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GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

ON THE ELECTROLYTIC GENERATION OF HYDRATED ELECTRON

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BHABHA ATOMIC RESEARCH CENTRE
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ABSTRACT

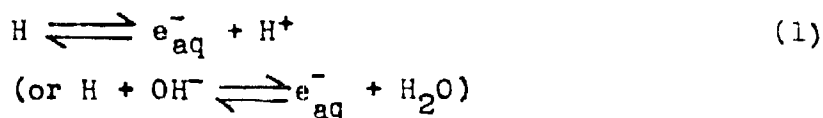
Investigations on the electrolytic generation of hydrated electron in oxygenated as well as oxygen free solutions at different pH were undertaken. Since e_{aq}^- is known to react rapidly with O_2 yielding the transient O_2^- ion, the latter was looked for through its interaction with phosphite ions resulting in their oxidation near the cathode. It appears from the results that in electrolytic processes, the primary electron ($e_{cathode}^-$) probably reacts directly with reactive solutes like oxygen, bypassing the hydration step. Data obtained in oxygen free solutions, however, support the possible formation of hydrated electron at least in alkaline solutions.

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It is known that hydrogen atoms are converted to hydrated electrons in alkaline solutions, and that the reverse reaction takes place in acidic solutions. p_K of the equilibrium reaction 1 has been established to be $3.6^{(1)}$.



Now, H atoms are generally assumed to be the precursors of electrolytic hydrogen gas evolved from aqueous solutions. Since the above equilibrium is also operative, *prima facie* there is no reason why hydrated electrons could not also be the precursors, at least in alkaline solutions. In that case H_2 would form according to the reaction 2.



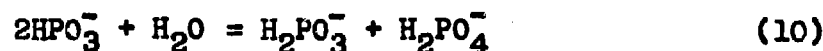
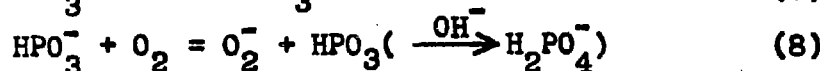
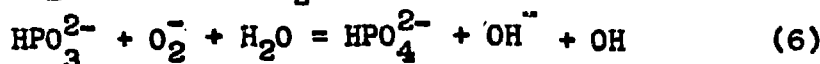
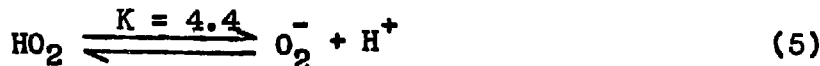
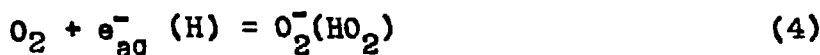
Experimental results in support of electrolytic generation of hydrated electron in N_2O saturated solutions, or in other oxygen free atmospheres have been published⁽²⁻⁴⁾. Critical examination^(5,6) of the results, however, reveal that the results could perhaps be explained by other mechanisms, not necessarily involving hydrated electrons. In any case, no attempt seems to have been made so far to generate and to detect e_{aq}^- in an oxygen atmosphere, presumably because of the

difficulty anticipated by virtue of its rapid reaction with O_2 yielding O_2^- , as is known from radiation chemical studies.



The present work was undertaken with the object of obtaining some clarifications regarding the question of electrolytic generation of e_{aq}^- in aqueous solutions, particularly in presence of oxygen.

In oxygen saturated solutions, hydrogen peroxide is a cathodic product. Hence detection of the transient O_2^- ion in presence of H_2O_2 was necessary in these investigations. Phosphite ions were used in these electrolytic experiments for this purpose. They are known to be unreactive towards H_2O_2 , but as established by radiation chemical studies^(7,8) they readily react with HO_2 or O_2^- leading to a chain reaction in presence of oxygen, and thereby get oxidized to phosphate ions:



In this investigation, therefore, we looked for "cathodic oxidation" of phosphite ions, under conditions that

the cathodic potential was negative enough for a sufficient flow of current to generate measurable concentration of detectable species, but not too negative to reduce the oxidized products.

It may be noted that phosphite ions might also be oxidized cathodically by H atoms (in absence of oxygen) through the hydrogen abstraction reaction 11⁽⁷⁻⁹⁾, followed by reaction 10.



