

KINETIC PARAMETERS FROM CHRONOPOTENTIOMETRIC WAVES

BY T. P. RADHAKRISHNAN AND A. K. SUNDARAM, F.A.Sc.

*Analytical Division, Bhabha Atomic Research Centre,
Modular Laboratories, Trombay, Bombay-85 (AS)*

Received March 21, 1972

ABSTRACT

A simplified expression is given for the potential-time relation of a cathodic chronopotentiometric wave which involves mixed control by diffusion and charge-transfer. The treatment of quasi-reversible chronopotentiometric waves has been considered in detail. The chronopotentiometric behaviour of a number of partially irreversible and totally irreversible systems has been studied. The kinetic parameters have been evaluated and compared.

INTRODUCTION

CHRONOPOTENTIOMETRIC equations applicable to reversible and totally irreversible electrode reactions in the absence of kinetic complications have long been established.^{1,2} The evaluation of kinetic parameters for fast electrode reactions by the single pulse galvanostatic method has been considered in detail by Berzins and Delahay³. The 'so-called' quasi-reversible (partially irreversible) chronopotentiometric waves have received very little attention. Anderson and Macero⁴ have derived a general expression applicable to quasi-reversible chronopotentiometric waves and their treatment allows the use of concentrations other than zero for both the oxidised and reduced forms. However numerical solution of their equation with three unknown parameters can be best carried out only by an involved iteration procedure either manually or by using a computer. In the present study we have used a simplified equation applicable to a cathodic chronopotentiometric wave involving mixed control by diffusion and charge transfer. The potential-time relationship and the limiting equation for totally irreversible reduction have been applied to the experimental data for some known systems and the kinetic parameters have been evaluated.

POTENTIAL-TIME RELATION FOR CATHODIC WAVES

Consider a first order electrode reaction



involving either two soluble species O and R or the product R soluble in the electrode as in the deposition of an amalgam-forming metal on a mercury cathode. The initial concentration of O in the bulk of the solution is C^0 and no reduction product R is present initially. The solution is unstirred and a large excess of indifferent electrolyte is present in the solution so that mass transfer is controlled by diffusion. It is assumed that the electrode is planar and that conditions for semi-infinite linear diffusion are satisfied. In this treatment of constant current electrolysis only the effect of superposed charge-transfer and diffusion rate-control on the potential-time curve has been taken into account and the influence of double layer charging has been neglected. The rate of the electrode reaction can be written as³

$$\begin{aligned} \frac{i}{nFA} = & C_O(o, t) k_s \exp \frac{-\alpha nF(E - E_s)}{RT} \\ & - C_R(o, t) k_s \exp \frac{nF(1 - \alpha)(E - E_s)}{RT} \end{aligned} \quad (2)$$

where 'i' is the magnitude of the constant current, A the electrode area, n the number of electrons involved, E the measured potential, E_s the standard potential of the system, k_s the standard rate constant and α the transfer coefficient, $C_O(o, t)$ and $C_R(o, t)$ are the concentrations of the oxidised and reduced species respectively at the electrode surface and other symbols have their usual significance.

Concentrations of both O and R as a function of time and distance from the electrode surface have been obtained⁵ by solution of the boundary value problem and

$$C_R(o, t) = \frac{2i}{\pi^{1/2} nFA D_R^{1/2}} \cdot t^{1/2} \quad (3)$$

$$C_O(o, t) = C^0 - \frac{2i}{\pi^{1/2} nFA D_O^{1/2}} t^{1/2} \quad (4)$$

$$C_O(o, t) = \frac{2i}{\pi^{1/2} nFA D_O^{1/2}} (\tau^{1/2} - t^{1/2}) \quad (5)$$

where D_O and D_R are the diffusion coefficients of the oxidised and reduced species respectively, t is the time elapsed after the beginning of electrolysis and τ is the transition time⁶ given by

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} nFA D_O^{\frac{1}{2}} C^0}{2i} \quad (6)$$

Equations (3) and (5) can be written as

$$C_R(o, t) = C^0 \left[\frac{t}{\tau} \cdot \frac{D_O}{D_R} \right]^{\frac{1}{2}} \quad (7)$$

$$C_O(o, t) = C^0 \left[\frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{\tau^{\frac{1}{2}}} \right] \quad (8)$$

Using relations (7) and (8), equation (2) can be rewritten as

$$\begin{aligned} \frac{i}{nFA k_s C^0} &= \left(\frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{\tau^{\frac{1}{2}}} \right) \exp \left[\frac{-\alpha nF(E - E_s)}{RT} \right] \\ &\quad - \left(\frac{t}{\tau} \cdot \frac{D_O}{D_R} \right)^{\frac{1}{2}} \exp. \frac{nF(1 - \alpha)(E - E_s)}{RT} \end{aligned} \quad (9)$$

or

$$\begin{aligned} \frac{i}{nFA k_s C^0} \exp. \frac{\alpha nF(E - E_s)}{RT} &= 1 - \left(\frac{t}{\tau} \right)^{\frac{1}{2}} \left[1 + \left(\frac{D_O}{D_R} \right)^{\frac{1}{2}} \exp \frac{nF(E - E_s)}{RT} \right] \end{aligned} \quad (10)$$

i.e.,

$$\left(\frac{t}{\tau} \right)^{\frac{1}{2}} = \frac{1 - \frac{i}{nFA k_s C^0} \exp \frac{\alpha nF}{RT} (E - E_s)}{1 + \left(\frac{D_O}{D_R} \right)^{\frac{1}{2}} \exp \frac{nF}{RT} (E - E_s)} \quad (11)$$

Equation (11) is identical with the expression derived by Oldham⁷ for the general galvanostatic condition using the diffusion layer concept.

