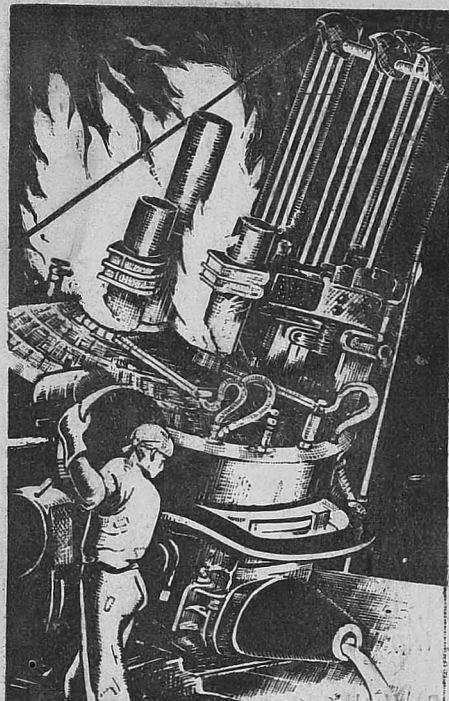




ACHESON GRAPHITE & NATIONAL CARBON ELECTRODES

FOR ALL
ELECTRO-THERMIC
AND
ELECTROLYTIC
APPLICATIONS

WRITE FOR
INFORMATION
AND PRICES TO

ALSO
CARBON LINING BLOCKS
BRICKS, PASTE ETC.

VOLTAS

BOMBAY. CALCUTTA. MADRAS. COCHIN

BULLETIN OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE KARAIKUDI

Vol. 2

JANUARY 1955

No. 1

CONTENTS

	Page
Dr. Shanti Swarup Bhatnagar.	3
Electrolytic Reduction of Keto Groups to Methylene Groups in Aliphatic Compounds. By Sherlock Swann, Jr.	6
On Dielectric Breakdown in Ozoniser Discharges. By N. A. Ramaiah & M. V. Ramakrishna Rao	12
Commercial Possibility of Producing Electrolytic Cuprous Oxide in India. By H. V. K. Udupa, S. Sampath & R. Viswanathan	17
Processing of Monazite. By C. S. Acharya	20
Electrolysis of Non-Aqueous Solutions. By N. Subramanyan	24
Alkaline Nickel-Cadmium Storage Battery. By Siddhartha Ghosh	26
NOTES AND NEWS	31
BOOK REVIEWS:	
"New Instrumental Methods in Electrochemistry"	33
"Ferromagnetic Domains"	34
"Survey of the Indian Chemical and Pharmaceutical Industry-1954"	35
"Annual Review of Physical Chemistry, Vol. 5"	35
"Titanium and Titanium Alloys"	36
"Rare Metals Hand Book"	37
"Non-Ferrous Foundry Metallurgy"	38
ABSTRACTS	39

HIGHEST Quality
ATTRACTIVE Prices
PROMPT Deliveries

CAUSTIC SODA
LIQUID CHLORINE
BLEACHING POWDER
HYDROCHLORIC ACID
FERRIC CHLORIDE



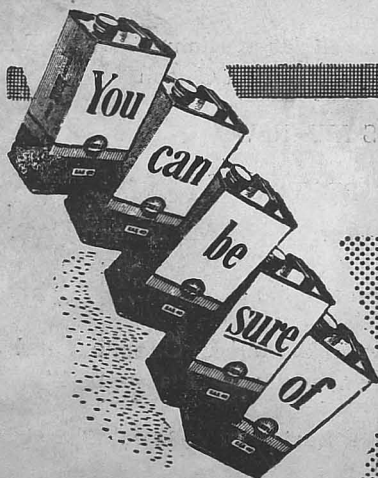
CAUVERY BRAND CHEMICALS
THE METTUR CHEMICAL &
INDUSTRIAL CORPN. LTD.

METTUR DAM. R. S., S. INDIA.

Managing Agents :

SESHASAYEE BROS. Ltd.

TIRUCHIRAPALLI.



SHELL X-100 motor oil



Dr. SHANTI SWARUP BHATNAGAR, F. R. S.

Dr. SHANTI SWARUP BHATNAGAR

1894 - 1955

On New Year's Day, 1955 India suffered a grievous loss in the passing away of Dr. S. S. Bhatnagar, the architect of scientific research in free India. A versatile genius who served his country in many ways by his rare combination of broad scientific knowledge, energy and executive ability, he wore himself out with the severe labours and worries which he undertook single-handed in the cause of science and education in India.

Dr. Bhatnagar was born on February 21, 1894 and lost his father when he was only eight months old. He had therefore to work his way up in life and was a self-made man in every sense of the word. He took his M. Sc. degree from the Forman Christian College, Lahore and then went to England in 1919 on a Dyal Singh Scholarship. He obtained the D Sc. degree of the London University in 1921 for his work on the subject of *Emulsions* under Prof. F. G. Donnan of the University College, London. During this period he worked also at the Sorbonne University, Paris and the Kaiser Wilhelm Institute, Berlin.

On returning to India, Dr. Bhatnagar joined the Banaras Hindu University as Professor of Chemistry. He remained in Banaras till 1924 and built up a vigorous school of physical chemistry there. In 1924 he was appointed as the Professor of Physical Chemistry and Director of the University Chemical Laboratories in Lahore. During the sixteen years of his stay there, his passion for research found full expression, and Dr. Bhatnagar and his students made important contributions in the field of colloids, surface chemistry, photo-chemistry and magneto-chemistry. The pioneering work which Dr. Bhatnagar carried out on the subject of magneto-chemistry opened a new frontier of research and the first English book on *Principles and Applica-*

tions of Magneto-Chemistry (1935) was written by him in collaboration with Dr. K. N. Mathur.

Dr. Bhatnagar did not by any means confine his interest to researches of a purely fundamental character during this period. He tackled successfully a number of oil problems for Messrs. Steel Brothers & Co., Ltd. and won an honoured name in the field of industrial research. Among the important contributions made by him were the solution of the mud problem, production of odourless waxes, refinement of kerosene oil to increase its flame height, lubrication, and prevention of metallic corrosion in hot axle boxes. It was characteristic of his selfless devotion to the cause of science that he donated to the University of Lahore all the large sums of money he received as royalties and awards from commercial firms.

With the breaking out of World War II, Dr. Bhatnagar was called to serve in the capacity of Director of Scientific and Industrial Research. He bore lightly the heavy administrative burden cast on him and found the time to take a personal interest in research work also. Several processes and products of great importance were developed during the war years by him and his staff, chief among them being antigas cloth and varnish, air-foam solution, vegetable oil blends as lubricants and fuels, unburstable containers, glass substitutes, dehydrated castor oil, and plastics from Indian wastes.

His appointment as Director of Scientific and Industrial Research gave Dr. Bhatnagar the opportunity to realize his life-long dream of putting India on the scientific and industrial map of the world. He rose equal to the occasion and Prime Minister Nehru found in him the

master-builder who could give shape to his determination to bring science to the fore in India's plan for the future. The creation of our 14 magnificent National Laboratories within an interval of barely 7 years is indisputably the biggest achievement of Dr. Bhatnagar. This would have been a remarkable feat anywhere in the world, and is little short of a miracle under the conditions existing in India. And it is a measure of the single-hearted devotion of Dr. Bhatnagar to his work that every one of these laboratories bears in its features, architectural as well as scientific, the unmistakable impress of his personality.

Dr. Bhatnagar was active in other ways too to promote the cause of scientific research in India. He instituted a scheme of grants-in-aid for scientific research in various institutions and university laboratories not directly connected with the Council of Scientific and Industrial Research. For the first time he made it possible for the science graduate with an enquiring mind to take up scientific research as a career and a vocation, unhampered by lack of finance or equipment.

When the Government formed the new Ministry for Natural Resources and Scientific Research, Dr. Bhatnagar became its first Secretary. Later, he was also entrusted with the Secretaryship of the Education Ministry. He was also called upon to be the first Chairman of the University Grants Commission. He thus shouldered the burden of four onerous offices, and yet carried out with signal distinction the multifarious duties arising from all of them. It was due to his efforts that the National Research Development Corporation of India was established to fill the gap between research and development, and contribute to India's economic and industrial progress. He was responsible for initiating the Industrial Research Association Movement in India, and three Research Associations have already come into being as a result of his efforts. Among other projects which owe their

origin to his enterprise and long-range planning are the establishment of *The Indian Rare Earths, Ltd.* for the processing of monazite sands, the intensification of the search for atomic minerals, sulphur bearing ores and petroleum deposits, and the installation of a Heavy Media Separation Plant for the beneficiation of manganese ores. It was Dr. Bhatnagar's persuasive influence and skill as a negotiator that was mainly responsible for the establishment of the oil refineries in India.

As Secretary to the Ministry of Education, Dr. Bhatnagar gave his active support to the setting up of a School of Asian languages at the Banaras Hindu University. He was also responsible for raising the emoluments of University professors and teachers, and increasing the financial assistance to Universities through the agency of the University Grants Commission.

Dr. Bhatnagar's outstanding services in such diverse fields won the recognition of many learned bodies and of the Government from the very beginning. He was awarded the O. B. E. in 1936 and knighted in 1941. Later, he was made an Honorary Fellow and then Vice-President of the Society of Chemical Industry. In the same year he was elected to fellowship of the Royal Society. Several universities, both Indian and foreign, conferred honorary doctorates on him. He had been elected President of the Indian Science Congress and also of the National Institute of Sciences. On Independence Day 1954, the Government of India honoured him with the award of Padma Vibhushan.

Dr Bhatnagar cultivated the writing of Urdu poetry as his chief relaxation. A collected volume of his poetry has been published which reveals him as a poet of no mean order, distinguished for his clarity of expression and soaring vision. Deeply attached to his associates, he placed implicit confidence in them and won their unreserved loyalty and love. He kept in close and personal

touch with every branch of activity under his care and had a marvellous capacity to assess people and situations rightly and come to quick decisions. He combined with these traits a dynamic energy and enthusiasm to achieve things. As Dr. Alagappa Chettiar so aptly pointed out, 'there has not been in recent times a scientist and statesman so beautifully integrated as Dr. Bhatnagar.' The loss of his precious life so suddenly and prematurely is a serious blow to scientific work in India, and it will be long before the void left by his departure can be suitably filled.

ELECTROLYTIC REDUCTION OF KETO GROUPS TO METHYLENE GROUPS IN ALIPHATIC COMPOUNDS

by

Sherlock Swann, Jr.

(University of Illinois Urbana, Illinois, U. S. A.)

Electrolytic reduction is an alternate to the Clemmensen method for the reduction of keto groups to methylene groups in aliphatic compounds both cyclic and acyclic (1).

