

ELECTRO-CHEMICAL REACTIONS IN ALTERNATING ELECTRIC FIELD

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1. INTRODUCTION

THE study of kinetics of electro-chemical reactions under the action of alternating fields has assumed a new importance in view of the recent interesting work of Randles.¹ The work of Randles distinctly indicates the possibility of a chemical reaction being brought about by the action of alternating field with a considerably high current efficiency. Very little work however has been done on the quantitative measurement of current efficiency for electrolysis using alternating current. The only important detailed study of recent times is by A. N. Kappanna,² who has determined the current efficiency using silver nitrate as electrolyte. It is however found that there were complications due to the electrode surfaces being altered by the deposits produced by the current. Further, there was formation of silver peroxy-nitrate at one of the electrodes. The present work has been confined to the electrolysis of ferric sulphate solutions using platinum electrodes, wherein the electrode reactions are simpler in character.

2. EXPERIMENTAL

The alternating current was obtained through a transformer giving a voltage of 45 to 90 volts, current being adjusted using a rheostat. The peak current was measured by making use of an oscillograph, from which the average value of the current was computed. The average value was confirmed by making use of a rectifier type microammeter. 0.33N ferric sulphate was used as the electrolyte. Platinum wire electrodes were employed. In any electrolytic cell the two electrodes were nearly of the same dimensions, the average area being taken for the calculation of current density. In many of the experiments, a number of electrolytic cells were put in series so as to minimise the effects due to change in nature and magnitude of the quantity of electricity passed while interpreting the effect of dimensions of the electrodes on current efficiency. In all these experiments the net reaction was

that of reduction, the ferric salt being reduced to the ferrous state. Evolution of hydrogen and oxygen was noticed in every case except with the lowest current density (when platinum discs were used as electrodes).

In the present work the discharge of hydrogen has been ignored and the current efficiencies are all calculated on the basis of the amount of ferrous salt produced. Since the net reaction is found to be reduction, the current efficiency is calculated by taking into account the total amount of cathodic current passed and the actual amount of net reduction that has taken place. The amount of reduction was determined by titrating the resulting ferrous salt against standard (0.01 N) permanganate. The electrolysis was conducted for a duration of 5 minutes, 10 minutes and 15 minutes. Duplicates were performed in each case. The average of each of the 6 sets of values are given in Table I. Some experiments were conducted with boiling electrolyte. Values obtained by experiments for 15 minutes duration are given in Table I.

TABLE I

No.	Electrode Dimensions		Current Density Amps./sq. cm.	Current efficiency % at Room temperature	Current efficiency % at Boiling temperature
1	Dia.	Length	6.7	15	..
			3.4	17	21
	0.0152 cm.	0.65 cm.	1.7	4.5	22
			.83	4.3	23
			.42	4.1	17
2	0.0229 cm.	0.65 cm.	4.4	15	..
			2.2	7.8	22
			1.1	3.3	20
			0.55	4.0	25
			0.28	3.3	26
3	0.0356 cm.	1.1 cm.	1.7	4.4	..
			0.85	3.9	20
			0.42	3.1	18
			0.21	1.4	15
			0.11	1.9	8.6
4	0.0356 cm.	2.1 cm.	.88	5.6	..
			.44	4.9	17
			.22	3.9	13
			.11	2.9	9.3
			.055	3.1	7.0
5	Disc electrode each of area 3.5 sq. cm.		0.06	1.9	..
			0.03	1.3	3.2
			0.015	0.7	3.0
			0.008	0.5	3.3
			0.004	..	4.6

3. DISCUSSION

The general results obtained in the preliminary investigation are as follows:—

Firstly it is found that the current efficiency for the net reduction reaction can be as much as 25% or even higher. Secondly there is a general parallelism between current densities and current efficiencies, the latter increasing with the increase of former. Finally experiments at the boiling temperature have yielded much higher current efficiencies than those obtained at the ordinary temperatures.

