Enthalpies of Activation for the Iron(II)–Iron(III) Redox Reaction at Platinum and Palladium Electrodes in Chloride and Sulphate Media

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Summary Exchange current densities and enthalpies of activation for the Fe^{2+}–Fe^{3+} redox reaction depend on the nature of the metal electrode in sulphate medium, $\Delta H^\ddagger$ being 6·0 kcal g ion^{-1} at Pt and 8·5 kcal g ion^{-1} at Pd; in 6M HCl, however, $\Delta H^\ddagger$ is almost independent of the metal, being 4·0 and 3·6 kcal g ion^{-1}, respectively, at Pt and Pd.

ALTHOUGH redox reactions at electrodes have been studied theoretically,[1] few measurements of $\Delta H^\ddagger$ are available. The Fe^{2+}–Fe^{3+} reaction at Pt and Au has been studied at one temperature,[2] and the temperature dependence of exchange current density (i_0) has been examined using Pt in perchlorate medium[3] and more recently with Pt, Pd, Rh, Ir, and Au in sulphate medium.[4,5] In this instance,[4,5] TABLE

Exchange current densities (i_0) *and activation enthalpies* ($\Delta H^{\ddagger}$) *for the* Fe^{2+}–Fe^{3+} *reaction*[a] *at* Pt *and* Pd *in sulphate and chloride media*

System		i_0 (mA cm^{-2}) 25 °C Ref. 5	25 °C Present work	50 °C Ref. 5	50 °C Present work	$\Delta H^{\ddagger}$ (kcal g ion^{-1}) Refs. 4, 5	$\Delta H^{\ddagger}$ Present work
SO_4^{2-}	Pt	8·0	7·5	18·0	16·5	5·0	6·0 ± 0·5
medium	Pd	12·5	1·0	16·5	3·0	2·4	8·5 ± 0·1
Cl^-	Pt	14	35·5	—	53	—	4·0 ± 0·1
medium	Pd	150	27[b]	—	44[c]	—	3·6 ± 0·6

[a] $[Fe^{2+}] = [Fe^{3+}] = 0{\cdot}1$M. [b] 41 mA cm^{-2}, including Pd dissolution. [c] 74 mA cm^{-2}, including Pd dissolution.

$\Delta H^{\ddagger}$ was claimed to be *independent of the metal*, with values of 5 to 6 kcal g ion^{-1}, except that Pd anomalously gave $\Delta H^{\ddagger} = 2{\cdot}4$ kcal g ion^{-1}. However i_0 showed strong dependence on the metal and a linear relationship of ln i_0 with electronic work function was proposed.[4,5] Different catalytic effects of Cl^- ion on i_0 were reported for Pt, Pd (Table) and Au, but no $\Delta H^{\ddagger}$'s were obtained for chloride medium.

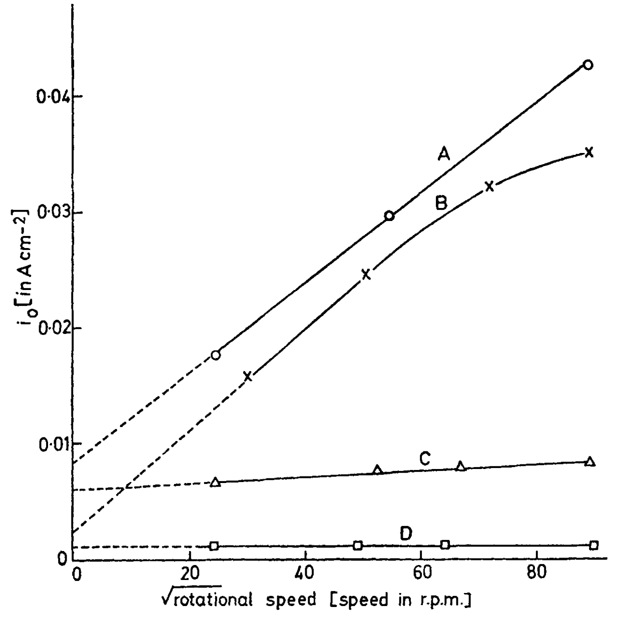

FIGURE 1. *Dependence of exchange current densities* (*in* A *cm*$^{-2}$) *at* ca. 25°C *on rotational speed for* 0·1M Fe^{2+}–0·1M Fe^{3+} *in acidic chloride and sulphate medium of equal ionic strength.* (*A*) Pd *in chloride* (*including metal dissolution*); (*B*) Pt *in chloride;* (*C*) Pt *in sulphate;* (*D*) Pd *in sulphate.*

The i_0's (see Table) were obtained with a rotating disc electrode,[6] used at its maximum rotational speed (8000 r.p.m.) to minimise mass transport overpotential. The value of i_0 was calculated, using $i_0 = iRT/\eta F$, from linear curves between current density (i) and overpotential (η) obtained potentiostatically for $-5\text{mV} < \eta < 5$ mV. Solutions 0·1M Fe^{2+} and 0·1M Fe^{3+} in each case, in 6M HCl or 1·92M H_2SO_4, were purified by 48h pre-electrolysis at 55 °C using Pt foil electrodes and N_2 stirring. Electrodes of 2 mm diameter rod were assembled in Kel-F rods, cleaned in solvents and in triple-distilled water and activated in 3M H_2SO_4 immediately before use, by generating and reducing a thin adsorbed oxygen layer.[7]

Figure 1 indicates that, in sulphate medium, mass transport hindrance was negligible, while for Pt in chloride a current *vs.* rotational speed plateau is almost reached at 8000 rpm. Only for Pd in chloride does the rate (i_0) depend linearly on the square root of rotational speed indicating substantial transport control at up to 8000 r.p.m.