From equation (10) it follows that

$$\begin{aligned} E = E_s + \frac{2.3 RT}{\alpha nF} \log \frac{nFA k_s C^0}{i} + \frac{2.3 RT}{\alpha nF} \\ \times \log \left[1 - \left(\frac{t}{\tau} \right)^{\frac{1}{2}} \left\{ 1 + \left(\frac{D_O}{D_R} \right)^{\frac{1}{2}} \exp \frac{nF}{RT} (E - E_s) \right\} \right]. \end{aligned} \quad (12)$$

Equation (12) is the general expression for the potential-time curve of a cathodic chronopotentiometric wave in terms of k_s , α , E_s , D_o and D_R . This relation is valid when E is cathodic to E_s and this condition is satisfied when

$$\frac{nFA C^o}{i} \leq \frac{1}{k_s}$$

Reversible Reduction

When diffusion overvoltage predominates in the electrode process, the contribution

$$\frac{i}{nFA k_s C^o} \exp. \frac{\alpha nF}{RT} (E - E_s)$$

due to the charge-transfer overvoltage, if any, can be neglected in comparison with unity and equation (11) becomes¹

$$\left(\frac{t}{\tau}\right)^{\frac{1}{2}} \left[1 + \left(\frac{D_o}{D_R}\right)^{\frac{1}{2}} \exp \frac{nF}{RT} (E - E_s) \right] = 1 \quad (13)$$

Simplifying

$$E = E_s + \frac{2.3 RT}{nF} \log \left(\frac{D_R}{D_o}\right)^{\frac{1}{2}} + \frac{2.3 RT}{nF} \log \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}} \quad (14)$$

or

$$E = E_{\tau/4} + \frac{2.3 RT}{nF} \log \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}} \quad (15)$$

where the quarter-wave potential $E_{\tau/4}$ is given by

$$E_{\tau/4} = E_s + \frac{2.3 RT}{nF} \log \left(\frac{D_R}{D_o}\right)^{\frac{1}{2}} \quad (16)$$

The standard potential E_s for the electrode reaction and particularly the diffusion coefficients D_o and D_R of the oxidised and reduced species may not be available under the experimental conditions. It is preferable in such cases to refer in terms of the formal standard potential E_f^o of the couple when the concentration of the supporting electrolyte is one molar and C_o/C_R is unity.

(ii) *Irreversible Reduction*

When the process is totally irreversible,

$$\left(\frac{D_o}{D_R}\right)^{\frac{1}{2}} \exp \frac{nF(E - E_s)}{RT}$$

becomes negligible in comparison with unity and equation (11) becomes

$$\left(\frac{t}{\tau}\right)^{\frac{1}{2}} = 1 - \frac{i}{nFAk_s C^o} \exp \frac{\alpha nF}{RT} (E - E_s) \quad (17)$$

i.e.,

$$E = E_s + \frac{2.3 RT}{\alpha nF} \log \frac{nFAk_s C^o}{i} + \frac{2.3 RT}{\alpha nF} \log \left[1 - \left(\frac{t}{\tau}\right)^{\frac{1}{2}} \right].$$

Or,

$$E = E_{t=0} + \frac{2.3 RT}{\alpha nF} \log \left[1 - \left(\frac{t}{\tau}\right)^{\frac{1}{2}} \right] \quad (18)$$

where

$$E_{t=0} = E_s + \frac{2.3 RT}{\alpha nF} \log \frac{nFAk_s C^o}{i}. \quad (19)$$

The same result was obtained by Delahay and Berzins² by neglecting the effect due to the backward reaction in equation (1). From a plot of

$$E \text{ vs. } \log \left[1 - \left(\frac{t}{\tau}\right)^{\frac{1}{2}} \right],$$

both k_s and α can be calculated provided E_s or E_f^o is known.

(iii) *Quasi-reversible Reduction*

When the rate of the electrode reaction is controlled by both diffusion and charge-transfer over-voltage, equation (12) should be applied and can be written as

$$E = E_s + \frac{2.3 RT}{\alpha nF} \log \frac{nFAk_s C^o}{i} + \frac{2.3 RT}{\alpha nF} \log \left[1 - \left(\frac{t}{\tau}\right)^{\frac{1}{2}} \left\{ 1 + \exp \frac{nF}{RT} (E - E_{\tau/4}^r) \right\} \right] \quad (20)$$

where the reversible quarter-wave potential $E_{\tau/4}^r$ is given by equation (16).

Combining equations (19) and (20)

$$E = E_{t=0} + \frac{2.3 RT}{\alpha n F} \log \left[1 - \left(\frac{t}{\tau} \right)^{\frac{1}{2}} \left\{ 1 + \exp \frac{nF}{RT} (E - E_{\tau/4}^r) \right\} \right] \quad (21)$$

i.e.,

$$E = E_{t=0} + \frac{2.3 RT}{\alpha n F} \log(1 - A)$$

where

$$A = \left(\frac{t}{\tau} \right)^{\frac{1}{2}} \left\{ 1 + \exp \frac{nF}{RT} (E - E_{\tau/4}^r) \right\}. \quad (22)$$

The reversible quarter-wave potential $E_{\tau/4}^r$ for a quasi-reversible reduction can be determined from anodic-cathodic polarograms or by amalgam polarography⁸. A plot of E vs. $\log(1 - A)$ should be linear and from the slope and intercept both α and k_s can be calculated. If the standard potential E_s is not known, an apparent rate constant k_s' can be calculated using the formal potential E_f^0 .

EXPERIMENTAL

Apparatus

An electrical circuit was assembled for the precise recording of potential-time curves⁹. A fully transistorised constant current source was fabricated and the electrolysis current was obtained by measuring the iR drop across a $1 \text{ K}\Omega$ G.R. standard resistance ($\pm 0.05\%$). The abrupt rise in potential in the initial portion of the $E-t$ curve was backed-off with a Pye potentiometer and only the useful segment of the $E-t$ curve was recorded at high sensitivity. A VOM-7 (Bausch and Lomb) or Elektronik-19 (Honeywell Brown) recorder with a series input resistance of $1 \text{ M}\Omega$ and a shunt resistance of $5 \text{ K}\Omega$ was used at recorder range $0.5 - 1 \text{ mV}$ so that the current drawn from the cell was negligible. The transition time was obtained by graphical methods^{2,10} and was about 30 secs in the present study.

An improved cell set-up was used and the anode compartment was isolated from the cathode by a high-porosity sintered glass disc partition. Platinum foil of area 1 cm^2 served as the anode. Mercury, purified by electrolysis and subsequent double distillation, was used as the cathode and was contained in a perspex cup of 2 cm. diameter. The perspex cup was

coated with Beckmann descicote to prevent wetting of the surface. The cathode compartment of the cell was provided with a side arm for fitting the Luggin capillary of a saturated calomel electrode. The tip of the reference electrode was kept within 1 mm of the surface of the working electrode. For studies with perchlorate solutions an agar-sodium chloride salt bridge was used. Polarographic measurements were made on a manual set-up using a dropping amalgam or dropping mercury electrode. All solutions were deoxygenated by bubbling tank nitrogen and the temperature was kept at $30 \pm 0.1^\circ \text{C}$.

