1-\alpha_1)Z_1 = 1.8 \qquad \alpha_2 Z_2 = 0.64 \qquad (\text{IX-4a})$$

$$W_I^- = 1.7 \qquad W_{\text{Feic}} = 0.76 \qquad (\text{IX-4b})$$

$$\vec{Fk}_1 = 1.09 \times 10^{-12} \text{ A M}^{-1.7} \qquad \vec{Fk}_2 = 7.87 \times 10^2 \text{ A M}^{-0.76} \qquad (\text{IX-4c})$$

$$i_{oo1} = 6.7 \times 10^{-3} \text{ A} \qquad i_{oo2} = 0.76 \text{ A} \qquad (\text{IX-4d})$$

The  $i_{ooj}$  values were calculated for each couple from its definition in eq. (I-18b), and the calculated quantities in expressions (4a) and (4c).

The quantities listed above (4a-4d) are not unreasonable, although they do not agree with any of the mechanisms mentioned in Chapter III. They probably represent various combinations of more fundamental quantities related to the intimate workings of the electron transfer of the couples under the particular conditions of this work. They reproduce the experimental kinetic reaction orders and catalytic rates almost exactly, which is a check on the consistency of the figures.

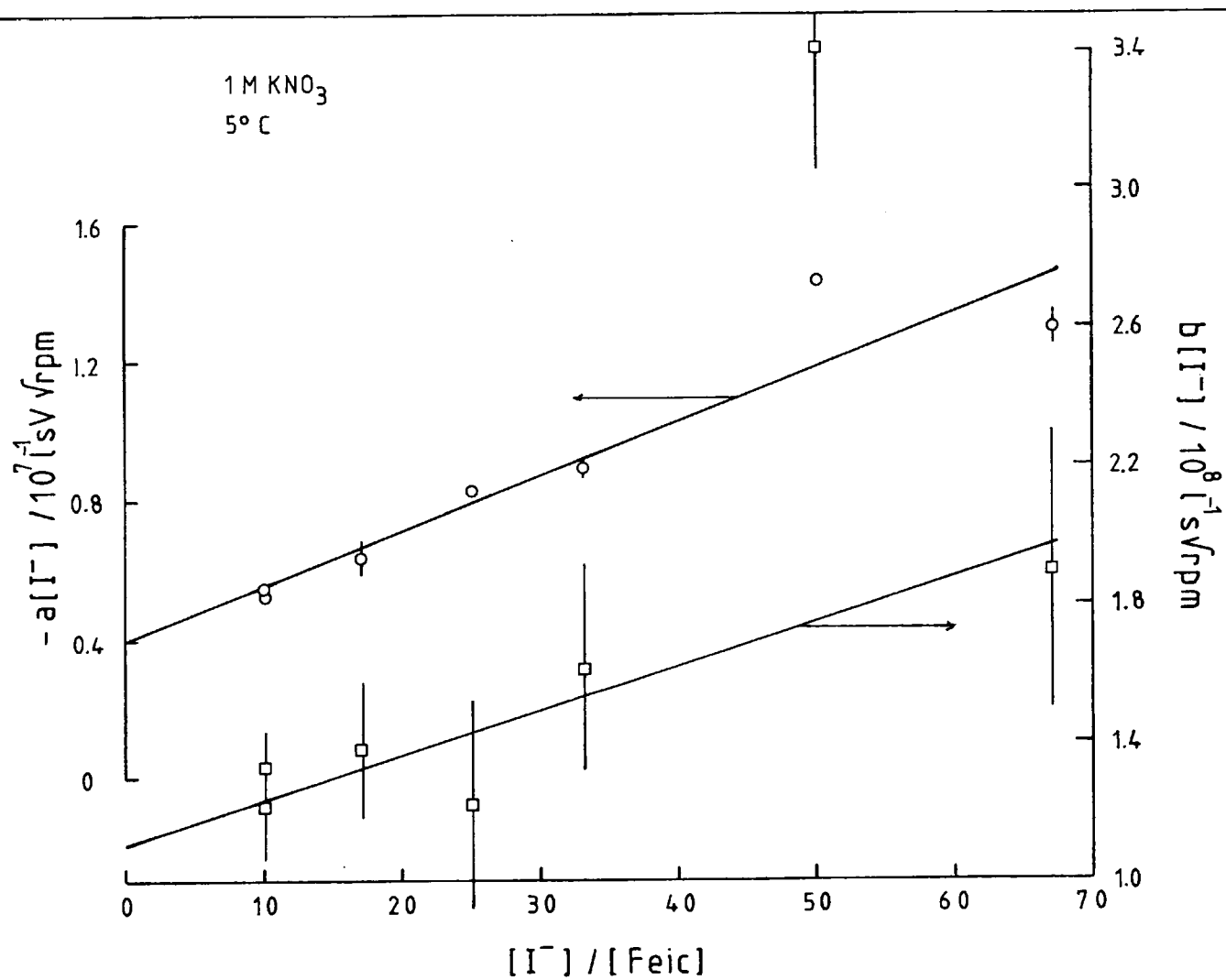
Further tests may be carried out with the slopes a and b in Table 10. According to eqs. (II-26) and (II-24), and since  $u'_{\text{cat}}$  is used in place of  $i_m$ :

$$a = (W_I^-/\sigma_I^- [I^-] - W_{\text{Feic}}/\sigma_{\text{Feic}} [\text{Feic}]) 2 r_2 F/\alpha_2 Z_2 f \qquad (\text{IX-5})$$

$$b = 2F(r_2 W_I^-/\sigma_I^- [I^-] + r_1 W_{\text{Feic}}/\sigma_{\text{Feic}} [\text{Feic}]) \qquad (\text{IX-6})$$

Therefore, plots of  $a[I^-]$  or  $b[I^-]$  vs.  $[I^-]/[\text{Feic}]$  should yield straight lines. They are shown in Figure 13. The scatter of the points is considerable, and no clear-cut relationship emerges. Least squares fitting to a straight line gives:

Figure IX-13



$$10^{-7} a [I^-] / \ell^{-1} \text{ s } V (\text{rpm})^{\frac{1}{2}} = -(0.4 \pm 0.1) - (0.016 \pm 0.003) [I^-] / [\text{Feic}] \quad (\text{IX-7})$$

$$10^{-8} b [I^-] / \ell^{-1} \text{ s } (\text{rpm})^{\frac{1}{2}} = (1 \pm 0.1) + (0.013 \pm 0.006) [I^-] / [\text{Feic}] \quad (\text{IX-8})$$

The standard deviations arising from the fitting alone are substantial. A full account of the errors should also include the error fittings of  $a$  and  $b$  (Table 12) which are about  $\pm 10\%$  of their absolute values (see Table 12). Thus, no definite numerical tests can be meaningfully carried out from eqs. (7) and (8). In spite of this, there seem to be some patent inconsistencies with eqs. (5) and (6), e.g., the fact that the slope in eqs. (7) and (8) is about two orders of magnitude smaller than the intercept, while eqs. (5) and (6) predict roughly similar values because all of the quantities involved are of about the same size. It is possible to test whether it is the slopes or the intercept that are likely to be correct. If one inserts into the appropriate equations the  $\alpha_j Z_j$  and  $W_j$  obtained (4a) and (4b), and the  $\sigma_j$  values calculated from the  $k_j$  measured in Chapter VI (which are related through the expression  $k_j = \sigma_j \omega^{\frac{1}{2}}$ , where  $\omega = 500 \text{ rpm}$ ; the resultant  $\sigma_j$  must then be multiplied by 1.29, i.e., the ratio of the geometric areas  $A(\text{glassy carbon})/A(\text{Pt})$ ), then  $a \approx 10^4 \ell^{-1} \text{ s} (\text{rpm})^{\frac{1}{2}} \text{ V}$  and  $b \approx 5 \times 10^5 \ell^{-1} \text{ s} (\text{rpm})^{\frac{1}{2}}$ . The slopes of eqs. (7) and (8) are 3-10 times larger than these values while the intercept furnished by eq. (7) is of a sign opposite to that expected from eq. (5).

In spite of the large uncertainties in the figures, one should not ignore these large numerical inconsistencies, in the sense that this probably indicates that a more complex system than that considered in Chapter II is at hand.

f) Dependence of the Catalytic Rate on the Concentration of the Products.

This is shown in Table 13. However, the data cannot be analysed with plots of  $1/u'_{\text{cat}}$  vs.  $1/\omega^2$  because eq. (II-24) is not valid in this situation:

TABLE IX.13    DEPENDENCE OF THE CATALYTIC RATE ON THE PRODUCT CONCENTRATIONS

$5 \times 10^{-2}$  M KI,  $3 \times 10^{-3}$  M Feic, 1 M KNO<sub>3</sub>, 5°C.

| $\omega/\text{rpm}$          | 100                                                              | 150  | 200  | 300  | 500  | 750  | 1000 |
|------------------------------|------------------------------------------------------------------|------|------|------|------|------|------|
| $10^3[\text{Feoc}]/\text{M}$ | $10^9 u'_{\text{cat}}/\text{mol s}^{-1} [\text{I}_2]_{t=0} = 0$  |      |      |      |      |      |      |
| 0.1                          | 1.54                                                             | 1.69 | 2.25 | 2.21 | 1.82 | 1.91 | 1.74 |
| 1.0                          | 1.92                                                             | 2.50 | 1.66 | 1.92 | 1.72 | 1.66 | 1.46 |
| $10^3[\text{I}_2]/\text{M}$  | $10^9 u'_{\text{cat}}/\text{mol s}^{-1} [\text{Feoc}]_{t=0} = 0$ |      |      |      |      |      |      |
| 0.05                         | 2.02                                                             | 2.29 | 2.39 | 3.11 | 3.19 | 3.17 | 3.72 |
| 0.10                         | 1.84                                                             | 2.01 | 2.16 | 2.46 | 2.92 | 3.32 | 3.21 |

the relatively significant product concentration would enhance the contribution of the back electrochemical reaction; also, the Tafel approximation is probably not valid for the couple whose product has been added to the reaction.

This last point is clearly illustrated in Figure 14, where the overpotential  $E_{\text{cat}} - E_j$  has been plotted as a function of time.  $E_j$  was calculated from the Nernst equation (I-9) for each couple, using the bulk concentrations of reactants and products. The latter were obtained from

the actual "total" values in eq. (V-14). No allowance was made for the homogeneously produced substances, as  $E_j$  respond to their "total" or net values, and not specifically to the heterogeneous component of the overall rate.

As shown in Figure 14, the overpotential for each couple is in the Tafel region ( $|\eta| > 50$  mV for  $I^-/I_3^-$  and  $> 100$  mV for the Feic/Feoc) during the first minutes of the reaction, and decrease steadily with time due to accumulation of the products in the bulk of the solution. However, if one of the products is present in significant amounts since the beginning of the reaction,  $\eta$  for the couple concerned is much reduced right from the beginning, while the other couple still shows Tafel behaviour and its  $\eta$  is not much affected, at least in these particular conditions. Therefore, the catalytic rate is deprived of much of its "driving force", i.e., the overpotential of one of the couples, and therefore is greatly reduced in the presence of the products. Because of the nature of the Butler-Volmer equation (I-16), that describes the individual couples, a decrease in  $|\eta|$  not only decreases the forward reaction, but correspondingly increases the back reaction. The inference follows that if the catalysis proceeds through the electrochemical path, then all products must have an inhibitory effect on the catalytic rate, provided that their concentration is large enough to decrease the overpotential of its couple. Quantitative analysis of these effects is complicated by the fact that the Tafel approximation cannot be used in one of the eqs. (II-56).

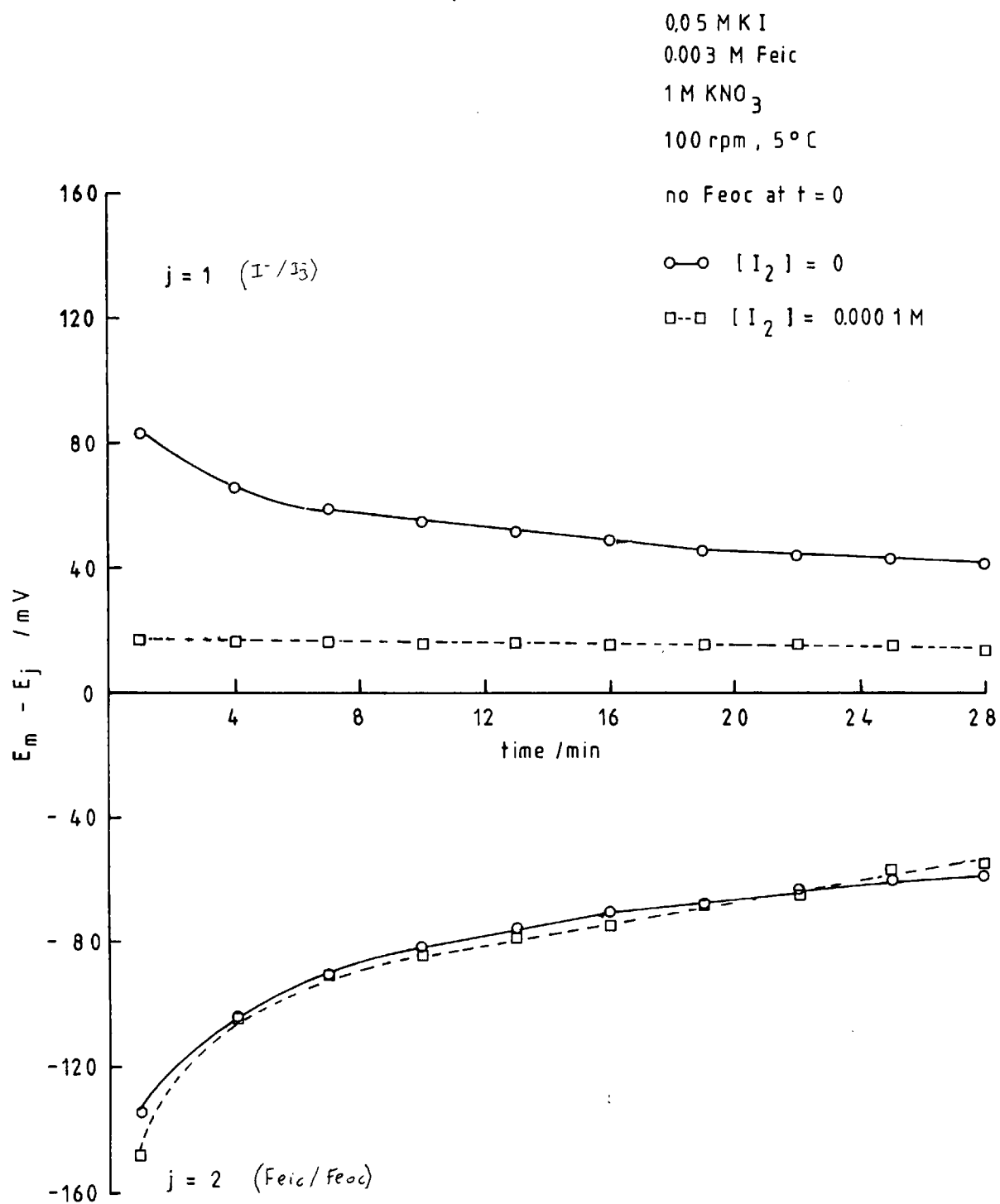


Figure IX - 14

g) Dependence of the Catalytic Rate on Temperature.