Arrhenius plots ($\log_{10} i_0$ *vs* $1/T$) for 25—55°C, shown in Figure 2, enable the enthalpy of activation of both cathodic and anodic reactions at the equilibrium potential ($\eta = 0$) to be obtained[8] as $\Delta H^{\ddagger}_{\eta=0} = -(2{\cdot}3R/F)[\partial \log_{10} i_0/\partial(1/T)]$. A corrected plot is also shown for the Pd–Cl^- case, because electrode dissolution, indicated by the temperature-dependent shift of equilibrium potential in this system, was occurring and had to be allowed for. Dissolution alone was measured at 8000 r.p.m. in *pure* 6M HCl, at the "observed" Fe^{2+}–Fe^{3+} zero-current potentials at each temperature.[9] Corrections for electrode roughening and possible retardation of the redox reaction were not attempted.

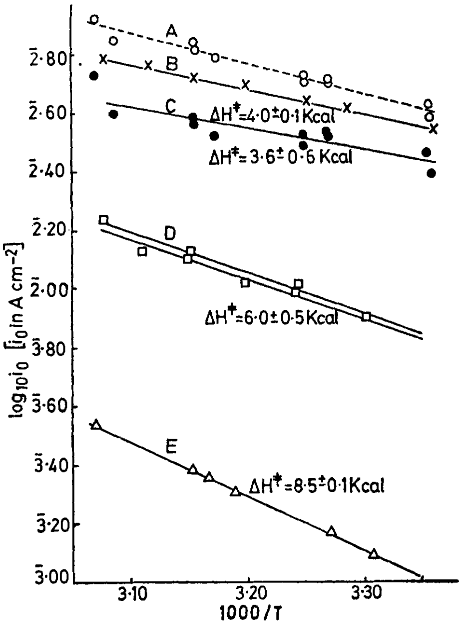

FIGURE 2. *Arrhenius plots of exchange current densities* (*in* A *cm*$^{-2}$) *for* 0·1M Fe^{2+}–0·1M Fe^{3+} *in acidic chloride and sulphate medium of equal ionic strength.* (*A*) Pd *in chloride, uncorrected for electrode dissolution;* (*B*) Pt *in chloride;* (*C*) Pd *in chloride, corrected;* (*D*) Pt *in sulphate;* (*E*) Pd *in sulphate.*

It is evident that both $\Delta H^{\ddagger}$ and i_0 *depend on the metal* when interfacial processes control the current (SO_4^{2-} case), in disagreement with earlier work.[4,5] Further, the solution phase affects the values of i_0 and $\Delta H^{\ddagger}$, the acceleration in the Cl^- system resulting in at least partial transport control with correspondingly low values of $\Delta H^{\ddagger}$. The condition of the electrode also affects i_0 and $\Delta H^{\ddagger}$, a dirty Pt electrode exhibiting lower i_0's and higher $\Delta H^{\ddagger}$ ($>$ 6 kcal). Deactivation of clean electrodes in insufficiently purified solution was accelerated at higher temperatures and resulted in time-dependent Arrhenius plots, the rising T plot leading to an apparently lower $\Delta H^{\ddagger}$ than the true value.[9]

The table indicates the catalytic effect of chloride in our work to be 5-fold at Pt and 25-fold at Pd at 25 °C, falling to 3-fold and 15-fold, respectively, at 50 °C. Bockris *et al.*[5] obtained 2-fold at Pt and 12-fold at Pd (not 50-fold as stated in ref. 4), both at 25 °C.

Solution composition affects reaction in two possible ways: (i) A bulk medium effect—in 6M HCl, the chloro-complexes are preponderant[10] (of 0·1M Fe^{3+} salt added, 0·053M becomes $FeCl_2^+$, 0·037M $FeCl_3$ and 0·009M $FeCl^{2+}$), complexing being less strong in H_2SO_4. The presence of a small strongly electronegative atom such as Cl in the chloro-complexes may result in a more rapid electron exchange with the metal through a process similar to "homogeneous" bridging.[11]

(ii) An electrode effect—specific adsorption of anions by the metal could facilitate closer approach of the ion's co-ordination sphere. In our concentrated media and at the Fe^{2+}–Fe^{3+} equilibrium potential, specific adsorption on all noble metals will be substantial—possibly reaching saturation for the more strongly adsorbed Cl^- ion.[12]

Evidence favourable to the second possibility is the persistence of higher electrode activity in SO_4^{2-} after previous exposure to the Fe^{2+}, Fe^{3+}, Cl^- system.[9] Specific adsorption of halide ions on noble metals is known to be only slowly reversible.[12]

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