Chemicals

Stock solutions (0.1 M) of zinc sulphate, nickel sulphate and cobalt sulphate were prepared from G.R. salts using double distilled water and were standardised by conventional methods. The stock solution of europium perchlorate (0.02 M) was obtained from pure Eu_2O_3 (Rare Earth Products Ltd., England). Bismuth perchlorate was obtained from A.R. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ by repeated fuming with perchloric acid. The final solution (0.05 M) in 1 N HClO_4 was standardised by EDTA titration. Vanadyl sulphate (0.05 M) in 1 M H_2SO_4 was prepared from A.R. ammonium metavanadate by SO_2 reduction and was standardised by oxidimetric titration after reduction to V^{2+} state. An aliquot of VO_2^+ was converted to vanadous sulphate by controlled potential electrolysis at a mercury cathode. The vanadous sulphate was then oxidised to vanadic salt by catalytic reaction with a large platinum foil in N_2 atmosphere (3 hrs.). Fresh solutions of vanadic sulphate were prepared before use. Other reagents used were AnalaR grade.

RESULTS AND DISCUSSION

The half-wave potential of reversible polarographic waves is known^{2, 9, 11} to be identical with chronopotentiometric quarter-wave potential. The reversible quarter-wave potential $E_{\tau/4}^r$ for partially irreversible reductions, e.g., Zn^{2+} in 1 M Na_2SO_4 , 1 M ethylenediamine (En) — 0.5 M KCl , 1 M NaOH — 1 M KCl , 1 M KNO_3 — 1 M Na OAc and BiO^+ in 1 M HClO_4 were determined by recording the anodic-cathodic polarograms with a dropping amalgam electrode. The concentrations of the depolarizer in the solution and in the amalgam phase were nearly equal (2mM) and since the diffusion coefficients of Zn and Bi in the amalgam phase were not known, the value of $E_{\tau/4}^r$ was taken as the formal standard potential E_f^0 in each case. For Eu^{3+} in 1 M KCl and also in 1 M NaClO_4 , the E_f^0 values were determined

from composite polarograms with equal concentrations (2mM) of Eu^{3+} and Eu^{2+} in solution. The reproducibility of the E_{f^0} values was better than ± 0.002 V in all the cases.

In the limiting case when $t \rightarrow 0$ equation (20) reduces to

$$E_{t=0} = E_s + \frac{2.3 RT}{anF} \log \frac{nFAk_s C^0}{i} \quad (19)$$

and this expression is applicable to both partially irreversible and totally irreversible waves. Assuming E_{f^0} as equal to E_s , the relation between $E_{t=0}$ and current density can be written as

$$E_{t=0} = E_{f^0} + \frac{2.3 RT}{anF} \log k_s' + \frac{2.3 RT}{anF} \log \frac{nFAC^0}{i} \quad (23)$$

i.e.,

$$\Delta E = \frac{0.06}{an} \log k_s' + \frac{0.06}{an} \log \frac{nFAC^0}{i} \quad (24)$$

It is clear that a plot of

$$\Delta E \text{ vs. } \log \frac{nFAC^0}{i}$$

should be linear and from the slope and intercept a and k_s' can be calculated.

The dependence of $E_{t=0}$ on cathodic current density at a constant concentration of the depolariser was studied for the reduction of Zn^{2+} in sodium sulphate, ethylenediamine (En), sodium hydroxide and sodium acetate (NaOAc) medium. The plot of

$$\Delta E \text{ vs. } \log \frac{nFAC^0}{i}$$

for the different systems is shown in Fig. 1, and the values of a and k_s' obtained therefrom are given in Table I. The values of a and k_s' obtained by other methods have also been included in Table I for comparison and it can be seen that the agreement is good particularly in view of the uncertainty and error involved in the direct recording of $E_{t=0}$. Further the $E_{t=0}$ values have not been corrected for (i) the iR drop due to the resistance of the solution between the tip of the Luggin Capillary of the reference electrode and the cathode (ii) the ohmic drop in the measuring circuit arising from the

current drawn by the input element of the recorder. The contribution due to (i) becomes appreciable at higher current densities and so accurate values of α and k_s' can be obtained only from the corrected values of $E_{t=0}$. In the present study no correction was applied to the measured potential and it is probable that the discrepancy in the values of α is due to this effect.