Let us picture the conditions at an electrode dipped in an electrolyte and subjected to the action of an alternating current. When the electrode experiences the cathodic half wave of the alternating current, reduction takes place and the reduction products are formed at the electrode. If these products are not removed by either phase separation or diffusion, there is a possibility of the reaction being reversed during the anodic half wave of the current. If the anodic half wave completely reverses the reaction brought about by the cathodic half wave, the net chemical reaction will be zero and the current efficiency as defined in this paper becomes zero. If however during the progress of reduction, the products of the reaction are partially removed by phase separation or diffusion, the anodic half wave will not have its full effect, especially as in these experiments when the original solution does not contain any oxidisable substance. The occurrence of a net electrochemical reaction is further favoured if the oxidative electrode process is slower than the reductive process under similar conditions.

Let us consider in a little detail the kinetics of the reduction process. During the cathodic half wave the electrode gets charged to higher and higher reductive potentials up to a maximum value after which the potential goes on falling to a zero value. According to the theory of Absolute Reaction Rates as applied to electrode processes,³ the instantaneous rate of the reduction process would be a function of the potential of the electrode at that instant. With the rise in the potential, the rate of reduction would increase exponentially. One may expect therefore that at higher current densities which should normally mean higher peak potential, one would get larger accumulation of the products of reaction at the electrode which would bring about a larger extent of diffusion and hence increase the current efficiency with reference to the net reduction reaction. Further, with the increase in current density, the overvoltage of the electrode surface for hydrogen evolution would be greatly exceeded by the electrode potential and hence vigorous

evolution of hydrogen takes place. This evolution would cause vigorous stirring at the electrode surface, and the resulting convection process would facilitate the movement of products of the reaction. This would again cause increase in current efficiency. This explains the general observation that the current efficiency increases with current density. The higher current efficiencies met with in the experiments at high temperatures are to be attributed to the higher diffusion rate and lower overvoltage for discharge of hydrogen.

A careful examination of Fig. 1 shows that the current efficiency may not be a single-valued function of current density, particularly at high values of current. There appears to be a tendency for high current efficiency with larger electrodes even at the same current density. This phenomenon is being investigated and further work is in progress.

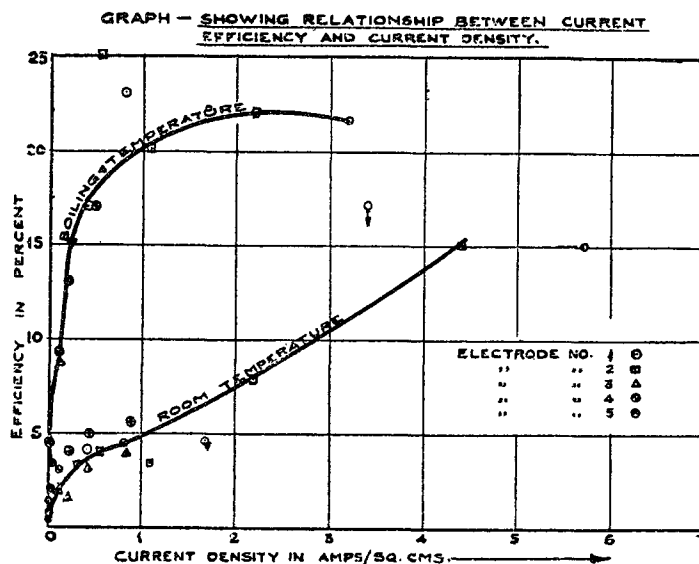


FIG. 1. Graph—Showing Relationship between Current Efficiency and Current Density

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5. SUMMARY

The reduction of ferric sulphate brought about by alternating current has been quantitatively studied. It is found that the current efficiency can be as much as 25% or even higher under favourable conditions. The current efficiency increases with increase in current density and rise in temperature. The results are qualitatively explained on the basis of the theory.

3. REFERENCES

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2. Kappanna, A. N. and Joshi, K. M. .. *Proc. Ind. Sci. Congress*, 1947, Part III, p. 99.
3. Glasstones Laidler and Eyring .. *The Theory of Rate Processes*, p. 575.