15. *Heterogeneous Catalysis in Solution. Part II.*[1] *The Effect of Platinum on Oxidation–Reduction Reactions.*

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The reactions Ce(IV)–Br^-, Ce(IV)–Hg(I), Ce(IV)–H_2O (in $HClO_4$), *p*-benzoquinone–Fe(II), I_3^-–Ti(III), and $Fe(CN)_6^{3-}$–$S_2O_3^{2-}$ are heterogeneously catalysed by platinum metal, whereas the reactions Ce(IV)–H_2O (in H_2SO_4), Fe(III)–Sn(II), and Fe(III)–$S_2O_3^{2-}$ are unaffected by the presence of platinum. Slight catalysis occurs for $Cr_2O_7^{2-}$–I^-, and for $Fe(CN)_6^{3-}$–I^- catalysis is more pronounced at 0° than at 25°. These reactions and those from more than seventy other aqueous catalytic studies collected from the literature have been tabulated. With only one definite exception, the results fit the double hypothesis that platinum is acting as a simple electron-conductor and that the current density–voltage curves of the couples concerned are roughly additive. Heterogeneous catalysis or its absence can therefore be predicted from the electrochemical properties of the reacting couples. Applications of the findings to other aspects of physical chemistry and to preparative work are discussed.

Redox reactions of the type

$$\mathrm{Ox_1} + \mathrm{Red_2} \longrightarrow \mathrm{Red_1} + \mathrm{Ox_2} \qquad (1)$$

are often heterogeneously catalysed by metals. It has been suggested [2-5] that here the metal acts simply as a conductor of electrons, and it was pointed out [1] that catalysis ought

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[1] Part I is considered to be, Spiro, *J.*, 1960, 3678.
[2] Prestwood and Wahl, *J. Amer. Chem. Soc.*, 1949, **71**, 3137.
[3] Garner, *J. Phys. Chem.*, 1952, **56**, 857.
[4] Waind, *Chem. and Ind.*, 1955, 1388.
[5] Baughan, *Discuss. Faraday Soc.*, 1960, **29**, 135.

then to occur with a given metal if both the Ox_1/Red_1 and the Ox_2/Red_2 couples are electrochemically reversible on the metal and that catalysis would not occur if either or both couples are electrochemically irreversible. The limited evidence originally presented to test this idea has now been considerably augmented by further experimental work and by information gathered both from recent publications and from the literature as far back as 1845. These facts are interpreted with the help of a more detailed theoretical picture based on current-density–voltage curves.

Electrochemical Reversibility.—The more reversible a couple, Ox/Red, the faster the velocities at equilibrium of both the forward and the reverse reactions

$$\mathrm{Ox} + ne^- \rightleftharpoons \mathrm{Red} \qquad (2)$$

at the metal surface. Reversibility is, therefore, expressed quantitatively by this velocity which, in electrochemical terms, is the exchange current density i_0 in amp. cm.$^{-2}$. Any uncertainty as to the concentrations to which i_0 refers is avoided by use of the standard exchange current density i_{00} which corresponds to the rate of the forward or backward reaction at equilibrium when each species involved in the reaction is present to the extent of 1 mole l.$^{-1}$. For first-order processes,

$$i_0 = i_{00}[\mathrm{Ox}]^{1-\alpha}[\mathrm{Red}]^{\alpha} \qquad (3)$$

where α is the transfer coefficient of the cathodic process. Although values of i_{00} at platinum electrodes are known for relatively few couples,[6] an estimate of the degree of reversibility can often be obtained from e.m.f. behaviour or from simple current–voltage curves. The latter are treated in more detail in the next Section, and it suffices to state here that high overpotentials or the occurrence of hysteresis loops are sure signs of irreversibility. E.m.f. criteria of reversibility have been given by Luther [7] and others; [8] they are, briefly, that if a couple rapidly sets up at an electrode a constant reproducible potential which varies with concentration as expected from the Nernst equation, and which is unchanged by shaking and by slight anodic or cathodic polarization, then that couple is reversible at the electrode in question and the exchange current density is probably at least 10^{-6} amp. cm.$^{-2}$. If the contrary behaviour is found, the couple is electrochemically irreversible and i_0 at the electrode is probably 10^{-10} amp. cm.$^{-2}$ or less. Table 1 summarizes the results at platinum electrodes obtained by all methods. In some cases no definite information is available, and in others (MoO_2^+/Mo^{3+}, V^{3+}/V^{2+}, Ti^{3+}/Ti^{2+}, Cr^{3+}/Cr^{2+}) measurements are difficult because the platinum electrode catalyses the reaction between the couple and the solvent, a point that will be taken up again later. Within each column the couples have been given in the order of decreasing E^0, the standard electrode potential in volts with the I.U.P.A.C. sign. Some of these E^0 values, taken for the most part directly from Latimer's compilation,[9] are actually formal and not standard potentials.

Current Density–Voltage Curves.—Fig. 1 shows curves of current density against electrode potential for three independent redox couples at platinum electrodes. The presentation conforms to polarographic usage, the upper half depicting reduction processes with positive cathodic currents and the potential V becoming more negative from left to right. The points B, E, and Q at which the curves cross the zero-current axis are the Nernst-equation potentials, the slopes at these points being given by [20]

$$(\partial i/\partial V)_{i\rightarrow 0} = -\boldsymbol{nF}i_0/\nu\boldsymbol{R}T \qquad (4)$$

where n is the number of electrons in reaction (2), $\boldsymbol{F}$ is Faraday's constant, $\boldsymbol{R}$ the gas constant, T the absolute temperature, and ν the stoicheiometric number.[20] The slope is thus proportional to the exchange current density i_0 of the couple concerned, so that PQR

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[6] Spiro, *Electrochem. Acta*, 1964, **9**, 1531.
[7] Luther, *Z. Elektrochem.*, 1907, **13**, 289.
[8] Das and Ives, *J.*, 1962, 1619.
[9] Latimer, " Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N.J., 2nd edn., 1952.

TABLE 1.

Standard electrode potentials at 25° in water (E^0) and reversibility characteristics of redox couples involved in the kinetic experiments.

Reversible couples	E° [9]	Reversibility	Other couples	E° [9]	Reversibility
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	+1·70	rev.[6,10]	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2·01	irrev.[21,22]
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	+1·51 [11]	rev.[6,11]	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1·84	irrev.[10]
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1·36	rev.[6,9]	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1·77	irrev.[23]
$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	+1·25	rev.[6,10]	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1·51	irrev.[22]
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \tfrac{1}{2}I_2 + 3H_2O$	+1·20	mod. rev.[10]	$ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O$	+1·45	
$NpO_2^{2+} + e^- \rightleftharpoons NpO_2^+$	+1·15	rev.[12,13]	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1·33	irrev.[9,22]
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1·09	rev.[6,10]	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1·23	irrev.[9,20,29]
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1·00	mod. rev.[10]	$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1·19	irrev.[24]
$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+0·92	rev.[10]	$NpO_2^+ + 4H^+ + e^- \rightleftharpoons Np^{4+} + 2H_2O$	+0·74	irrev.[12]
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0·77	rev.[6,14]	$H_2MoO_4 + 2H^+ + e^- \rightleftharpoons MoO_2^+ + 2H_2O$	+0·5	uncertain [10]
$C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_4(OH)_2$	+0·70	rev.[6,9,10]	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0·15	irrev.[10]
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0·54 [15]	rev.[6,16]	$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0·1	irrev.[25]
$MB^+ + H^+ + 2e^- \rightleftharpoons MW$	+0·53	rev.[17]	$HCHO + 2H^+ + 2e^- \rightleftharpoons CH_3{\cdot}OH$	+0·19	irrev.[25a]
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	+0·36	rev.[6,9,10]	$CH_3{\cdot}CHO + 2H^+ + 2e^- \rightleftharpoons CH_3{\cdot}CH_2{\cdot}OH$	+0·19	irrev.[25a]
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0·34	rev.[18]	$MoO_2^+ + 4H^+ + 2e^- \rightleftharpoons Mo^{3+} + 2H_2O$	0·0	unknown
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0·34	mod. rev.[10]	$CO_2(g) + 4H^+ + 4e^- \rightleftharpoons HCHO + H_2O$	−0·07	irrev.[25a]
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+0·33	mod. rev.[10]	$CH_3{\cdot}CO_2H + 2H^+ + 2e^- \rightleftharpoons CH_3{\cdot}CHO + H_2O$	−0·12	
$TiO_2^+ + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$	+0·1	rev.[10]	$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	−0·20	irrev.[25a,26]
$Co(NH_3)_6^{3+} + e^- \rightleftharpoons Co(NH_3)_6^{2+}$	+0·1	rev.[19]	$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0·25	unknown
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	±0·00	rev.[9,20]	$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}$	−0·4	unknown
$Eu^{3+} + e^- \rightleftharpoons Eu^{2+}$	−0·43	rev.[10]	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	−0·41	unknown
			$2CO_2(g) + 2H^+ + 2e^- \rightleftharpoons (CO_2H)_2$	−0·49	irrev.[27]

MB+ is Methylene Blue; MW is Methylene White.

represents a fairly irreversible couple whereas ABC and DEF are reversible. Let us now consider a solution in which two of the couples, say ABC and PQR, are present together. If they do not interfere or interact with each other at the electrode surface, their joint effect can be represented by a curve in which the current, at any given potential, is the sum of the currents which ABC and PQR individually display at that potential.[28] The current density–voltage curve for the mixture will therefore cross the line BEQ of zero net current at a point, b, such that the cathodic current density, ab, caused by ABC is numerically equal to the anodic current density, bc, arising from the PQR couple. The mixture potential, b, is seen to be much closer to the e.m.f., B, of the reversible system than to that (Q) of the irreversible one. The rate at which the ABC system is reduced at potential b, and that at which the PQR system is oxidised, is given by the current density ab (or bc), and it is this which represents the rate of the heterogeneous reaction on the platinum surface. This conclusion is a phenomenological one and is valid whether the slow step at the mixture potential for either couple is due to electron transfer at the surface or to diffusion to or from the surface. In the latter case the appropriate current density–voltage curve would be horizontal (limiting current), and this does not affect the additivity principle.[28] As regards units, amp. cm.$^{-2}$ is equal to coulomb sec.$^{-1}$ cm.$^{-2}$, and by means of Faraday's

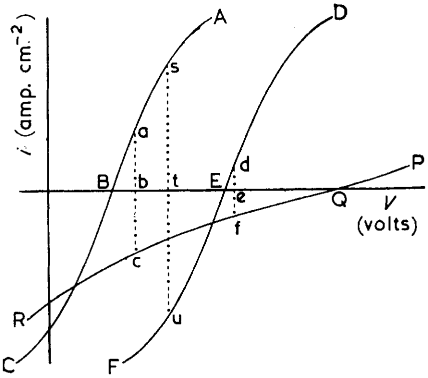

FIG. 1. Schematic diagram of current density–voltage curves for two reversible couples (ABC, DEF) and one irreversible couple (PQR).