The data are shown in Table 14, and at infinite  $\omega$  in Table 15.

TABLE IX.14    DEPENDENCE OF THE CATALYTIC RATE ON TEMPERATURE.

$5 \times 10^{-2}$  M KI,  $3 \times 10^{-3}$  M Feic, 1 M KNO<sub>3</sub>, 5°C.

| $\omega/\text{rpm}$  | 100                                      | 150  | 200  | 300  | 500  | 750  | 1000 |
|----------------------|------------------------------------------|------|------|------|------|------|------|
| $T/^{\circ}\text{C}$ | $10^9 u'_{\text{cat}}/\text{mol s}^{-1}$ |      |      |      |      |      |      |
| 5                    | 2.2                                      | 2.5  | 2.8  | 3.1  | 3.2  | 3.6  | 3.8  |
| 15                   | 1.48                                     | 1.59 | 1.81 | 2.14 | 2.67 | 2.88 | 2.75 |
|                      | 1.72                                     | 2.23 | 2.21 | 2.46 | 2.81 | 2.94 | 3.05 |
| 25                   | 1.54                                     | 1.40 | 1.63 | 1.93 | 2.10 | 2.33 | 2.31 |

TABLE IX.15    EFFECT OF TEMPERATURE ON THE CATALYTIC RATE AT  $\omega = \infty$

$5 \times 10^{-2}$  M KI,  $3 \times 10^{-3}$  M Feic, 1 M KNO<sub>3</sub>, 5°C

| $T/^{\circ}\text{C}$ | $10^9 u'_{\text{cat}}/\text{mol s}^{-1}$ | $10^{-9} b/\text{mol}^{-1} \text{s}(\text{rpm})^{\frac{1}{2}}$ |
|----------------------|------------------------------------------|----------------------------------------------------------------|
| 5                    | $5.6 \pm 0.9$                            | $2.8 \pm 0.4$                                                  |
| 15                   | $5 \pm 1$                                | $4.3 \pm 0.7$                                                  |
| 25                   | $3.4 \pm 0.5$                            | $4.1 \pm 0.6$                                                  |

The Arrhenius plot of the data in Table 15 gives an apparent activation energy of  $-4 \pm 0.1 \text{ Kcal mol}^{-1}$ . The actual value of the apparent activation energy is subject to large uncertainties as the poor reproducibility at 15°C shows, but the decrease of  $u'_{\text{cat}}$  with increasing temperature seems genuine. This result does not contradict

the electrochemical model. If one uses eq. (II-17) to define  $E_a^{\text{app}}$

$$E_a^{\text{app}} = -R \frac{\partial \ln i_m}{\partial (1/T)} = r_2 E_{001}^{\text{app}} + r_1 E_{002}^{\text{app}} + \alpha_2 Z_2 r_1 \Delta H^0 \quad (\text{IX-9})$$

where the  $E_{00j}^{\text{app}}$  s are the activation energies of the standard exchange current densities:

$$E_{00j}^{\text{app}} = -R \partial \ln i_{00j} / \partial (1/T) \quad (\text{IX-10})$$

As shown in Chapter VI, the standard enthalpy change of the reaction  $\Delta H^0$  is  $-7.72 \text{ Kcal mol}^{-1}$ . It seems likely that the exchange current densities would increase with increasing temperature so that the  $E_{00j}$  values would be positive. The overall balance in eqs. (9) could therefore be of either sign. In the case of complete mass transport control (Chapter VI), the net balance was shown to be negative in good agreement with experiment.

#### IX.4. Conclusions.

The results described in this chapter are concerned only with the kinetics of the catalysis of reaction (I-1) on glassy carbon. Some effort was devoted towards finding a suitable pretreatment of the electrode that would furnish a stable long term performance of the catalyst. Polishing with teecepol was effective in this respect, but the reproducibility was still not wholly satisfactory.

It was found that different electrochemical treatment following polishing markedly affected the catalytic rate, which was twice as fast on "reduced" glassy carbon than on an "oxidised" surface at  $\omega = \infty$ .

The dependence of the catalytic rate and the catalyst potential on concentration may be represented by equations of the form of eqs. (II-56) in the Tafel region. The values of the different parameters required to

achieve such representation are quite plausible from an electrochemical point of view, but they do not agree with any of the mechanisms which have been proposed for the two couples in the literature. It is quite possible, however, that the electrochemical parameters of each couple are affected by the presence of the other couple, i.e., that undisturbed overlap of the  $i$ - $E$  curves might not hold for this system. The results with the "reduced" and "oxidised" catalyst strongly suggests participation of chemical surface groups in the reaction.

The rate decreases upon raising the temperature. This is consistent with the electrochemical mechanism according to eq. (II-17) since it has been shown (Chapter VI) that the difference in the standard equilibrium potentials becomes less favourable for the reaction.

A better understanding of the mechanism of this catalysis will require a detailed study of the kinetics of the electron transfer of the couples  $\text{Feic}/\text{Feoc}$  and  $\text{I}^-/\text{I}_3^-$  on glassy carbon electrodes.

## CHAPTER TEN

### SOLVOLYSIS REACTIONS

#### X.1. Acid-Base Catalysis.

a) Catalysis in solution by acids or bases involves proton transfer to or from a reactant or an intermediate in the reaction. The proton donor or acceptor "is said to be a catalyst in a homogeneous system when its concentration occurs in the velocity expression to a higher power than it does in the stoichiometric equation" (Bell).<sup>128</sup> The step in question need not be rate-determining but the fact that it occurs at all allows the appearance of a new low activation reaction path.<sup>129</sup> If the reaction is catalysed by  $H^+$  or  $OH^-$  only, the reaction is said to be subject to specific acid-base catalysis. If any other weak acid or base, able to undergo acid-base intercourse with the reactant, speeds up the rate too, then general acid-base catalysis is said to be operative.

If proton transfer with the substrate,  $S$ , is the slow step in the reaction, the rate  $v$  is given by<sup>130</sup>:

$$v = k[S] \quad (X-1)$$

The rate constant  $k$  is<sup>130</sup>:

$$k = k_0 + k_H[H^+] + k_{OH^-}[OH^-] + \sum_j (k_{HX_j}[HX_j] + k_{X_j}[X_j]) \quad (X-2)$$

where  $HX_j$  and  $X_j$  are weak acids and bases, respectively. If only specific catalysis is operative, then  $k_{HX_j} = k_{X_j} = 0$ . At very low pH values  $[OH^-]$  may be neglected, and most of  $X_j$  will be protonated, so that  $[X_j] = 0$ . At very high pH,  $[H^+]$  may be neglected, and  $[HX_j] = 0$ . Thus,  $k$  becomes:

$$k = k_o + k_H^+ [H^+] + \sum_j k_{HX_j} [HX_j]_o \quad (X-3)$$

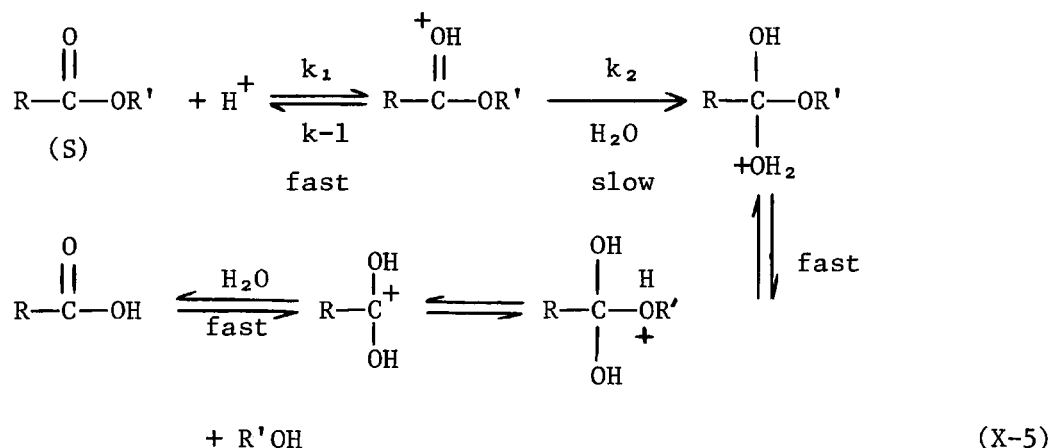
in very acid pH while for very alkaline pH:

$$k = k_o + k_{OH^-} [OH^-] + \sum_j k_{X_j} [X_j]_o \quad (X-4)$$

where the subindexed brackets refer to the stoichiometric concentrations. Then it is possible to obtain  $k_H^+$  or  $k_{OH^-}$  from plots of  $k$  vs.  $[H^+]$  or  $[OH^-]$ , respectively. The intercept furnishes the rate constant,  $k_o$ , of the uncatalysed reaction plus the general acid-base component; the latter may be calculated if  $k_o$  is known, e.g., from runs in the absence of the  $HX_j$  s and  $X_j$  s. However, in order to prove that general acid-base catalysis takes place it is necessary to show that the rate depends on the stoichiometric concentration of the suspected catalyst, and not just on the equilibrium  $H^+$  concentration.<sup>129</sup>

#### b) The Hydrolysis of Esters.

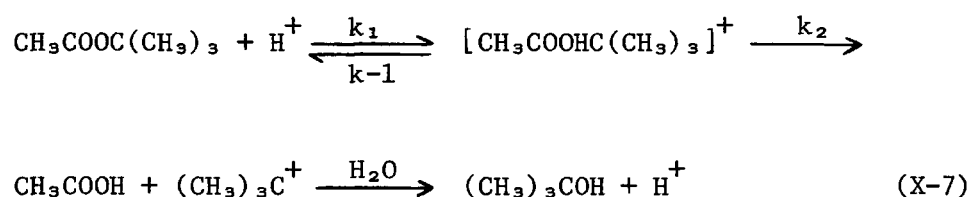
The hydrolysis of esters is an acid-base catalysed process. Current textbooks<sup>131</sup> list several proven mechanistic pathways. The acid catalysis of simple esters is reckoned to follow the sequence:



The rate  $v$  is given by:

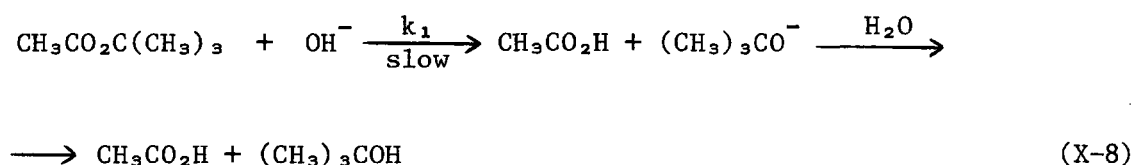
$$v = (k_2 k_1 / k_{-1}) [H^+] [S] \quad (X-6)$$

However, in the case of *t*-butyl acetate, the stability of the *t*-butyl cation allows another reaction path, which occurs simultaneously with (5)<sup>132</sup>:



This also leads to a rate law as in eq. (6). Path (7) contributes > 80% in the 25–85°C temperature range.<sup>132</sup> The key step in the reaction is the protonation of the acyl oxygen, which allows subsequent nucleophilic attack by a water molecule. Acid catalysis should also be effective if the proton is provided by a weak acid HX.

The  $\text{OH}^-$  ion is a nucleophile more powerful than  $\text{H}_2\text{O}$  and it can attack the acyl carbon without previous "sensitisation" of the substrate<sup>133</sup>:



The rate is given by:

$$v = k_2 [\text{OH}^-] [S] \quad (X-9)$$

Other nucleophiles could act as catalysts too, but then the carboxylic acid would not necessarily be produced. The carboxylic acid itself may act as a catalyst if the reaction is subject to general acid catalysis.

In solutions around neutral pH, and in the absence of catalysts other than  $H^+$  or  $OH^-$  130:

$$k = k_o + k_H^+ [H^+] + k_{OH^-} K_W/[H^+] \quad (X-10)$$

The value of  $k$  passes through a minimum at a certain  $[H^+]_{min}$ , given by

$$dk/d[H^+] = 0 = k_H^+ - k_{OH^-} K_W/[H^+]_{min}^2 \quad (X-11)$$

$$[H^+]_{min} = (k_{OH^-} K_W/k_H^+)^{\frac{1}{2}} \quad (X-12)$$

Introducing this expression into eq. (10):

$$k_{min} = k_o + 2(k_H^+ k_{OH^-} K_W)^{\frac{1}{2}} \quad (X-13)$$

Taking  $-\log_{10}$  on both sides of eq. (12)

$$pH_{min} = pH_N - \frac{1}{2} \log_{10}(k_{OH^-}/k_H^+) \quad (X-14)$$

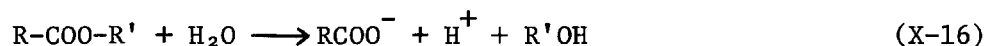
If a weak acid HY of total concentration  $A_o$  also catalyses the reaction:

$$k = k_o + k_H^+[H^+] + k_{OH^-} K_W/[H^+] + k_{HY} A_o [H^+]/(K_{HY} + [H^+]) \quad (X-15)$$

If the dissociation constant  $K_{HY}$  is small compared with the prevailing acidity, the general catalytic component will appear as part of the uncatalysed reaction ( $k_o + k_{HY} A_o$ ). If it is large, it will appear as part of the acid component ( $k_H^+ + k_{HY} A_o/K_{HY}$ ); however, in this case the concentration of undissociated HY will be small and therefore its catalytic effects small too.

c) Measurement of Rates.

The overall reaction of ester hydrolysis is:



In near neutral solutions it may be followed by continuously titrating the  $\text{H}^+$  produced with a strong base, in the so-called "pH-stat method".<sup>134</sup> However, a correction must be made to the experimental data to allow for the partial dissociation of the weak carboxylic acid. Let  $y$  stand for the total acid produced (dissociated plus undissociated) at any time,  $t$ , and let  $x$  represent the carboxylate concentration. Therefore:

$$y = [\text{RCOOH}] + x \quad (\text{X-17})$$

and also

$$[\text{RCOOH}] = [\text{H}^+]x/K_D \quad (\text{X-18})$$

where  $K_D$  is the dissociation constant of  $\text{RCOOH}$ . Thus,

$$y = fx \quad (\text{X-19})$$

where

$$f = 1 + [\text{H}^+]/K_D \quad (\text{X-20})$$

From eqs. (6) and (9) it follows that the rate is first order in  $[\text{S}]$ , since the concentration of catalyst remains constant. One can therefore write

$$\ln(a - y) = \ln a - kt \quad (\text{X-21})$$

where  $a$  is the initial amount of ester and  $y$  is given by eq. (17). In order to relate the course of the reaction to the observed  $\text{H}^+$  produced,  $x$ , eq. (18) must be introduced to give:

$$\ln(a/f - x) = \ln(a/f) - kt$$

(X-22)

## X.2. Displacement Reactions.

Displacement reactions are of the general form:



R is usually an alkyl group, X a halide, and Y the attacking nucleophile, i.e., a Lewis base, which may be either a polar molecule like water or ethanol, or an anion like  $\text{OH}^-$ .