1. EXPERIMENTAL

Electrolyses were carried out in a glass apparatus in which the cathode compartment, about 12 cm in height and 2.5 cm in diameter, was separated from the anode compartment by means of a filter paper packing. The cathode was of platinum foil, usually 14 cm², unless otherwise stated, the anode being always a platinum-rhodium wire. The electrode potential with respect to a saturated calomel electrode was measured with a Beckman G.S. model pH/Potentiometer. A stabilized power supply "Aplab" make, 0 - 25 V, D.C. and 5 A maximum, was used for obtaining the electrolytic current. The anolyte was a millimolar solution of sodium sulphate. Solutions for electrolyses were prepared in bidistilled water by suitable dilution of standard sodium phosphite solutions, prepared from Na₂HPC₃·5H₂O (Lab Reagent, B.D.H.). Acidity and alkalinity were measured either by titration or pH measurement, and were

adjusted by the addition of known quantities of standard NaOH or H₂SO₄.

Electrolyses were carried out in presence of one of the following gases: oxygen, nitrogen (Indian Oxygen Ltd.) argon and nitrous oxide (Matheson gas products USA). For removing oxygen from the last three gases, a train of three traps of alkaline pyrogallol was used. The efficiency of the purifying train was checked by an extremely sensitive method⁽¹²⁾, which is based on the current induced cathodic oxidation of As(III) in presence of O₂. The gas was allowed to bubble through the catholyte continuously during electrolysis for stirring also. Before being allowed in the cell, the gas was passed through water of the same acidity or alkalinity as that of the electrolyte.

Analysis: For the estimation of traces of phosphate in presence of a large excess of phosphites, the molybdenum blue method suitably modified was used. We have checked that the method recommended by Daniels⁽¹⁰⁾ for arsenic(V) in presence of arsenic(III), based on a preliminary extraction of the molybdenum complex in isobutyl alcohol, is applicable in the case of phosphate also, the extinction coefficient of the molybdenum blue being 1.95×10^4 ($\pm 3\%$) at 730 nm.

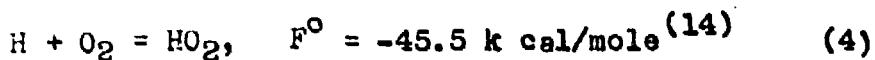
2. RESULTS AND DISCUSSION

A few typical results are compiled in Table I from which it seems clear that phosphite ions are not oxidized in electrolytic runs carried out in presence of oxygen and with cathodes prepolarized anodically, that is to say when there is only an

adsorbed layer of oxygen free from any possible contamination of hydrogen on the electrode surface. We have checked that under these conditions oxygen is reduced to hydrogen peroxide (estimated by the method of Allen et al⁽¹¹⁾), which being unreactive towards phosphates, accumulates in the solution up to a certain steady state concentration. In alkaline and neutral solutions the observed extent of oxidation in blank runs (i.e. due to spontaneous oxidation in contact with platinum and in absence of current) is almost negligible being very close to the reagent blank. In acid solutions, however, the spontaneous oxidation in the blank runs is slightly higher, but are not significantly different from those of the experimental runs. In separate experiments with alkaline arsenite, taken in lieu of phosphite, we have observed formation of arsenate near a cathode in presence of oxygen⁽¹²⁾. Such an oxidation is understandable since arsenite is rapidly oxidized by hydrogen peroxide, provided of course the cathodic potential is not too negative.

Appreciable oxidation of phosphite ions takes place, on the other hand, if the cathode undergoes a cathodic prepolarization in absence of oxygen, and then brought in contact with oxygen (Sr. nos. 8-21). Oxidation takes place both in the presence and in the absence of a cathodic current. Oxidation is, however, inhibited if the prepolarization be effected in oxygen. Our interpretation is that during cathodic prepolarization in absence of oxygen, the platinum electrode surface is covered at least partially with adsorbed hydrogen atoms⁽¹³⁾. The moment the adsorbed hydrogen atoms come in contact with

oxygen, the following reactions take place:

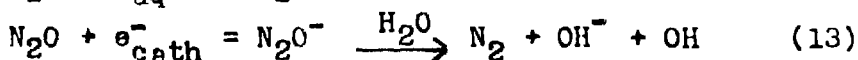
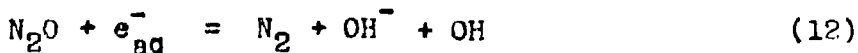


The highly negative free energy of reaction 4 is evidently responsible for the desorption of the radicals formed. That is not surprising since W_d , the heat of hydrogen adsorption on platinum is reported to change from about 20 to about 4 k cal/mole, depending upon θ , the coverage^(13,15). Once the peroxy radicals come in contact with phosphite ions, then the subsequent oxidation of the latter is understandable in terms of reactions 6-10, mentioned before. Comparison of the results of solutions having different pH shows that the observed effect is much more marked in the case of neutral and acid solutions than in the case of alkaline solutions (run nos. 20 and 21). In the latter case, since cathodic prepolarization was also done in alkaline solutions, hydrogen atoms were either not formed, or even if formed got destroyed because of the equilibrium reaction 1 with a pK of 9.6.