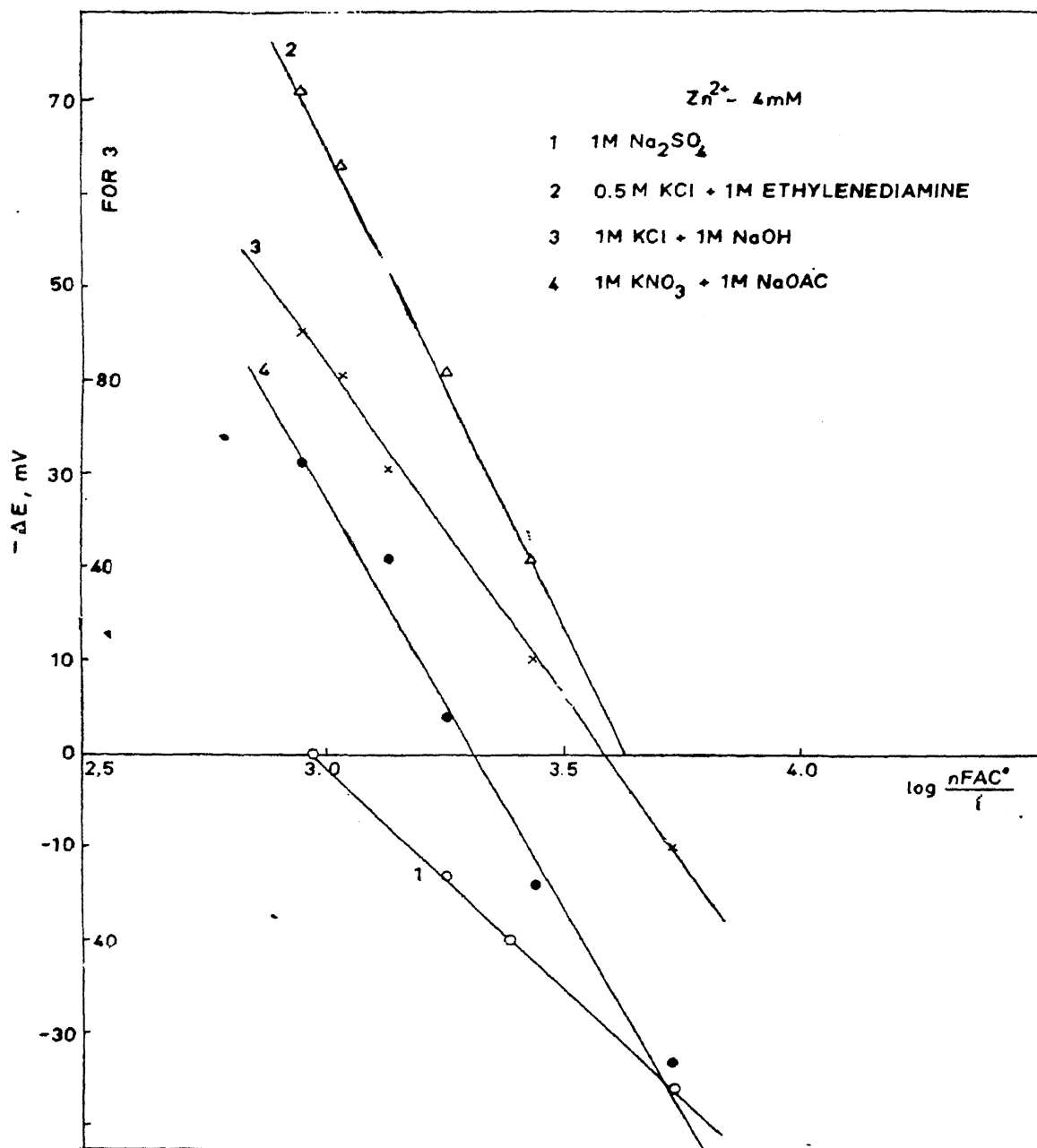


FIG. 1. Log-plot for zinc.

Accurate values of $E_{t=0}$ can be obtained by graphical extrapolation of the plot of E vs. $\log(1 - A)$. It is clear from equation (22) that as $t \rightarrow 0$,

Kinetic Parameters From Chronopotentiometric Waves

TABLE I
 Values of E_j^0 , $E_{t=0}$, α and $\log k_s'$ for metal ions in different media

Metal ion	Base electrolyt.	Current density mA/cm ²	$E_{t=0}$ — V vs. S.C.E.	Slope	E_j^0 — V vs. S.C.E.	α		$-\log k_s'$	
						a	b	a	b
4 mM Zn ²⁺	1 M Na ₂ SO ₄	0.144	0.980	0.05	1.016	0.63	0.31 ¹²	2.97	2.71 ¹²
		0.750	1.016						
4 mM Zn ²⁺	1 M En ‡0.5 M KCl	0.289	1.396	0.10	1.375	0.29	0.68 ¹³	3.63	3.81 ¹³
		0.866	1.446						
4 mM Zn ²⁺	1 M KCl ‡1 M NaOH	0.144	1.400	0.143	1.420	0.21	0.42 ¹⁴	3.59	3.31 ¹⁴
		0.866	1.511						
4 mM Zn ²⁺	1 M KNO ₃ ‡1M NaOAc	0.144	1.011	0.09	1.044	0.34	0.37 ¹⁵	3.31	3.21 ¹⁵
		0.866	1.075						
4 mM Eu ³⁺	1 M KCl	0.144	0.623	0.103	0.614	0.58	..	3.52	3.68 ¹⁶
3 mM BiO ⁺	1 M HClO ₄	0.35	-0.0246	0.034	-0.024	0.59	..	3.38	3.43 ¹⁷

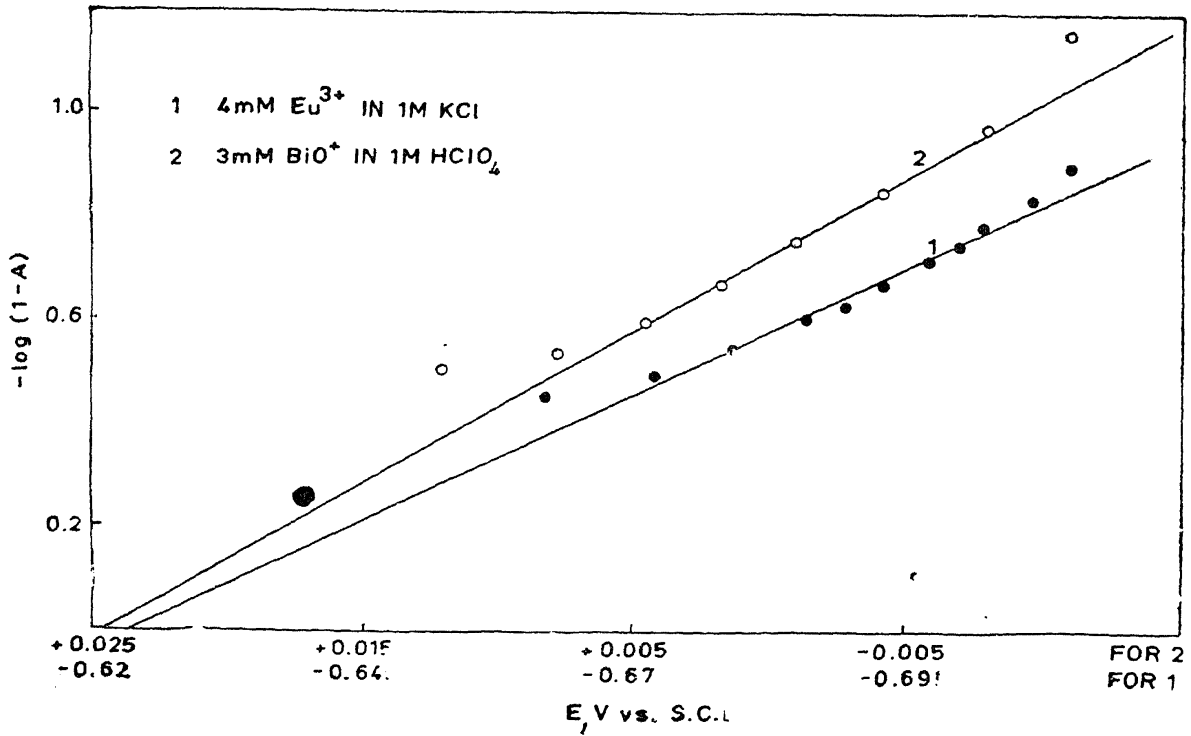


FIG. 2. Plot of $\log^2(1-A)$ vs. E .