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[10] According to the e.m.f. references listed in Latimer, ref. 9.

[11] Grube and Huberich, *Z. Elektrochem.*, 1923, **29**, 8.

[12] Hindman, Magnusson, and La Chapelle, *J. Amer. Chem. Soc.*, 1949, **71**, 687.

[13] Cohen and Hindman, *J. Amer. Chem. Soc.*, 1952, **74**, 4679.

[14] Peters, *Z. phys. Chem.*, 1898, **26**, 193.

[15] Riddiford, *Z. Elektrochem.*, 1957, **61**, 752.

[16] According to the e.m.f. references listed by Riddiford, ref. 15.

[17] (*a*) Clark, Cohen, and Gibbs, " Studies on Oxidation–Reduction I—X," *Hygienic Lab. Bull.* No. 151, Washington, D.C., 1928, Part VIII, p. 224; (*b*) Holst, *Z. phys. Chem.*, 1935, **175***A*, 99, 120; (*c*) Vetter and Bardeleben, *Z. Elektrochem.*, 1957, **61**, 135.

[18] Hillson, *Trans. Faraday Soc.*, 1954, **50**, 385.

[19] Bjerrum, " Metal Ammine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1957, pp. 242—243.

[20] Bockris, in " Modern Aspects of Electrochemistry," ed. Bockris, Butterworths, London, 1954, Vol. I, ch. 4.

[21] Fredenhagen, *Z. anorg. Chem.*, 1902, **29**, 396.

[22] Weigert, *Z. phys. Chem.*, 1907, **60**, 513.

[23] Gerischer and Gerischer, *Z. phys. Chem.* (*Frankfurt*), 1956, **6**, 178; Winkelmann, *Z. Elektrochem.*, 1956, **60**, 731.

[24] Sugino and Aoyagi, *J. Electrochem. Soc.*, 1956, **103**, 166.

[25] Thatcher, *Z. phys. Chem.*, 1904, **47**, 641; Scheffer and Böhn, *Z. Elektrochem.*, 1929, **35**, 484.

[25a] Liang and Franklin, *Elektrochim. Acta*, 1964, **9**, 517.

[26] v. Euler and Ölander, *Z. phys. Chem.*, 1928, **137***A*, 29; Gottlieb, *J. Electrochem. Soc.*, 1964, **111**, 465; Fleischmann, Johnson, and Kuhn, *ibid.*, p. 602.

[27] Lingane, *J. Electroanal. Chem.*, 1960, **1**, 379; Johnson, Wroblowa, and Bockris, *Electrochim. Acta*, 1964, **9**, 639.

[28] Wagner and Traud, *Z. Elektrochem.*, 1938, **44**, 391; Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1940, **62**, 2170.

constant this is readily converted into equiv. sec.$^{-1}$ cm.$^{-2}$, the rate of a chemical surface reaction.

A number of special cases can now be treated in terms of this picture. (1) Both couples are reversible, *e.g.*, ABC and DEF. The current density–voltage curves of both are steep, and the cathodic and anodic currents (st, tu) at the mixture potential are then very large and so result in a rapid heterogeneous reaction. Catalysis by platinum is thus to be expected and, as the kinetic results will show, is always found unless obscured by the speed of the homogeneous reaction. (2) One couple is reversible (ABC or DEF) and the other irreversible (PQR). Fig. 1 shows that the mixture potential (b or e) is in each case much closer to the e.m.f. of the reversible couple (B or E) than to that of the irreversible one (Q). The current (ab or de) at the mixture potential is smaller than that (st) in case (1) but is nevertheless appreciable, with current ab much greater than de. The heterogeneous reaction between the two couples can thus be quite fast even if one couple is irreversible and, other things being equal, the rate increases the further apart the e.m.f.s of the two couples. That this increase is exponential follows from Tafel's equation:[20]

$$\eta = b_{\text{cath(anod)}} \log_{10} (i/i_0), \quad (|\eta| \geqslant ca.\ 0{\cdot}1\ \text{v}) \qquad (5)$$

where the overpotential η is here the difference between the mixture potential and the Nernst potential, and where the Tafel slope b_{cath} is equal to $2{\cdot}303\nu\boldsymbol{RT}/n\boldsymbol{F}\alpha$ and b_{anod} to $2{\cdot}303\nu\boldsymbol{RT}/n\boldsymbol{F}(1 - \alpha)$. As an example, for the couple

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

$i_0 = 2 \times 10^{-10}$ amp. cm.$^{-2}$ and $b_{\text{anod}} = 0{\cdot}09$, $b_{\text{cath}} = 0{\cdot}11$.[29] Then, overpotentials of 0·2, 0·5, and 1·0 v give values for the current density i of approximately 10^{-8}, 10^{-5}, and 1 amp. cm.$^{-2}$, respectively. In practice the current density in the last case will be much less and will be controlled by the rate of diffusion. (3) Where both couples are irreversible the situation is similar to (2) except that the mixture potential, instead of being near the e.m.f. of

TABLE 2.

Catalytic effect of platinum on isotopic oxidation–reduction exchange reactions.

Oxidant	Reductant	Medium	Temp.	Form of Pt	Catalysis	Ref.
Ce^{4+}	Ce^{3+}	3M-$HClO_4$	0°	foil	marked	30
Tl^{3+}	Tl^{+}	2·5M-$HClO_4$ + 1·1M-$NaClO_4$	37·3	platinized	marked	2, 31
$Co(NH_3)_6{}^{3+}$	$Co(NH_3)_6{}^{2+}$	ammonia buffer	64·5	foil	marked	32
$NpO_2{}^{2+}$	$NpO_2{}^{+}$	3·0M-$HClO_4$	0	foil?	slight	33
$NpO_2{}^{+}$	Np^{4+}	M-$HClO_4$	47	foil	slight	34
		0·1M-$HClO_4$ + 0·9M-$NaClO_4$	47	foil	none	34
$MnO_4{}^{-}$	Mn^{2+}	3·16M-$HClO_4$	25	platinized	slight	35
Co^{3+}	Co^{2+}	1·0M-$HClO_4$	3·2	foil	none	36

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[29] Bockris and Huq, *Proc. Roy. Soc.*, 1956, *A*, **237**, 277.
[30] Fronaeus and Östman, *Acta Chem. Scand.*, 1956, **10**, 769.
[31] Challenger and Masters, *J. Amer. Chem. Soc.*, 1956, **78**, 3012.
[32] Biradar, Stranks, and Vaidya, *Trans. Faraday Soc.*, 1962, **58**, 2421.
[33] Cohen, Sullivan, and Hindman, *J. Amer. Chem. Soc.*, 1955, **77**, 4964.
[34] Sullivan, Cohen, and Hindman, *J. Amer. Chem. Soc.*, 1954, **76**, 4275.
[35] Adamson, *J. Phys. Chem.*, 1951, **55**, 293.
[36] Bonner and Hunt, *J. Amer. Chem. Soc.*, 1960, **82**, 3826.
[37] Shaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 2169.
[38] Engler and Wöhler, *Z. anorg. Chem.*, 1902, **29**, 1, 17.
[39] Vondracek, *Z. anorg. Chem.*, 1904, **39**, 24.
[40] Gilks and Waind, *Discuss. Faraday Soc.*, 1960, **29**, 102.
[41] Millon, *Ann. Chim. Phys.*, 1845, **13**, 29; Lemoine, *Compt. rend.*, 1907, **144**, 357; 1921, **173**, 7.
[42] Schwabe, *Z. Elektrochem.*, 1957, **61**, 744.
[43] Bredig and Sommer, *Z. phys. Chem.*, 1910, **70**, 34.
[44] Just, *Z. phys. Chem.*, 1908, **63**, 513.
[45] Spiro, Johnston, and Wagner, *Electrochim. Acta*, 1961, **3**, 264.
[46] Bennett and Sheppard, *J. Phys. Chem.*, 1962, **66**, 1275.
[47] Nicol and Rosseinsky, *Chem. and Ind.*, 1963, 1166.
[48] Nicol and Rosseinsky, *Proc. Chem. Soc.*, 1963, 16.

TABLE 3.

Catalytic effect of platinum on various oxidation–reduction reactions.