If electrolysis be carried out in an inert atmosphere of argon/nitrogen (sr. nos. 22-36), then slight oxidation is detected only in neutral and acid solutions, probably through reaction 11 with H atoms generated cathodically in these media, followed by the disproportionation reaction 10. Moreover, concentration of phosphate formed at very negative potentials are almost negligible (sr.nos. 28, 29, 35 and 36). Under these

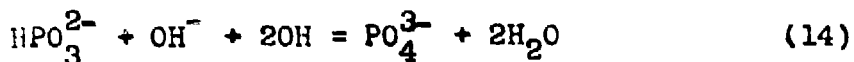
conditions, back cathodic reduction of the intermediate P(IV) species becomes possibly more favourable than the disproportionation reaction 10, through which phosphate ions are formed*. In any case, the extent of this hydrogen abstraction reaction is much less than the oxidation induced by chain reaction involving perhydroxy radicals. Since H atoms cannot exist at a pH greater than 9.6, oxidation does not take place as expected in alkaline solutions (runs nos. 22-24).

Finally, a few experiments were carried out in N₂O saturated alkaline solutions, in the hope that OH radicals would be generated cathodically through either the reaction 12 or reaction 13.



* In acid solutions P(IV) species might exist as H₂PO₃ or its dimer H₄P₂O₆, the latter being known to be stabler than the former. Redox potentials for the reduction couple H₄P₂O₆ + 2H⁺ + 2e⁻ = 2H₃PO₃, and H₄P₂O₆ + 2e⁻ = 2H₂PO₃⁻, are reported to be +0.38 V and + 0.275 V respectively (16). These values correspond to free energy changes of -16.53 and -12.6 k cal/mole, compared to -30 k cal/mole, estimated for the disproportionation reaction, H₄P₂O₆ + H₂O = H₃PO₃ + H₃PO₄ (14). Thus at potentials, no more negative than the foregoing equilibrium values, the disproportionation reaction should be competing more favourably, at least from energetic considerations. At potentials further away towards negative side, the competition would obviously go more and more in favour of the cathodic reduction of P(IV) species, until the disproportionation reaction leading to the formation of phosphate ions becomes insignificant. Since the radical H₂PO₃ or the radical ion HPO₃⁻, which are supposed to enter in the mechanism postulated (and for which free energy data are not available), are expected to be more energetic than $\frac{1}{2}$ H₄P₂O₆, the foregoing quantitative values of free energies would surely be somewhat different. Yet the qualitative picture as envisaged would not perhaps be altered seriously.

and that these oxidizing radicals would react with phosphite ions to yield phosphate ions according to the well known exo-energetic reaction 14



Our attempts to detect phosphate ions under these conditions were, however, not successful (sr. nos. 37,38). It can be shown from the potentials reached during electrolysis that the possibility of back cathodic reduction of phosphate ions formed, if any, should be ruled out as an explanation for the negative results. It is rather felt that OH radicals are probably formed at the cathode but that they are reduced immediately before reacting with P(III) species to produce the intermediate P(IV) species (reaction 7), this reaction being the initial step before the overall oxidation reaction 14 can proceed to P(V) species. Such a hypothesis is supported at least by energetic considerations, since the E_B^0 of the reaction 7 can be shown to be no more than +1.74 V, compared to +2.0 V for the OH-OH⁻ couple. The other experiments (sr. nos. 39,40) concerning N₂O, however, support the picture envisaged in the foregoing: the slight oxidation noticed in oxygen saturated alkaline solutions with cathodically prepolarized electrodes is completely absent when the prepolarization is carried out in presence of N₂O in lieu of in nitrogen/argon, since N₂O destroys e⁻_{cathode} or e⁻_{aq} the precursor of H atom. As expected N₂O is ineffective in acid solutions (sr.no. 13).