In  $\text{S}_{\text{N}}1$  reactions (unimolecular nucleophilic substitution) the alkyl halide dissociates relatively slowly into a carbonium ion and a halide ion, followed by a swift attack by the nucleophile<sup>135</sup>:

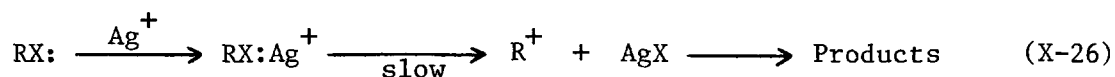


The rate is expressed by:

$$v = k[\text{RX}] \quad (X-25)$$

It is independent of the nucleophile concentration. Thus, if the nucleophile is  $\text{OH}^-$ , the rate is independent of pH. If several nucleophiles are present (say, water, ethanol and  $\text{OH}^-$  ion) they compete for the carbonium ion, and there will be a mixture of products. In addition, elimination of hydrogen may occur, producing alkenes.

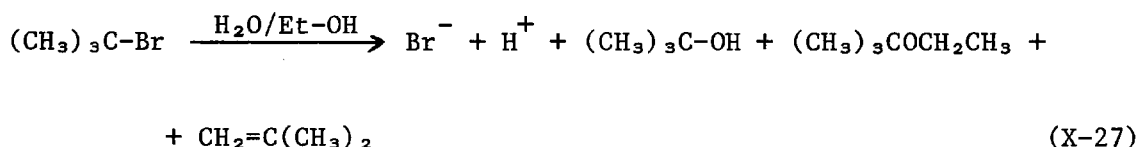
Catalysis of  $\text{S}_{\text{N}}1$  reactions by heavy metal ions of silver, mercury and copper is well known; it is due to complexing with the unshared electrons of the halide<sup>135</sup>:



Such solvolyses are also heterogeneously catalysed by solid silver halides and by silver metal.<sup>139</sup> The solvent for its part plays two important roles: separation of the two ions, for which solvents with a high

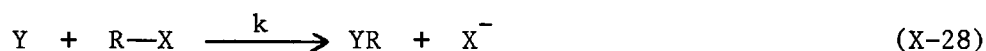
dielectric constant are more suitable, and stabilisation of the ions by solvation, which is easier in polar solvents than in less polar ones.

The solvolysis of t-butyl bromide (t-BuBr) is an  $S_N1$  reaction,<sup>136,137</sup> which in ethanol and water mixtures proceeds according to:



In such solvent mixtures the first order rate constant increases some 1000 times when the water content, i.e., one of the nucleophiles, is increased from 10% to 60% v/v, in apparent violation of its  $S_N1$  mechanism. Actually, the water effects have to do with charge separation and ion solvation, rather than with a change in the reaction path.<sup>138</sup>

In  $S_N2$  reactions (bimolecular nucleophilic substitution) dissociation of the alkyl halide does not occur: nucleophilic attack and loss of the halide happen simultaneously:



The rate in this case is directly proportional to the nucleophile concentration:

$$v = k[\text{Y}][\text{RX}]
 \tag{X-29}$$

## CHAPTER ELEVEN

### AN INVESTIGATION OF NON-FARADAIC ELECTROCATALYSIS.

#### XI.1. Introduction.

Despić et al.<sup>140</sup> have claimed that the hydrolysis of t-butyl acetate (t-BuOAc) is accelerated by gold and silver electrodes when their potential was pulsed by a square wave from the potential of zero charge ( $E_{pzc}$ ) in the anodic direction. As the ester does not undergo charge transfer reactions in that potential region, and the electrodes at open circuit did not significantly enhance the rate, it was proposed that the electric field polarised suitable bonds on the adsorbed ester in a way that facilitated hydrolysis. This mechanism was termed "non-faradaic electrocatalysis". Under their most favourable experimental conditions on gold (0.5 M Na<sub>2</sub>SO<sub>4</sub>; 40°C; electrode area/solution volume ratio of 0.08 cm<sup>-1</sup>; 10<sup>-1</sup> M < [t-BuOAc] < 10<sup>-4</sup> M; pulses at 0.5 Hz between 0.25 V ( $E_{pzc}$ ) and 0.75 V vs. SHE; starting at pH 6) they obtained a 27-fold increase in the first order rate constant w.r.t. the homogeneous uncatalysed reaction.

The results of a study of non-faradaic electrocatalysis are reported here. The reactions concerned are the hydrolysis of t-BuOAc in 0.5 M Na<sub>2</sub>SO<sub>4</sub> on gold and silver pulsed electrodes, and the solvolysis of t-butyl bromide (t-BuBr) in 80% v/v Et-OH/H<sub>2</sub>O on silver electrodes. As metallic silver at open circuit catalyses the reaction,<sup>139</sup> it seemed pertinent to study the effect of pulsation in the hope that it would enhance the catalytic rate.

## XI.2. Experimental.

### a) Chemicals.

The t-BuOAc (Aldrich) and t-BuBr (BDH) were purified by fractional distillation. The middle fraction was collected and stored in the dark. Prior to distillation, the t-BuBr was shaken with anhydrous  $\text{Na}_2\text{CO}_3$  and filtered through No. 1 Whatman filter paper. Potassium hydrogen phthalate (KHP, AnalaR),  $\text{NaNO}_3$  (AnalaR),  $\text{Na}_2\text{SO}_4$ , and stock 0.5 M NaOH solution (carbonate free) AVS, were from BDH. J. Burrough AR ethanol containing 0.3% water was used without further purification. All water was doubly distilled.

The ca. 0.02 N NaOH solution was prepared by diluting the stock NaOH solution with de-aerated water inside a nitrogen-filled dry box. It was titrated potentiometrically with 20 ml of ca. 0.001 N KHP solution, which had been prepared by dissolving an accurately weighed amount of ca. 0.1 g of the oven-dried salt (overnight at  $100^\circ\text{C}$ ) in 500 ml of water. Titration was accomplished with the pH-stat equipment described below, by automatic recording of the first derivative of the titration curve.

The 80% v/v ethanol/water mixture was prepared by weighing 300 g of ethanol, and adding 94.0 g of water.

### b) Equipment.

A thermostat like the one described in Chapter V was used, except that no cooling unit was necessary.

The solvolysis of t-BuOAc and t-BuBr produces one hydrogen ion per reacted molecule of substrate (Chapter IX). Thus, the reactions were followed

by titrating the  $H^+$  produced at constant pH with NaOH solution. The pH-stat equipment in Figure 1 (Radiometer, Copenhagen), consisted of a pH meter (PHM62), an automatic burette (ABU 12) provided with a plastic reservoir bottle containing ca. 0.02 N NaOH, an automatic titrator (TTT 60), and a recorder (REC 61) fitted with a derivative unit (REA 260). It operates by delivering alkali if the pH drops below a preset value. The volume of solution delivered is displayed in the digital counter of the burette, and in the recorder chart as a function of time; it can be operated automatically or manually. The pulsing equipment consisted of a Farnell LMF 2 oscillator, which supplied the square wave and operated at 1 Hz, connected to the external input of a TR 70/2A Chemical Electronics potentiostat (0.3  $\mu$ s, rise time). The reaction vessel and electrochemical cell (Figure 2) was a 50 ml straight walled, concave bottomed, pyrex glass Quickfit vessel, containing a Teflon-covered magnetic bar, the latter actuated by a submersible magnetic stirrer (Rank Brothers, Bottisham). Its tightly fitting vitrathene lid was secured by six clamps to the horizontal lip around the edge, and had enough holes to hold the delivery tip for the alkali, the glass and saturated calomel electrodes, the gold or silver working electrodes, and a short glass tube sealed with a Beckman frit at the lower end and containing the coiled platinum wire counter electrode. This tube was filled with supporting electrolyte. Another lid with fewer holes was used for the homogeneous runs. The electrodes and other tubing were tightly wrapped with PTFE tape at the point of contact with the lid to avoid leaks of volatile material during the runs.

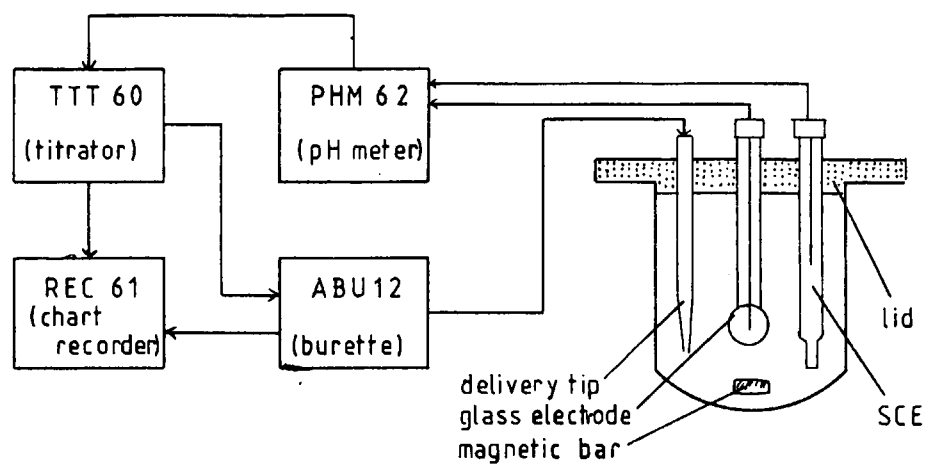


Figure XI-1

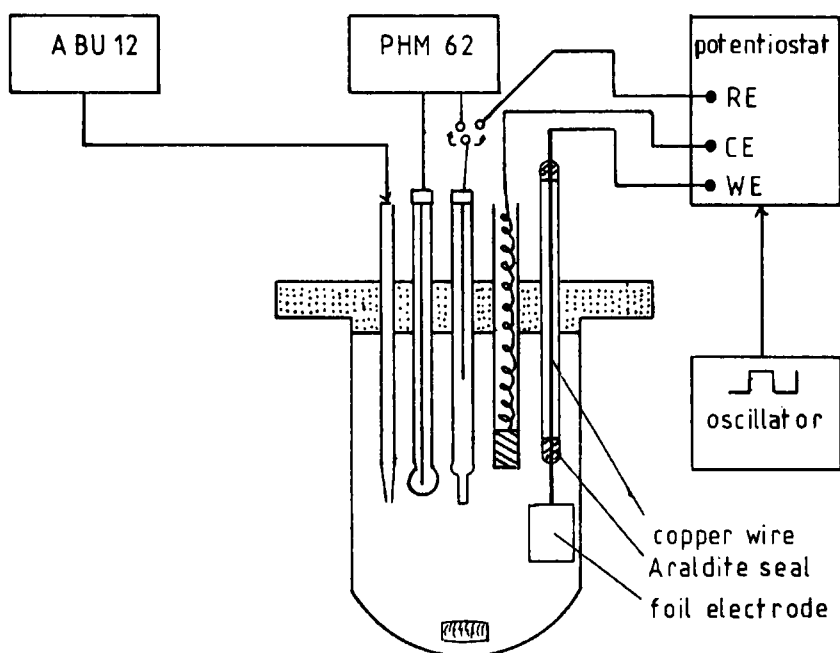


Figure XI-2

It was found that automatic operation of the pH-stat with simultaneous pulsing of the gold or silver WE was not feasible, as the pH meter readings fluctuated by  $\pm 0.2$  pH units at roughly the same frequency as the pulses. Manual operation was therefore adopted, with the pH meter left in standby for, typically, 10-20 min during which the pulses were applied. However, in order to keep the pH at a constant value and to monitor the extent of the reaction, the solution was regularly titrated during that time (every 5 min for t-BuOAc, 3 min for t-BuBr) by briefly returning the WE to open circuit, reading the pH and delivering enough alkali to restore the pH to its initial value (the titration took 15-20 s; the total volume delivered up to that time had to be written down). Pulsing was then resumed. To highlight the effect of the electric field at the WE (either pulsing or constant applied potential), potential-controlled periods were alternated with open circuit periods. During the latter the solution was also regularly titrated. The saturated calomel electrode was switched, from the pH meter to the potentiostat and vice versa, according to the operation being performed, which took an additional 40 s.

c) The Gold and Silver Electrodes.

The gold (1 cm x 1 cm) and silver foil (3 cm x 5 cm) electrodes (Figure 2) were attached to a gold or silver wire, respectively. These wires were soldered to a copper wire which was enclosed in a glass tube and sealed in with Araldite. That part of the seal nearer the foil was tightly wrapped with PTFE tape to avoid softening upon prolonged contact with water.

Both electrodes were treated once by Despic's procedure : they were first degreased in hot concentrated NaOH (a beaker half-full of NaOH pellets with just enough water to cover them, and dissolved by vigorous

stirring), rinsed, briefly immersed in concentrated nitric acid, and rinsed again. No apparent changes were detected in the gold electrode. The silver electrode, initially grey, acquired a uniform white metallic lustre, although it became appreciably thinner and brittle. Its lower edge was badly corroded and had to be cut away with scissors, to give the final dimensions quoted above. This treatment can thus be used only once in the lifetime of the electrode. However, degreasing in NaOH was occasionally carried out for both electrodes.

Before every run, the gold electrode was electrochemically pre-treated in 0.5 M  $\text{Na}_2\text{SO}_4$  by holding it for 30 s at each potential of the sequence 0.5, 0.0, 0.5, 0.0, 0.5 V (SCE). If a final reducing treatment was desired, it was polarised in 1 M  $\text{H}_2\text{SO}_4$  for 30 s at 1.5 V, followed by 30 s at -0.25 V (SCE). The electrode was then thoroughly washed and used within a few minutes. The silver electrode was preconditioned by holding it at -0.7 V (SCE) for 2 minutes in 1 M  $\text{KNO}_3$ . However, in some runs this was omitted.

#### d) Experimental Procedure.

For the runs with t-BuOAc, either homogeneous or in the presence of the gold electrode, 100  $\mu\text{l}$  of the ester were injected quickly beneath the surface of 100 ml of de-aerated 0.5 M  $\text{Na}_2\text{SO}_4$ , and shaken for ca. 15 s at room temperature. This gave a concentration of 0.0075 M, calculated from the density of the ester at 25°C,<sup>127</sup> and the volumes employed. Then 50 ml were transferred to the reaction vessel, already in position inside the thermostat, through the SCE hole; this was promptly plugged with the electrode, and stirring started. Previous work by Dr. M.C.P. Lima<sup>141</sup> had shown that if the ester was simply injected into the reaction vessel already containing the supporting electrolyte, it just collected at the surface, even under stirring, and volatilised

in the 4 ml dead space between the solution and the lid. Low rate constants were then obtained. However, solutions prepared by shaking between 5 s and 2 min led to a higher and reproducible value of the rate constant.<sup>141</sup> Lima also showed that passing nitrogen over the surface of the reaction mixture during the run progressively depleted the ester, and the rate dropped to zero because of evaporation of the ester. It was therefore preferable to allow some air to be present during the runs. However, the pulsing range used [0.15 to 1.05 V (SCE)] is too anodic to cause electrochemical reactions of oxygen.