Reaction	Medium	Temp.	Form of Pt	Catalysis	Ref.†
$2Ce(IV) + Tl(I) \longrightarrow 2Ce(III) + Tl(III)$	N-H_2SO_4	25°	black	* positive	37
$2Ce(IV) + 2Br^- \longrightarrow 2Ce(III) + Br_2$	M-H_2SO_4	20	foil	* marked	p.w.
$Ce(IV) + Hg(I) \longrightarrow Ce(III) + Hg(II)$	2M-$HClO_4$	15	foil	* marked	p.w.
$H_2O_2 + 2H^+ + 2Cl^- \longrightarrow 2H_2O + Cl_2$	dil. HCl	hot	black	positive	38
$ClO_3^- + 6H^+ + 6Fe(II) \longrightarrow Cl^- + 3H_2O + 6Fe(III)$			black	positive	39
$Tl(III) + 2Fe(II) \longrightarrow Tl(I) + 2Fe(III)$	0·57M-$HClO_4$ + 0·3M-$NaClO_4$	room	foil	* positive	40
$2IO_3^- + 2H^+ + 5(CO_2H)_2 \longrightarrow I_2 + 10CO_2 + 6H_2O$			black	positive	41
$2Fe(III) + 3I^- \longrightarrow 2Fe(II) + I_3^-$			black	* positive	4
		25	foil	* positive	1
	0·5M-KNO_3	0	foil	* marked	p.w.
$2Fe(III) + HCO_2H \longrightarrow 2Fe(II) + CO_2 + 2H^+$		25?	powder	positive	42
$C_6H_4O_2 + 2Fe(II) + 2H^+ \longrightarrow C_6H_4(OH)_2 + 2Fe(III)$	0·38M-$HClO_4$ + 0·2M-$NaClO_4$	20	foil	* marked	p.w.
$2MB^+ + HCHO + H_2O \longrightarrow 2MW + CO_2 + 2H^+$	2% gelatin	70	sol	positive	43
$MB^+ + HCO_2H \longrightarrow MW + CO_2 + H^+$	0·004% gelatin	25	sol	positive	26, 43
$I_3^- + 2Ti(III) \longrightarrow 3I^- + 2Ti(IV)$	0·13M-HCl + 0·1M-KI	20	foil	* marked	p.w.
$2Fe(CN)_6^{3-} + 3I^- \longrightarrow 2Fe(CN)_6^{4-} + I_3^-$	dil. KI	room	bright	* positive	44
			black	* positive	4
	M-, 2M-KNO_3	25	foil	* positive	45, p.w.
	M-KNO_3	0	foil	* marked	p.w.
$2Fe(CN)_6^{3-} + 2S_2O_3^{2-} \longrightarrow 2Fe(CN)_6^{4-} + S_4O_6^{2-}$	M-KCl	20	foil	marked	p.w.
$Cr_2O_7^{2-} + 14H^+ + 9I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_3^-$	0·4M-NaCl + 0·04M-H^+	5, 25	foil	slight	p.w.
$S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-$		room	wire	none	1
$Co(III) + Fe(II) \longrightarrow Co(II) + Fe(III)$	M-$HClO_4$	0	foil	none	46
$Mn(III) + Fe(II) \longrightarrow Mn(II) + Fe(III)$	M-H^+, 3M-ClO_4^-	15		* none	47
$V(V) + Fe(II) \longrightarrow V(IV) + Fe(III)$	M-ClO_4^-			* none	48
$2Fe(III) + Sn(II) \longrightarrow 2Fe(II) + Sn(IV)$	0·1M-HCl	0	foil	none	p.w.
$2Fe(III) + 2S_2O_3^{2-} \longrightarrow 2Fe(II) + S_4O_6^{2-}$	0·25M-KNO_3	0	foil	none	p.w.

† p.w. = present work; details are given in the Experimental section.

one couple, is now some distance away from both e.m.f.s. The cathodic (or anodic) current at density the mixture potential, and hence the heterogeneous rate, will be small unless the two e.m.f.s are far apart.

Kinetic Results.—Table 2 summarises the catalytic effect of platinum on isotopic exchange reactions of the kind

$$\mathrm{Ox_1 + Red_1^* \longrightarrow Red_1 + Ox_1^*} \qquad (6)$$

which may be regarded as particularly simple cases of general redox reactions of type (1). The effect of platinum on the latter is contained in Table 3 while Table 4 is restricted to redox reactions involving the H^+/H_2 couple and Table 5 to those involving O_2/H_2O or O_2/OH^-. Although care has been taken in these Tables to describe accurately the degrees of catalysis, and although such important variables as medium, temperature, and the type of catalyst have been stated explicitly, it should be borne in mind in comparing these results that other important factors (stirring rate, real area of catalytic surface and the ratio of this area to solution volume) cannot usually be assessed from the published information. It is possible, therefore, that in a few cases slight catalysis has been exaggerated by extreme experimental conditions and that in others positive catalysis has been overlooked because of unfavourable circumstances. An example is provided by the Ce^{4+}–Ce^{3+} exchange reaction. Fronaeus and Östman [30] (Table 2) shook the cerium solutions during their exchange experiments and found marked catalysis by platinum with diffusion to the metal surface as a rate-determining step. No appreciable catalytic effect would therefore be expected under quiescent conditions. This probably explains why Duke and Parchen,[78] who appear to have agitated their solution at the beginning of a run only, found virtually no catalysis by platinum.

Let us now examine all the isotopic exchange reactions in Table 2. Current–voltage diagrams become trivial when products and reactants are chemically identical, and a test for electron-transfer through the metal is simply that, given good stirring,[30] catalysis should occur with electrochemically reversible couples and be absent for irreversible ones. Comparison with Table 1 shows this to be true for the first 4 reactions in Table 2 as well as the last one. It is doubtful whether the NpO_2^+–Np^{4+} exchange is an exception; the catalysis was slight even in concentrated perchloric acid solution and the e.m.f. evidence of irreversibility refers [12] to M-hydrochloric acid, a different medium in which complexing must have occurred. The MnO_4^-–Mn^{2+} result, too, is not strictly comparable with the others, for the platinum induced the formation of some manganese dioxide [35] through whose presence on the metal surface other catalytic processes could well become possible. Altogether, then the exchange reactions provide some good support for an electron-transfer-through-platinum mechanism and no real evidence against it.

We turn now to Tables 3, 4, and 5.† To make the discussion more concise, an asterisk denotes any reaction between couples both of which are reversible or moderately reversible at platinum. It is immediately apparent that positive catalysis by platinum has been observed for all asterisked processes except Mn(III)–Fe(II) and V(V)–Fe(II). In these two cases, however, the homogeneous rates were too fast for the effect of added platinum to

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† The actual charges of ions have been given in Tables 1 and 2, as these deal with infinitely dilute solutions or with those containing perchloric acid. Tables 3—5 list reactions in various complexing media and therefore the valence of ions is written more generally, *e.g.*, Co(III) instead of Co^{3+}.

[49] Boutry, Bloch, and Balaceanu, *Bull. Soc. chim. France*, 1962, 988.
[50] Cooke, *Chem. News*, 1888, **58**, 103.
[51] Ernst, *Z. phys. Chem.*, 1901, **37**, 448.
[52] Boutry, Bloch, and Balaceanu, *Bull. Soc. chim. France*, 1961, 1098.
[53] Rosenblatt, *J. Amer. Chem. Soc.*, 1940, **62**, 1092.
[54] Eggert, *Z. Elektrochem.*, 1914, **20**, 370.
[55] Clark and Cohen, "Studies on Oxidation–Reduction I—X," *Hygienic Lab. Bull.* No. 151, Washington, D.C., 1928, Part III, p. 34; Clark, Cohen, and Gibbs, *ibid.*, Part VIII, p. 181.
[56] Chilesotti, *Z. Elektrochem.*, 1906, **12**, 146, 160.
[57] Luther and Michie, *Z. Elektrochem.*, 1906, **14**, 826.
[58] Vavon, *Ann. Chim.*, 1914, **1**, 144, 168.

TABLE 4.

Catalytic effect of platinum on various oxidation–reduction reactions involving hydrogen.

Reaction	Medium	Temp.	Form of Pt	Catalysis	E° of other couple	Ref.
$2Ce(IV) + H_2 \longrightarrow 2Ce(III) + 2H^+$		30°	sol, Pt/C	* positive	1·5?	49
$ClO_3^- + 3H_2 \longrightarrow Cl^- + 3H_2O$	satd. $KClO_3$	room	black	positive	1·45	50
$Cl_2 + H_2 \longrightarrow 2Cl^- + 2H^+$		room	black	* positive	1·36	50
$Cr_2O_7^{2-} + 8H^+ + 3H_2 \longrightarrow 2Cr^{3+} + 7H_2O$	acid	room	black	positive	1·33	50
$O_2 + 2H_2 \longrightarrow 2H_2O$			sol	positive	1·23	51
$Br_2 + H_2 \longrightarrow 2Br^- + 2H^+$		room	black	* positive	1·09	50
$2HgCl_2 + H_2 \longrightarrow Hg_2Cl_2 + 2Cl^- + 2H^+$		room	black	* positive	0·92	50
$2Fe(III) + H_2 \longrightarrow 2Fe(II) + 2H^+$	chloride soln.		black, sol	* positive	0·77	21, 50
	sulphate soln.	30	black, sol, Pt/C	* positive		50, 52
$C_6H_4O_2 + H_2 \longrightarrow C_6H_4(OH)_2$	5% HCl	room	Pt/C	* positive	0·70	53
$V(V) + H_2 \longrightarrow V(III) + 2H^+$	2N-H_2SO_4	room	platinized	* positive	0·67	54
$MB^+ + H_2 \longrightarrow MW + H^+$		room	Pt/asbestos, black	* positive	0·53	55, 17*b*
$2Mo(VI) + H_2 \longrightarrow 2Mo(V) + 2H^+$	concd. HCl	room	platinized	positive	0·5	56
	2N-H_2SO_4	room	platinized	positive		54
$2Fe(CN)_6^{3-} + H_2 \longrightarrow 2Fe(CN)_6^{4-} + 2H^+$		room	black	* positive	0·36	50
$U(VI) + H_2 \longrightarrow U(IV) + 2H^+$	0·1N-H_2SO_4	room	black	* positive	0·33	57
$CH_3{\cdot}CHO + H_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}OH$		room	black	positive	0·19	58
$2Ti(IV) + H_2 \longrightarrow 2Ti(III) + 2H^+$	N-H_2SO_4	25, 30	platinized, sol, Pt/C *	* positive	0·1	59, 49
$Mo(III)$ (green) $+ 2H^+ \longrightarrow Mo(V) + H_2$	2N-HCl, N-H_2SO_4	room	platinized	positive	0·0	60
$2V(II) + 2H^+ \longrightarrow 2V(III) + H_2$		room	platinized	positive	−0·25	61
$2Ti(II) + 2H^+ \longrightarrow 2Ti(III) + H_2$	dil. HCl	0	foil?	positive	−0·4	62
$2Cr(II) + 2H^+ \longrightarrow 2Cr(III) + H_2$	N-HCl	25	platinized	positive	−0·41	14, 63
$2Cr(II) + 12NH_3 + 2H^+ \longrightarrow 2Cr(NH_3)_6^{3+} + H_2$	4—6M-NH_4Cl + 8M-NH_3	20	reduced	positive		64
$2Eu(II) + 2H^+ \longrightarrow 2Eu(III) + H_2$	concd. HCl + $NaClO_4$	39·4?	platinized	* positive	−0·43	65
$Cu(II) + H_2 \longrightarrow Cu + 2H^+$		30	sol, Pt/C	init. positive	0·34	49
$2Co(CN)_6^{4-} + 2H^+ \longrightarrow 2Co(CN)_6^{3-} + H_2$		cold	platinized	slight		14, 66
$ClO_4^- + H_2 \longrightarrow ClO_3^- + H_2O$		room	black	none	1·19	50, 67
$HCHO + H_2 \longrightarrow CH_3{\cdot}OH$		room	black	none	0·19	58

TABLE 5.