HISTORICAL

Although Tafel (2) had carried out the reduction of the carbonyl group of a lactam in a catholyte of sulfuric acid at a lead cathode, the first reduction of a carbonyl group of a ketone to the methylene was reported by Piccinini (3) when he obtained N-methylgranatanine from the cyclic amino ketone pseudopelletierine under similar conditions. The method was used later to prepare N-methylgranatanine by Willstätter and Veraguth (4) who found in addition some of the alcohol N-methylgranatoline. The first hydrocarbon to be prepared by the electrolytic reduction of an aliphatic ketone was 2-methylhexane from 5-methyl-2-hexanone by Tafel (5). In this reduction the superiority of cadmium over lead as a cathode was also demonstrated for the first time. A lower yield of hydrocarbon was obtained at lead on account of the simultaneous formation of a metallo-organic compound of lead. The keto acid levulinic and its dimethyl derivative were reduced to valeric acids at both lead and mercury cathodes by Tafel and Emmert. (6) At the mercury cathode the lactone of the hydroxy acid formed from dimethyllevulinic acid was also found. The first study of the lower members of the series of straight chain aliphatic ketones was carried out by Tafel (7) and coworkers who found that acetone was reduced quantitatively to propane and that ethyl methyl and

diethyl ketones were reduced to their corresponding hydrocarbons at cadmium. Some propane was also found at lead. It was also found that no hydrocarbon was obtained when acetone was subjected to reduction in an alkaline solution at a cadmium cathode. The reduction of a cyclic aliphatic ketone, menthone to the hydrocarbon, although not pure, was carried out by Matsui and Shimizu (8). A number of cathodes, mercury, amalgamated lead, amalgamated tin, lead, tin and nickel were tried. The best results were obtained with mercury and amalgamated lead. No reduction of menthone took place at nickel in acid or at any cathode in alkali. The reduction of menthone was studied, further, by Schall and Kirst (9), at the following cathodes: cadmium, lead, mercury, copper, platinum and palladium. Excellent yields of the hydrocarbon were obtained at cadmium, poorer at lead and mercury and none at all at the last three cathodes. The influence of the physical structure of the cathode on the reduction of ketones was reported for the first time in this work. It was found that the ratio of menthane to menthol in the product was greater at a polished lead cathode than at one which had been "prepared" by the Tafel (10) procedure. A lead cathode was used by Read and Fletcher (11) to carry out the reduction of the carbonyl group of the hydroxy ketone diacetone alcohol to the methylene group. Some reduction to the carbinol also took place. The first study of the behavior of cathodes in the reduction of acetone was carried out by Müller (12). Those used were silver, platinum, copper, cadmium, amalgamated zinc, mercury and lead.

This was also the first report of the use of amalgamated zinc for the reduction of an aliphatic ketone. It turned out to be the best by far for the reduction of acetone to propane, with cadmium next. Poorer yields were obtained at mercury, lead and silver while negative results were obtained at platinum and copper. The method of Tafel and Emmert (6) was used by Lükcs (13) in the reduction of 4-oxononanoic acid to peltargonic acid. Optimum conditions for the electrolytic reduction of a typical aliphatic ketone, methyl propyl, to the hydrocarbon at a cathode of cadmium were determined by Swann, (14) since such information was fragmentary in the previous literature. It was found that over wide ranges there was little variation in the yield of pentane with current density or with temperature, but that lower yields resulted when the acid concentration at the beginning of the run was not high enough. The behavior of cathodes of cadmium, unamalgamated and amalgamated, was compared in the reduction of cyclohexanone and cyclopentanone by Stanger (15). He found, surprisingly, that cyclohexanol was the main product from cyclohexanone along with some cyclohexane and that the amount of product was greater at unamalgamated cadmium. The products of the reduction of cyclopentanone were not investigated. The study of the reduction of methyl propyl ketone (14) was extended by Swann and Feldman (16) to include other cathodes. It was shown that metals of the second group of the periodic table and lead in the fourth group are the most active for the reduction of the ketone to the hydrocarbon and that the optimum current densities and acid concentrations depend on the cathode materials. The behavior of cathodes in aqueous solution was compared with that in glacial acetic acid-sulfuric acid by Swann, Deditius and Pyhrr (17). The cathodes most active in aqueous solution (16) were also most active in glacial acetic acid. In addition, however, tin was equally active in glacial acetic acid. The best yield of

pentane was obtained in aqueous solution at cadmium (14). The relationship between the yield of pentane and the composition of the cathode in the reduction of methyl propyl ketone at a series of cadmium amalgams was shown by Swann, Read and Howard (18). It was shown that there is a close correlation between the yield of hydrocarbon and the melting point diagram, evidence that the physical structure of the cathode is of major importance. In connection with another study it became necessary to repeat the reduction of methyl propyl ketone (16) at room temperature. As a result it was found by Swann and Field (19) that the only marked increase in the yield of pentane with temperature occurred at the lead cathode. It should be stated here that at 75°C, the yield of hydrocarbon at mercury is considerably greater than at 55°C (18). The method of Schall and Kirst (9) was successfully used to prepare menthane from l-menthone and dl-isomenthone by Keats (20). The reduction of a branched chain aliphatic ketone with substituents adjacent to the carbonyl group was carried out for the first time by Wibaut et al. (21). 3,3-Dimethylbutanone was reduced at a cadmium cathode to the hydrocarbon as main product with some olefine and alcohol. A very pure cast zinc cathode was shown by Clapp (22) to give yields of pentane from methyl propyl ketone equal to those obtained at cadmium (14). He showed also that the yields of hydrocarbon in the reduction of methyl propyl ketone at cathodes of zinc and cadmium were unaffected by the physical structure of the metal. The cathode study made with methyl propyl ketone (16) was repeated with ethyl methyl ketone by Swann et al. (23). It was shown that, as with methyl propyl ketone, the best yields of hydrocarbon were obtained at cathodes of cadmium and zinc, but that with the ketone of lower molecular weight the yields of hydrocarbon were lowered by the presence of secondary alcohol and that the reduction was affected by the physical structure of the cathode. The reduction of methyl propyl

ketone to pentane at alloy cathodes (18) was extended by Read (24) to the cadmium-bismuth system. In comparison with the solid solution system previously studied the latter, a eutectic system, showed no resemblance. There was little relation between the yield of pentane and the melting point diagram of the cadmium-bismuth system. Compared with the other active cathodes (16) bismuth was somewhat less active than mercury, but much more active than cathodes other than the select group mentioned above. Wolfrom, Konigsberg, Moody and Goepp (24a) assumed that D-fructose was reduced to 2-desoxysorbitol in alkaline solution at a cathode of amalgamated lead. It was shown by Ershov and Zepalova-Mikhailova (25) that 5-hydroxy-2-pentanone was reduced successfully to amyl alcohol at a cathode of cadmium.

Lukeš and Šorm (26) following the procedure of Tafel and Emmert (6) carried out the reduction of a number of ketonic acids to simple aliphatic acids. Presumably mercury was used as cathode in addition to the lead mentioned in the experimental part. This work was followed by the reduction of the cyclic ketonic acid 4-methyl-3-oxocyclohexylic acid to 4-methylcyclohexanecarboxylic acid at a lead cathode by Šorm and Arient (27). Reduction of acetone at a cadmium cathode has been used to prepare propane of almost 100% purity by Gordon and Heimel (28). They have suggested this method for the preparation of propane-2- C^{13} . Recently the reduction of the ring aminoketone 2-ethyl-1-methyl-3-piperidone has been studied at cathodes of cadmium, lead, tin, and copper by Leonard, Swann and Dryden (29). Under the same conditions the straight chain amino ketone presumably formed by scission of the carbon-nitrogen bond was reduced to the amine at cathodes of both cadmium and lead, but unexpectedly in better yield at lead. Recent work by Leonard, Swann and Figueras (30) and by Leonard, Swann and Fuller (31) has shown that the carbonyl group in certain ring amino

ketones is reduced to methylene, the extent of conversion being dependent on the structure of the amino ketone. Finally, it has been shown by Krone (32) that the two protecting methyl groups on either side of the carbonyl group cause an increase in the yields of secondary alcohol and pinacol at the expense of hydrocarbon as compared with a straight chain aliphatic ketone (16), and that the physical structure of cathodes of zinc and cadmium was an important factor in the reduction.

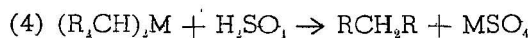
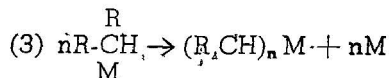
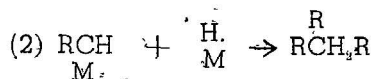
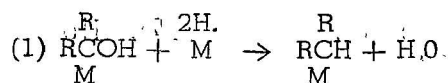
DISCUSSION

Electrolytic reduction of the carbonyl group of an aliphatic ketone to a methylene group generally takes place only in acid solution. Although many studies of the reduction in alkaline solution have been carried out, some examples of which are found in references 6, 7, and 8, there has been no report of the formation of methylene except in the case of fructose (24a). A study of different mineral acids in the reduction has shown no difference in the yield of hydrocarbon (33).

The most active cathodes for the reduction of aliphatic ketones in acid solution are cadmium, zinc, lead and mercury, of the single metals, and amalgamated zinc, cadmium, and lead, of the alloys. The most active cathode of all seems to be amalgamated zinc (12), although there has been no record of its use with the ketones of higher molecular weight. The close relationship between the electrolytic and Clemmensen reductions has been indicated and metallo-organic compounds as intermediates postulated (9). It was pointed out that while the active cathodes have high hydrogen overvoltages, the "catalytic" effect on activity was more important (12). Thus in the reduction of acetone the cathode potential at silver was found to be less than that at platinum or at copper, but the yield of propane was higher. In the reduction of ethyl methyl ketone (23), of 2-ethyl-1-methyl-3-piperidone (29) and methyl propyl ketone (16) lead is an active cathode while tin

is not, although both have high hydrogen over-voltages and are in the same group of the periodic table. It has been postulated that the reduction is not simply brought about by hydrogen alone (12) but that the metal of the cathode enters in. This seems entirely reasonable and is supported by the fact that the physical structure of the cathode has been shown to be important (9, 18, 23, 24, 32).