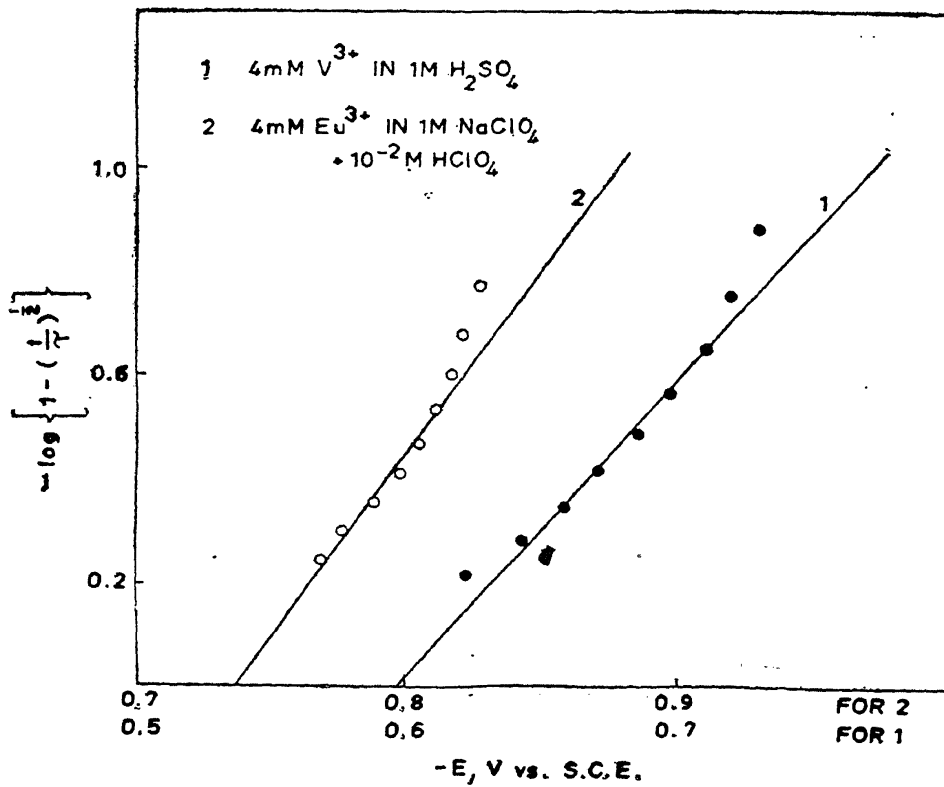


FIG. 3. Log-plot for V^{3+} and Eu^{3+} .

TABLE II

Values of $E_{t=0}$, α and $\log k_s'$ for metal ions in different media

Metal ion	Base electrolyte	Current density mA/cm ²	$E_{t=0}$ — V vs. S.C.E.	Slope	α		$-\log k_s'$	
					a	b	a	b
4 mM V ³⁺	1 M H ₂ SO ₄	0.139	0.596	0.174	0.35	0.59 ¹⁸	3.76	3.22 ¹⁸
4 mM Eu ³⁺	1 M NaClO ₄ ⁺	0.144	0.736	0.142	0.42	0.49 ¹⁹	4.37	3.82 ¹⁹
	0.01 M HClO ₄					0.49 ²⁰		4.70 ²⁰
4 mM Ni ²⁺	1 M KCl	0.318	1.095	0.093	0.33	0.35 ⁹	9.88	9.62 ⁹
4 mM Ni ²⁺	1 M KBr	0.318	1.020	0.06	0.50	..	12.2	..
4 mM Ni ²⁺	1 M KI	0.318	1.005	0.063	0.48	..	11.6	..
2 mM Co ²⁺	1 M K ₂ SO ₄	0.159	1.240	0.145	0.21	..	8.36	..
2 mM Co ²⁺	1 M KNO ₃	0.159	1.015	0.06	0.50	0.38 ^{21*}	11.67	11.0 ^{21*}

* 0.2 M NaClO₄ medium.

$\log(1 - A) \rightarrow 0$ and the intercept of the plot should give $E_{t=0}$ whereas α could be obtained from the slope. The chronopotentiometric reduction of Eu^{3+} in 1 M KCl and bismuthyl perchlorate in 1 M HClO_4 were studied and the plot of E vs. $\log(1 - A)$ is given in Fig. 2. The values of α and k_s' calculated from the plot are in good agreement with those reported in the literature (Table I).