Catalytic effect of platinum on various oxidation–reduction reactions involving oxygen.

Reaction	Medium	Temp.	Form of Pt	Catalysis	$E°$ of other couple	Ref.†
$2Co(III) + H_2O \longrightarrow 2Co(II) + 2H^+ + \frac{1}{2}O_2$	N-H_2SO_4	0°	platinized	positive	1·84	68
$2Ce(IV) + H_2O \longrightarrow 2Ce(III) + 2H^+ + \frac{1}{2}O_2$	2M-$HClO_4$	18	foil	positive	1·70	p.w.
	M-H_2SO_4	20	foil	none	1·44	p.w.
$Cl_2 + H_2O \longrightarrow 2Cl^- + 2H^+ + \frac{1}{2}O_2$		room	black	positive	1·36	69
$Tl(III) + H_2O \longrightarrow Tl(I) + 2H^+ + \frac{1}{2}O_2$	0·2M-H_2SO_4?	18	platinized	very slight	1·25	70
$Tl(I) + 2H^+ + \frac{1}{2}O_2 \longrightarrow Tl(III) + H_2O$	N-HNO_3?	room	black	very slight	1·25	71
$2V(IV) + 2H^+ + \frac{1}{2}O_2 \longrightarrow 2V(V) + H_2O$	2N-H_2SO_4	17	platinized	none	1·00	54
$2Fe(II) + 2H^+ + \frac{1}{2}O_2 \longrightarrow 2Fe(III) + H_2O$	0·05N-HCl	room	sol	slight	0·77	21
$C_6H_4(OH)_2 + \frac{1}{2}O_2 \longrightarrow C_6H_4O_2 + H_2O$	N-H_2SO_4	17	platinized	slight	0·70	54
$3I^- + 2H^+ + \frac{1}{2}O_2 \longrightarrow I_3^- + H_2O$	dil. H_2SO_4	room	black	positive	0·54	72
$2V(III) + 2H^+ + \frac{1}{2}O_2 \longrightarrow 2V(IV) + H_2O$	2N-H_2SO_4	17	platinized	positive	0·34	54
$U(IV) + 2H^+ + \frac{1}{2}O_2 \longrightarrow U(VI) + H_2O$	0·1N-, 2N-H_2SO_4	17	platinized	positive	0·33	57, 54
$CH_3{\cdot}CH_2{\cdot}OH + \frac{1}{2}O_2 \longrightarrow CH_3{\cdot}CHO + H_2O$	acetate buffer	20	powder	positive	0·19	73
	0·1M-NaOH	20	powder	positive	0·19	73
$2S_2O_3^{2-} + H_2O + \frac{1}{2}O_2 \longrightarrow S_4O_6^{2-} + 2\,OH^-$		room	platinized	slight	0·1	74
$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$			sol	positive	0·00	51
$H{\cdot}CHO + O_2 \longrightarrow CO_2 + H_2O$		room	sponge	positive	−0·07	75
$CH_3{\cdot}CHO + \frac{1}{2}O_2 \longrightarrow CH_3{\cdot}CO_2H$	acetate buffer	20	powder	slight	−0·12	73
	0·1M-NaOH	20	powder	positive	−0·12	73
$HCO_2H + \frac{1}{2}O_2 \longrightarrow CO_2 + H_2O$		20	Pt/$BaSO_4$	positive	−0·20	76
$(CO_2H)_2 + \frac{1}{2}O_2 \longrightarrow 2CO_2 + H_2O$		room—50	sponge, sol	positive	−0·49	77

† p.w. = present work; details are given in the Experimental section.

have been detected. From details kindly provided by Dr. Rosseinsky, we calculate that under his experimental conditions [47,48] any heterogeneous process, even if diffusion-controlled, would have been equivalent to a first-order reaction with a half-time of at least 5000 seconds. The half-times of the homogeneous reactions were less than 20 seconds.

The other fact that quickly emerges when asterisks and catalytic effects are compared is that numerous reactions involving irreversible couples are positively catalysed. Table 5, entirely devoted to the irreversible oxygen couple, is the most striking demonstration of this. We note first that, apart from the oxidation of water by chlorine, hardly any catalysis is observed for a group of reactions near the top of Table 5 which all involve couples with E^0 values around that of the oxygen couple itself, 1·23 v. The reason becomes clear when we recall from the previous Section that, to provide current densities of *ca.* 10^{-8}, 10^{-5}, and 1 amp. cm.$^{-2}$, the oxygen couple must be subject to overpotentials of 0·2, 0·5, and 1 v, respectively. It is then not surprising that we found the reaction

$$2\mathrm{Ce(IV)} + H_2O \longrightarrow 2\mathrm{Ce(III)} + 2H^+ + \tfrac{1}{2}O_2$$

to be catalysed by platinum in perchloric acid, where the formal Ce(IV)/Ce(III) potential is 1·70 v [9] ($\eta = 0·47$ v), and not catalysed in sulphuric acid in which the formal potential is only 1·44 v [9] ($\eta = 0·21$ v). Similarly, the fact that O_2 in the presence of platinum oxidises V(III) to V(IV) but not to V(V), although the latter product is thermodynamically feasible, is readily understood when we remember (Table 1) that both the V(IV)/V(III) and the V(V)/V(IV) couples are reversible but that their E^0 values are, respectively, 0·34 and 1·00 v. An adequate overpotential for the oxygen couple is therefore provided on the platinum surface by the first-named vanadium couple but not by the second. In the same way we can explain the virtual absence of catalysis in the Tl(I)–O_2 and Tl(III)–H_2O reactions, the slight positive catalysis in the oxidation by oxygen of Fe(II) and quinol and the greater catalysis in the oxidation of I^-, U(IV), and H_2. In the $S_2O_3^{2-}$–O_2 reaction both couples are irreversible [case (3) of the theory] but the large difference of *ca.* 0·7 v between the two electrode potentials in neutral solution should be sufficient to provide both a cathodic overpotential for the oxygen couple and an anodic one for $S_4O_6^{2-}/S_2O_3^{2-}$ big enough to account for the small catalytic effect observed. A similar interpretation applies to the influence of platinum on the oxidation by oxygen of the various organic reagents: in the case of oxalic acid, $(CO_2H)_2$, an adequate overpotential for both couples is provided with the platinum surface at around 0·8 v [27] and at lower potentials [25a,26] for ethanol, formaldehyde, and formic acid. The only reaction in Table 5 that does not seem to agree with the theory is the catalysed evolution of oxygen from chlorine water, since the E^0 values in

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[59] Diethelm and Foerster, *Z. phys. Chem.*, 1908, **62**, 129, 145; Denham, *ibid.*, 1910, **72**, 641.

[60] Foerster, Fricke, and Hausswald, *Z. phys. Chem.*, 1930, **146**, 81, 177.

[61] Rutter, *Z. anorg. Chem.*, 1907, **52**, 368.

[62] Forbes and Hall, *J. Amer. Chem. Soc.*, 1924, **46**, 385.

[63] Jablczynski, *Z. phys. Chem.*, 1908, **64**, 748.

[64] Schäffer, in Kirschner, ed., " Advances in the Chemistry of the Coordination Compounds," Macmillan, New York, 1961, p. 628.

[65] Meier and Garner, *J. Phys. Chem.*, 1952, **56**, 853; Garner, *ibid.*, p. 857.

[66] Manchot and Herzog, *Ber.*, 1900, **33**, 1742.

[67] Gall and Manchot, *Ber.*, 1925, **58***B*, 482.

[68] Oberer, " Beiträge zur Kenntnis des Kobaltisulfates," Diss., Zürich, 1903, pp. 52—53.

[69] Schönbein, *J. prakt. Chem.*, 1866, **98**, 76.

[70] Grube and Hermann, *Z. Elektrochem.*, 1920, **26**, 291.

[71] Abegg and Spencer, *Z. anorg. Chem.*, 1905, **44**, 379, 400.

[72] Schönbein, *J. prakt. Chem.*, 1868, **105**, 198 (see footnote on p. 207).

[73] Müller and Schwabe, *Kolloid-Z.*, 1930, **52**, 163.

[74] Thatcher, *Z. phys. Chem.*, 1904, **47**, 641, 686.

[75] Delépine, *Bull. Soc. chim. France*, 1897, **17**, 938.

[76] Müller and Schwabe, *Z. Elektrochem.*, 1928, **34**, 170.

[77] Sulc, *Z. phys. Chem.*, 1899, **28**, 719; Sano, *Bull. Chem. Soc. Japan*, 1939, **14**, 121; 1940, **15**, 196, 204.