A tentative mechanism is shown below. As was stated previously, the similarity between the electrolytic and Clemmensen reductions was recognized and mechanisms similar to the present one proposed for both (9, 12, 35, 36). The carbonium ion RCOHR^+ formed from the starting ketone and acid might, for example, be discharged at the cathode and the resulting free radical $\text{RCOHR}^\cdot$ be adsorbed to the extent of compound formation with the active but not with the inactive cathodes. It has been shown that higher concentrations of sulfuric acid cause an increase in the yield of hydrocarbon at cathodes of cadmium, (14) conditions favorable for the formation of carbonium ion. The metallo-organic compound formed at the cathode might then be reduced to the hydrocarbon directly or through the intermediate formation of a metallo-alkyl, which would be decomposed to the hydrocarbon in the presence of water. The alcohol as an intermediate seems to be ruled out since a number of attempts to reduce secondary alcohols to hydrocarbons at active cathodes have resulted in failure (6, 7, 9, 12, 21). The reduction of the olefine formed during the reaction has been suggested (9) as a mechanism for the formation of the saturated hydrocarbon. This also may be eliminated as it has been shown that unconjugated olefines are not reduced electrolytically (21, 34).



The equations are written to show the metal of the cathode taking part in the reaction. Since the reduction of an aliphatic ketone takes place at or near the potential for hydrogen evolution, (37, 38, 39, 40, 41), it may be assumed that the active reducing agent is adsorbed atomic hydrogen (42). Evidence of the possibility of Reaction 3 is to be found in the formation of dialkylmercury compounds by the discharge of RHg^+ at a cathode (43). It would appear that Reactions (3) and (4) are more important than Reaction (2) in the formation of hydrocarbons. It has been shown that at cathodes of mercury and lead the formation of stable metallo-organic compounds from straight chain and certain cyclic aliphatic ketones lowers the yield of hydrocarbon (5, 6, 9, 12, 16, 23, 44, 45, 46, 47, 48, 49, 50). With menthone the presence of the organomercury compound has been noted, but not that of the organo-lead compound (9). It may be presumed by analogy that similar zinc and cadmium (9) compounds are formed but they would be hydrolysed by water and acid to the hydrocarbon (51) and the metal sulfate from which the metal would be redeposited on the cathode. No extensive corrosion of zinc and cadmium cathodes has been noted as compared with lead (14, 16). Evidently the reduction of the carbonyl group in certain substituted ketones does not proceed through the metallo-organic compound. No mention was made of the appearance of organic lead or mercury compounds in the reduction of pseudopelletierine (3, 4), and of levulinic acid

and others (6, 13, 26, 27). No lead compound was found in the products of the reduction of ring α -amino ketones or straight chain aliphatic amino ketones (29, 30, 31) and no lead or mercury compounds in the reduction of diisopropyl ketone (32). The structure of the ketone is also a deciding factor in the extent of reduction of the carbonyl to the methylene group. The tendency toward hydrocarbon formation increases with molecular weight from ethyl methyl ketone to methyl isoamyl ketone (7, 16, 23). The reverse is true in the case of ketones with groups protecting the carbonyl group. (21, 32). On the basis of the mechanism proposed above the combination of two metallo-organic radicals in the latter case to form the metallo-organic compound (see equation 3) may be hindered. In glacial acetic acid-sulfuric acid (17) it is probable that no metallo-organic compound is formed.

It may be seen from the bibliography that comparatively little research has been carried out on the relation of the structure of the starting ketone to the products obtained at the active cathodes. Before a mechanism can finally be established, such studies must be carried out, particularly on steric effects.

The author wishes to thank Dr. N. J. Leonard and Mr. R. A. Strehlow for their advice.

REFERENCES:

1. S. Swann, Jr., *Trans. Electrochem. Soc.* **69**, 287 (1936); **77**, 459 (1940); **88**, 103 (1945); *J. Electrochem. Soc.* **99**, 219 (1912).
2. J. Tafel, *Ber.* **32**, 3194 (1899).
3. A. Piccinini, *Gazz. chim. ital.* **32i**, 260 (1902).
4. R. Willstätter and H. Veraguth, *Ber.* **38**, 1984 (1905).
5. J. Tafel, *Ber.* **42**, 3146 (1909).
6. J. Tafel and B. Emmert, *Z. Elektrochem.* **17**, 569 (1911).
7. J. Tafel, et. al. *Z. Elektrochem.* **17**, 972 (1911).
8. M. Matsui and S. Shimizu, *Mem. Coll. Sci. Kyoto Imp. Univ.* **4**, 245 (1920).
9. C. Schall and W. Kirst, *Z. Elektrochem.* **29**, 537 (1923).
10. J. Tafel, *Ber.* **33**, 2209 (1900).
11. R. R. Read and F. A. Fletcher, *Trans. Am. Electrochem. Soc.* **47**, 93 (1925).
12. E. Müller, *Z. Elektrochem.* **33**, 253 (1927).
13. R. Lukeš, *Collection Czechoslov. Chem. Commun.* **1**, 119 (1929).
14. S. Swann, Jr., *Trans. Electrochem. Soc.* **62**, 177 (1932).
15. H. Stanger, *Diss., Univ. Wurzburg* (1933).
16. S. Swann Jr. and J. Feldman, *Trans. Electrochem. Soc.* **67**, 195 (1935).
17. S. Swann Jr., L. F. Deditius, and W. A. Pyhrr, *Trans. Electrochem. Soc.* **68**, 321 (1935).
18. S. Swann Jr., H. J. Read, and F. C. Howard, *Trans. Electrochem. Soc.* **69**, 345 (1936).
19. S. Swann, Jr., and E. W. Field, *Trans. Electrochem. Soc.* **72**, 327 (1937).
20. G. H. Keats, *J. Chem. Soc.* (1937) 2003.
21. J. P. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoff, and J. Smit-tenberg, *Rec. trav. chim.* **58**, 329 (1939).
22. J. T. Clapp, *Thesis, Univ. of Illinois* (1940).
23. S. Swann, Jr., R. W. Benoliel, L. R. Lyons and W. H. Pahl, *Trans. Electrochem. Soc.* **79**, 83 (1941).
24. H. J. Read, *Trans. Electrochem. Soc.* **80**, 133 (1941).
- 24a. M. L. Wolfrom, M. Konigsberg, F. B. Moody and R. M. Goepp, Jr., *J. Am. Chem. Soc.* **68**, 122 (1946).

25. B. P. Ershov and L. A. Zepalova-Mikhailova, *Zhur. Priklad. Khim.* **16**, 383 (1943).
26. R. Lukeš and F. Šorm, *Collection Czech. Chem. Commun.* **13**, 585 (1948). See also the following patents: Spolek pro chemickou a hutní výrobu Belg. 453, 373 (1943); Swiss 240, 790 (1946); French 908, 727 (1946); and Ital. 426, 633 (1947).
27. F. Šorm and Arient, *Collection Czech. Chem. Commun.* **15**, 175 (1950).
28. A. S. Gordon and S. Heimel, *J. Am. Chem. Soc.* **73**, 2942 (1951).
29. N. J. Leonard, S. Swann Jr., and H. L. Dryden, Jr., *J. Am. Chem. Soc.* **74**, 2871 (1952).
30. N. J. Leonard, S. Swann Jr., and J. Figueras, Jr., *J. Am. Chem. Soc.* **74**, 4620 (1952).
31. N. J. Leonard, S. Swann Jr., and G. Fuller, *J. Am. Chem. Soc.* **76**, 3193 (1954).
32. L. H. Krone, *Diss. Univ. of Illinois*, (1953).
33. W. Triebel, *Thesis, University of Illinois*, (1951).
34. C. L. Wilson, *Trans. Electrochem. Soc.* **75**, 353 (1939).
35. G. Tiller, *Diss. Univ. of Wurzburg*, (1930).
36. C. R. Noller: *A Textbook of Organic Chemistry*, pp. 216 - 17 Saunders, Philadelphia (1951).
37. G. Semerano, *Gazz. Chim. Ital.* **62**, 959 (1932).
38. E. Adkins and F. W. Cox, *J. Am. Chem. Soc.* **60**, 1151 (1938).
39. G. Scaramelli, *Boll. sci. facolta chim. ind.* **2**, 129 (1941).
40. M. I. Bobrova and P. N. Sokolov, *Zhur. Obschei Khim.* **21**, 1779 (1951); *J. Gen. Chem. U. S. S. R.* **21**, 1965 (1951).
41. N. J. Leonard, F. E. Fischer, E. Barthel, Jr., J. Figueras, Jr., and W. C. Wildman, *J. Am. Chem. Soc.* **73**, 2371 (1951).
42. W. M. Leslie and J. A. V. Butler, *Trans. Faraday Soc.* **32**, 989 (1936).
43. J. L. Maynard and H. C. Howard, Jr., *J. Chem. Soc.* **123**, 960 (1923).
44. N. M. Melnikov and M. S. Rokitschaya *Zhur. Obschei Khim.* **7**, 2596 (1937).
45. J. Tafel, *Ber.* **39**, 3626 (1906).
46. J. Tafel, *Ber.* **44**, 323 (1911).
47. B. Renger, *Ber.* **44**, 331 (1911).
48. J. Tafel, *Ber.* **45**, 3321 (1912).
49. H. Hibbert and R. R. Read, *J. Am. Chem. Soc.* **46**, 983 (1924).
50. C. J. Haggerty, *Trans. Am. Electrochem. Soc.* **56**, 421 (1929).
51. C. Schall, *Z. Elektrochem.* **38**, 31 (1932).
52. E. Krause and A. von Grosse: *Die Chemie der metall-organischen Verbindungen*, Borntraeger, Berlin (1937).