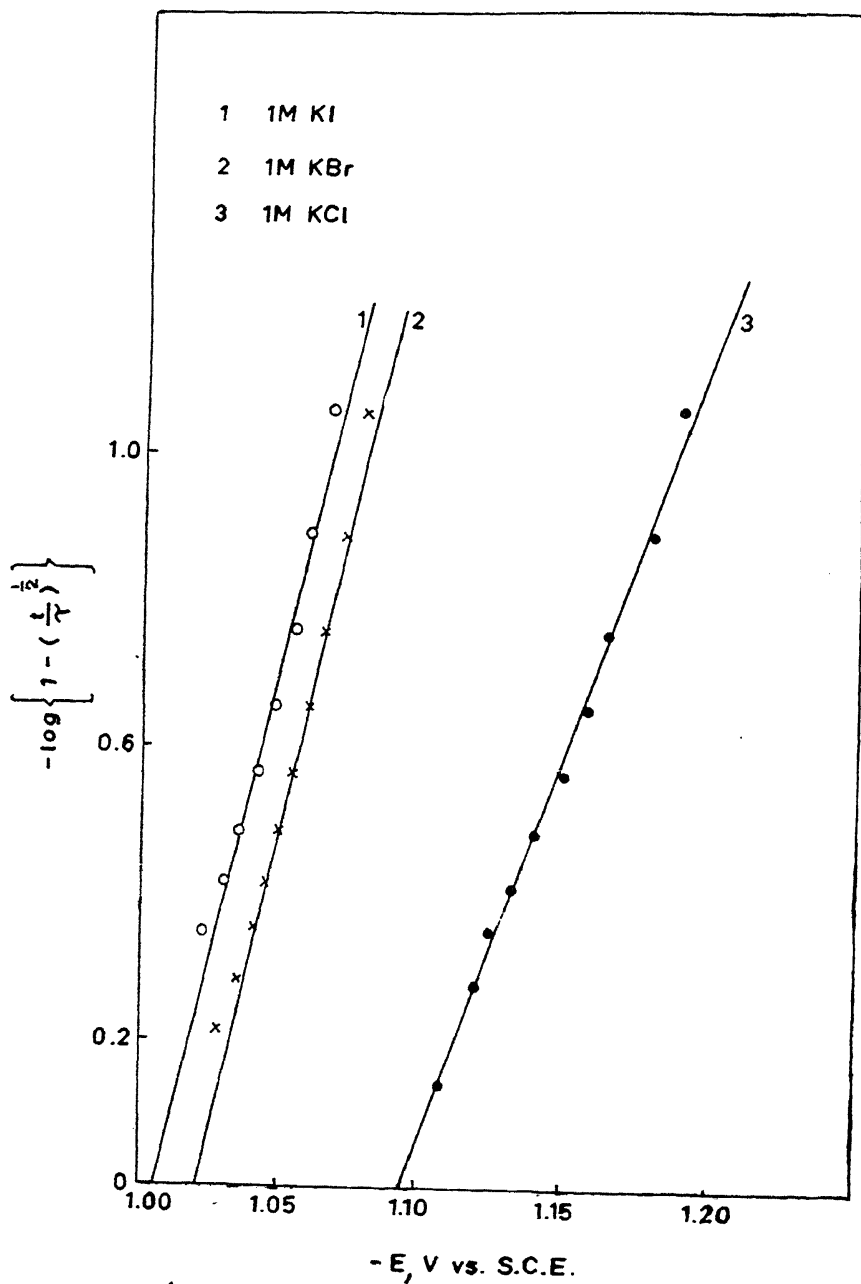


FIG. 4. Log-plot for 4 mM Ni^{2+} .

When $\exp nF(E - E_{\tau/4})/RT$ is negligible in comparison with unity, equation (21) reduces to equation (19) and the latter expression is valid for irreversible reductions. This condition is virtually satisfied when $k_s \leq 10^{-4}$ cm./sec. The plot of

$$E \text{ vs. } \log \left[1 - \left(\frac{t}{\tau} \right)^{\frac{1}{2}} \right]$$

for the reduction of V^{3+} in 1 M H_2SO_4 and Eu^{3+} in 1 M $NaClO_4 + 0.01$ M $HClO_4$ is given in Fig. 3 and from the slope, intercept and E_f^0 the values

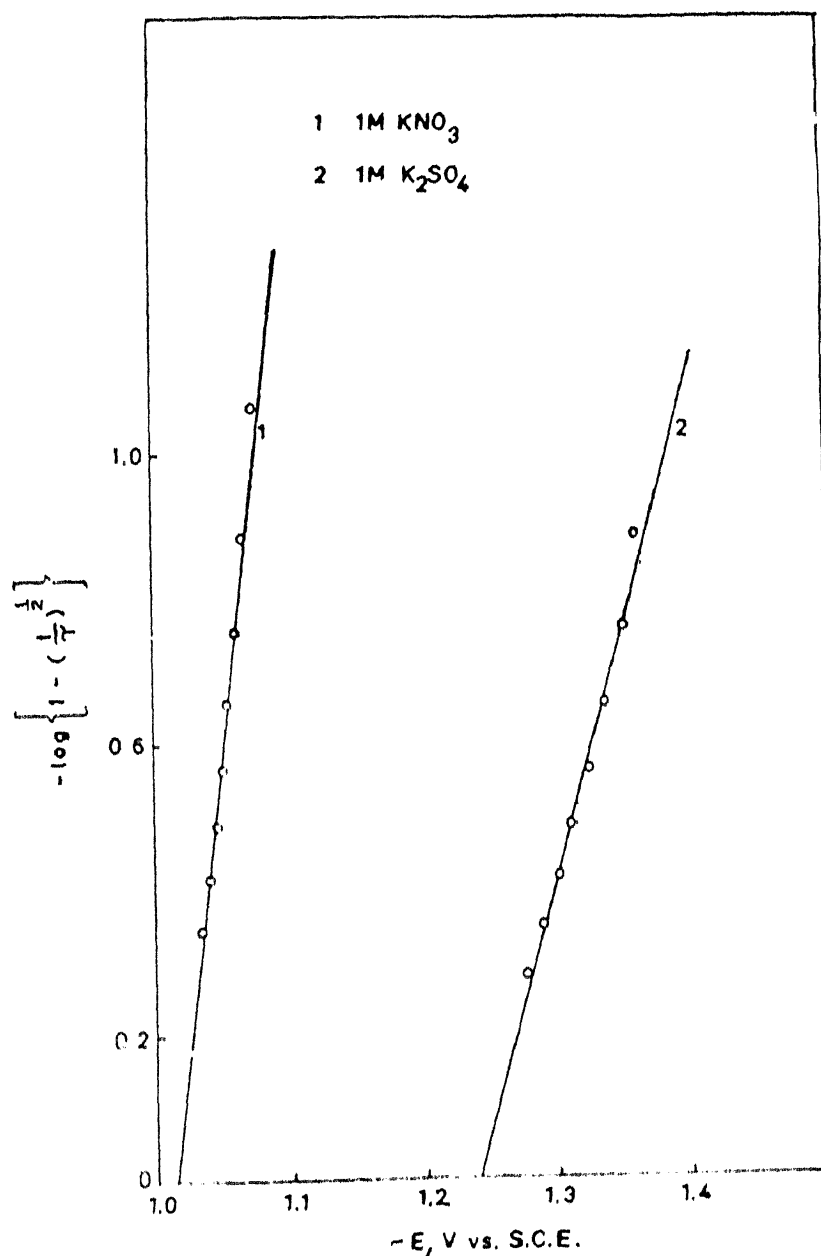


FIG. 5. Log-plot for 2 mM Co^{2+} .

of α and k_s' were calculated (Table II). For V^{3+} in 1 M H_2SO_4 , E_f^0 was taken as -0.541 V vs S.C.E.²² whereas for Eu^{3+} in 1 M $NaClO_4 + 0.01$ M

HClO₄ the value determined polarographically was -0.602 ± 0.002 V vs. S.C.E. in agreement with -0.601 V vs. S.C.E. reported by Timmer *et al.*²³. The kinetic parameters for these systems are comparable with those reported by other workers and it has been pointed out that deviation from expected behaviour is due to double layer¹⁹ and adsorption effects¹⁸. It is interesting to observe that for Eu³⁺ in 1 M NaClO₄ medium the value of $\log k_s'$ is close to the average of the values observed^{19,20} with and without double-layer correction.