[78] Duke and Parchen, *J. Amer. Chem. Soc.*, 1956, **78**, 1540; Parchen and Duke, *U.S. Atom. Energy Comm.*, 1955, ISC–671.

Table 1 are only 0·13 v apart. It is, however, not the difference in standard potentials but rather the difference in the actual potentials in the solution concerned that determines the overpotential. In a saturated solution of chlorine in water at 25° the activities of the H^+ and Cl^- ions produced by hydrolysis can be calculated to be 0·03, and, if we also correct $E^0(Cl_2/Cl^-)$ for the free energy [9] of Cl_2(aq.) as compared with Cl_2(g), we obtain

$$E(Cl_2/Cl^-) = 1{\cdot}46 \text{ v}, \quad E(O_2/H_2O) = 1{\cdot}14 \text{ v}.$$

An anodic overpotential of 0·32 v would give rise to a current density for the oxygen couple of almost 10^{-6} amp. cm.$^{-2}$, and the observation of positive catalysis is therefore no longer in conflict with theory. Moreover, with intermediates such as OCl^- present, it is by no means unlikely that the current density–voltage curves of the Cl_2/Cl^- and O_2/H_2O couples interact with each other at the platinum surface.

Returning now to Tables 3 and 4, we are faced with the fact that exchange current densities and Tafel slopes are not known for most of the other irreversible couples, and indeed even qualitative indications of reversibility are often lacking (Table 1). We can therefore say no more than that, with reactions involving two couples of known or possible irreversibility, a finding of positive catalysis is not unreasonable in terms of our theory if the E^0 values of the two reacting couples are fairly far apart. This applies to all the non-asterisked processes in the upper half of Table 4 and to several reactions in Table 3 such as HIO_3–$(CO_2H)_2$ and $Cr_2O_7^{2-}$–I^-. On the other hand, our theory would not lead us to expect catalysis by platinum if the E^0 values are close together. Where a couple is known to be as highly irreversible as ClO_4^-/ClO_3^-, it could be predicted that reactions even with partners of greatly different E^0 would be uncatalysed, and the results at the ends of Tables 3 and 4 bear this out.

There remain a few reactions that do not seem to fit into the theoretical scheme. In most cases this is due to extenuating circumstances; for example, the rapid fall-off with time of the catalytic rate of the Cu(II)–H_2 reaction in Table 4 is caused by the fact that the copper formed coats the platinum particles. Catalysis then ceases because the H^+/H_2 couple is far less reversible on copper than on platinum.[20] In Table 3 the observed catalysis of the H_2O_2–Cl^- reaction is more easily understood when it is noted that the reaction mixture was warmed on a water-bath. Not only would the rise in temperature affect the E^0 values but, more important, the exchange current densities would rise considerably. A more difficult problem is posed by the apparent inconsistency of the data involving the Co(III)/Co(II) couple. It has been reported that the potential of the couple shows irreversible behaviour at a platinum electrode (Table 1), that the Co(III)–H_2O reaction is catalysed by platinum (Table 5), and that the Co^{3+}–Co^{2+} and Co(III)–Fe(II) reactions are not so catalysed (Tables 2 and 3). Two interpretations other than a breakdown of the theory can be put forward. First, the standard exchange current density i_{00} of the Co(III)/Co(II) couple at platinum could be very low and the observed catalysis of the Co(III)–H_2O reaction largely photochemical, as in the analogous Ce(IV)–H_2O [79] and Tl(III)–H_2O [70] cases, or perhaps the result of dissolution of the platinum itself.[80] The second possibility is that i_{00} for the couple is really fairly high, the reported e.m.f. behaviour being the result of the electrode-catalysed interaction of Co(III) and the solvent. That no heterogeneous catalysis was found in the Co(III)–Fe(II) and Co^{3+}–Co^{2+} studies could then be ascribed to a masking effect by the rapid homogeneous reactions as in the analogous Mn(III)–Fe(II) and V(V)–Fe(II) cases discussed earlier. Were this so, catalysis in the Co(III) reactions might have been detected with faster stirring and a larger surface area of catalyst. A reinvestigation of all these cobaltic studies is clearly desirable.

We have found only one unequivocal exception to the predictions of the theory, *viz.*, the rapid catalysis by platinum of the ferricyanide–thiosulphate reaction in spite of the

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[79] Baur and Glaessner, *Z. Elektrochem.*, 1903, **9**, 534.

[80] Ravnö and Spiro, following Paper.

irreversibility of the $S_4O_6^{2-}/S_2O_3^{2-}$ system and the small difference of $0{\cdot}2_6$ v in the E^0 of the two couples. Since the theory involved two separate hypotheses, any disagreement with experiment can be due to two separate reasons. One is that the current density–voltage curves are not independent and additive but interact at the metal surface. The other is that the metal may catalyse not by acting as an electron-bridge but by stabilizing some adsorbed reaction intermediate as in heterogeneous gas-phase catalysis. The second reason may well account for the marked catalysis in the $Fe(CN)_6^{3-}$–$S_2O_3^{2-}$ reaction, especially since the homogeneous reaction is very complicated kinetically and almost certainly involves radical intermediates.[81,82]

Apart from this one exception, however, and within the limitations imposed by the scarcity of electrochemical data, the evidence from the more than 70 reactions in Tables 2—5 has been shown to be consistent with the dual hypotheses that the platinum catalyses through being an electron-conductor and that the current density–voltage curves of the reacting couples are roughly additive. Similar theoretical considerations may apply to the less-well-documented heterogeneous catalyses by other metals and by semiconductors. Further work to test these ideas quantitatively is in progress. It must be added that Tables 3—5 are almost certainly incomplete. Consideration of the effect of platinum on a solution reaction frequently forms only a small part of papers devoted mainly to other ends, and a thorough coverage of the literature is virtually impossible. We have, moreover, not listed numerous references in which either the rates of reactions in the presence of platinum were not contrasted with those of blank experiments or in which there is appreciable doubt as to the stoicheiometry of the reaction. An early example is Schönbein's observation [83] in 1858 and 1859 that platinum catalysed the disappearance of the blue colour of indigo on addition of $HClO_3$, HIO_3, or H_2O_2, without proof as to whether leucoindigo or isatin, or both, were formed. Finally, Tables 3—5 contain only a few organic reactions although it is well known [84] that many more, particularly hydrogenations, are catalysed by platinum and other metals. Whether their function here is partly or wholly that of electron-bridges can be judged better when we acquire more electrochemical information not only for aqueous solutions but more especially for the non-aqueous media in which these reactions are normally carried out.

Decomposition Reactions.—We now turn to a group of decomposition reactions which are effectively internal oxidation–reduction processes and which are often platinum-catalysed. Some of these are listed in the first column of Table 6. Since each reaction can be formally split up into an oxidation and a reduction half-reaction (column 2), we propose that here too the platinum acts simply as an electron-conductor. On its surface both half-reactions are assumed to proceed simultaneously and independently, so that the two current density–voltage curves are additive. This idea is strongly supported by the experimental finding of Gerischer and of Winkelmann [23] that for the decomposition of hydrogen peroxide solutions on platinum this is indeed the case. In one other instance (the decomposition of HN_3 solutions) we have enough electrochemical information for a partial test. The exchange current density of the half-reaction

$$2N_3^- \longrightarrow 3N_2(g) + 2e^-$$

is known [91] to be *ca.* 10^{-76} amp. cm.$^{-2}$, a value so small that at first sight the idea of an electrochemical mechanism seems absurd. However, the application of equation (5), with a Tafel slope of 0·058,[91] shows that this half-reaction can produce an appreciable

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[81] Sandved and Holte, *Tidsskr. Kjemi Bergvesen*, 1940, **20**, 106.

[82] Barreira, D.I.C. Thesis, Imperial College, 1962.

[83] Schönbein, *Ann. Physik u. Chem.*, 1858, **15**, 258; *J. prakt. Chem.*, 1859, **78**, 63, 90.

[84] Schiller, in Müller, ed. "Die Methoden der Organischen Chemie," G. Thieme, Stuttgart, 1955, vol. IV, part 2, p. 241; Houben, "Die Methoden der Organischen Chemie," G. Thieme, Leipzig, 3rd edn., 1925, vol. II.

[85] Calculated from standard free energies listed by Latimer, ref. 9.

TABLE 6.

Decomposition reactions catalysed by platinum.

Overall reaction	Half-reactions	E^0 [85]	Ref.
$2H_2O_2 \longrightarrow 2H_2O + O_2(g)$	$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1·77	86
	$H_2O_2 \longrightarrow O_2(g) + 2H^+ + 2e^-$	+0·68	
$3HN_3 \longrightarrow 4N_2(g) + NH_3$	$HN_3 + 3H^+ + 2e^- \longrightarrow N_2(g) + NH_4^+$	+1·96	87
	$2HN_3 \longrightarrow 3N_2(g) + 2H^+ + 2e^-$	−3·1	
$3N_2H_4 \longrightarrow N_2(g) + 4NH_3$, in acid or neutral solution	$N_2H_5^+ + 3H^+ + 2e^- \longrightarrow 2NH_4^+$	+1·28	88
	$N_2H_5^+ \longrightarrow N_2(g) + 5H^+ + 4e^-$	−0·23	
$4NH_2{\cdot}OH \longrightarrow 2NH_3 + N_2O(g) + 3H_2O$	$NH_2{\cdot}OH + 2H^+ + 2e^- \longrightarrow NH_3 + H_2O$	+1·25	89
	$NH_2{\cdot}OH \longrightarrow \frac{1}{2}N_2O(g) + \frac{1}{2}H_2O + 2H^+ + 2e^-$	−0·22	
$NH_4^+ + NO_2^- \longrightarrow N_2(g) + 2H_2O$	$NO_2^- + 4H^+ + 3e^- \longrightarrow \frac{1}{2}N_2(g) + 2H_2O$	+1·52	90
	$NH_4^+ \longrightarrow \frac{1}{2}N_2(g) + 4H^+ + 3e^-$	+0·27	
$HCO_2H \longrightarrow H_2(g) + CO_2(g)$	$2H^+ + 2e^- \longrightarrow H_2(g)$	±0·00	76
	$HCO_2H \longrightarrow CO_2(g) + 2H^+ + 2e^-$	−0·20	

current-density of, say, 10^{-5} amp. cm.$^{-2}$ at an overpotential of 4·1 v. A more negative E^0 value and a smaller Tafel slope of 0·043 found by Thomas [92] after extensive purification would require a similar overpotential. According to Table 6, this still leaves nearly 1 v to spare as the cathodic overpotential for the other half-reaction

$$HN_3 + 3H^+ + 2e^- \longrightarrow N_2(g) + NH_4^+$$

provided the rate of the azide oxidation is not markedly pH-dependent. Thus, even in this seemingly unfavourable case, the limited evidence available is consistent with a catalytic mechanism of electron-transfer through the metal.