3. MECHANISM FOR THE ELECTROLYTIC REDUCTION OF OXYGEN

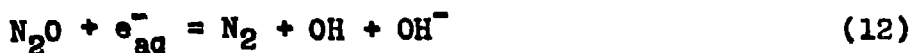
The results seem to establish very clearly that during the electrolytic reduction of oxygen, HO_2 radical or O_2^- ions are not formed in the solution phase, provided of course the system be free from hydrogen initially, and even if these transient intermediates are formed on the cathode surface in an adsorbed state, they are quickly reduced to HO_2^- or H_2O_2 . The results, therefore, provide a direct experimental evidence in support of the mechanism generally assumed for the cathodic formation of hydrogen peroxide from oxygen⁽¹⁷⁾, according to which, HO_2 formed as an intermediate remains adsorbed on the electrode surface, and only the stable product viz. H_2O_2 may either desorb, or be further reduced leading to the formation of water.

4. ELECTROLYTIC GENERATION OF HYDRATED ELECTRON/HYDROGEN ATOM

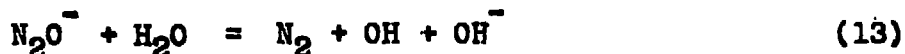
The redox potential of hydrated electron is calculated to be -2.77 V ⁽¹⁸⁾ in European convention. Thus, if one aims to generate electrolytically even a very low concentration of hydrated electron, say $10^{-7} \text{ moldm}^{-3}$ at a pH of 11, the cathode should have to be made as negative as -1.7 V (vs n h e). On the other hand, one may argue that if hydrated electron be, in fact, the precursor of cathodically produced hydrogen gas, then a finite concentration of the former must certainly be present at more positive potentials. In analogy to the picture commonly assumed in one of the mechanisms for explaining hydrogen over voltage through hydrogen atoms formed in a primary step,

one expects that hydrated electrons if formed at more positive potentials would remain adsorbed on the electrode surface, combination of two hydrated electrons providing the energy for desorption of the final product viz. hydrogen molecules.

In view of the above considerations, for chemical identification of hydrated electron (adsorbed on an electrode surface), it is necessary to use a reagent which would react with e_{aq}^- exo-energetically furnishing the energy of desorption of the products. Walker⁽²⁾ used N_2O and measured N_2 produced according to reaction 12, ΔF° of which is pretty high being about -118 k cal/mole (ΔF° is calculated assuming $F^\circ N_2O = 25$ k cal/mole).



It is therefore interesting to note that Walker could measure significant amount of N_2 , even though he used a very low current density $\sim 50 \mu A/cm^2$, with a platinum electrode and with 0.25 mol dm^{-3} of Na_2SO_4 solution. Under these conditions hydrogen gas evolution is hardly noticeable. Of course this experiment, as stated before⁽⁵⁾ does not prove unequivocally the cathodic formation of e_{aq}^- since N_2O can readily react with $e_{cathode}^-$ giving N_2O^- which can then decompose as follows giving the same products:



In regard to oxygen saturated solutions, our results show as stated before that O_2^- (or HO_2) is not detectable in

the solution phase. But that does not preclude the possibility of its formation in an adsorbed state on the electrode surface. Since the free energy of formation of e_{aq}^- (63.9 k cal/mole⁽¹⁸⁾) is more positive than that of O_2^- (13 k cal/mole), the formation on the electrode surface of the former, in preference to the latter, is rather improbable. Moreover, if e_{aq}^- (or H) were formed on the electrode surface, then the same would have reacted with O_2 with a free energy change of about - 50 k cal/ (or -45 k cal/mole). This energy being highly negative, O_2^- (or HO_2) should have been desorbed and detected by the technique employed by us. Therefore, from our results, it would seem almost certain that e_{aq}^- cannot form in presence of oxygen either in solution phase or on the electrode surface in an adsorbed state.

"Cathodic oxidation" of phosphite ions observed in electrolyses carried out in an inert atmosphere of nitrogen/argon, and also the results obtained with electrodes prepolarized cathodically in the same atmosphere are readily explicable on the basis of electrolytic formation of H atoms in acid and neutral solutions. Moreover, our data concerning pH effect conform to the equilibrium 1, and hence support albeit indirectly, the formation of e_{aq}^- in oxygen free (i.e. in nitrogen/argon) alkaline solutions. The data are, however, inadequate to throw light on the question whether it is formed in a primary electrode process, or subsequently from H atom.