A different arrangement was used for runs in the presence of the silver electrode, because at the very cathodic potentials employed here [-1.0 to -0.5 V (SCE)] oxygen is reduced. This is an undesirable factor in studies of non-faradaic phenomena. Therefore, nitrogen was passed through the supporting electrolyte in the reaction vessel for one hour, with stirring. The nitrogen stream was then switched through a bubbler flask immersed in the bath and containing pure t-BuOAc; nitrogen flow and continuous supply of ester was thus provided. The ester concentration in the reaction mixture soon reached an approximately steady state value as it was removed by evaporation with the nitrogen outflow and by hydrolysis. Because the resulting ester concentration was relatively high, the experiments with silver electrodes were carried out at the lower temperature of 35°C.

The initial unadjusted pH of the reaction mixture was ca. 5.4. If the run was to be carried out at a more basic value a few  $\mu\text{l}$  of 0.5 M NaOH were added with a microsyringe. If a more acid pH was needed, a few microlitres of diluted (usually 1 M)  $\text{H}_2\text{SO}_4$  were added until the pH dropped to the intended value.

The experiments with *t*-BuBr were carried out at 25°C in 80% v/v ethanol/water mixtures containing 0.3 M NaNO<sub>3</sub>, chosen as supporting electrolyte because of several possible inorganic salts quoted in the literature it was the most soluble in this solvent mixture. Fifty ml were placed in the reaction vessel, thermostated and nitrogen passed for at least 1 hour under stirring. During this time the pH slowly rose and stabilised at ca. 8.5. Nitrogen was then allowed to pass over the surface for the rest of the run. The reaction was started by injecting beneath the surface 50 μℓ of a mixture of 20 μℓ of *t*-BuBr in 1 ml pure EtOH, to give a substrate concentration of  $1.8 \times 10^{-4}$  M.

e) Treatment of Experimental Data.

The laboratory data are the volumes of alkali delivered, *x* (in μℓ), up to given times, *t*. Thus it is convenient to express the initial amount of ester, *a*, in eq. (X-22) as μℓ of NaOH solution, according to the formula:

$$a/\mu\ell = 10^6 v\rho/M[\text{NaOH}] \quad (\text{XI.1})$$

where *v* is the volume of ester (ml) in the 50 ml reaction mixture, *ρ* its density (g cm<sup>-3</sup>) and *M* its molecular weight (g mol<sup>-1</sup>); the [NaOH] is that of the titrant delivered by the ABU12 (mol ℓ<sup>-1</sup>).

The hydrolysis rates of *t*-BuOAc were corrected according to section X.1.c., and equation (X-19). This correction required values of the dissociation constant of acetic acid (*K<sub>D</sub>*) in 0.5 M Na<sub>2</sub>SO<sub>4</sub>. It is known that the temperature dependence of *K<sub>D</sub>*, both in zero ionic strength (*μ*) and in concentrated solutions, is given by<sup>142</sup>

$$\log K_D - \log K_\theta = -p(t - \theta)^2 \quad (\text{XI.2})$$

where  $t$  is the temperature in degrees centigrade and  $K_\theta$  and  $\theta$  are constants independent of  $t$  but dependent on  $\mu$ ;  $p$  equals  $5 \times 10^{-5}$  irrespective of  $\mu$  or  $t$ . The values of  $K_\theta$  and  $\theta$  in water ( $\mu = 0$ ) were calculated from the data of  $K_D$  at several temperatures by Harned and Owen and are listed in Table 1.

TABLE XI.1  $K_D$  IN WATER.<sup>142</sup>

|                                  |       |       |       |       |
|----------------------------------|-------|-------|-------|-------|
| $t/^{\circ}\text{C}$             | 45    | 50    | 55    | 60    |
| $10^5 K_D/\text{mol } \ell^{-1}$ | 1.670 | 1.633 | 1.589 | 1.542 |

By plotting  $\log (10^5 K_D) + pt^2$  vs.  $t$ , the values found were  $\theta = 29.34^{\circ}\text{C}$ ,  $10^5 K_D = 1.715$  ( $r = 0.9996$ ).  $K_D$  at higher temperatures obtained by extrapolation were:

TABLE XI.2  $K_D$  IN WATER.

|                                  |       |       |       |
|----------------------------------|-------|-------|-------|
| $t/^{\circ}\text{C}$             | 65    | 70    | 75    |
| $10^5 K_D/\text{mol } \ell^{-1}$ | 1.483 | 1.419 | 1.350 |

Data for  $K_D$  in  $\text{Na}_2\text{SO}_4$  were not available. Therefore  $K_\theta$  and  $\theta$  in 0.5 M  $\text{Na}_2\text{SO}_4$  ( $\mu \approx 1.5$ ) were assumed to be equal to the values in 1.5 M  $\text{NaCl}$  solutions. Data are available<sup>142</sup> for 1 and 2 M  $\text{NaCl}$  solutions, and values for 1.5 M  $\text{NaCl}$  were obtained by linear interpolation (Table 3).

TABLE XI.3 DATA IN 1 M  $\text{KCl}$ .

|       |                     |                   |
|-------|---------------------|-------------------|
| $\mu$ | $-\log K_\theta$    | $\theta$          |
| 1.01  | 4.4957              | 35.7              |
| 1.5   | 4.5324 <sup>a</sup> | 39.4 <sup>a</sup> |
| 2.01  | 4.5875              | 45.0              |

<sup>a</sup> Interpolated value.

The values of  $K_D$  calculated from eq. (2) are then given in Table 4.

TABLE IX.4. ESTIMATED VALUE OF  $K_D$  in NaCl ( $\mu = 1.5$ )

| $t/^{\circ}\text{C}$               | 35   | 40   | 60   | 70   |
|------------------------------------|------|------|------|------|
| $10^5 K_D / \text{mol } \ell^{-1}$ | 2.94 | 2.93 | 2.80 | 2.64 |

A list of  $f$  values calculated from eq. (X-20) is shown in Table 5, for conditions appropriate to the work carried out here and by Lima.<sup>141</sup>

TABLE XI.5. CORRECTION FACTORS  $f$ , UNDER VARIOUS EXPERIMENTAL CONDITIONS

| Medium                         | $t/^{\circ}\text{C}$ | pH          | $f$  |
|--------------------------------|----------------------|-------------|------|
| WATER                          | 60                   | 6.40        | 1.03 |
|                                | 65                   | 6.40        | 1.03 |
|                                | 70                   | 5.50        | 1.22 |
|                                | 70                   | 6.40        | 1.03 |
|                                | 70                   | 7.00        | 1.00 |
|                                | 70                   | 7.50        | 1.00 |
|                                | 70                   | 8.30        | 1.00 |
|                                | 75                   | 6.40        | 1.03 |
| 0.5 M $\text{Na}_2\text{SO}_4$ | 40                   | 5.44        | 1.12 |
|                                | 60                   | 4.07        | 4.04 |
|                                | 60                   | 4.12        | 3.71 |
|                                | 60                   | 4.45        | 2.27 |
|                                | 60                   | 4.81        | 1.55 |
|                                | 60                   | 5.25        | 1.20 |
|                                | 60                   | 5.44        | 1.13 |
|                                | 60                   | 6.40        | 1.01 |
|                                | 60                   | 7.62        | 1.00 |
|                                | 60                   | $\geq 8.00$ | 1.00 |

The  $[H^+]$  values in eq. (X-20) were estimated from  $[H^+] \approx 10^{-pH}$ , which will differ somewhat from the true concentration because of lack of knowledge about the activity coefficient of  $H^+$  and because the pH measurements include the liquid junction potential between the saturated KCl solution of the SCE and the reaction mixture.<sup>143</sup> However, it can be seen from Table 5 that above pH 6.40 the correction factor,  $f$ , may almost be ignored in the calculations and that it exceeds 1.20 only below pH 5.5.

f) Extracts from Despic' et al.'s<sup>140</sup> Experimental Procedure.

" t-BuOAc was hydrolysed in 0.5 M  $Na_2SO_4$  starting at pH 6, at constant temperature in an inert atmosphere "

" Hydrolysis was carried out in a closed glass vessel, thermostated by an ultrathermostat to  $0.01^\circ C$ . The lid [of the vessel] had provisions for inlet and outlet of inert gas and for taking out samples for titration. It also served as a support for the three electrodes: the gold plate electrode, a saturated sulphate reference electrode connected to the former via a Luggin capillary and a counter electrode. The latter was a gold wire enclosed in a glass tube with a glass frit at the end through which it was filled with electrolyte upon immersion and which served as electrolytic junction with the bulk of the solution. Titrations of the acid formed were made with the standardised NaOH solution (0.00063 M) in the usual way with potentiometric end-point determination. "

"In a typical experiment 100 ml of the aqueous  $Na_2SO_4$  solution were placed into the cell, thermostated to a desired temperature [30, 35 or  $40^\circ C$ ] and freed of dissolved oxygen by bubbling inert gas [nitrogen]. Ester was then added to form a solution of the initial concentration in

the range of  $10^{-4}$  -  $10^{-1}$  M. Samples of 2 ml were taken out at time intervals of 20 min and the acid titrated. After some 200 minutes the solution was heated to  $70^{\circ}\text{C}$  for half an hour and the acid titrated again as to establish the final value after hydrolysis is completed."

### XI.3. Results and Discussion.

#### a) Homogeneous Runs with t-BuOAc.

The first order rate constant  $k$  was calculated from plots of  $\ln[a/f-x]$  vs.  $t$ , according to eq. (X-22). Good linear plots were obtained (Figure 3) although they curve at long times probably because of slow evaporation of the ester. The rate constants obtained under several experimental conditions (but in the absence of gold or silver electrodes) are listed in Table 6.

The reproducibility in the automatic mode was better ( $\pm 0.2\%$ ) than in the manual one ( $\pm 1-2\%$ ); the latter also gave  $k$  values some 3-6% lower. As expected from the acid/base catalysis of this reaction,  $k$  passes through a minimum at about pH 6. The  $\log k$  values are plotted vs. pH in Figure 4. The rate constants obtained from first order plots not corrected for the partial dissociation of acetic acid are also shown. These give the wrong impression that the reaction is inhibited at acid pH values. The value of  $k$  at pH 6.40 in 0.5 M  $\text{Na}_2\text{SO}_4$  (auto mode) of  $0.291 \times 10^{-3} \text{ min}^{-1}$  is markedly higher than that in water in the same conditions,  $0.240 \times 10^{-3}$ , obtained by Lima.<sup>141</sup> This larger value could be due to a combination of factors such as catalysis by the  $\text{HSO}_4^-$  ion and changes in the activity coefficients of the reactants (ester and hydrogen ion) and of the activated complex<sup>129-131</sup> (the primary salt effect) or to changes in the  $\text{pK}_a$  of the alkyl-bound oxygen in the ester (the secondary salt effect).

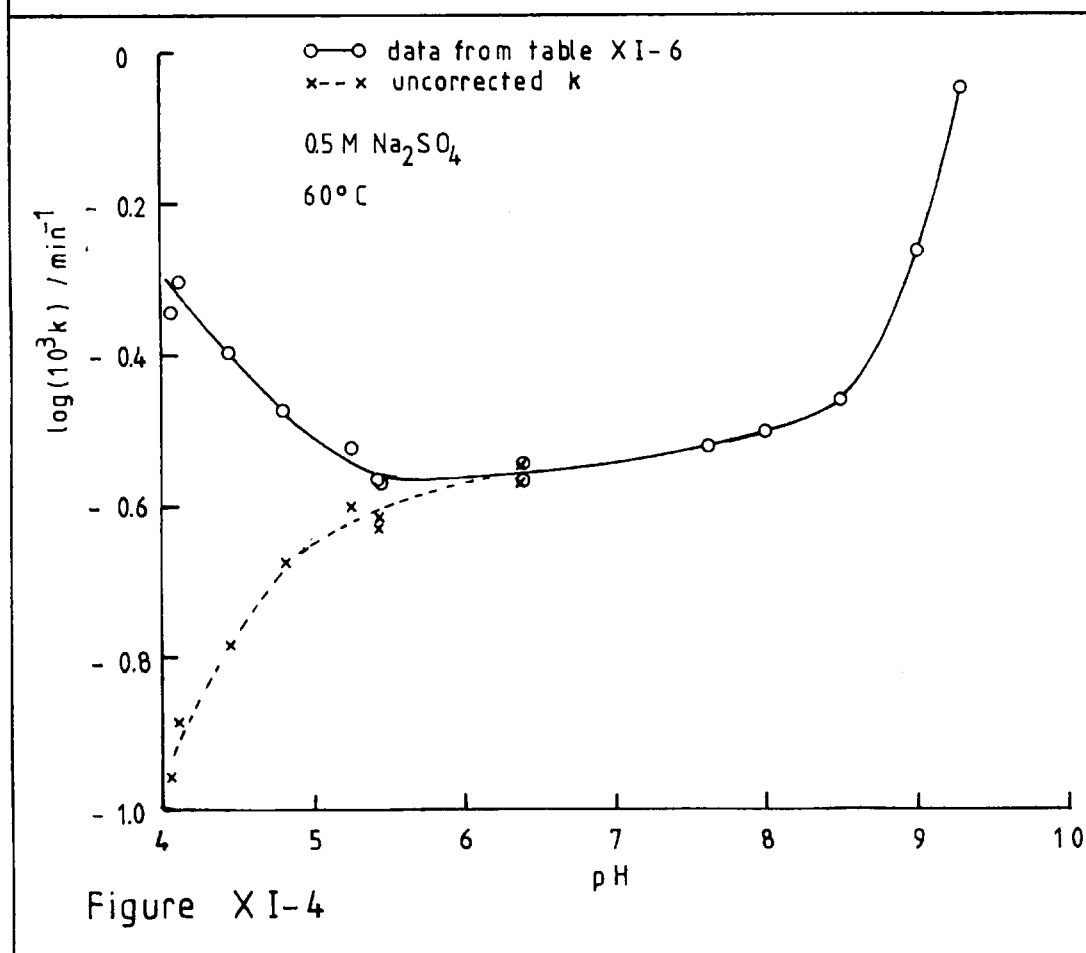
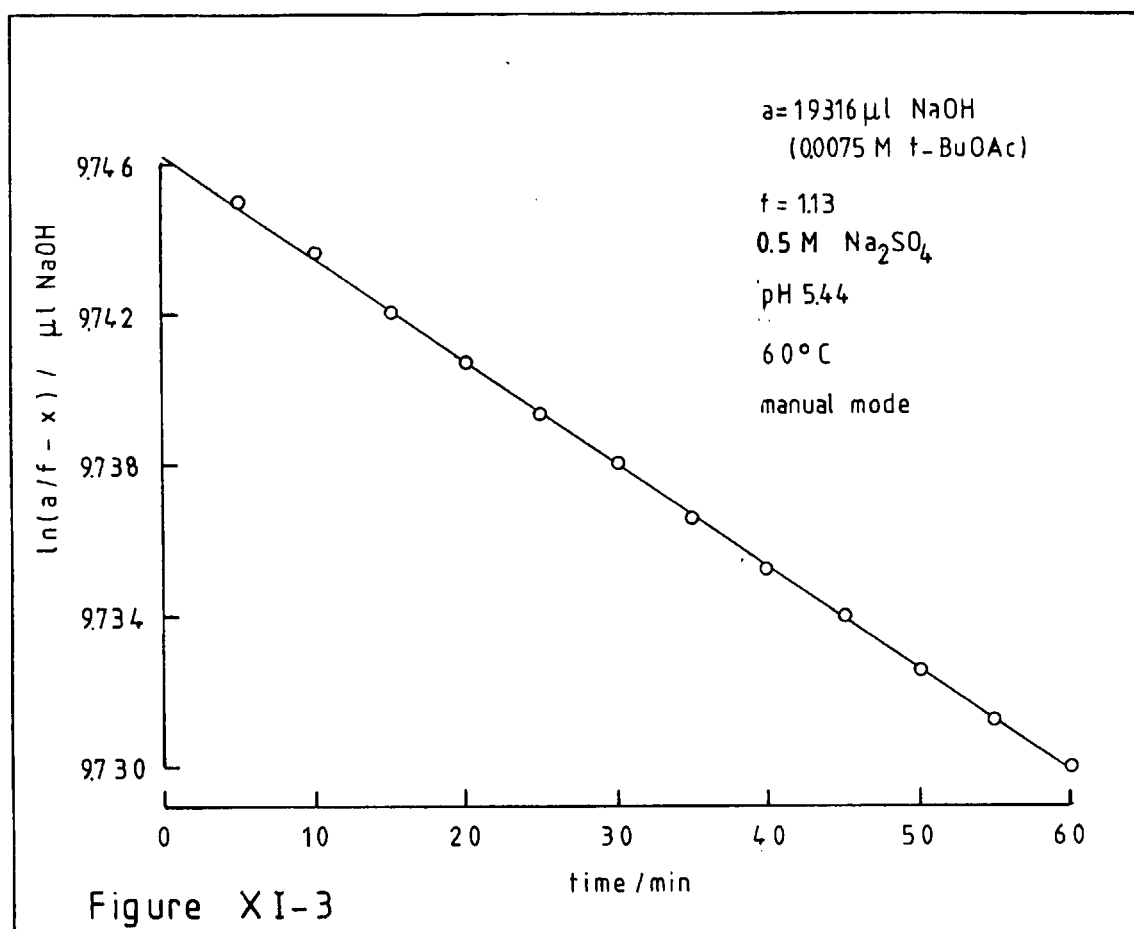