Reactions involving aqueous formic acid appear in Table 6 as well as in Tables 3 and 5, and they can all be related within our theoretical framework. The CO_2/HCO_2H couple is a fairly irreversible one.[25a, 26] This in turn explains why the decomposition of formic acid solutions is catalysed only slightly by platinum, for, although the H^+/H_2 system is reversible on platinum, the difference in the E^0 values of the two couples is only 0·2 v. It would then be expected that the oxidising partner of a reversible couple of rather higher E^0, such as Ce(IV), Fe(III), or Methylene Blue, would attack formic acid quite rapidly on a platinum surface, and Table 3 shows that this is what does happen. The marked catalysis by platinum of the oxidation of HCO_2H by O_2 (Table 5) is also in line with this picture since the standard electrode potentials differ by almost 1·5 v, and a big enough overpotential for both half-reactions is therefore provided at the mixture potential. Schwabe [42] has already pointed out that the rate of decomposition of HCO_2H increases when electrons are withdrawn from the platinum catalyst by raising the mixture potential with a couple of high E^0.†

It is worth noting that formic acid does not decompose in solution, as it can do in the gas phase, according to

$$HCO_2H \longrightarrow CO + H_2O$$

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† Evidence published [92a] since this Paper was submitted confirms that the formic acid–oxygen reaction on platinum proceeds by a purely electrochemical mechanism.

[86] Bredig and Müller, *Z. phys. Chem.*, 1899, **31**, 258.

[87] Loew, *Ber.*, 1891, **25**, 2947; Oliveri-Mandala, *Gazzetta*, 1916, **46**, 137.

[88] Loew, *Ber.*, 1887, **20**, 144; Tanatar, *Z. phys. Chem.*, 1902, **40**, 475; 1902, **41**, 37; Gutbier and Meundlinger, *ibid.*, 1913, **84**, 203.

[89] Tanatar, *Z. phys. Chem.*, 1902, **40**, 475.

[90] Loew, *Ber.*, 1890, **23**, 1443, 3018; Vondracek, *Z. anorg. Chem.*, 1904, **39**, 24.

[91] Stout, *Trans. Faraday Soc.*, 1945, **41**, 64; Bockris, ref. 20, p. 230.

[92] Thomas, *Trans. Faraday Soc.*, 1962, **58**, 1412.

[92a] Hoffman and Kuhn, *Electrochim. Acta*, 1964, **9**, 835.

a reaction for which no partial electrochemical equations can be written. This line of thought may allow one to distinguish between mechanisms of catalysis. It has been found,[93] for example, that the decomposition of nitroamide is enhanced by platinum sol, but the products were assumed [93] to be the same as in the homogeneous reaction

$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$

Were this true, a mechanism of simple electron-transfer through the metal could be ruled out since the latter requires different products such as N_2 and NO or HNO_2.

The literature contains a few examples of heterogeneous decomposition and redox reactions occurring simultaneously on a given catalyst. Thus Loevenhart and Kastle [94] in 1903 found that the addition of platinum black to a mixture of H_2O_2 and HCO_2H (or HCHO) at 60° considerably increased the rate of decomposition of the peroxide as well as the rate of oxidation by H_2O_2 of the organic substrate to carbon dioxide. Potassium oxalate, however, was hardly oxidised at all under the same conditions. These results can be easily described on an extended current density–voltage diagram such as Fig. 2 where the curves for the three half-reactions are sketched. On the assumption that each curve is unaffected by the presence of the others, the mixture potential B (*i.e.*, the potential at which AB = BC) with H_2O_2 alone is shifted to Y when HCO_2H (or HCHO) is added. YU then represents the rate of oxidation of HCO_2H (or HCHO) to CO_2, YZ the rate of production of oxygen gas, and the sum

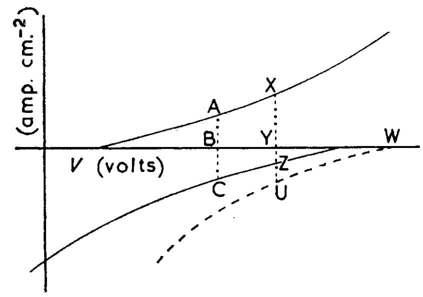

FIG. 2. Schematic diagram of current density--voltage curves for the two half-reactions of a decomposition process (full lines) and for another redox half-reaction (broken line) occurring simultaneously. Thus, curve AX could represent the reduction

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O,$$

curve CZ the oxidation

$$H_2O_2 \longrightarrow O_2(g) + 2H^+ + 2e^-,$$

and curve UW the oxidation

$$HCO_2H \longrightarrow CO_2(g) + 2H^+ + 2e^-.$$

$$XY + YZ = YU + YZ + YZ$$

the rate of disappearance of H_2O_2. As far as one can judge from available electrochemical data,[25a-27] YU is likely to be quite large when the organic substance is HCO_2H or HCHO but much smaller for $(CO_2K)_2$, and this would account for the experimental observations. It would be interesting to examine such a case in detail, as well as one in which the Nernst potential of the added redox couple lies between those of the two decomposition half-reactions. The oxidation of Cl^- by H_2O_2 (Table 3) falls into this category.

Practical Applications.—Heterogeneous catalysis in solution can obviously be put to good use in inorganic and organic syntheses. Work on vanadium has provided several excellent examples. Rutter,[61] for instance, prepared V(II) solutions by electrochemical reduction at cathodes of high hydrogen overpotential such as lead or mercury and, whenever he wanted V(III) solutions free from V(II), simply inserted a platinized platinum foil to promote the catalytic reaction

$$V(II) + H^+ \longrightarrow V(III) + \tfrac{1}{2}H_2$$

Eggert,[54] using a platinum catalyst, was readily able to reduce V(V) to V(III) with hydrogen

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[93] King, *J. Amer. Chem. Soc.*, 1938, **60**, 144.

[94] Loevenhart and Kastle, *Amer. Chem. J.*, 1903, **29**, 397; Wieland and Fischer, *Ber.*, 1926, **59**, 1180.

gas but found that the passage of oxygen through a V(III) solution produced only V(IV) and not V(V). As discussed in an earlier Section, all these phenomena are consistent with a catalytic mechanism of electron-transfer through the metal, and thus there appears to be much scope for applying the same idea to other synthetic problems.

Platinum and other metals have many opportunities of interacting with solutions when they are used as electrodes in physicochemical measurements. Such interactions are usually no more than heterogeneous catalyses, and the theoretical ideas discussed earlier now enable us to explain rationally several puzzling or seemingly inconsistent observations in the literature and to predict under what conditions similar phenomena may arise. The first set of examples concerns attempts to measure the standard electrode potentials of couples that attack the solvent. As Table 4 shows, the reduced forms of the Mo(V)/Mo(III), V(III)/V(II), Ti(III)/Ti(II), Cr(III)/Cr(II), Eu(III)/Eu(II), and $Co(CN)_6^{3-}/Co(CN)_6^{4-}$ couples all react with hydrogen ions to produce hydrogen gas under the catalytic influence of platinum, the chemist's normal first choice of electrode material. If the couple is fairly irreversible, the catalytic rate is likely to be slow and the mixture potential will then be close to that of the H^+/H_2 couple. This seems to be true [95] for the $Co(CN)_6^{3-}/Co(CN)_6^{4-}$ [or $Co(CN)_5(H_2O)^{2-}/Co(CN)_5(H_2O)^{3-}$] couple which is irreversible at mercury and which may well be irreversible also at platinum. If the redox couple is electrochemically reversible, as is the H^+/H_2 couple, catalysis will be marked [case (1) of the theory] and the mixture potential will become equal to the equilibrium potential of the whole system.[45] The only way to overcome this difficulty so as to obtain the potential of the redox couple under investigation is to decrease the rate of the catalytic process. This has usually been achieved in the past [10,96] by employing an electrode such as mercury, tin, or lead, at which the H^+/H_2 couple is irreversible. An alternative method is to slow down the rate of diffusion of hydrogen ions to the platinum surface by employing a solution of fairly high pH. Thus McCoy,[97] who used a formate buffer with only a " small and variable excess of formic acid," found constant Eu(III)/Eu(II) potentials at a platinum electrode despite the later finding [65] that in acid solutions there is marked catalysis by platinum of the reaction

$$\mathrm{Eu(II)} + H^+ \longrightarrow \mathrm{Eu(III)} + \tfrac{1}{2}H_2$$

In accurate conductance work it has long been known that care must be taken to guard against interaction between the platinized platinum electrodes and the solution. Catalytic decompositions such as those in Table 6 are obvious examples, and special measures are necessary to determine the conductances of the corresponding solutions. For hydrogen peroxide, either as solute [98] or solvent,[99] it has been found effective to replace the platinum electrodes with ones of tin plate [98] or pure tin [99] on which overpotentials are higher. Even normally stable solvents may decompose catalytically under extreme conditions as was shown recently [100] by the discovery of the reaction

$$CH_3\cdot CH_2\cdot OH \longrightarrow H_2 + CH_3\cdot CHO$$

at platinum electrodes at 245°. A more indirect interaction was reported by Auerbach and Zeglin [101] who found the conductance of aqueous sodium formate solutions to decrease with time. This they traced to the oxidation of the solute by oxygen adsorbed on the platinized electrodes,

$$HCO_2^- + \tfrac{1}{2}O_2 \longrightarrow HCO_3^-$$

a reaction known to be catalysed by platinum in acid solutions (Table 5). The trouble

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[95] Hume and Kolthoff, *J. Amer. Chem. Soc.*, 1949, **71**, 867.