In view of the above, it appears that in electrolytic processes, hydration of the primary electron ($e_{cathode}^-$) may or

may not take place, depending upon the nature of solutes. With relatively more reactive solutes like oxygen, for example, it can very well react directly, bypassing the transient formation of e_{aq}^- . The negatively charged species thereby formed could of course remain adsorbed on the electrode surface and undergo further reactions with $e_{cathode}^-$ or with other aqueous species, till favourable conditions are reached for desorption. The above conclusion seems to be somewhat analogous to that of Hamill⁽¹⁹⁾ according to whom dry electrons, produced in a primary event during radiolysis of aqueous solutions, need not have to be always hydrated before reacting with certain solutes.

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Table I

OXIDATION OF PROSPHITE^(a) TO PHOSPHATE AT A PLATINUM CATHODE^(b) PREPOLARIZED UNDER VARIOUS CONDITIONS

Sr. No.	pH	Treatment given to cathode	Conditions for spontaneous/electrolytic oxidation				Phosphate formed		
			Gas ^(c)	Cathodic current μ A	Cathodic potential V, (vs SCE)	Time of run	O.D. ^(d)		%
1	2	3	4	5	6	7	8	9	10
IN OXYGEN SATURATED SOLUTIONS									
1	11	A.P. (g)	O ₂	79 to 22	-0.07 to -0.03	2.0 h	0.012		
2	11	"	O ₂	78 to 40	-0.06 to +0.01	2.0 h	0.007		
3	7.5	"	O ₂	5	+0.34 to +0.17	1.0 h	0.023	0.017	
4	7.5	"	O ₂	70 to 20	+0.27 to +0.12	1.0 h	0.008	0.01	
5	7.5	Electrode just washed after expt.4	O ₂	Spontaneous		1.0 h	0.012		
6	1	A.P. (g)	O ₂	5	+0.85 to +0.505	1.0 h	0.055	0.036	
7	1	"	O ₂	5	+0.5	1.0 h	0.053	0.038	
IN OXYGEN, BUT WITH ELECTRODES CATHODICALLY PREPOLARIZED IN NITROGEN/ARGON ATMOSPHERES									
8	1	C.P. (1)	O ₂	Spontaneous		30 min	1.6		40.8
9	1	"	O ₂	30	+0.48 to +0.55	30 min	1.47		37.5
10.	1	A.P. (g)	N ₂	50	+0.10 to -0.27	1.0 h	Gas changed		

Table I contd.,.

1	2	3	4	5	6	7	8	9	10
11	1	Cathode after expt. 10 just washed	O ₂		Spontaneous	1.0 h	1.36		34.7
12	1	A.P. (g) Run continued	N ₂ O ₂	50	+0.59 to -0.275 Spontaneous	1.0 h 1.0 h	G.C. (k) ~2		51.0
13	1	A.P. (g) Run continued	N ₂ O O ₂	5 5	+0.83 to +0.085 +0.085 to +0.57	1.0 h 1.0 h	G.C. (k) 1.55		39.5
14	7.5	C.P. (j)	O ₂		Spontaneous	30 min	0.51		13.0
15	7.5	"	O ₂	36 to 48	+0.2 to +0.23	30 min	0.583		14.9
16	7.5	A.P. (g) Run continued with high current	N ₂ O ₂	40 80 to 73	+0.53 to -0.665 -0.665 to +0.18	1.0 h 1.0 h	G.C. (k) 0.53		13.5
17	7.5	A.P. (g) Run continued	N ₂ O ₂	40	+0.47 to -0.66 Spontaneous	1.0 h 1.0 h	Current stopped and G.C. (k) 0.98		25.0
18	7.5	A.P. (g) Run continued	N ₂ O ₂	5	+0.31 to -0.2 Spontaneous	1.0 h 1.0 h	C.S. (l) and G.C. (k) ~2		51.0
19	7.5	A.P. (g) Run continued	N ₂ O ₂	5	+0.27 to -0.49 Spontaneous	1.0 h 1.0 h	C.S. (l) and G.C. (k) 1.95		49.7
20	11	A.P. (g) Run continued	N ₂ O ₂	98 to 35	+0.04 to -0.7 Spontaneous	1.0 h 1.0 h	C.S. (l) and G.C. (k) 0.055		1.4
21	11	A.P. (g) Run continued	N ₂ O ₂	35 to 39 39	+0.125 to -0.775 +0.05 to +0.13	1.0 h 1.0 h	G.C. (k) 0.062		1.6

Table I contd...