TABLE IX.6 RATE CONSTANT IN 0.5 M Na<sub>2</sub>SO<sub>4</sub>, 0.0075 M t-BuOAc, 60°C.

| pH   | $10^3 k/\text{min}^{-1}$ | Method |
|------|--------------------------|--------|
| 4.07 | 0.461                    | manual |
| 4.12 | 0.507                    | manual |
| 4.45 | 0.404                    | manual |
| 4.81 | 0.340                    | manual |
| 5.25 | 0.302                    | manual |
| 5.43 | 0.264                    | auto   |
| 5.44 | 0.267                    | auto   |
| 5.44 | 0.276                    | manual |
| 5.44 | 0.272                    | manual |
| 6.40 | 0.272                    | manual |
| 6.41 | 0.290                    | auto   |
| 6.41 | 0.291                    | auto   |
| 6.41 | 0.291                    | auto   |
| 7.62 | 0.300                    | manual |
| 8.00 | 0.316                    | manual |
| 8.50 | 0.349                    | manual |
| 9.00 | 0.552                    | manual |
| 9.30 | 0.948                    | manual |

Analysis of the data according to eqs. (X-3) and (X-4) is shown in Figure 5. Assuming that the value of  $K_w = 9.61 \times 10^{-14} \text{ M}^2$  at 60°C in pure water applies to the data in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at 60°C, the following data are obtained:

$$k_o = 0.29 \times 10^{-3} \text{ min}^{-1}$$

$$k_{\text{H}^+} = 2.5 \text{ M}^{-1} \text{ min}^{-1}$$

from  $k$  vs.  $[\text{H}^+]$

$$k_o = 0.27 \times 10^{-3} \text{ min}^{-1}$$

$$k_{\text{OH}^-} = 3.8 \text{ M}^{-1} \text{ min}^{-1}$$

from  $k$  vs.  $1/[\text{H}^+]$

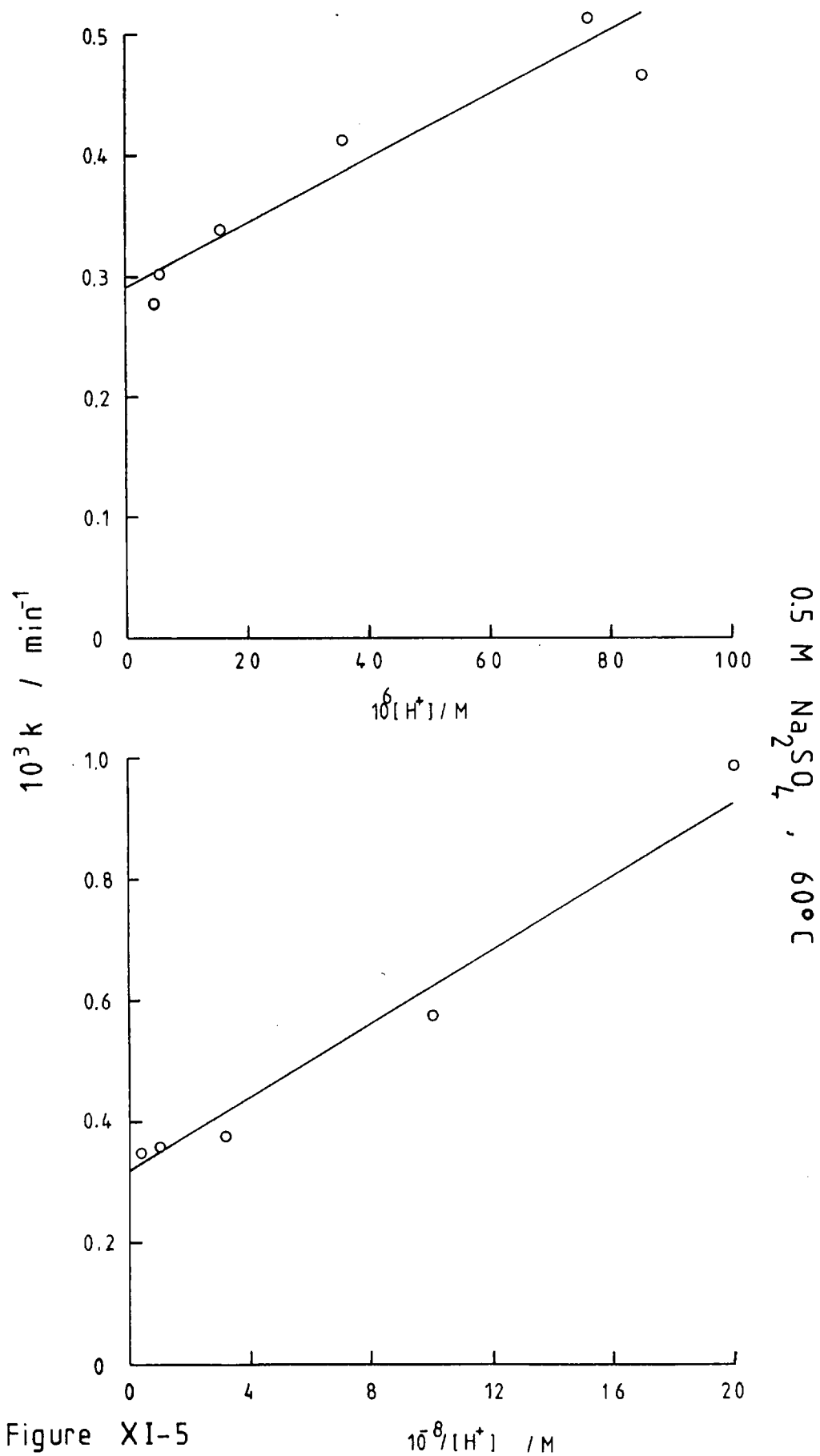


Figure XI-5

These values are probably affected by the SCE/0.5 M Na<sub>2</sub>SO<sub>4</sub> liquid junction potential and by the fact that, in ideal conditions, the pH furnishes the value of  $a_{H^+}$ , not  $[H^+]$ . The  $k_{H^+}$  value is considerably higher than 0.82 M<sup>-1</sup> min<sup>-1</sup> found by Adam, et al.<sup>132</sup> in 0.93 M HCl at 60°C. If it is assumed that the difference is due to catalysis by the HSO<sub>4</sub><sup>-</sup> ion, its rate constant can be estimated from eq. (X-15) as:

$$k_{HSO_4^-} = \frac{(2.5 - 0.82) \text{ M}^{-1} \text{ min}^{-1} \cdot 0.5 \text{ M}}{0.5 \text{ M}} = 1.7 \text{ M}^{-1} \text{ min}^{-1}$$

where  $A_0 = [Na_2SO_4] = 0.5 \text{ M}$  and  $K_{HSO_4^-}$  (the dissociation constant of the HSO<sub>4</sub><sup>-</sup> ion) has been taken as 0.5 M for an ionic strength of 1.5 at 25°C.<sup>10c,144</sup> The actual value for  $k_{HSO_4^-}$  is probably smaller, once salt effects have been eliminated. Indeed, it should be smaller than  $k_{H^+}$ . However, this appears to be the first evidence to show that this hydrolysis is subject to general acid/base catalysis, and not just to specific catalysis by H<sup>+</sup> and OH<sup>-</sup>.

The value for  $k_{OH^-}$  at 6.6°C is 0.0248 M<sup>-1</sup> min<sup>-1</sup>,<sup>145</sup> and 0.1082 at 25°C.<sup>133</sup> This leads to a value of 1.09 M<sup>-1</sup> min<sup>-1</sup> at 60°C, well below the value in 0.5 M Na<sub>2</sub>SO<sub>4</sub>. However, it is the result of a long extrapolation, and therefore subject to considerable error, but it nevertheless suggests that the presence of Na<sub>2</sub>SO<sub>4</sub> might be having a catalytic effect on the rate.

The value of  $k$  reported by Despić et al.<sup>140</sup> at 40°C in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at an initial pH of 6 is  $2.1 \times 10^{-4} \text{ min}^{-1}$ , which is ten times higher than the value of  $2.9 \times 10^{-5} \text{ min}^{-1}$  found by Lima.<sup>141</sup> A value of  $1.7 \times 10^{-5} \text{ min}^{-1}$  can be estimated for  $k$  in pure water from Adam et al.'s data.<sup>132</sup> Thus

Despić's data are out by a factor of 10. Lima has found that heating the ester at 70°C (Section XI.2.f) leads to only 6% of ester hydrolysed, whereas Despić, et al. assumed that half an hour at 70°C caused complete hydrolysis. Their  $k$  values were therefore much too small, and this would have given them abnormally high homogeneous rate constants since in the early stages of the reaction  $kt \approx x/a$ .

b) Hydrolysis of t-BuOAc in the Presence of Gold and Silver Electrodes.

Figure 6 shows a typical run with the gold electrode at 60°C. Its presence at open circuit (marked OC) does not modify the rate. Application of various pulsing regimes at 1 Hz (a: 0.25-0.75 V; b: 0.15-0.65 V; c: 0.35-0.85 V; d: 0.25-1.05 V, vs. SHE) did not affect the rate either. Under our experimental conditions, rate increases of 15 times w.r.t. the homogeneous value were expected according to Despić's data. Table 6 suggests that enhancements as small as 50% (i.e., a factor of 1.5-fold) would have been detected as an increase in the slope during the pulsing period. Instead, the whole run can be described by a smooth line with a slope of  $0.291 \times 10^{-3} \text{ min}^{-1}$ , very similar to the homogeneous rate constant. The slight curvature was probably caused by slow evaporation of the ester, as the run lasted for nearly 3 hours.

Figure 7 shows that on silver too, pulsation between -0.75 ( $E_{\text{pzc}}$ ) and -0.25 V (SHE) at 35°C did not enhance the rate, although 70-fold increase in  $k$  would have had to occur in these conditions.<sup>140</sup> Runs with silver had to be carried out at pH 9. At lower values, application of pulses actually led to apparent negative rates, i.e., the pH actually went up rather than down. It was probably caused by electrochemical reduction of residual oxygen or of water:

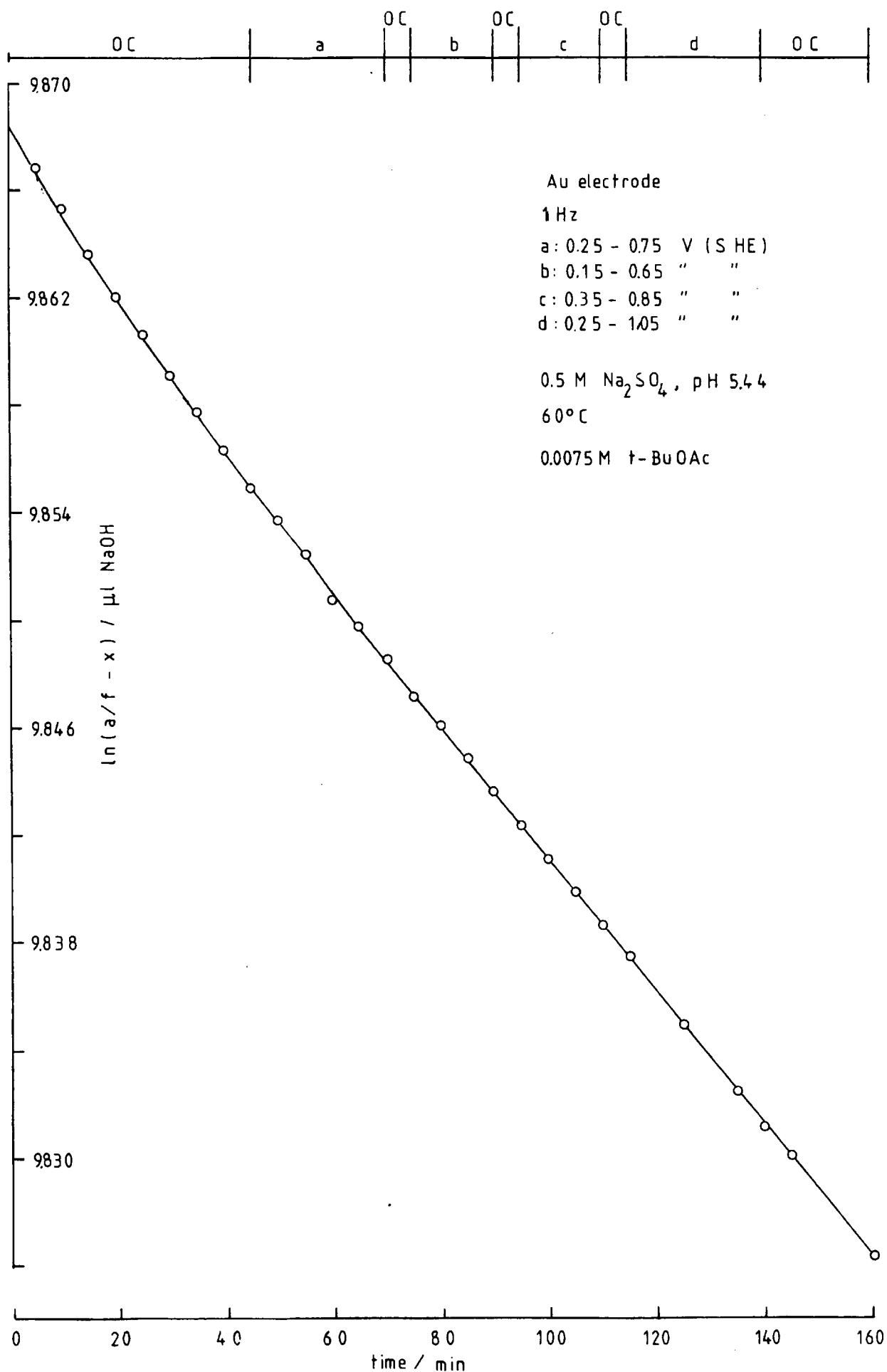


Figure XI-6

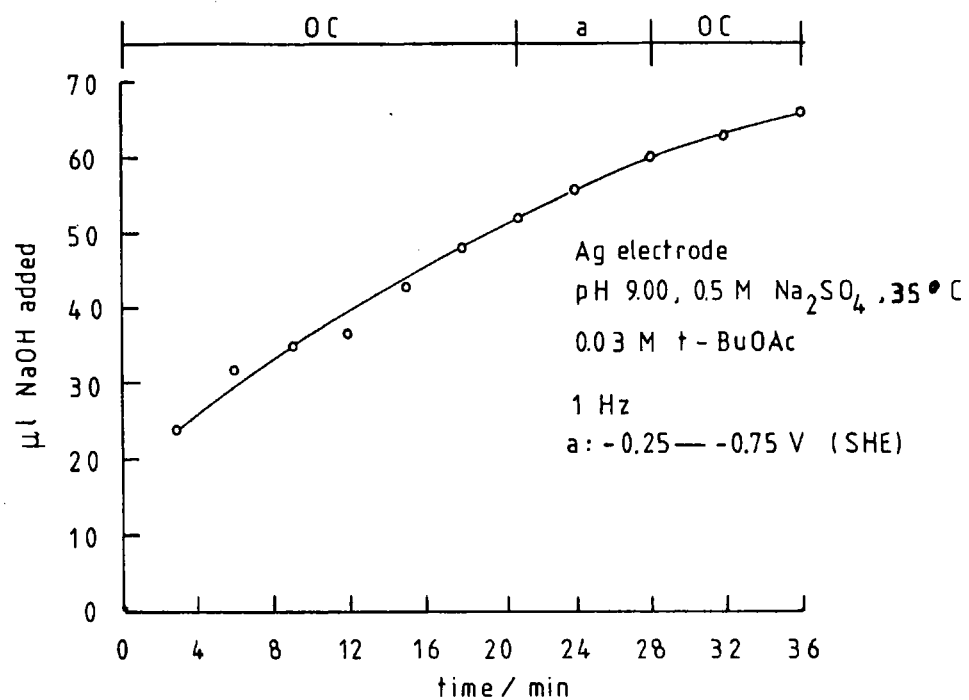


Figure XI-7

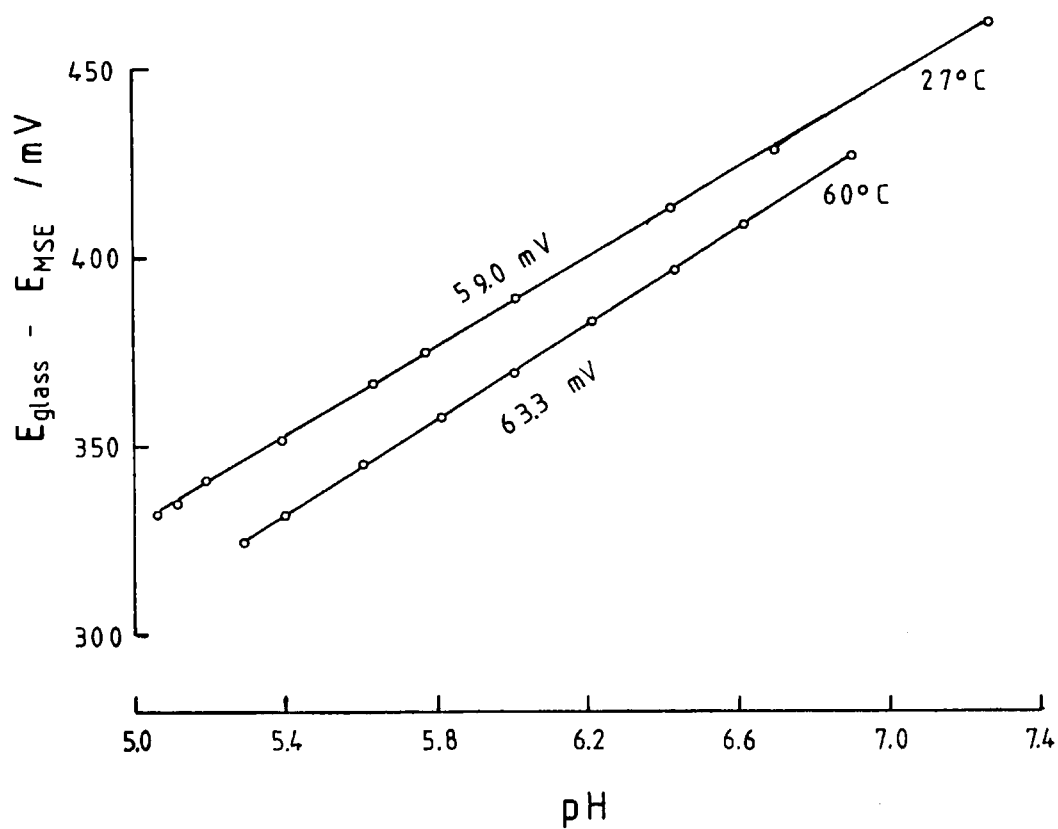
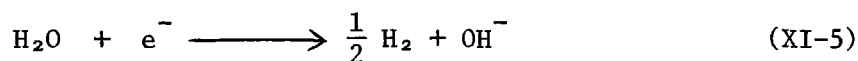
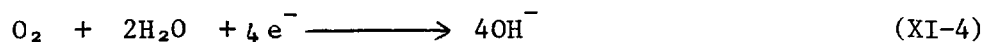


Figure XI-8



In case these negative results were due to impurities preferentially adsorbed on the electrodes, or to  $\text{Cl}^-$  ions leaked from the SCE, the runs were repeated with the following precautions: the  $\text{Na}_2\text{SO}_4$  was carefully recrystallised (155 g plus 400 ml water, heated to  $95^\circ\text{C}$ , filtered while hot, cooled at  $5^\circ\text{C}$ , precipitate recovered by filtration, rinsed with chilled water and dried at  $160^\circ\text{C}$  for 18 hours). The SCE was replaced with a Radiometer K601 mercurous sulphate reference electrode (MSE). It had a potential of +0.2199 V vs. SCE at  $60^\circ\text{C}$ . The mV scale of the pH meter was calibrated by reading the pH of various NaOH dilutions in 0.5 M  $\text{Na}_2\text{SO}_4$  with the glass/SCE pair, and the corresponding mV with the glass/MSE pair. Calibration curves at  $27^\circ\text{C}$  (room temperature) and at  $60^\circ\text{C}$  are shown in Figure 8. The  $27^\circ\text{C}$  calibration was used for all runs. Another point to consider is that Despić et al. did not mention the use of stirring during their runs. Stirring should have speeded up any diffusion-controlled steps in the catalytic process and so, if anything, have increased the effect of pulsing. However, as an extra check, the run with the gold electrode was carried out with discontinuous stirring. The stirrer was operated only for 8 min at the beginning of the run to achieve thermal equilibrium with the bath and thereafter only during the short periods in which the acid produced was being titrated. The resulting plot at  $60^\circ\text{C}$  for the gold electrode is shown in Figure 9, with no effect being caused by pulsation at 1 Hz between 0.25 and 0.75 V (SHE). Figure 10 shows a run at  $60^\circ\text{C}$  with the silver electrode, with the usual continuous mechanical stirring, but with recrystallised salt and MSE, which shows that pulsation does not seem to have any effect.

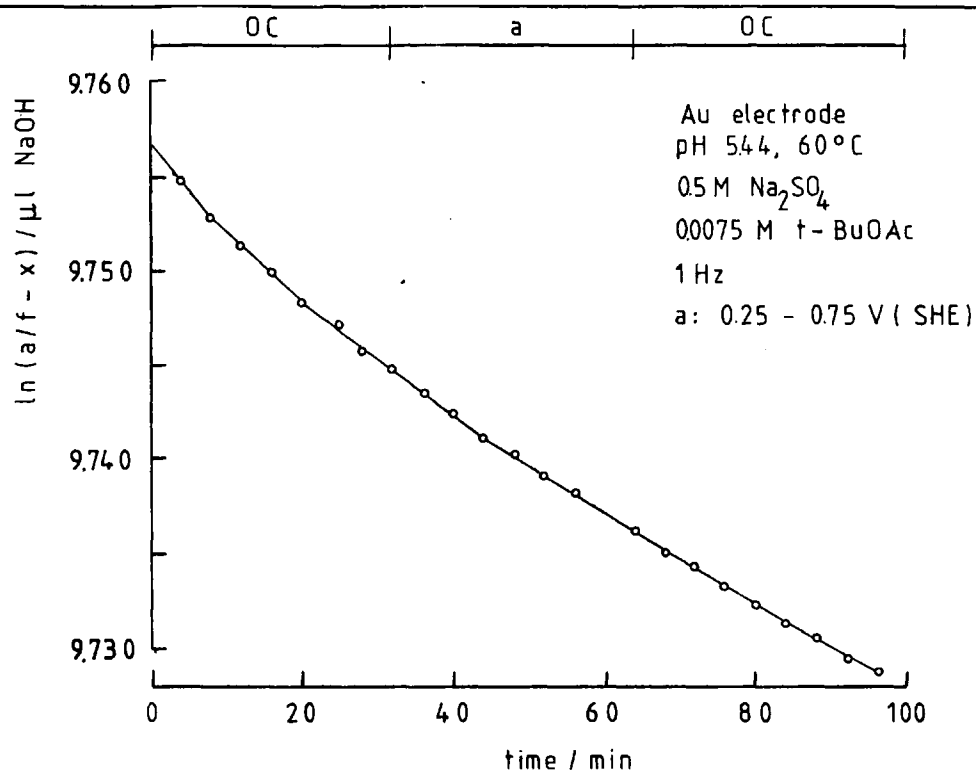


Figure XI-9

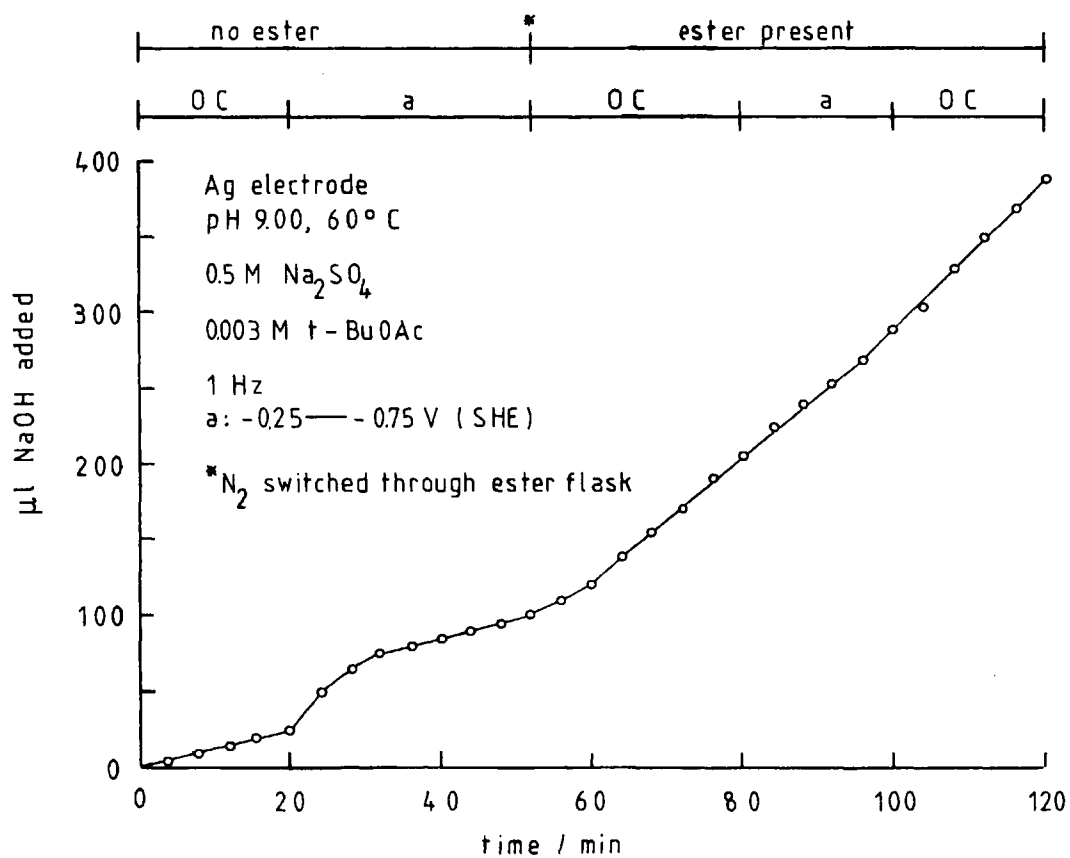


Figure XI-10

c) Homogeneous Runs with t-BuBr.

The results of the homogeneous solvolysis of t-BuBr in 80% v/v EtOH/H<sub>2</sub>O are summarised in Table 7.

TABLE XI.7 HOMOGENEOUS SOLVOLYSIS OF t-BuBr 80% v/v EtOH/H<sub>2</sub>O, 25°C.

| Medium                  | pH   | $10^4 \text{ k/s}^{-1}$ |
|-------------------------|------|-------------------------|
| no salt                 | 8.50 | 3.58                    |
| no salt                 | 8.50 | 3.63                    |
| no salt                 | 8.50 | 3.65                    |
| 0.3 M NaNO <sub>3</sub> | 7.95 | 3.63                    |
| 0.3 M NaNO <sub>3</sub> | 8.70 | 2.96                    |
| 0.3 M NaNO <sub>3</sub> | 8.00 | 3.83                    |
| 0.3 M NaNO <sub>3</sub> | 8.80 | 3.83                    |
| 0.3 M NaNO <sub>3</sub> | 8.70 | 3.83                    |

The values of k are somewhat scattered but they confirm that the rate constant is independent of pH (Chapter X). The presence of 0.3 M NaNO<sub>3</sub> exerts only a small increase in k as would be expected from an uncharged reactant. The rate constants in the absence of the salt are close to the value of  $3.58 \times 10^{-4} \text{ s}^{-1}$  in the same conditions reported elsewhere.<sup>146</sup>

d) Solvolysis of t-BuBr in the Presence of Gold and Silver Electrodes.