[96] Jones and Colvin, *J. Amer. Chem. Soc.*, 1944, **66**, 1573, and refs. therein.

[97] McCoy, *J. Amer. Chem. Soc.*, 1936, **58**, 1577.

[98] Calvert, *Z. phys. Chem.*, 1901, **38**, 513.

[99] Shanley, Roth, Nichols, and Kilpatrick, *J. Amer. Chem. Soc.*, 1956, **78**, 5190; Thomas and Maass, *Canad. J. Chem.*, 1958, **36**, 449.

[100] Newton, Copeland, and Benson, *J. Chem. Phys.*, 1962, **37**, 339.

[101] Auerbach and Zeglin, *Z. phys. Chem.*, 1923, **103**, 178.

was overcome by filling the conductance cell and its oxygen-laden electrodes with hydrogen gas until the catalytic process

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

had gone to completion—a clear case of heterogeneous catalysis being used on the principle of " set a thief to catch a thief." Adsorbed oxygen probably accounts also for the observed oxidation of alcoholic solutions in contact with platinized conductance electrodes.[102]

The greatest possibility between interaction of an electrode and a solution exists when the kinetics of a reaction are being determined by electrochemical means, whether potentiometric, amperometric, or conductometric. As an example, the marked difference in the rates of the reaction

$$Br_2 + Tl(\text{I}) \longrightarrow 2Br^- + Tl(\text{III})$$

found [103] by spectrophotometry and by potential measurements was probably caused by heterogeneous catalysis at the platinum electrode. In future it should be possible to decide whether an electrometric method is suitable for following the rate of a given redox reaction on the basis of the theoretical hypotheses discussed above. These should, moreover, prove equally useful guides for work with many fuel cells and in certain electrosyntheses where electrode catalysis is much sought after.

In numerous analytical methods, too, one or more electrodes are in contact with a reaction mixture. Errors may therefore arise from unsuspected electrode–solution interaction and we have found, for example, that the well-known potentiometric ceric–ferrous titration, usually performed satisfactorily in a sulphuric acid medium, cannot be carried out in a perchloric acid solution where ceric ions decompose the solvent on the platinum surface. This result was of course predictable from the data in Table 5, and it should now be possible to foresee many such effects. Indeed, there seems some scope for deliberately seeking out cases of heterogeneous catalysis and turning them to analytical advantage.

EXPERIMENTAL

The rates of eleven aqueous redox reactions were measured in the presence and in the absence of platinum foil. The homogeneous (or blank) solutions and those containing platinum were examined under identical experimental conditions, both being agitated either on a Griffin SD-100 shaker or else with a glass-paddle stirrer driven by a Towers variable-speed motor. An excess of some supporting electrolyte was always present to keep salt effects and pH constant, and the rates were followed by titration or spectrophotometrically on a Unicam S.P. 500 spectrophotometer or a Perkin-Elmer Spectracord 4000. Wherever possible, the experimental procedure was checked by comparing the homogeneous rate with literature values. The bright platinum foil used was either 12 cm.^{2} (both sides of a piece 1 in. square) or 114 cm.^{2} in area, and was cleaned in concentrated hydrochloric acid between experiments. The solution volume was normally 100 ml. All reagents were of AnalaR quality unless stated otherwise.

Wherever necessary, tests were carried out to ensure that any catalysis observed was genuinely heterogeneous and not due to one of several other kinds of platinum–solution interaction. The theory and experimental details of these tests are given in the following Paper.[80]

Ce(IV)–Br$^-$ *Reaction.*—The reacting solutions contained 5×10^{-4}M Hopkin and Williams $Ce(SO_4)_2$, 5×10^{-2}M-KBr, and 0·92M-H_2SO_4. The rate at 20 ± 1° was determined spectrophotometrically at 356 mμ where Ce(IV) absorbs strongly. The homogeneous reaction was first-order with respect to Ce(IV) (Fig. 3) with a velocity constant at 20° of $0{\cdot}04_6$ l. mole^{-1} min.$^{-1}$. King and Pandow's results [104] at 25° for a similar medium lead to a value of 0·06. Fig. 3 shows that platinum markedly catalysed the reaction and that the extent of catalysis was roughly proportional to the area of metal surface present.

Ce(IV)–H_2O *Reaction.*—With a solution 5×10^{-4}M in $Ce(SO_4)_2$ and 0·92M in H_2SO_4, no

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[102] Partington, *J.*, 1911, **99**, 1937.

[103] Carpenter, Ford-Smith, Bell, and Dodson, *Discuss. Faraday Soc.*, 1960, **29**, 92; Ford-Smith, Sutin, and Dodson, *ibid.*, p. 134.

[104] King and Pandow, *J. Amer. Chem. Soc.*, 1953, **75**, 3063.

reaction was observed spectrophotometrically at 356 mμ during 2 hr. at 20° either in the blank solution or in one containing 114 cm.^{2} platinum foil. However, in a medium of 2M-$HClO_4$ at 18 ± $\frac{1}{2}$°, half the 5 × 10^{-4}M-$Ce(SO_4)_2$ solute was reduced in 6 days in the blank solution and in 2 hr. when 114 cm.^{2} platinum foil was present. Although the stability of homogeneous Ce(IV) solutions has been investigated in the past,[105] the literature evidence on possible platinum catalysis is incomplete. Fronaeus and Östman [30] found only a slow reaction in 2·82M-$HClO_4$ at 0° even in the presence of platinum, whereas Sherrill, King, and Spooner [106] postulated catalysis by their platinum electrode to account for the decrease of potential with time in Ce(IV) + Ce(III) solutions in perchloric acid at 25°. Baur and Glaessner [79] reported a positive Ce(IV)–H_2O reaction in nitric acid in the presence of platinized platinum, but it is not clear whether they carried out a blank experiment without platinum.

Ce(IV)–Hg(I) *Reaction.*—The rate of the reaction between 4·2 × 10^{-4}M Hopkin and Williams $Ce(SO_4)_2$ and 5 × 10^{-3}M-$Hg_2(NO_3)_2$ in 2M-$HClO_4$ at 15 ± $\frac{1}{2}$° was measured spectrophotometrically at 356 mμ. A calibration curve had to be constructed because Beer's law was not obeyed by Ce(IV), presumably because of polymer formation.[107] The half-times were 7 min. for the solution containing 114 cm.^{2} platinum foil and 10 hr. for the homogeneous reaction. The latter has been studied from 50 to 70° by McCurdy and Guilbault; [108] their points and ours fit on the same smooth curve of log (rate constant) against 1/(abs. temp.).

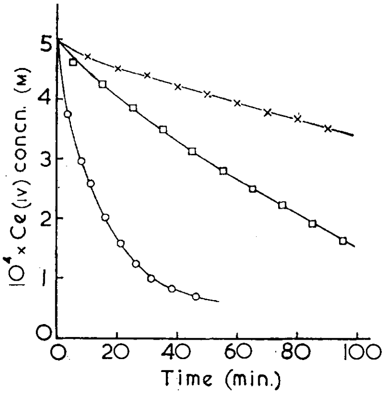

FIG. 3. Kinetic results at 20° for the Ce(IV)–Br^- reaction. The initial solution was 5 × 10^{-4}M in $Ce(SO_4)_2$, 5 × 10^{-2}M in KBr, and 0·92M in H_2SO_4. Crosses mark a homogeneous run, and squares and circles show runs in the presence of 12 and 114 cm.^{2} platinum foil, respectively.

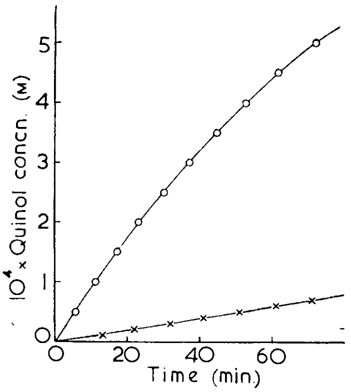

FIG. 4. Kinetic results at 20° for the quinone–Fe(II) reaction. The initial solution was 1 × 10^{-3}M in benzoquinone, 0·0127M in $Fe(ClO_4)_2$, 0·2M in $NaClO_4$, and 0·3767M in $HClO_4$. Crosses and circles mark runs in the absence and presence, respectively, of 114 cm.^{2} platinum foil.

p-*Benzoquinone*–Fe(II) *Reaction.*—Fig. 4 shows the marked catalysis observed when 114 cm.^{2} platinum foil was present in a mixture 1 × 10^{-3}M in B.D.H. *p*-benzoquinone, 0·0127M in G. F. Smith $Fe(ClO_4)_2$, 0·2M in G. F. Smith $NaClO_4$, and 0·3767M in $HClO_4$. The reactions were followed spectrophotometrically at 280 mμ where quinol is the main absorbing species. The rate constants at 20 ± 1° were 0·7$_6$ l. [mole (quinol)]$^{-1}$ min.$^{-1}$ for the catalysed reaction and 0·08$_5$ for the solution without platinum. A blank run at 20° in relative darkness gave 0·07 l. mole^{-1} min.$^{-1}$ which may be compared with a thermal rate of 0·06 calculated from literature figures [109] for the activation energy and the velocity at 25°.