* ON DIELECTRIC BREAKDOWN IN OZONISER DISCHARGES

by

N. A. Ramaiah and M. V. Ramakrishna Rao

(Department of Chemistry, University of Delhi, Delhi)

Siemen's ozoniser is widely used in Physico-chemical Laboratories for varied purposes; for example, preparation of ozone; active hydrogen,¹ etc., investigation of chemical reactions in ionized gases,² and the like. Recently we employed the same for studies of Langmuir adsorption on glass of I_2 and H_2O vapour under discharge.³ The Siemen's tube is preferred for a number of reasons, especially due to absence of metallic electrodes which sputter under discharge leading to unknown and uncontrollable circumstances; combine readily with excited media to yield irreproducible results; and complicate

the data on the disappearance of gas or adsorption effects.⁴ It is favoured also on account of the considerable ease in obtaining the electrode surface free from impurities and adsorbed gases by well-known processes of washing, drying and degassing under vacuum.^{5,6} However, there is one significant limitation in the usage of the ozoniser: quantitative investigation of any problem related with the working of the ozoniser,⁸ appears difficult.⁷ It is so, because one is unable to have a knowledge of the exact field acting on the gas phase of the system. In practice, a known alternating voltage is applied to the outer

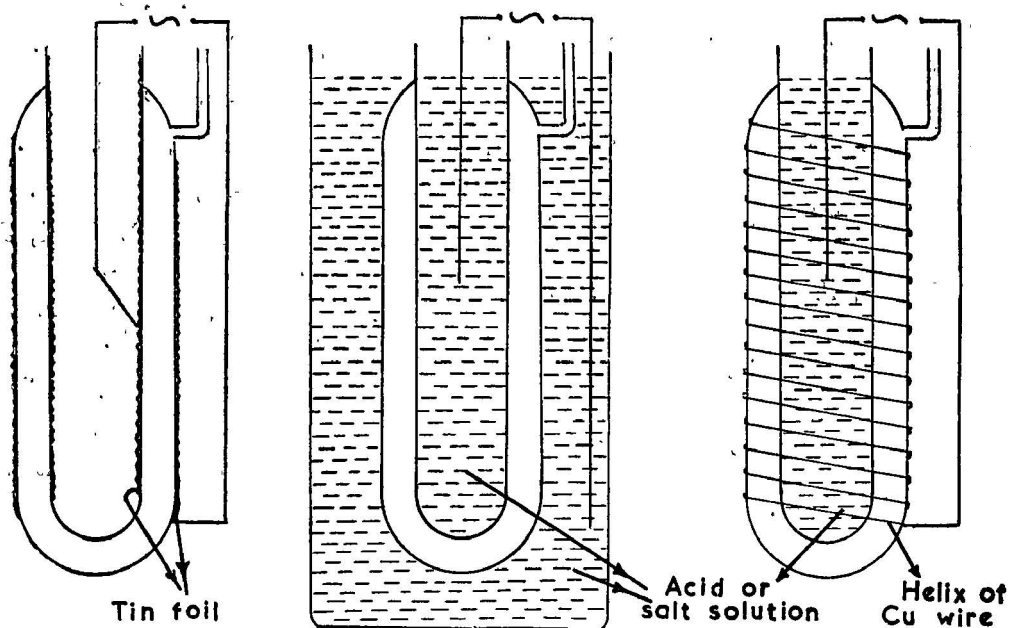


Fig. 1. Excitation of the ozoniser by different electrodes.

* Paper presented at the symposium on "Electrochemical Processes and their Applications to Indian Industry" March, 1954; and based on the thesis submitted for the M. Sc. degree (B. H. U. 1952) by one of the authors (M. V. R.)

§ For a mathematical treatment of the overall capacity of the ozoniser see Warburg, E., *Verhandl. deut. Phys. Ges.*, **1**, 382 (1903); *Z. techn. Phys.*, **4**, 450 (1923); **5**, 165, (1924); Lunt, R. W., *Phil. Mag.*, **3**, 1025 (1927). It may be added that the constant k of equation (1) can be calculated from purely electrostatic considerations; the processes are however, cumbersome and applicable to the conditions prior to the breakdown potential V_m . Their validity under circumstances above V_m is doubtful.

surface of the outer cylinder and the inner surface of the inner cylinder of the ozoniser (see Fig. 1) by means of suitable electrodes; in the familiar experiments on ozone preparation tin foil is used, while in a few series of other experiments acid or salt solution or/and a helix of bright copper wire wound tightly on the glass surface have been employed, as the electrodes (Fig. 1). On account of the dielectric nature of the glass walls and the capacity thereof, a fraction of the applied voltage only will be acting on the gaseous medium of the ozoniser. If V_0 is the peak value of the alternating potential, the voltage across the gas phase is given by

$$V_g = k V_0 \quad \dots (1)$$

Here the constant k may be denoted as the *ozoniser constant*, analogous to the *cell constant* which is familiar to workers in electrochemistry; it depends upon the capacity of the ozoniser or its dimensions. For an ozoniser of fixed geometry, it varies with the dielectric properties of the glass, the roughness of its surface or/and the gas layers adsorbed thereon. Theoretically, k is less than unity. If the value of k is computed for a fixed vessel filled with a gas of which the fundamental characteristics like ionization potential, mean free path, etc., are known, it can be utilised for mathematical development of any studies in other media enclosed in the same ozoniser. It may be too early to emphasise that the constant k can be employed with suitable changes to study the nature of the glass, changes in the character of a surface with different adsorbed layers, etc. A simple method for the calculation of the *ozoniser constant* k is given here, which when applied to experimental data, presents a new problem on the dielectric breakdown of a gas.

BREAKDOWN POTENTIAL V_m

The calculation of the *ozoniser constant* is based upon the truth of the statement that in electric discharge, ionization by gas particles occurs primarily by electron impact.^{7, 8, 9, 10.} That is, an

electron moving in the field direction acquires energy and imparts the same to a gas atom or molecule in an inelastic collision. When the energy received by the gas particle is equivalent to or greater than the corresponding ionization potential, ionization takes place resulting in the production of an additional electron. This process, viz. ionization by electron collision, is the fundamental feature of electric discharge and predominates at a potential applied to the electrodes of the system to give such a field that an electron passing through one mean free path distance acquires at

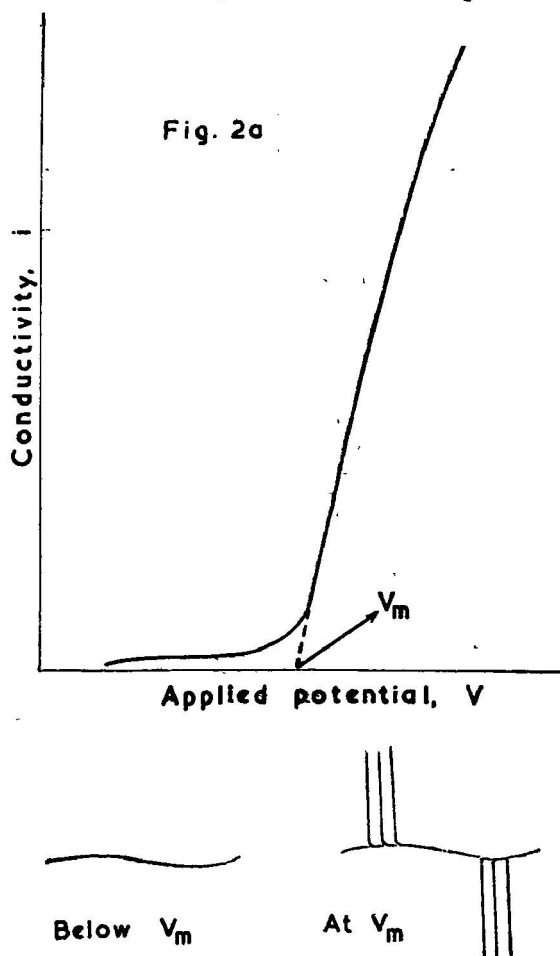


Fig. 2. Determination of the 'breakdown potential' V_m

least the energy corresponding to the ionization potential of the medium. This voltage is referred to as the 'threshold potential' or 'breakdown potential' V_m at which the system breaks down as dielectric, i. e. a large proportion of even normal gas particles are ionised leading to a marked increase of the conductivity i with rise of applied potential V , and appearance of glow in the discharge tube. V_m corresponds also to the onset potential of a self-maintained discharge for which the secondary emission from the cathode is primarily important.^{1, 2} It is found fairly accurately by extrapolation of $V-i$ curves to the potential axis (Fig. 2a) and by noting the voltage at which pulses of sustained character appear on the otherwise smooth sinusoidal current trace (Fig. 2b), when the observations are made by a current measuring instrument (like micro-ammeter, galvanometer actuated by a vacuo-junction, diode, etc.) and cathode-ray oscillograph.¹¹

CALCULATION OF THE OZONISER CONSTANT

The method employed for calculation of the *ozoniser constant* involves two stages: (i) computation of the actual voltage across the homogeneous gas phase (this is possible from the knowledge of ionization potential and mean free path of molecule of the medium, *vide infra*) and (ii) comparison of V_g with the peak value of the potential applied to the ozoniser and sufficient enough to cause dielectric breakdown (cf. equation 1).

At a given pressure and temperature of a gas, the mean free path λ of a molecule is given by⁸

$$\lambda = \frac{RT}{\sqrt{2} \pi \sigma^2 NP} \quad (2)$$

The symbols have been defined in Table I. The values of λ for most of the gases at NTP are appended in standard text books;^{7, 8, 12, 13} from these, λ at any experimental temperature (T) and pressure (P) can be calculated from⁸

$$\frac{\lambda}{\lambda_0} = \frac{T \cdot T_0}{T_0 \cdot P} \quad (3)$$

where λ_0 , P_0 and T_0 refer to the values at NTP. It is known that electron mean free path λ_e is $4\sqrt{2}$ times λ of a molecule.⁷

Let a and b be the radii of the outer surface of the inner cylinder (A), and the inner surface of the outer cylinder (B) of

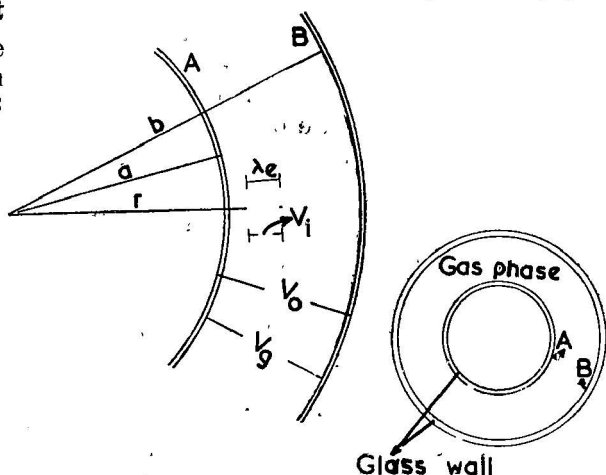


Fig. 3. Diagrammatic representation of the cross section of an Ozoniser and of the Potential Distribution.

the ozoniser respectively (see Fig. 3). V_g refers to the total potential across AB . The field at any point r in the space between the concentric cylinders is given by

$$X = \frac{V_g}{\log(b/a)} \frac{1}{r} \quad \dots \quad (4)$$

X is, however, not uniform but variant with the distance of r from A or B . The energy that an electron acquires during the passage of its mean free path distance, i. e. from r to $r + \lambda_e$, in the discharge space can be obtained from (4) and is roughly given by

$$E = \varepsilon X_{r, r + \lambda_e} = \varepsilon \cdot X \int_r^{r + \lambda_e} \frac{dr}{r} = \varepsilon \cdot V_g \frac{1}{\log_e \frac{b}{a}} \int_r^{r + \lambda_e} \frac{dr}{r} \quad (5)$$

Since ionization by electron impact predominates at the breakdown potential V_m , E corresponds to the ionization potential V_i of the medium. Therefore,

$$V_i = \frac{V_g}{\log_e b/a} \log_e \frac{r + \lambda e}{r} \quad \dots (6)$$

From (1) and (6), one gets that

$$k = \frac{V_i \cdot \log_e b/a}{\sqrt{2} V_m \log_e \frac{r + \lambda e}{r}} \quad \dots (7)$$

In the above calculation of the *ozoniser constant*, the following assumption has been made: in the inelastic collision between an electron and a neutral particle, the energy of the electron acquired over one mean free path distance is completely transferred to the gas particle.