The presence of the gold electrode at open circuit did not affect the rate. Pulsing was not tried because the aim of this section was to study pulsing effects when the metal by itself catalyses the reaction.

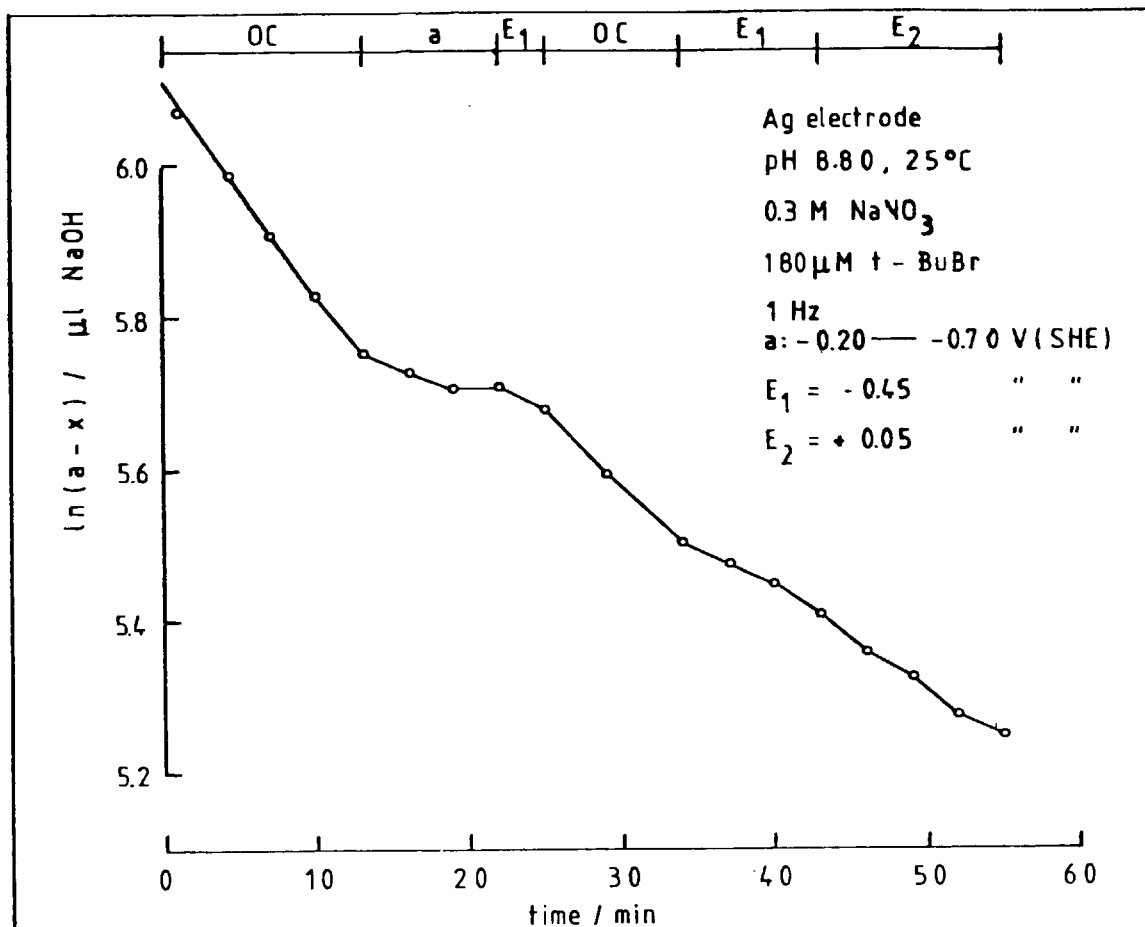


Figure XI - 11

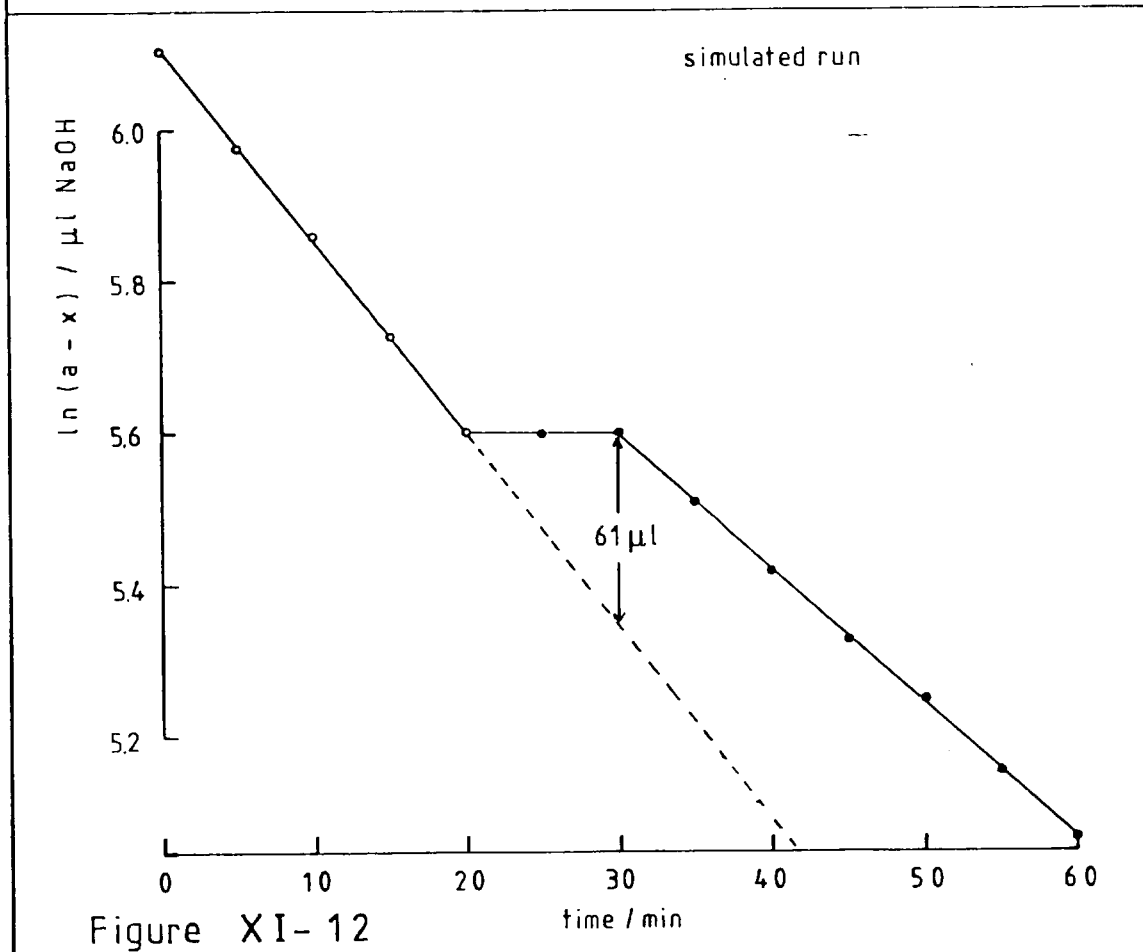


Figure XI- 12

In the presence of the silver electrode at open circuit (no salt present) the rate constant rose to  $5.7 \times 10^{-4} \text{ s}^{-1}$ . Silver is known to catalyse this reaction through adsorption of the alkyl halide by its bromide end.<sup>139</sup> In the presence of 0.3 M  $\text{NaNO}_3$  the rate constant decreased to  $4.5 \times 10^{-4} \text{ s}^{-1}$  probably due to competitive adsorption of the  $\text{NO}_3^-$  ions. After repeated use of the silver electrode as a catalyst, the rate constant stabilised at  $4.20 \times 10^{-4} \text{ s}^{-1}$ .

As Figure 11 shows, pulsation at 1 Hz between -0.70 and -0.20 V (SHE) actually decreases the rate constant (catalytic plus homogeneous) to negligible values. During the subsequent open circuit period, the rate constant increased again but stayed at  $2.47 \times 10^{-4} \text{ s}^{-1}$ , well below its homogeneous value. Holding the potential at constant values [ $E_1 = -0.45 \text{ V}$  and then  $E_2 = +0.05 \text{ V}$  (SHE)] is seen to reduce the rate constant again, but less than during pulsing. In a separate run, the rate was apparently brought to a halt when a constant potential of -0.7 V (SHE) was applied. At the same time some 0.3-0.4 mA were observed to flow through the counting resistor. The subsequent rate constant on open circuit was again only  $2.47 \times 10^{-4} \text{ s}^{-1}$ .

It is possible that the apparent decrease in rate might have been to reactions (4) and/or (5) or to  $\text{NO}_3^-$  reduction. In fact, if the observed current produces one  $\text{OH}^-$  ion per electron, it would be equivalent to  $6-8 \times 10^{-8} \text{ mol OH}^- \ell^{-1} \text{ s}^{-1}$ . The rate of  $\text{H}^+$  production after ca. 15 min of reaction ( $a = 1.8 \times 10^{-4} \text{ M t-BuBr}$ ) is:

$$\text{rate} = \frac{-d[\text{t-BuBr}]}{dt} = -a k \exp(-kt) \quad (\text{XI-6})$$

or  $5.2 \times 10^{-8} \text{ mol H}^+ \ell^{-1} \text{ s}^{-1}$ , which would be almost completely "titrated" by the current, if a reaction like (5) is taking place.

That the rate did not return to its open circuit value on removal of the polarising potential can be shown to be a mathematical artifact. For suppose that the electrochemical reaction has removed  $b$  molar  $H^+$  ions from the reaction mixture. Then the concentration of acid formed by the solvolytic reaction and neutralised by NaOH will seem to be only  $x'$ , where  $x' = x - b$ . It is thus  $\ln(a - x')$  that will be plotted against time to give the first order rate constant. However, it follows from eq. (X-21) that:

$$\ln(a - x') = \ln(a - x + b) = \ln(a e^{-kt} + b) \quad (XI-6)$$

so that the slope of the plot will be

$$k' = \frac{-d \ln(a - x')}{dt} = \frac{a k e^{-kt}}{a e^{-kt} + b} < k \quad (XI-7).$$

Figure 12 simulates this behaviour. The open circles represent the open circuit overall rate (homogeneous plus heterogeneous) calculated from eq. (X-21) using  $a = 450 \mu\ell$  and  $k = 4.2 \times 10^{-4} s^{-1}$ , which are typical of these runs. The filled circles represent the plot calculated according to eq. (6), with  $b = 61 \mu\ell$ , i.e., the volume of NaOH that failed to be delivered to the reaction mixture during the 10 min period of pulsation (horizontal section). The final rate constant is  $2.86 \times 10^{-4} s^{-1}$ , well below the homogeneous value and close to that obtained experimentally.

#### XI.4. Conclusions.

None of the experiments reported here, whether with t-BuOAc at gold or at silver electrodes, or with t-BuBr at silver electrodes, has provided any evidence for the phenomenon of non-faradaic electrocatalysis. The experimental technique used here is very similar to Despić et al.'s and some of the differences were examined in special experiments. As shown by Lima<sup>141</sup> their homogeneous rate constants are 10 times too high, almost certainly because they used erroneously low values for the total ester concentration,  $a$ . Their catalytic rate constants are probably out by the same factor. It is difficult to estimate these rate constants, as Despić, et al.'s model requires diffusion of the ester towards the electrode, adsorption, charging of the double layer and bond polarisation, desorption of the products away from the electrode and discharge of the double layer. Any of these steps may be rate determining. However, it is possible to estimate the maximum possible rate by assuming it to be equal to the frequency of pulsing, and based on complete coverage of the electrode. A Leybold molecular model of the t-BuOAc molecule was found to project an area of some  $50 \text{ \AA}^2$  on a flat surface, which leads to a maximum coverage of  $2.7 \times 10^{-9} \text{ mol}$  on the  $8 \text{ cm}^2$  gold electrode used by Despić. We shall assume that all these adsorbed molecules react at the moment of switching the potential from 0.25 V to 0.75 V (SHE), since according to the model put forward by Despić no further adsorption of ester should take place at 0.75 V, because it is so far away from the  $E_{\text{pzc}}$ . This leads to a rate of  $5.4 \times 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$ , because Despić's solution volume is 0.1 l and the whole pulse lasts 0.5 s under their most favourable conditions. From Table 2 in Despić's paper,  $k \approx 2 \times 10^{-4} \text{ s}^{-1}$  at  $40^\circ\text{C}$ , which leads to initial rates of  $2 \times 10^{-5}$

$\text{mol l}^{-1} \text{ s}^{-1}$  when  $[\text{t-BuOAc}] = 10^{-1} \text{ M}$  to  $2 \times 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$  at  $10^{-4} \text{ M}$ .

These rates should be reduced by a factor of 10 to account for the error in the initial ester concentration, giving  $2 \times 10^{-6} - 2 \times 10^{-9} \text{ mol l}^{-1} \text{ s}^{-1}$ . Thus, at the higher ester concentrations, Despić's initial rates are higher than the maximum possible rate by a factor of up to  $10^2$ .

Another test of their pulsed rates can be made by examining their activation energies  $E^\ddagger$  between 35 and 40°C. Taking only the values for gold electrodes pulsed between 0.25 and 0.75 V (SHE) at frequencies,  $\nu$ , of 0.5 or 1 Hz, we have

| $\nu/\text{Hz}$ | R | $E^\ddagger/k \text{ cal mol}^{-1}$ |
|-----------------|---|-------------------------------------|
| 0.5             | 1 | 41.6 mean of Table 2 <sup>140</sup> |
| 1               | 1 | 51.6 from Table 1 <sup>140</sup>    |
| 0.5             | 9 | 42.5 from Table 1 <sup>140</sup>    |

Here R is the ratio of the periods during which the electrode was held at the lower and at the upper potential limit for each pulse. Despić et al. themselves quote a figure of  $39.9 \text{ kcal mol}^{-1}$  without specifying the frequency regime. Such enormous activation energies are far larger than one would expect for a heterogeneously catalysed process. Furthermore, they are at least ten times greater than the activation energy for any diffusion-controlled process. These high temperature coefficients are very hard to reconcile with the large magnitude of the reported catalytic rate constants themselves.

No genuine effects of changes in the interfacial electric field at the silver electrode on the catalysis of the t-BuBr solvolysis could be found. t-BuBr is a polar molecule so that its degree of adsorption on the electrode would be expected to be influenced by the field, and hence the catalysis by silver. It could be, of course, that these effects are small and were masked by the other faradaic effects. In

any case, no significant non-faradaic electrocatalysis appears to operate in this case either.