Fe(III)–I^- *Reaction.*—The rate of formation of iodine was followed by titration with 0·01M-sodium thiosulphate. For a solution 0·01M in $Fe(NO_3)_3$, 0·01M in KI, and 0·5M in KNO_3, the initial homogeneous rate was 1·8 × 10^{-5} mole (iron) l.$^{-1}$ min.$^{-1}$ at 0°. If the reaction is initially

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[105] Weiss and Porret, *Nature*, 1937, **139**, 1019; Heidt and Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 2476; Kolp and Thomas, *ibid.*, 1949, **71**, 3047; Grant, *J. Inorg. Nuclear Chem.*, 1964, **26**, 337.

[106] Sherrill, King, and Spooner, *J. Amer. Chem. Soc.*, 1943, **65**, 170.

[107] King and Pandow, *J. Amer. Chem. Soc.*, 1952, **74**, 1966.

[108] McCurdy and Guilbault, *J. Phys. Chem.*, 1960, **64**, 1825.

[109] Baxendale, Hardy, and Sutcliffe, *Trans. Faraday Soc.*, 1951, **47**, 963.

first-order in Fe(III) and second-order in I^-, as has been found [110] in other media, our results lead to a third-order rate constant of 18 l.^{2} mole^{-2} min.$^{-1}$. The initial rate at 0° in the presence of 114 cm.^{2} bright platinum foil was 15 × 10^{-5} mole (iron) l.$^{-1}$ min.$^{-1}$, and plots of the progress of the catalysed and uncatalysed reactions resembled in shape those in Fig. 4. The Fe(III)–I^- reaction is known to be catalysed by platinum black [4] and by platinum foil at room temperature.[1]

I_3^-–Ti(III) *Reaction.*—The mixture used was 0·01M in B.D.H. $TiCl_3$, 5 × 10^{-4}M in iodine, 0·1M in KI, and 0·125M in HCl, and the disappearance of tri-iodide was measured spectrophotometrically at 475 mμ. The half-times at 20 ± ½° were 3½ min. with 114 cm.^{2} platinum foil present and 18 min. in the homogeneous solution. The latter figure compares fairly well with a half-time of 14 min. at 25° calculated for the same medium from the data of Johnson and Winstein.[111]

$Fe(CN)_6^{3-}$–I^- *Reaction.*—It is well known [1,4,44] that this reaction is catalysed by platinum, and it was decided to investigate the effect of temperature upon the catalysis. Aliquots were titrated with 0·01M-sodium thiosulphate by an established procedure [112] and the results are shown in Figs. 5 and 6 for solutions 0·075M in $K_3Fe(CN)_6$, 0·2M in KI, and M in KNO_3. In the homogeneous reaction at 25°, half the equilibrium concentration of iodine was produced in 8·0 min. which compares well with the value interpolated from the graphically presented literature results.[113] The activation energy of the homogeneous reaction was 8·$_4$ kcal., in good agreement with a figure of 8 kcal. obtained by Howlett.[114] Since the effect on the rate of adding 114 cm.^{2} platinum foil was much more pronounced at 0 than at 25°, the activation energy for the heterogeneous process must be appreciably less than 8 kcal. This is consistent with other evidence [115] that the catalysis is at least partly diffusion-controlled.

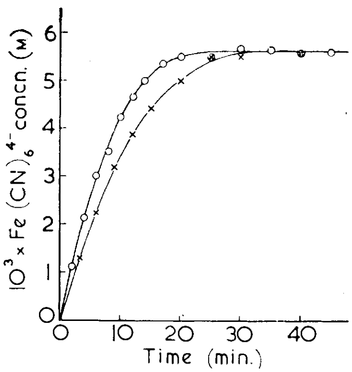

FIG. 5. Kinetic results at 25° for the $Fe(CN)_6^{3-}$–I^- reaction. The solution was initially 0·075M in $K_3Fe(CN)_6$, 0·2M in KI, and M in KNO_3. Crosses mark the homogeneous run and circles the run with 114 cm.^{2} platinum foil present.

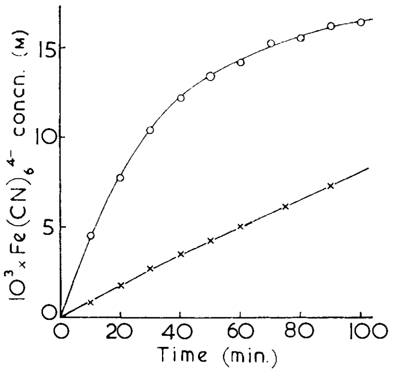

FIG. 6. Kinetic results at 0° for the $Fe(CN)_6^{3-}$–I^- reaction. The solution was initially 0·075M in $K_3Fe(CN)_6$, 0·2M in KI, and M in KNO_3. Crosses mark the homogeneous run and circles the run with 114 cm.^{2} platinum foil present.

$Fe(CN)_6^{3-}$–$S_2O_3^{2-}$ *Reaction.*—The decrease in ferricyanide concentration was followed spectrophotometrically at 450 mμ in solutions of composition 0·004M-$K_3Fe(CN)_6$, 0·04M-$Na_2S_2O_3$, 0·100M-$CH_3{\cdot}CO_2H$, 0·125M-$CH_3{\cdot}CO_2Na$, and M-KCl. The results at 20 ± 0·3° are shown in Fig. 7, and it is evident that the introduction of 114 cm.^{2} platinum foil has markedly increased the rate. The homogeneous run is very complicated kinetically; the half-time of 80 min. at 20° in Fig. 7 is consistent with one of 53 min. at 25° obtained independently in this laboratory.[82]

[110] Hershey and Bray, *J. Amer. Chem. Soc.*, 1936, **58**, 1760; Fudge and Sykes, *J.*, 1952, 119, and earlier Papers referred to therein.

[111] Johnson and Winstein, *J. Amer. Chem. Soc.*, 1951, **73**, 2601.

[112] La Mer and Sandved, *J. Amer. Chem. Soc.*, 1928, **50**, 2656.

[113] Friedman and Anderson, *J. Amer. Chem. Soc.*, 1939, **61**, 116.

[114] Howlett, personal communication.

[115] Spiro and Ravnö, unpublished work.

$Cr_2O_7^{2-}$–I^- *Reaction.*—Using the method of Beard and Taylor,[116] kinetic measurements were carried out with solutions 5 × 10^{-4}M in $K_2Cr_2O_7$, 0·015M in KI, 0·04M in $HClO_4$, and 0·4M in NaCl. The results at 5 ± 0·01° of the homogeneous reaction and of one with 114 cm.^{2} platinum foil present are shown in Fig. 8; catalysis is seen to be slight. A similar result was obtained at 25°. Positive catalysis by platinum black of the oxidation of iodide by dilute chromic acid of unspecified composition was reported by Schönbein [83] over a century ago.

Fe(III)–Sn(II) *Reaction.*—The reaction in a mixture 0·1M in $FeCl_3$, 0·03M in $SnCl_2$, and 0·1M in HCl was followed at 0° by removing aliquots and then titrating the ferrous iron formed with 0·04N-$K_2Cr_2O_7$. The half-time (with respect to tin) of 15 min. is not inconsistent with literature [117] values obtained for rather different conditions. There was no change in rate on the addition of 114 cm.^{2} platinum foil.

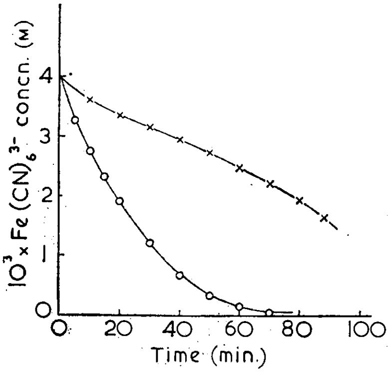

FIG. 7. Kinetic results at 20° for the $Fe(CN)_6^{3-}$–$S_2O_3^{2-}$ reaction. The starting solution was 0·004M in $K_3Fe(CN)_6$, 0·04M in $Na_2S_2O_3$, 0·1M in $CH_3{\cdot}CO_2H$, 0·125M in $CH_3{\cdot}CO_2Na$, and M in KCl. Crosses mark the homogeneous run and circles the run with 114 cm.^{2} platinum foil present.

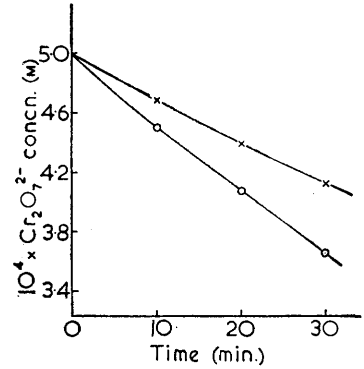

FIG. 8. Kinetic results at 5° for the reaction $Cr_2O_7^{2-}$–I^-. The initial mixture was 5 × 10^{-4}M in $K_2Cr_2O_7$, 0·015M in KI, 0·04M in $HClO_4$, and 0·4M in NaCl. Crosses indicate the homogeneous run and circles the run with the addition of 114 cm.^{2} platinum foil.

Fe(III)–$S_2O_3^{2-}$ *Reaction.*—The velocity in a mixture 0·025M in $Fe(NO_3)_3$, 0·025M in $Na_2S_2O_3$, and 0·25M in KNO_3 was followed at 0 ± 0·2° by iodine titration according to a previously established method.[118] The times of half and of three-quarter change were 2 and 14 min., respectively, and are in fair agreement with the results in the literature [118] when variations in medium are borne in mind. There was no effect on introducing 114 cm.^{2} platinum foil.

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[116] Beard and Taylor, *J. Amer. Chem. Soc.*, 1929, **51**, 1973.

[117] Kahlenberg, *J. Amer. Chem. Soc.*, 1894, **16**, 314; Timofeew, Muchin, and Gurewitsch, *Z. phys. Chem.*, 1923, **115**, 161; Robinson and Law, *Trans. Faraday Soc.*, 1935, **31**, 899.

[118] Hewitt and Mann, *J.*, 1913, **103**, 324; Page, *Trans. Faraday Soc.*, 1960, **56**, 398.