A NEW PROBLEM FROM EXPERIMENTAL DATA

The threshold potential V_m for oxygen at a pressure of 52 mm Hg (28°C) was found to be 800 volts (rms), with an ozoniser of the following dimensions:¹⁴

Outer diameter of the outer cylinder	...	20.5 mm.
Inner diameter of the outer cylinder	...	17.5 "
Outer diameter of the inner cylinder	...	14.0 "
Inner diameter of the inner cylinder	...	11.0 "
Inter electrode distance	..	1.75 "
Length of the electrodes	...	432 "

The ionization potential of O_2 is 14.1 ev.¹⁵ and λ at NTP is 6.44×10^{-6} cm.⁸. These data gave a value of 5.88 for k . Similar results were obtained for systems containing iodine vapour and chlorine in studies of which the experimental inaccuracy was not greater than 3 percent. The observed abnormal value of k , which is about 500 per cent greater than the

theoretical value (<1) appears to be not due to the experimental error. This indicates that the dielectric breakdown in ozoniser discharge occurs at much lower fields than those calculated theoretically; the mechanism(s) responsible therefor merits investigation.

TABLE 1: *Nomenclature*

V	— Applied alternating potential
V_m	— Rms value of the 'breakdown potential'
V_o	— Peak value of the 'breakdown potential'
V_g	— Potential across the gas phase
V_i	— Ionization potential of the gaseous medium
X	— Field strength in volts/cm.
σ	— Diameter of the gas molecule
N	— Avagadro number
λ	— Mean free path of a molecule
λe	— Mean free path of an electron
E	— Electron energy
e	— Electronic charge
i	— Conductivity
a	— Outer diameter of the inner cylinder of the ozoniser
b	— Inner diameter of the outer cylinder of the ozoniser
r	— Distance of any point in the discharge space from the axis of the ozoniser
k	<i>Ozoniser constant</i>

REFERENCES:

- 1 Elliot, G. A., *Trans. Farad. Soc.*, **23**, 75 (1927).
- 2 Elliot, G. A., Joshi, S. S. & Lunt, R. W., *ibid.*, **23**, 57 (1927); Joshi, S. S., *ibid.*, **25**, 143 (1929).
- 3 Saxena, A. P., Bhatawdekar, M. G. & Ramaiah, N. A., *Nature*, **171**, 929 (1953).
- 4 Johnson, M. C., *Proc. Roy. Soc.*, **125**, 603 (1923).

5. Ramaiah, N. A., *Jour. Phys. Chem.*, **56**, 218 (1952); *Jour. Chim. Phys.*, **49**, 327 (1952); cf. also MacBain, J. W., 'Sorption of Gases on Solids', (Routledge, 1939).
6. Razouk, R. I. & Salem, A. S., *Jour. Phys. & Colloid Chem.*, **52**, 1208 (1948).
7. Loeb, L. B., 'Fundamental Processes of Electrical Discharge in Gases' (John Wiley, N. Y., 1939).
8. Maxfield, F. H. & Benedict, R. H.: 'Theory of Gaseous Conduction and Electronics' (McGraw-Hill Book Corp., N. Y., 1941).
9. Townsend, J. S., 'Electrons in Gases' (Hutchison's Sci. & Techn. Publications, London, 1947).
10. Korff, S. A., 'Electron and Nuclear Counters' (D. Van Nostrand Co., N. Y., 1947).
11. Ramaiah, N. A., Bhatawdekar, M. G., & Subramaniam, N., *Jour. Chem. Phys.*, **21**, 1160 (1953).
12. Kennard, E. H., 'Kinetic Theory of Gases' (McGraw-Hill Book Corp., N. Y., 1938).
13. Loeb, L. B., 'Kinetic Theory of Gases' (McGraw-Hill Book Corp., N. Y., 1934).
14. Mohanty, S. R., *Jour. Ind. Chem. Soc.*, **25**, 506 (1948).
15. cf. International Critical Tables, Vol. VI (McGraw-Hill Book Corp.).

Noted added in proof: In the above, electron energy over one mean free path has been calculated; the same over a free path is apparently nearer to the actual circumstances. The difference arising out of this will be discussed later.

For the dielectric breakdown at low fields of $50-10^7$ cycles/sec., recently Harries and von Engel (*Nature*, **171**, 517, 1953) suggested a new mechanism taking into consideration "quantum avalanches." This will be considered in a later communication.

COMMERCIAL POSSIBILITY OF PRODUCING ELECTROLYTIC CUPROUS OXIDE IN INDIA

by

H. V. K. Udupa, S. Sampath and R. Viswanathan

(Central Electrochemical Research Institute, Karaikudi.)

Cuprous oxide is utilised by the Navy in antifouling formulations. It is also valuable as a seed treatment material to control seed-borne and soil-borne disease organisms and is also the best fungicide available for certain crop treatments. In finely divided condition, cuprous oxide finds considerable use in sprays or dusts for the control of fungus diseases in plants. To a minor extent, the compound is used in the production of copper salts, in ceramics for the development of porcelain red glaze, in the manufacture of ruby glass and as a catalyst in some organic syntheses.

Though Indian Standards Specification No. IS:70 of 1950¹ prescribes a minimum purity of 96% for samples of cuprous oxide for use in making paints, U. S. Navy specification 52C4C details² two grades—one of 97% purity and the other of 90% purity. The colour of cuprous oxide varies according to particle size. The finer sizes are yellow and the coarser ones red.

Import figures for cuprous oxide are not available. According to private communication received from one of the manufacturing firms in India, about 25 tons of cuprous oxide are required per year for making antifouling paints for the Indian Navy. Increase in consumption can be expected with further additions to the Navy. If India takes seriously to using cuprous oxide in agriculture, over 1000 tons can find an outlet in this trade. Bureau of Census figures³ show that roughly 3600 tons of cuprous oxide was produced in U. S. in 1943 and about 5600 tons in 1944. Groggins³ of the War Food Adminis-

tration estimated that 5000 tons of copper calculated as copper sulphate (hydrated) were needed by the U. S. in agriculture as fungicide in 1945. These figures will serve to gauge the potential demand in India, an essentially agricultural country.

Considering the huge quantity of copper scrap that can be expected from a vast country like ours in the form of rejected cables, wires etc. from the electrical industry and borings, clippings, turnings etc. from the engineering and metal goods industry, it is quite safe to assume that we will not be in short supply of the valuable starting material, viz. copper. Besides, scrap from the electricity departments like bare overhead wires which is essentially pure copper can be purchased at a fairly reasonable price—much below that of pure copper and can be directly cast into anodes and used. This category of scrap itself can meet the entire requirement of cuprous oxide for the antifouling compositions. Poorer scraps, cheaper in price, have to be refined prior to use. The production of cuprous oxide, if taken up, will satisfy most, if not all, of our needs. A cut in imports by utilizing the metal scrap will effect a twin saving of the national resources. It should also be pointed out here that the final cost of the cuprous oxide is a function of the original cost of the scrap and the cost of refining the same, when necessary.

Two methods are universally adopted in commerce for making this useful compound. One involves the application of furnace technology while the other

employs the electrochemical technique. The thermal method consists in the careful and controlled oxidation of copper in a fine state of subdivision. Though simple, this process calls for a regulation of temperature within close limits beyond which results are not favourable. The product is likely to contain cupric oxide and free copper as impurities. The electrolytic method, on the other hand, gives rise to a product of exceptionally high purity. By controlling the operating conditions, the process can yield products of varying shades to suit any particular demand.

An electrolytic method has been developed⁴ and patented⁵ in these laboratories for the preparation of cuprous oxide. The optimum conditions of working have been arrived at after careful investigation. The process can be briefly described as follows: cast copper sheets are used as anodes in a divided cell with sheet copper cathodes, the electrodes being separated by a cloth diaphragm. An alkaline solution of sodium chloride is used as the electrolyte. Brine heated to 80°C is fed at a constant predetermined rate into the cathode compartments of the cell. Cuprous oxide formed near the anode is withdrawn with the electrolyte through an opening at the bottom of the cell. The slurry is filtered free of cuprous oxide and the clear filtrate run back into the cell after adjusting the composition. The cake of cuprous oxide is then washed, stabilised and dried preferably under reduced pressure. The current density employed is 5 amp./cm². The product should be stored in air-tight steel drums in a cool, dry place.

A few noteworthy features have been developed for the process. The continuous circulation of the electrolyte prevents an unnecessary build-up of alkali at the cathode and maintains an optimum

and constant alkalinity at the anode required for the formation of cuprous oxide. Feeding of the electrolyte at a constant predetermined rate is carried out by equipment of a special design, the rate depending on the current strength and ratio of anolyte to catholyte.

After standardising the operating conditions in the laboratory, experiments were conducted employing a monel cell with a rated capacity of 1/4 lb. per hour. After these studies a unit capable of producing one pound per hour was designed, fabricated and operated successfully. Continuous runs of eight hours with this unit yielded products comparable to the imported material both in colour and in purity.

The current efficiency of the process has been found to be not less than 94% and the energy consumption (D. C. needed for electrolysis) 0.36 kWh. or less per pound of cuprous oxide formed. These results compare favourably with figures reported in literature. Purity of the product is not less than 96%.

The Naval Dockyard Laboratory, Bombay, have found the sample produced by this process very satisfactory. The purity and colour are, according to them, up to their requirements. Some firms, to whom samples were sent, have approved of the product for use in paint formulations and for making porcelain red glaze and colouring glass. A number of Indian firms have shown keen interest in taking up production on a commercial scale.

The cost of production of cuprous oxide is worked out below assuming that a plant is installed and operated with a throughput of 6 cwt in a 24 hr. day. It is also assumed that the plant is run for 300 days in a year.

A. Land and building costs :	Rs. 60,000
B. Equipment costs: (M. G. sets, boiler, copper melting furnace, vacuum shelf-drier, filtration equipments, tanks etc.)	1,07,000
C. Raw Materials costs per year:	
(i) Copper scrap valued at Rs. 1—10—0 per lb, and other chemicals.	3,41,000
(ii) Power, fuel etc.	32,000
D. Cost of labour and supervision per year.	39,000
E. Fixed charges (Insurance, 0.5% of A plus B, and depreciation 10% of A plus B)	17,500
Total capital investment	<u>5,96,500</u>

Approximately Rs. 6 lakhs.

Annual Operating costs :

Raw Materials :	3,73,000
Labour and supervision	39,000
Maintenance (5% of A plus B)	8,500
Fixed charges, interest on capital, management distribution and other overheads	73,000
Total	<u>4,93,500</u>
Profit 10%	<u>49,400</u>
	<u>5,42,900</u>

Annual Production = 90 tons or 2,01,600 lbs.