We remain at a loss, however, to account for the qualitative differences between the work reported here and Despić et al.'s. Following a conversation with Professor Despić, and from their published experimental procedure [reference 140 and Section XI.2.f.], it seems that his student, Mrs. Ivić, was not aware of the experimental problems associated with the high volatility of the t-BuOAc. Thus, the much higher rates she obtained by pulsation could be due to her plugging all of the holes in the lid of the reaction vessel with the various electrodes, thus reducing evaporation; these holes would presumably remain unplugged during homogeneous runs in which no electrodes are needed, thus allowing most of the ester to volatilise and leading to an apparently far lower rate. However, this hypothesis does not explain why their rate constants on pulsed gold electrodes have a maximum around the  $E_{pzc}$ . Professor Despić has told us that further work to try and resolve the discrepancy is being carried out in his laboratory, and his results are awaited with interest.

## APPENDIX ONE

### SIMULTANEOUS HOMOGENEOUS AND HETEROGENEOUS RATES

The Setting: The  $\text{Feic} + \text{I}^-$  reaction on platinum RDE and in the bulk of solution.

Qualitative Description: The reaction comes almost to equilibrium at the platinum surface (Chapter VI). Therefore the catalytic rate is completely controlled by the concentration gradient across the diffusion layer (DL). The homogeneous reaction must contribute to this gradient; hence the catalytic rate is affected. The purpose here is to try to evaluate the extent of these homogeneous effects.

Semi-Quantitative Description: Because of the variation of the concentration of reactants and products in the DL the homogeneous rate  $R_H$  varies along it. At  $x = 0$ ,  $R_H = 0$  because of the equilibrium condition; at  $x \geq \delta_N$ ,  $R_H = R_H^b$  (the bulk value of  $R_H$ ). Using Fick's second law:

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2} - v_j R_H \quad (\text{A1-1})$$

where  $v_j$  is the stoichiometric coefficient ( $v_j > 0$  for reactants; and  $< 0$  for products).  $R_H$  depends on all  $C_j(x)$  (thus eq.(1) represents a system of  $n$  coupled differential equations), and its full dependence is required to solve (1). We do not know this dependence. To estimate the homogeneous effect, it will be assumed that  $R_H$  varies linearly inside the DL:

$$R_H = (R_H^b / \delta_N) x \quad (\text{A1-2})$$

A steady state will be assumed so that  $\partial C_j / \partial t = 0$ . Because of (2), it is now enough to solve only one equation. Take  $j = I_3^-$ ,  $v_j = -1$ . Then:

$$D \partial^2 C / \partial x^2 + (R_H^b / \delta_N) x = 0 \quad (A1-3)$$

Integrating once from  $x = 0$  to  $x = x$ :

$$D(\partial C / \partial x) - F^\sigma + (R_H^b / 2\delta_N) x^2 = 0 \quad (A1-4)$$

where  $F^\sigma = D(\partial C / \partial x)_{x=0}$ . Integrating again from  $x = 0$  to  $x = \delta_N$ :

$$D(C^b - C^\sigma) - F^\sigma \delta_N + R_H^b \delta_N^2 / 6 = 0 \quad (A1-5)$$

Then:

$$u_{cat}^{app} = -F^\sigma A = (C^\sigma - C^b) DA / \delta_N - R_H^b \delta_N A / 6 \quad (A1-6)$$

where  $u_{cat}^{app}$  is the apparent catalytic rate, which includes the homogeneous contribution inside the DL.  $C^b$  is the bulk  $[I_3^-]$  from homogeneous and catalytic origin. Therefore, the first term on the extreme right hand side term in (6) is not the 'true' catalytic rate  $u_{cat}$ .  $A\delta_N$  is the volume of the DL so that the second term on to the right is insignificant compared to the first. However, for the sake of completeness a relation between  $u_{cat}^{app}$  and the observed value  $u_{cat}^{obs*}$  (in mols per second) will be obtained. The overall rate  $u_T$  (homogeneous plus catalytic) is:

$$u_T = u_{cat}^{app} + R_H^b V' \quad (A1-7)$$

where  $V' = V - A\delta_N$ ;  $V$  = volume of solution.  $V'$  is used instead of  $V$  because  $u_{cat}^{app}$  includes the homogeneous contribution inside the DL. But by definition [Eq. (II-7)]:

$$u_{cat}^{obs} = u_T - R_H^b V \quad (A1-8)$$

---

\*  $u_{cat}^{obs} = u'_{cat}$

Therefore:

$$u_{\text{cat}}^{\text{obs}} = u_{\text{cat}}^{\text{app}} + (V' - V) R_H^b = (C^\sigma - C^b) AD / \delta_N - 7 A \delta_N R_H^b / 6 \quad (\text{A1-9})$$

The second term is still small. Thus:

$$u_{\text{cat}}^{\text{obs}} = u_{\text{cat}}^{\text{app}} = (C^\sigma - C^b) AD / \delta_N \quad (\text{A1-10})$$

If  $C^b$  is expressed as a contribution of catalytic origin plus another ( $C_H^b$ ) of homogeneous origin:

$$u_{\text{cat}}^{\text{obs}} = u_{\text{cat}} - AD C_H^b / \delta_N \quad (\text{A1-11})$$

If  $u_{\text{cat}}^{\text{obs}}$  is evaluated at  $t = 0$ , at which  $C_H^b = 0$ , then  $u_{\text{cat}}^{\text{obs}} = u_{\text{cat}}$ , and no homogeneous effect will be observed.

## APPENDIX TWO

The following computer program fits by least squares a set of N pairs of data (X, Y) to the parabola:

$$Y = A_1 + (A_2)X + (A_3)X^2$$

PROGRAM POLYN2

```

00100 DIM X(15), Y(15)
00105 X1=X2=X3=X4=P1=P2=P3=P4=P5=Y1=Y2=Y3=A1=A2=A3=A4=S=0
00110 PRINT "ENTER NUMBER OF DATA POINTS "
00120 INPUT N
00130 PRINT "ENTER DATA AS X, Y "
00140 FOR I=1 TO N
00150 INPUT X(I), Y(I)
00160 NEXT I
00170 FOR I=1 TO N
00180 X1=X1+X(I)
00190 X2=X2+X(I)**2
00200 X3=X3+X(I)**3
00210 X4=X4+X(I)**4
00220 Y1=Y1+Y(I)
00230 Y2=Y2+X(I)*Y(I)
00240 Y3=Y3+(X(I)**2)*Y(I)
00250 NEXT I
260 X1=X1/N
261 X2=X2/N
262 X3=X3/N
264 X4=X4/N
265 Y1=Y1/N
266 Y2=Y2/N
267 Y3=Y3/N
00270 P1=Y2-X1*Y1
00280 P2=Y3-X2*Y1
00290 P3=X2-X1**2
00300 P4=X3-X1*X2
00310 P5=X4-X2**2

```

```
00320 A3=(P1/P3-P2/P4)/(P4/P3-P5/P4)
00330 A2=P2/P4-(P5/P4)*A3
00340 A1=Y1-A2*X1-A3*X2
00350 FOR I=1 TO N
00360 S=S+(Y(I)-A1-A2*X(I)-A3*(X(I)**2))**2
00370 NEXT I
00375 S=SQR(S/(N-1))
00380 PRINT "A1=" ; A1
00390 PRINT "A2=" ; A2
00400 PRINT "A3=" ; A3
00410 PRINT "S=" ; S
00412 A4=A2*(10**(-7))/(60*0.21)
00415 PRINT "INITIAL RATE=" ; " MOLAR PSECOND"
00420 PRINT "ANOTHER RUN?"
00430 INPUT Q
00440 IF Q=1 THEN 100
00450 END
```

### APPENDIX THREE

The following computer program solves numerically eqs. (II-31) and (II-32) for  $i_m$  (as  $v_{cat}$ ), and calculates  $E_m$  from eqs. (II-30) for the  $Feic/I^-$  system by the Newton-Raphson method,<sup>93</sup> under the conditions stated on lines 100-160 in the program.

PROGRAM CATRATE

```

00100 REM
00110 REM THIS PROGRAM CALCULATES THE INITIAL CATALYTIC RATE AND
00120 REM THE MIXTURE POTENTIAL BETWEEN FERRICYANIDE AND IODIDE
00130 REM ON A SMOOTH ROTATING PLATINUM DISK ELECTRODE OF 11.2 CM
00140 REM SQ., AT 500RPM, 5 DEG. CETN., IN 1M POTASSIUM NITRATE,
00150 REM IN A VOLUME OF 0.210 LITERS.
00160 REM 1 IS FOR FEIC, 2 FOR FEOC, 3 FOR TRI-IODIDE, 4 FOR IOD
00170 PRINT " ENTER MILLIMOL/LITER OF"
00180 PRINT " FEIC, IODIDE, FEOC, TRI-IODIDE"
00190 INPUT C1, C4, C2, C3
00200 PRINT " ENTER RATE ESTIMATE IN UNITS OF NMOLAR/SECOND"
00210 INPUT X1
00220 X1=4.053E-5*X1
00230 M=0.00178389
00240 L1=2.665E-3*C1
00250 L2=2.425E-3*C2
00260 L3=0.006588*C3
00270 L4=4.717E-3*C4
00280 IF L1>L4 THEN 00310
00290 P=L1
00300 GOTO 00320
00310 P=L4
00320 F=(L3+X1)*((L4-X1)**(-3))*(((L2+X1)/(L1-X1))**2)
00330 D=F*(2/(L2+X1)+1/(L3+X1)+3/(L4-X1)+2/(L1-X1))
00340 X2=X1+(M-F)/D
00350 IF X2<P THEN 00380
00360 X1=(X1+P)/2
00370 GOTO 00320
00380 IF ABS(1-F/M)>1E-10 THEN 00480

```

```

00390 IF ABS(1-X1/X2) > 1E-10 THEN 00480
00400 E=0.02396*LOG((0.001*C1-X2/2.665)/(0.001*C2+X2/2.425))
00410 E=0.2598+E
00420 PRINT
00430 X3=2.467E-5*X2
00440 PRINT " RATE=" ;X2;" MOLAR/SECOND"
00450 PRINT
00460 PRINT " EMIX=" ;E; " VOLTS VS. SCE"
00470 GOTO 500
00480 X1=X2
00490 GOTO 00320
00500 END

```

The following computer programme solves numerically eqs. (II-31) and (II-32) for  $i_m$  (as  $u'_{cat}$ ) and calculates  $E_m$  from eqs. (II-30) for the Feic/ $I^-$  system. The method used is that of halving successively the interval where  $i_m$  is known to belong, under the conditions stated on lines 100-140 in the program.

#### PROGRAM OEDIPUS

```

00100 REM THIS PROGRAM CALCULATES THE INITIAL CATALYTIC RATE AND
00110 REM THE MIXTURE POTENTIAL UNDER TOTAL MASS TRANSPORT CONTROL
00120 REM OF THE REACTION BETWEEN FERRICYANIDE AND IODIDE AT A
00130 REM PLATINUM RDE OF 11.2CM SQ, 500 RPM, 5 DEGREES CENT.,
00140 REM 1M POTASSIUM NITRATE
00150 REM 1=FERRICYANIDE, 2=FERROCYANIDE, 3=TRI-IODIDE, 4=IODIDE
00160 M=0.00178389
00170 PRINT " ENTER NUMBER OF CALCULATIONS TO BE DONE"
00180 INPUT N
00190 FOR I=1 TO N
00200 PRINT " ENTER MILLIMOLES/LITER OF"
00210 PRINT " FEIC, IODIDE, FEOC, TRI-IODIDE"
00220 INPUT C1, C4, C2, C3
00230 L1=2.665E-3*C1
00240 L2=2.425E-3*C2
00250 L3=6.588E-3*C3
00260 L4=4.717E-3*C4

```

```

00270 IF L1<L4 THEN 00300
00280 X1=L4
00290 GOTO 00310
00300 X1=L1
00310 X2=0
00320 X3=X1/2
00330 F=(L3+X3)*((L4-X3)**(-3))*(((L2+X3)/(L1-X3))**2)
00340 IF ABS(F/M-1)<1E-10 THEN 00360
00350 GOTO 00490
00360 IF ABS(X2/X3-1)<1E-10 THEN 00380
00370 GOTO 00490
00380 E=0.02396*LOG((0.001*C1-X3/2.665)/(0.001*C2+X3/2.425))
00390 E=0.2598+E
00400 A=5.18135E-6*X3
00410 B=4.6262E-7*X3
00420 PRINT
00430 PRINT " RATE=" ; A; " MOLES/SECOND"
00440 PRINT "      =" ; B; " MOLES/SECOND CM2"
00450 PRINT
00460 PRINT " EMIX=" ; E; " VOLTS VS SCE"
00470 PRINT
00480 GOTO 00570
00490 X2=X3
00500 IF F<M THEN 00530
00510 P=-1
00520 GOTO 00540
00530 P=1
00540 X3=X2+(P/2)*ABS(X2-X1)
00550 X1=X2
00560 GOTO 00330
00570 NEXT I
00580 END

```

## APPENDIX FOUR

The following computer programme fits a set of N pairs of data (X,Y) to a straight line

$$Y = B + MX \quad (A4-1)$$

by the least squares method. The standard deviation of intercept, W, and of the slope, Z, are defined as:

$$W = \left\{ \sum_j [B - (Y_j - MX_j)]^2 / (N-1) \right\}^{1/2} \quad (A4-2)$$

and

$$Z = \left\{ \sum_j [M - (Y_j - B) / X_j]^2 / N-1 \right\}^{1/2} \quad (A4-3)$$

respectively. In the case of eq. (3), pairs  $(X_j, Y_j)$  for which  $X_j = 0$  are rejected by the program.

PROGRAM LMS

```

00100 PRINT " ENTER NUMBER OF DATA POINTS "
00110 INPUT N
00120 P=N
00130 PRINT " ENTER DATA AS X,Y"
00140 FOR I=1 TO N
00150 INPUT X,Y
00160 S1=S1+X
00170 S2=S2+X**2
00180 S3=S3+Y
00190 S4=S4+Y**2
00200 S5=S5+X*Y
00210 IF X=0 THEN 00280
00220 S6=S6+1/X
00230 S7=S7+X**(-2)
00240 S8=S8+Y/X
00250 S9=S9+(Y/X)**2
00260 T=T+Y/(X**2)
00270 GOTO 00290
00280 P=P-1
00290 NEXT I

```

```

00300 M=(N*S5-S1*S3)/(N*S2-S1**2)
00310 B=(S3-M*S1)/N
00320 R=(N*S2-S1**2)/(N*S4-S3**2)
00330 R=M*SQR(R)
00340 W=S4-2*M*S5-2*B*S3+S2*(M**2)+2*M*B*S1+N*(B**2)
00350 W=SQR(W/(N-1))
00360 IF P<2 THEN 390
00370 Z=P*(M**2)-2*M*S8+2*M*B*S6+S9-2*B*T+S7*(B**2)
00380 Z=SQR(Z/(P-1))
00390 PRINT
00400 PRINT " Y=" ;M;" X+";B
00410 PRINT
00420 PRINT " CORRELATION COEFF. =      ";R
00430 PRINT " STD. DEVTN. OF INTERCEPT=" ;W
00440 IF P<2 THEN 470
00450 PRINT " STD. DEVTN. OF SLOPE=      "; Z
00460 GOTO 00480
00470 PRINT " STD. DEVTN. OF SLOPE CANNOT BE CALCULATED"
00480 END.

```

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