The reduction of Ni²⁺ in 1 M KCl, KBr and KI and Co²⁺ in 1 M K₂SO₄ and KNO₃ are totally irreversible in nature. The plots of

$$E \text{ vs. } \log \left[1 - \left(\frac{t}{\tau} \right)^{\frac{1}{2}} \right]$$

are shown in Figs. 4 and 5. Latimer²⁴ reports a value of -0.491 V vs. S.C.E. for the standard potential of the couple Ni²⁺ — Ni and -0.518 V vs. S.C.E. for Co²⁺ — Co system respectively. With the latter values and from the $E_{t=0}$ values obtained graphically the kinetic parameters (Table II) for these systems were calculated.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. M. Sankar Das, Head, Analytical Division, for his kind interest in the work and Shri R. Sundaresan for helpful discussions.

REFERENCES

1. Karaoglanoff, Z. .. *Z. Elektrochem.*, 1906, **12**, 5.
2. Delahay, P. and Berzins, T. *J. Am. Chem. Soc.*, 1953, **75**, 2486.
3. Berzins, T. and Delahay, P. *Ibid.*, 1955, **77**, 6448.
4. Anderson, L. B. and Macero, D. J. *Anal. Chem.*, 1965, **37**, 322.
5. Delahay, P. .. *New Instrumental Methods In Electrochemistry*, Interscience Publishers, Inc., New York, 1954, p. 180.
6. Sand, H. J. S. .. *Phil. Mag.*, 1901, **1**, 45.
7. Oldham, K. B. .. *Electrochim. Acta*, 1966, **11**, 1475.
8. Chandrasekharan, V. R., Sundaresan, R., Saraiya, S. C. and Radhakrishnan, T. P. *Report B.A.R.C.-370*. 1968., p. 8.
9. Delahay, P. and Mattax, C. C. *J. Am. Chem. Soc.*, 1954, **76**, 874.

10. Reinmuth, W. H. .. *Anal. Chem.*, 1961, **33**, 485.
11. Reilly, C. N., Everett, G. W. and Johns, R. H. *Ibid.*, 1955, **27**, 483.
12. Anne Marie Baticle, C. R. *Acad. Sci., Paris*, 1962, **254**, 668.
13. Sundaresan, R., Saraiya, S. C. and Sundaram, A. K. *Proc. Ind. Acad. Sci.*, 1967, **66** (2), 120.
14. Matsuda, H. and Ayabe, Y. *Z. Elektrochem.*, 1959, **63**, 1164.
15. —, — and Adachi, K. *Ibid.*, 1963, **67**, 593.
16. Randles, J. E. B. and Somerton, K. W. *Trans. Farad. Soc.*, 1952, **48**, 937.
17. Moussa, A. A. and Sammour, H. M. *J. Chem. Soc.*, 1960, p. 2151.
18. Satyanarayana, S. .. *J. Electroanal. Chem.*, 1964, **7**, 403.
19. Gierst, L. and Cornellissen, R. *Coll. Czech. Chem. Comm.*, 1960, **25**, 3004.
20. Gierst, L. .. *Trans. Symp. Electrode Proc. Philadelphia*, 1959, p. 109.
21. Saraby-Reintjes, A. and Overbeck, J. Th. G. *Trans. Farad. Soc.*, 1966, **62**, 182.
22. Randles, J. E. B. .. *Can. J. Chem.*, 1959, **37**, 238.
23. Timmer, B., Sluyters-Rehbach M. and Sluyters, J. H. *J. Electroanal. Chem.*, 1967, **14**, 181.
24. Latimer, W. M. .. *Oxidation Potentials*, Prentice-Hall, Inc., N.J., 1959.

RIS-
1-8-1972
GRATIS

Supplement to the

"Proceedings of the Indian Academy of Sciences"

INDEX TO VOL. LXXV (A)

AUTHORS' INDEX

- Anantharaman, T. R. .. See Furrer and others.
- Bhagavantam, S. .. Crystal symmetry and non-linear optical properties, 1.
- Bhatnagar, K. G. .. See Bhiday and others.
- Bhiday, M. R., Bhatnagar, K. G. and Chaudhari, N. M. .. *e-e* scattering cross-section measurements using page type geometry, 138.
- Chakravarty, S. C. and Ramanathan, K. R. .. A comparison of field-strengths of 164 kHz radio waves transmitted from Tashkent and received at Ahmedabad with flare-time solar X-ray emissions measured in satellites, 249.
- Chakravorti, M. C. .. See Mande and others.
- Chandrasekhariah, D. S. .. On plane problems in magneto-thermo-elastostatics, 73.
- Chaudhari, N. M. .. See Bhiday and others.
- Dahiya, R. S. .. Some expansion formulae $\tilde{\omega}_{\mu_1, \dots, \mu_n}(x)$ involving exponential functions and trigonometrical functions, 199.
- Furrer, P., Warlimont, H. and Anantharaman, T. R. .. Electron-microscopic examination of a splat-cooled silver-germanium alloy, 103.
- Gaur, Y. N. .. See Verma and Gaur.
- Gupta, K. C. .. See Mittal (Mrs.), P. K.
- Gupta, T. R. .. Response of heat transfer from a moving flat plate in a parabolic flow, 158.
- Harinath, K. S. .. Semi-split sequences, I, II, 13, 19.