Cost per lb. of product = Rs. 2-11-0.

Acknowledgment: The authors wish to thank to Dr. B. B. Dey, Director of the Institute and Dr. A. Jogarao, Assistant Director (Plg) for their sustained interest and constant encouragement throughout the investigation of the problem.

REFERENCES :

1. Indian Standards Specification, No. IS:70 (1950) Cuprous Oxide for paints.
2. Encyclopedia of Chemical Technology, (Interscience Encyclopedia Inc., New York, 1953) Vol. IV, p. 473.
3. *ibid*, Vol. VI, p. 984
4. Dey, B. B., *et al.*, *J. Sci. Ind. Research (India)* 13B, 219-220 (1954)
5. Indian Patent, 52,394, Oct. 29, 1954

PROCESSING OF MONAZITE

by

C. S. Acharya

(Central Electrochemical Research Institute, Karaikudi.)

Rapid developments in the fields of metallurgy and nuclear physics have been the cause of a renewal of interest in the rare earth and thorium metals during the past decade. The rare earth metals and their compounds are now finding increasing use in improving the forging and heat-resisting qualities of metals and alloys, in addition to their well known applications in glass and ceramic technology. Thorium, though not in itself a nuclear fuel, is a fertile material and by irradiation with neutrons may be converted to the fissionable product U^{233} which can be used in reactors in place of the naturally occurring U^{235} .¹ In the vast deposits of monazite found in the beaches of Travancore and Andhra lies much of the potential atomic mineral wealth of our country. The monazite found in the Travancore beaches is particularly high in thorium content which ranges from 8–10%. Besides, it also contains about 0.3–0.35% of uranium oxide. The various processes for the production of the compounds of thorium and the rare earths from this mineral are briefly surveyed here.

In the separation of monazite sand from the beach sands, gravity methods are used to bring about a preliminary concentration of the mineral. These concentrates are then passed through magnetic separators whereby the monazite is separated from the more magnetic minerals like garnet and ilmenite as well as the less magnetic rutile and sillimanite. By careful adjustment of the magnetic fields it is possible to obtain a product consisting of 97–99% monazite.

The extraction of the pure thorium and rare earth compounds from monazite

is a difficult process. The mineral is generally opened by either the acid or alkaline process depending mainly on the quality of the ore and the purity desired for the products. In the acid process the mixture of monazite and sulfuric acid is heated in cast iron pots fitted with covers and heavy anchor type agitators. The fumes of H_2SO_4 are drawn off through scrubbers from which the acid is recovered. The pots are heated externally. The reaction is exothermic and the heating is therefore carefully controlled.² The products formed depend on the amount of sulfuric acid used. When the sand is heated with an approximately equal weight of 98% H_2SO_4 to which some fuming sulfuric acid has been added, the product contains thorium pyrophosphate, which, unlike the corresponding rare earth salts, is insoluble in dilute mineral acid, and hence may be readily separated. If the amount of sulfuric acid is increased, the product consists of anhydrous thorium and rare earth sulfates, both of which are soluble in water. In either case the reaction mixture is added to cold water to dissolve out the sulfates leaving behind the heavy unchanged grains of sand. If the monazite is baked with only a limited quantity of sulfuric acid, thorium also will remain in the residue left after the solution of the rare earth sulfates. If, however, the thorium also is formed as a soluble product, it is precipitated either as pyrophosphate by the addition of sodium pyrophosphate³ or as orthophosphate by suitably adjusting the pH by the addition of a base like lanthanum hydroxide or carbonate⁴. After the removal of thorium, the rare earths are recovered from the solution by precipitation, to free them from the phosphoric

acid liberated during the digestion of the sand with H_2SO_4 . These metals are precipitated either as oxalates or as double sodium sulfates. In the former method the recovery of rare earths is complete while with sodium sulfate most of the yttrium earths remain in solution. Marsh, however, has indicated that virtually complete precipitation of the heavy lanthanon double sulfates may be accomplished by salting out with brine⁵.

Monazite also contains small amounts of radium and mesothorium and these can be recovered if a barium compound is added to monazite before treatment with sulfuric acid. The barium sulfate picks up the minute quantities of mesothorium and radium and remains as an insoluble residue when the sulfates of rare earths and thorium are dissolved out, and may be readily separated from the unreacted sand particles⁶.

The acid process is satisfactory for the decomposition of the sand, but the resulting solution contains nearly all the phosphate contained in the sand, in the form of phosphoric acid. The presence of this introduces serious problems in the subsequent treatment of this solution for the separation of thorium and the rare earths. The alkali treatment of the mineral is supposed to eliminate some of the difficulties inherent in the acid process. Buddeus and Preussner⁷ proposed to fuse monazite with sodium hydroxide whereby the hydroxides of thorium and the rare earths are formed along with sodium phosphate. Extraction of the mass after fusion with water should remove the sodium phosphate, leaving behind the metal hydroxides. Although this method is theoretically attractive, in practice it is difficult to ensure complete decomposition of the mineral and the reaction product is a hard solid mass, which is difficult to handle⁸. The use of sodium carbonate in place of sodium hydroxide, suggested by Urbain is not likely to bring about an improvement in the process.

Bearse and collaborators⁹, working at the Battelle Memorial Institute have

successfully evolved a process in which a caustic solution is used for the treatment of the mineral. They decompose the finely ground sand (-325 mesh) with 1.4 times its weight of sodium hydroxide in the form of a 45% solution. The mixture is heated at 280°F for 2-3 hours. The decomposition of the mineral is almost quantitative. The slurry obtained by this process is diluted and the hydrous metal oxides separated from the dissolved trisodium phosphate and excess NaOH . After two washings, the soluble phosphate content of the residual cake is reduced to 0.4% of P_2O_5 . The hydrous metal oxides are then dissolved in dilute HCl and the thorium separated from the rare earths by selective precipitation at pH 5.8–6.0, when the major portion of thorium and uranium comes down along with small amounts of rare earths. The filtrate on further neutralization gives a high grade rare earth product. These operations have been carried out on a pilot plant scale, treating 10 lbs. of sand per batch. The Indian Rare Earths Ltd. at Alwaye are presumably following a similar procedure, which is protected by a patent in the name of the Societe de Produits Chimiques de Terra Rares.

The processing costs are about the same for the acid and alkaline processes. The alkaline process is simpler than the acid one. Moreover, it makes possible the preparation of phosphate- and thorium-free rare earth compounds¹⁰. However, the process is more suitable only when the recovery of thorium is of secondary importance. The thorium oxide that is precipitated by partial neutralization of the chloride solution is contaminated with considerable amounts of rare earths and no simple method has been worked out so far for the removal of these contaminants, so as to obtain a very pure thorium product.

Many proposals have been made from time to time for alternative methods of decomposing the mineral. In most of these phosphorus is removed either in the elementary form or as a volatile compound. Considerable work has been

carried out in the field of chlorination. A Russian patent¹¹ refers to the chlorination of monazite under pressure in the presence of a reducing agent and KCl. The chlorinated product is worked up in the usual manner. Hartley and Wylie¹² working on Australian ores have evolved a method wherein finely ground monazite and charcoal powder in the ratio of 6.6:1 were briquetted and chlorinated at temperatures of about 700°C. Phosphorus volatilized as the oxychloride leaving behind the rare earth chlorides. The yield of these chlorides was 89–93%. Most of the thorium remained unattacked, the maximum chlorination of thorium being 18–19%. Chlorine efficiency was 75%. In a report on further research, Hartley¹³ refers to chlorination at temperatures above the melting point of the mixed lanthanon chlorides. At temperatures of over 900°C, thorium also was completely chlorinated, and it volatilized with impurities such as chlorides of Fe, Al, Cr and Ti. Phosphorus was removed partly in the elemental form and partly as trichloride and oxychloride. By suitable adjustment of flow rates and at temperatures of over 1000°C it was possible to remove most of the phosphorus in the elementary form. Some of the advantages claimed by the authors for these methods are: the phosphorus is eliminated and the rare earth metal chlorides obtained in a single operation; removal of impurities like Fe, Ti, Cr etc. is also accomplished simultaneously; the process directly gives anhydrous rare earth chlorides, which, by adjustment of working conditions may be obtained free from thorium and these anhydrous chlorides may be extracted in non-aqueous solvents or recovered in the molten state in which case they can be used directly for electrolysis. Sharma and Gupta¹⁴ working on similar lines were able to chlorinate the Travancore sand satisfactorily. Unground monazite, charcoal and molasses in the ratio of 5:1.5:2 were briquetted and chlorinated at 710°–750°C. The volatile chlorides⁵ of Ti, P, Fe etc. distilled over and were collected by

condensation. A maximum of 98.5% efficiency for rare earth recovery and 84% for thorium recovery was attained by these investigators. Chlorine efficiency was slightly less than 80%. Chlorination methods can be successfully adopted in our country, where chlorine obtained as a byproduct in the alkali industry is available in plenty.

It has also been proposed to heat the mineral with carbon in an electric furnace, the rare earth oxides being extracted from the mass after cooling by treatment with mineral acids. Weiss¹⁵ heated a mixture of monazite and carbon in an electric furnace, whereby the phosphides and carbides of the metals were formed. Baskerville¹⁶ proposed to volatilize the phosphorus by heating a mixture of monazite, coke, lime and fluorspar in the approximate ratio of 5:5:4:1 in an electric furnace. He deliberately produced CaC_2 within the mass, which facilitates its disintegration into a fine powder when thrown into water. The dissolved and suspended calcium hydroxide was removed by washing. The residue was treated with HCl and the thorium separated by the usual methods. The phosphorus which volatilized off was recovered by condensation.

In a similar procedure patented by Schulze¹⁷, the monazite is mixed with carbon and a compound of Mg or an alkaline earth metal and heated in an electric furnace. Phosphorus volatilizes and is recovered by condensation. The rare earths are left behind in the form of calcium or magnesium compounds which are soluble in HCl and are completely free from phosphorus. Excess of carbon is avoided so as to prevent the formation of phosphides and to remove all the phosphorus in the elementary form. Temperatures of 1650°–1750°C are used, at which reduction takes place rapidly and completely and easily fusible melts are formed. The melt is run into water and the granules thus obtained are ground before dissolving in acid.

No thermal reduction method is, however, known to have been adopted in

manufacture on a large scale. With cheap hydroelectric power progressively becoming available in our country, an efficient electrothermal process can be successfully exploited for the large scale decomposition of monazite. A thermal process directly produces elementary phosphorus, the requirements of which, in our country, are at present met entirely by foreign imports. The phosphorus produced in an electrothermal process, will therefore have a ready market. Moreover, such a process is particularly suitable for continuous operation, unlike the acid or alkaline digestion methods mentioned above. With this end in view, investigations are being carried out in this Institute for evolving a suitable electrothermal process for the working up of monazite sands. The results of these investigations will be reported in a separate communication in due course.