1	2	3	4	5	6	7	8	9	10
IN OXYGEN FREE SOLUTIONS									
22	11	A.P. (g)	N ₂	5	+0.3 to +0.03	1.0 h	0.012		
23	11	"	N ₂	95 to 29	+0.065 to -0.75	1.0 h	0.017		
24	11	"	N ₂	40	+0.29 to -0.65	1.0 h	Close to reagent blank		
25	7.5	"	A	5	+0.7 to -0.17	1.0 h	0.053	0.021(m) 0.021	0.8
26	7.5	A.P. (g)	N ₂	5	+0.22 to -0.215	1.0 h	0.07	0.011(m) 0.0081	1.5
27	7.5	"	"	5	+0.16 to -0.245	1.0 h	0.068		1.5
28	7.5	"	"	100 to 93	+0.37 to -0.74	1.0 h	0.015	0.012	
29	7.5	"	A	650 to 5	+0.13 to -0.75	1.0 h	0.012	0.0121(m) 0.0081	Negligible
30	1	"	"	10 to 1.5	+0.26 to +0.02	1.0 h	0.113	0.065	1.2
31	1	"	"	5	+0.77 to +0.04	1.0 h	0.06	0.032	0.8
32	1	"	N ₂	40 to 10	+0.3 to +0.155	1.0 h	0.108	0.0651(m) 0.0631	1.1
33	1	"	"	5	+0.28 to +0.15	1.0 h	0.133	0.0631(m) 0.0661	1.7
34	1	"	"	5	+0.65 to +0.15	1.0 h	0.112	0.068	1.1

Table I contd...

1	2	3	4	5	6	7	8	9	10
35	1	A.P. (g)	A	40	+0.68 to -0.245	1.0 h	0.038	0.032 (m) 0.035	
36	1	"	N ₂	100	+0.71 to -0.29	1.0 h	0.033	0.035	
37	11	"	N ₂ O	45 to 22	-0.22 to -0.265	1 h 45 min	0.009		
38	11	"	N ₂ O	5	+0.22 to +0.015	1.0 h	0.023	0.021	
39	11	" Run continued	N ₂ O O ₂	85 to 30 Spontaneous	+0.1 to -0.135	30 min 1.0 h	C.S. (l) 0.008	and G.C. (k)	
40	11	A.P. (g) Run continued	N ₂ O O ₂	61 to 32 32 to 30	+0.19 to -0.16 -0.16 to +0.125	1.0 h 1.0 h	G.C. (k) 0.017		

- a) Initial phosphite ion concentration: $10^{-3} \text{ moldm}^{-3}$; volume of electrolyte: 16 cm^3 .
- b) Cathode size: 14 cm^2 .
- c) Gas flow rate: about 3 bubbles/s.
- d) O.D. measured at 730 nm and in a cell of 1 cm path length. Molybdenum blue colour developed in 5 cm^3 sample diluted to 25 cm^3 .
- O.D. of 0.01 = $2.55 \times 10^{-6} \text{ moldm}^{-3}$ of phosphate ions in the sample.
- e) Blank includes the amount spontaneously oxidized in contact with platinum, and also the reagent blank, i.e., the amount of phosphate ions present in the original solution.
- f) The reagent blank determined in a number of experiments with $10^{-3} \text{ moldm}^{-3}$ phosphite solutions lie between 0.008 to 0.018 in terms of O.D. which corresponds to 0.25 - 0.5% of phosphate ions.
- g) Anodic prepolarization was carried out by making the platinum electrode an anode for 10 min in 1:4 nitric acid and passing a current of 0.2A. The electrode was then thoroughly washed in double distilled water to remove even traces of nitric acid, and finally used for regular electrolysis.
- i) Cathodic prepolarization was carried out by making the platinum electrode the cathode for 10 min in a current of about 0.2A in a sulphuric acid solution of pH ~ 1 , under conditions of copious hydrogen gas evolution.
- j) Same as (i) except that the cathodic prepolarization was carried out in a neutral solution of $0.1 \text{ moldm}^{-3} \text{ Na}_2\text{SO}_4$.
- k) Gas changed (G.C.)
- l) Current stopped (C.S.)
- m) Blank runs carried out before and after electrolytic run.