- Jha, Kamal Kant .. Analysis of bounded sets in a topological tensor product, 176.
- Karguppikar, A. M. .. See Radhakrishna and Karguppikar.
- Katyal, K. N. .. Couette flow of dipolar fluids, 39.
- Kaul, C. L. .. Fourier series of a generalised function of two variables, 29.
- Khare, P. L. .. See Modak and others.
- Kumar, N., Muthanna (Miss), M. and Sinha, K. P. On mass quantisation of elementary particles, 57.
- Lal, B. and Sahai, Baldev .. Study of levels in ^{51}Cr through ^{51}V (p, n, γ) reaction, 269.
- Mande, Chintamani, Pendharkar, A. V. and Chakravorti, M. C. The shapes of the L_{III} X-ray absorption discontinuity of rhenium in compounds, 209.
- .. See Modak and others
- Mittal (Mrs.), P. K. and Gupta, K. C. An integral involving generalized function of two variables, 117.
- Modak, S. G., Khare, P. L. and Mande, Chintamani An NMR study of the thiomalic acid complex of cobalt, 262.
- Moselhy, Moselhy Mohamed Spectroscopic determination of traces of some elements in cadmium carbonate, 217.
- Muthanna (Miss), M. .. See Kumar and others.
- Naidu, R. Raghava .. Spectrophotometric investigation of beryllium-2'-hydroxy chalcone complex, 124.
- Naidu, P. R. .. See Raman and Naidu.
- .. See Rao and Naidu.
- Narayan, B. .. Spectra and ionisation potential of cyanoacetylene, 92.
- Pendharkar, A. V. .. See Mande and others.
- Radhakrishnan, T. P. and Sundaram, A. K. Kinetic parameters from chronopotentiometric waves, 278.
- Radhakrishna, S. and Karguppikar, A. M. Raman spectra of irradiated NaClO_3 and KClO_3 crystals, 132.
- Ramakrishnan, V. T. .. See Shanmugam and Ramakrishnan,

- Ramanathan, K. R. .. See Chakravarty and Ramanathan.
- Ranganath, G. S. .. Faraday rotation tensor-extraction of components, 237.
- Rao, G. K. Raman and Naidu, P. R. Viscosities of binary solutions of non-electrolytes, 68.
- Rao, G. Venkoba and Venkatasubramanian, N. Salt effects in the alkaline hydrolysis of dicarboxylic esters in aqueous DMSO—the mechanism of half-ester hydrolysis, 8.
- Rao, K. C. Mohan and Naidu, P. R. Determination of acridine in non-aqueous media, 86.
- Rao, P. Mangeshwara and Rao, S. Brahmaji Polarographic study of iron (III)-resacetophenone-oxime complex, 50.
- Rao, S. Brahmaji .. See Rao and Rao.
- Rao, V. V. Ramana .. Secondary flow of a conducting fluid in a rotating straight annular pipe, 189.
- Rao, V. V. Ramana and Sithapathi, A. Laminar boundary layers along an infinite porous plate in the presence of a transverse magnetic field, 227.
- Sahai, Baldev .. See Lal and Sahai.
- Shanmugam, P. and Ramakrishnan, V. T. Synthesis of 3:4 dihydro 2H-pyrano (2, 3-*b*) quinolines, 96.
- Sinha, K. P. .. See Kumar and others.
- Sithapathi, A. .. See Rao and Sithapathi.
- Sudersanan, M. and Sundaram, A. K. Solvent extraction studies of indium, II, 151.
- Sundaram A. K. .. See Sudersanan and Sundaram.
.. See Radhakrishnan and Sundaram.
- Venkatasubramanian, N. .. See Rao and Venkatasubramanian.
- Verma, P. D. and Gaur, Y. N. On the unsteady flow and temperature distribution of a viscous incompressible fluid between two parallel flat plates, 108.
- Warlimont, H. .. See Furrer and others.

TITLE INDEX

- Acridine in non-aqueous media, determination of (Rao and Naidu), 86.
- Beryllium-2'-hydroxy chalcone complex, spectrophotometric investigation of (Naidu), 124.
- Binary solutions of non-electrolytes, viscosities of (Raman and Naidu), 68.
- Cadmium carbonate, spectroscopic determination of traces of some elements in (Moselhy), 217.
- Chronopotentiometric waves, kinetic parameters from (Radhakrishnan and Sundaram), 278.
- Cobalt, thiomalic acid complex of, an NMR study of the (Modak and others), 262.
- Couerte flow of dipolar fluids (Katyal), 39.
- ^{51}Cr , study of levels in, through $^{51}\text{V}(p, n\gamma)$ reaction (Lal and Sahai), 269.
- Crystal symmetry and non-linear optical properties (Bhagavantam), 1.
- Cyanoacetylene, spectra and ionisation potential of (Narayan), 92.
- Dicarboxylic esters in aqueous DMSO, salt effects in the alkaline hydrolysis of, —the mechanism of half ester hydrolysis (Rao and Venkatasubramanian), 8
- e-e* scattering cross-section measurements using page type geometry (Bhiday and others), 138.
- Elementary particles, on mass quantisation of (Kumar and others), 57.
- Expansion formula $\omega_{\mu_1, \dots, \mu_n}(x)$ involving experimental functions and trigonometrical functions (Dahiya), 199.
- Faraday rotation tensor-extraction of components (Ranganath), 237.
- Field-strengths of 164 kHz radio waves transmitted from Tashkent and received at Ahmedabad, a comparison of, with flare-time solar X-ray emissions measured in satellites (Chakravarty and Ramanathan), 249.
- Flow, parabolic, moving flat plate in a, response of heat transfer from a (Gupta), 158.
- Flow, secondary, of a conducting fluid in a rotating straight annular pipe (Rao), 189.
- Fourier series of a generalised function of two variables (Kaul), 29.

- Indium, solvent extraction studies of, II (Sudersanan and Sundaram), 151.
- Integral involving generalized function of two variables (Mittal and Gupta), 117.
- Iron (III)-resacetophenoneoxime complex, polarographic study of (Rao and Rao), 50.
- Laminar boundary layers along an infinite porous plate in the presence of a transverse magnetic field (Rao and Sithapathi), 227.
- Magneto-thermo-elasto-statics on plane problems in (Chandrasekhariah), 73.
- Quinolines, 3:4 dihydro 2H-pyrano (2, 3-b), synthesis of (Shanmugam and Ramakrishnan), 96.
- Raman spectra of irradiated NaClO_3 and KClO_3 crystals (Radhakrishna and Karguppikar), 132.
- Rhenium in compounds, the shapes of the L_{III} X-ray absorption discontinuity (Mande and others), 209.
- Semi-split sequences, I, II (Harinath), 13, 19.
- Silver-germanium alloy, splat-cooled, electron-microscopic examination of a (Furrer and others), 103.
- Topological tensor product, analysis of bounded sets in a (Jha), 176.
- Viscous incompressible fluid between two parallel flat plates, on the unsteady flow and temperature distribution of a (Verma and Gaur), 108.