REFERENCES :

1. S. Glasstone: *Source Book on Atomic Energy* (D. Van Nostrand Co. Inc., New York, 1950).
2. Kirk E. R. & Othmer D. F., *Encyclopedia of Chemical Technology*, Vol. III, (1949) p. 639-642.
3. Campbell E. D. & Carney R. J., *U. S. Patent* 1,182,880 (1916).
4. Powell, A. R. *British Patent* 510,198 (1930).
5. Marsh J., *Nature* **163**, 998 (1949).
6. Soddy, *Proc. Chem. Soc.* **26**, 336 (1910).
7. Buddeus W. & Preussner, L. *German Patent* 95,061 (1896).
8. Levy S. I., *The Rare Earths* (Edward Arnold & Co., London, 1924).
9. Bearse A. E., Calkins G. D., Clegg J. W., & Filbert R. B., *Chem. Eng. Progress* **50**, 235 (1954).
10. Kirk R. E. & Othmer D. F., *Encyclopedia of Chemical Technology*, Vol. XI (1953) p. 506.
11. Aleksandrov G. P., *Russ.* **57**, 668 (1940).
12. Hartley F. R. & Wylie A. W., *J. Soc. Chem. Ind.* **69**, 1 (1950).
13. Hartley F. R., *J. App. Chem.* **2**, 24 (1952).
14. Sarma B. and Gupta J., *J. Sci. Ind. Research (India)* **12B**, 14, (1953).
15. Weiss L., *German Patent* 129,416 (1901).
16. Baskerville C., *Intern. Cong. Appl. Chem.* **8**, ii, 17 (1912).
17. Schulze R., *U. S. Patent* 1,981,126 (1935).

ELECTROLYSIS OF NON-AQUEOUS SOLUTIONS

by

N. Subramanyan

(Central Electrochemical Research Institute, Karaikudi.)

Electrochemical research has been by and large confined to a study of aqueous solutions. Even so, dilute solutions have received the greatest attention, though only comparatively concentrated solutions and salts in the fused state are generally employed in industrial electrolysis. And no very systematic work has been done with regard to either concentrated aqueous solutions or fused electrolytes. It is being slowly realised at present that the electrochemistry of non-aqueous solutions has been largely a neglected field and that water, though unique, is only one of several ionizing solvents.

Reactions in non-aqueous solvents¹ have been found to be of four types in which the solvent plays a prominent role, namely metathetical reactions, acid-base neutralisations, solvolysis and solvations. The function of the reactants and the nature of the products will thus depend on the nature of the solvent and sometimes a precipitation reaction in aqueous medium can be reversed in non-aqueous solution. And it is only very recently that a non-aqueous solvent like liquid ammonia has been used in the manufacture of barbiturates on an industrial scale in the U. K., U. S. A. and Germany. In electrolysis also, it is well known that in aqueous solution, certain electropositive metals like sodium, magnesium, calcium and aluminium cannot be deposited. Generally organic solvents of the Grignard compound type are used for successfully plating aluminium. Metals like magnesium, lithium, sodium and potassium can be deposited by electrolysis of suitable salts in ethylene diamine. Similarly it has been found^{3,6} possible to deposit various metals

like Be, As, Sb, Bi, Sn and Zn from solvents like liquid ammonia, acetic acid pyridine, benzonitrile etc. Rare earth amalgams have been prepared by the electrolysis of ethyl alcohol solutions of the chlorides; and magnesium has been quantitatively deposited by electrolysis of other solutions of Grignard reagents. In suitable solvents, the less electropositive elements can act as anions and may be deposited on the anode in a coherent form. For example lead can be got as an anion in liquid ammonia and deposited⁴.

Apart from the applications of electrolysis of non-aqueous solutions, there are the interesting aspects of the mechanism of conduction of electricity by them. It has been found⁵ that the conductance of a solution of sodium or potassium in liquid ammonia at infinite dilution is considerably higher than that of salts dissolved in water. The conductance decreases as usual as more metal is added. However when still more metal is added, the conductance is increased tremendously and it has been postulated that concentrated solutions of sodium in ammonia exhibit *metallic* conduction. Studies of ionization in non-aqueous solutions have been made by various workers. It has been generally accepted that the higher the dielectric constant of a solvent, the greater is its ionizing power. Several solvents like hydrofluoric acid, ethylene diamine and furfural have been studied by means of conductance measurements and divergence of non-aqueous solutions from aqueous solutions in their behaviour has been attributed variously to the formation of complex ions, proton-donating capacity of the solvents and the dielectric constant of

solvents. The problem of evolving a general acidity scale applicable to both aqueous and non-aqueous solvents has been indicated and some work has been done on acidity functions. The effect of the solvent on oxygen and hydrogen overpotentials⁶ has been investigated with reference to some select solvents containing oxygen and hydrogen.

A brief indication has been given of the lines of work, of practical value and of theoretical interest that have been pursued in the case of electrolysis of non-aqueous solutions. It will be realised that there is vast scope for research in this branch of electrochemistry. While the possibilities of preparing some elements like silicon and the rarer metals that have lately come into prominence have to be explored, the need for systematizing the electrochemistry of non-aqueous solutions cannot be overlooked. Diverse types of solvents have to be classified properly and studied from various points of view, as there are aprotic and amphiprotic solvents, organic and inorganic solvents. Not much work has been done on electrodes suitable for measuring potentials in various types of non-aqueous solutions and special cells may have to be developed for conductance measurements in non-aqueous solutions, because of certain

inherent difficulties in the use of solvents, volatile or toxic and of solvents which absorb moisture or gases from the atmosphere. Fundamental properties like ionic mobilities and the degree of ionization which depend on the properties of the solvent can be examined critically with respect to the viscosity and the dielectric constant of various media. In conclusion it can be said that the electrochemistry of non-aqueous solution is a branch of study which is bound to be fascinating and fruitful.

REFERENCES :

1. J. R. M., *Chemical Products*, **16**, 364 (1953).
2. Dikse T. P and Briscoe H. T., *Metal Ind. (N Y)* **36**, 284 (1938).
3. Davidson A. W., *J. Chem. Edn.*, **14**, 218 (1937).
4. Kraus, C. A., *Trans. Electrochem. Soc.* **45**, 175 (1924).
5. M. Dole, 'Principles of Experimental and Theoretical Electrochemistry' McGraw-Hill Book Co., Inc., New York and London, (1935) p. 123.
- 6a. Bockris, J. O' M., *Nature*, **159**, 401 (1947).
- b. Bockris, J. O' M., *ibid.* **158**, 584 (1946).

ALKALINE NICKEL-CADMIUM STORAGE BATTERY

by

Siddhartha Ghosh

(Central Electrochemical Research Institute, Karaikudi.

HISTORY:

Half a century after the invention of the Plante type lead acid battery, Waldermar Jungner in Sweden and Thomas A. Edison in the United States almost simultaneously made their invention of alkaline nickel-cadmium and nickel-iron batteries. Prior to 1910 the nickel cadmium battery had been developed and manufactured by Waldermar Jungner and Karl Ludvig Berg in Sweden. Berg with his sons separated from Jungner and opened the Nickel-Cadmium Battery Co. in England, subsequently, known as Alklum Company, in 1917. Afterwards NIFE Battery was started by Jungner in 1919, and was a serious competitor to Alklum. In about 1923, the French SAFT company started making ionic nickel cadmium batteries and later in 1926 the famous German company AFA opened a subsidiary company in England in the name of Britannia Battery Company.

The opening of all these nickel-cadmium battery manufacturing companies became a threat to the manufacturers of lead acid batteries in England, particularly the Chloride Storage Co. Ltd. The Electric Storage Company of Philadelphia, makers of "Exide" Battery, owns nearly 50% of the shares in England's Chloride. So they jointly bought the stocks in part of British NIFE in 1923, and Britannia Batteries in 1928. The interests of the French SAFT company had also been taken over by some means, which made the Alklum company the only manufacturer of nickel cadmium batteries in England. So Chloride had acquired full control over the manufacture of nickel-cadmium and lead acid batteries in 1935. The British Nickel

Cadmium Battery Co. continued its manufacture of nickel-cadmium batteries, whereas the Electric Storage Company of Philadelphia did not, nor did they allow anybody to import these batteries to the United States. This was possible by virtue of one of the provisions of the Cartel Agreement binding together Electric Storage Battery Company of Philadelphia, Chloride of England, and AFA of Germany, that none of them would export the nickel cadmium battery into the territory of the others without expressed permission. In 1945 a complaint was filed against Electric Storage Company and Willard Storage Battery Company, a subsidiary company of the former, by the Anti-Trust-Division of the United States Department of Justice, that due to the Cartel arrangements U. S. entered World War II with "neither the commercial experience nor the manufacturing facilities necessary to determine the advantages of cadmium batteries over lead acid batteries". The complaint was settled in 1948 by a "consent decree" and the defendant companies renounced their cartel agreement with AFA and Chloride. Sometime previously, one of the high executives of Electric Storage Company of Philadelphia visited Chloride's plant where he had discussions with their staffs carrying on comparative tests of flat plate Exide with NIFE and Alklum batteries, and was convinced of the high standard of performance of these batteries. These were being used for starting Diesel engines and the British War Department had practically adopted the nickel cadmium batteries for military use on account of the fact that they could be stored for considerable periods of time without appreciable loss

in capacity. The United States Army and Navy battery experts were also interested in the nickel cadmium battery and they pursued their investigation on the old batteries manufactured in Germany which they captured during the war. In England, France, Sweden, Russia and almost the whole of Europe, nickel cadmium batteries are manufactured extensively. After the end of hostilities in Europe, an investigation mission from the U. S. Navy visited AFA factory in Germany to study the manufacture of nickel-cadmium batteries in detail. Subsequently the Army reports on the nickel cadmium batteries have been made public by the U. S. Department of Commerce, wherein they have stressed the following advantages and disadvantages:-

- (i) Long life.
- (ii) High capacity at moderate rates of discharge above 0°C .
- (iii) Poor high temperature characteristics.
- (iv) High retention of charge (Low self-discharge)
- (v) Capacity per unit weight in comparison to lead acid battery is low.
- (vi) Care-free maintenance.

An American procurement officer, Lt. Col. H. B. Nichols made contacts with Berg Brothers, one of the pioneers in the manufacture of nickel-cadmium battery and started the Nickel Cadmium Battery Company, East Hampton, Mass. in United States. They are engaged in the production of various batteries for industrial use. They are also conducting experiments in collaboration with the U. S. Signal Corps to produce "sintered plate" type nickel cadmium batteries which were developed in Germany in 1930. In Hanover² AFA has constructed a factory to produce batteries for starting purposes, capable of operating at high discharge rate and low temperatures. The U. S. Signal

Corps Engineering Laboratory, Fort Monmouth, New Jersey explored the "know-how" of the process of manufacture and successfully carried out tests to satisfy special military requirements.

From the history of the manufacture of alkaline accumulators and from the available information there is good reason to believe that the commercial development of the nickel-cadmium battery has been deliberately prevented in the United States. Further, it may also be observed that the big interests in lead acid battery have tried to keep down the use of the alkaline accumulator in the field of automobile and heavy diesel applications to a certain extent in order to maintain the extensive popularity of lead acid storage batteries throughout the world. But both the lead acid and alkaline type accumulators have their merits and demerits and it is for the future to prove the superiority of the one over the other.

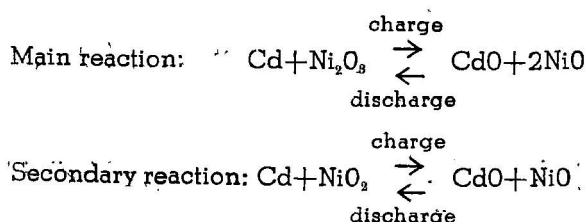
INTRODUCTION:

The manufacture of nickel-cadmium batteries has been undertaken in the United States of America only since 1946, though these batteries have been known in Europe for a very long time. Nickel cadmium batteries have got promising performance at high rate of discharge and low temperature, and the ability to be on floating charge for a long time without damage or loss in capacity. The average voltage of a cell on discharge is about 1.2 volts. In constructional details nickel cadmium batteries are similar to Edison's nickel-iron cells, the negative and the positive plates being similar in construction, and of the "pocket type" as developed by Jungner. The active material of the positive plate is nickel oxide and that of the negative plate metallic cadmium, and the electrolyte is a solution of caustic potash (KOH) with a little addition of lithium hydroxide. Some further advances have been made in the manufacture of 'sintered plate' batteries using nickel oxide as the positive active

material and cadmium as the negative active material; they differ from other nickel cadmium batteries in the method of support. These thin plate batteries are claimed to be replacing the lead-acid type batteries.

THEORY:

The actual mechanism of chemical reactions in the case of nickel-cadmium batteries has not been well understood, as is the case with lead acid batteries also. The probable reactions of charge and discharge may be viewed as follows:-



Actually we get hydroxide at the electrodes³ and not anhydrous nickel or cadmium oxides. The part which water plays in the reaction has not been properly understood, so only the oxidation and reduction reactions have been shown. The electrolyte is not involved in the reaction which is the case with lead acid batteries, but seems to serve only as a conducting medium.

The main reaction is responsible for supplying the major part of the current, but the secondary reaction may supply in part if discharge is made within a few hours after finishing the previous charge.

DETAILS:

PLATES: The positive and the negative electrodes are of the pocket type and are similar in construction to the negative plate of Edison nickel iron battery. These pockets or compartments are made from sheet steel which is perforated and the edges are ground off. They are then nickel plated, and the plating is homogenized by annealing the strips in an atmosphere of hydrogen. It is important that the plating should be impervious, so that contact between the

active material and iron may be avoided. The active material is fed into pocket electrodes in the proper quantity through a controlled adjustable slide on the outlet of the hopper⁴. The positive pocket electrode is fed with finely divided graphite or nickel flakes in homogeneous mixture with highly purified nickel oxide. The negative electrode consists of cadmium metal and cadmium oxide.

The production of suitable nickel oxide for the positive active material is one of the outstanding problems in the manufacture of nickel cadmium batteries. There are many patents covering the production of nickel oxide, but most manufacturers prepare it by reacting nickel sulphate with caustic soda solution to get nickel hydroxide, which is usually a bulky precipitate containing adsorbed ions from the solution. As reactions of the charge and discharge take place mainly in the solid phase, the original structure of nickel hydroxide is very important. The structure is more or less dependent on the precipitation and drying conditions, and to an even greater extent on the ionic concentrations and temperature of the nickel sulphate and caustic soda solutions. Usually the nickel hydroxide is heated to a high temperature to obtain the desired nickel oxide.

Similarly the negative pocket type plates are filled with metallic cadmium, CdO, and Cd(OH)₂ which is mostly contaminated with iron. During the formation i.e. charging, the nickel oxide is converted to Ni(OH)₃ and while discharging it is reduced to Ni(OH)₂ in the positive plates; similarly in the negative plate, during charge cadmium is converted to hydroxide and during discharge back to metallic cadmium. In the positive plates very pure graphite (free from iron) or nickel flakes are added for making the active material more conductive and in the negative plates addition of iron serves to increase the electrical conductivity of the CdO material. It has been noted that the internal resistance

of the battery is also decreased by the addition of iron in the active material of the negative plates. It is assumed that during discharge iron in the negative plate is not oxidised, so it serves only as a conductor. But it has also been noted that cadmium oxide itself is a good conductor and iron-free nickel cadmium battery is not in any way inferior to batteries containing iron.

ASSEMBLY :

The assembly of the positive and negative plates is done in groups similar to lead acid type batteries. Here the positive and negative groups are connected together by "connecting rods"⁵ which pass through holes at the top end of the plates separated from one another by means of washers, fitting on the rod and locked in place by a lock washer and nut on the end of the rod. The positive and negative groups are intermeshed to form a complete element as in the lead acid battery, with separators of hard rubber or PVC plastic pins. At the sides flat insulating hard rubber sheets are inserted; also the element is insulated from the walls of the container, which is made of nickel plated sheet steel. The bottom of the cell, and after insertion of the element, the top of the container are welded, these being previously nickel plated. The terminal posts for the plate groups which project through the holes at the top of the cells are sealed with hard and soft rubber gaskets and bushings. Generally the bushing in the positive pole is red and in the negative black. In the centre of the lid a combination valve and filler hole is provided, so that when the valve is closed no air from outside can enter the cell. The terminal posts are tapered, nickel plated and suitably provided with nuts to make inter-cell and outside connections.

ELECTROLYTE :

The electrolyte used in the nickel-cadmium cell is a solution of pure caustic potash (KOH) in water which generally contains some small percentage of

lithium hydroxide. The specific gravity usually varies between 1.19 to 1.25. For operation in cold climates a higher specific gravity is chosen. The effect of lithium hydroxide is said to be to prolong the life of the cell and especially to protect the cell from deterioration at higher temperatures of operation. Carbon dioxide absorbed through water or otherwise has a harmful effect on the life of the Nickel Cadmium battery, so it is advisable to change the electrolyte once in a year.

PERFORMANCE :

Like the Edison nickel-iron batteries different ratings have been specified for different applications of these batteries. Generally 5 hr, 7 hr, and 10 hr. ratings are given. At high rates of discharge the fall in voltage is considerable. To make these batteries suitable for use in starting automobiles and Diesel engines 'thin plate' and also 'sintered plate' batteries have been evolved. The internal resistance of these batteries is kept sufficiently low by making some additions of conducting materials to the active mass of the plates. These have been found to give better voltage characteristics at high discharge even at low temperature.

The temperature characteristic depends on the nature of construction of the cell and the nature of service it has to perform. Usually the ampere-hour output is increased to a certain extent and does not become passive as in the case of nickel-iron batteries.

The self-discharge characteristic is quite low, and with the use of purer material it may be kept sufficiently low. In commercial batteries self discharge ranges from 20 to 40 per cent per year.

The maximum recommended temperature for the operation of the nickel cadmium battery by the manufacturers is 115°F or 46°C. The electrolyte freezes at -28°C irrespective of the state of charge in the batteries.

These batteries are not easily spoilt by overcharging and can be kept on float charge for a long time.

LIFE:

The service life of nickel-cadmium batteries is very good, even under service conditions where maintenance is poor and neglect and abuse are encountered. Some batteries are found to render service even on use for 15 to 20 years. Comprehensive data on the life of these batteries are not available, but batteries manufactured in France for automobiles are guaranteed for four years.

USES:

Nickel-cadmium batteries can be used to replace lead-acid type batteries in many fields like train lighting and air-conditioning, signals, mine lamps, radios, emergency lightings, marine services, electric trucks, diesel starting etc. In India considerable numbers of these types of batteries are used in our railways.

DEVELOPMENTS:

Research towards the production of batteries with higher ampere hour capacity per pound weight, minimum volume and better performance and life is being carried out by several workers throughout the world, and many advances have been made in this field in recent years. The development of the 'sintered plate' nickel-cadmium battery is well under way and is reaching the manufacturing stage in U. S. A. In Germany during World War II, 'sintered plate' batteries were being actually produced. Another type of alkaline battery, namely, zinc-silver peroxide⁶ battery

has been known for a considerable time, but its practical development has been effected by H. G. Andre only quite recently. The outstanding characteristic of this type of battery is the high output per unit weight and space. Its merits have yet to be established in actual use.

CONCLUSION:

Alkaline batteries were known and developed in Europe earlier than in other countries of the world. The United States took up the problem as recently as 1946, and has acquired much of the 'know-how' from Germany. Though in India we have presumably made good progress in the production of lead acid storage batteries nothing has yet been done to produce alkaline batteries in any form here. It is pertinent to point out that for the past many years considerable numbers of these batteries are being imported, especially for the use of the Railways and the Defence Department. This is the time when we should endeavour to produce these batteries here in India.

REFERENCES:

1. Wesley, G. F., *The Battery Man*, 30, No. 8, p. 3 (1949)
2. Ellis, G. B., Mandel, H. & Linden, D. *J. Electrochem Soc.*, 99, 250C (1952)
3. Haul, A. P., *Trans. Electrochem. Soc.*, 76, 435 (1939)
4. B. I. O. S. Final Report No. 708.
5. George W. Vinal: *Storage Batteries* (Third Edn., John Wiley, New York) p. 82.
6. Eidensohn, S., *J. Electrochem. Soc.* 99, 252 (1952)

NOTES AND NEWS

DR. B. B. DEY RETIRES

Dr. B. B. Dey, D. Sc. (Lond), F. R. I. C., F. N. I., Director of the Central Electrochemical Research Institute proceeded on leave preparatory to retirement on 26-12-1954. Dr. Dey was the first Director of the Institute and joined in February, 1953 soon after the formal opening of the Institute by Dr. S. Radhakrishnan, Vice-President of India.

It was indeed fortunate for the newly started Electrochemical Research Institute to have got a man of Dr. Dey's eminence to shape its character and destiny. He brought with him an established reputation in the field of electro-organic chemistry based on the vigorous programme of research which he had been directing in Presidency College, Madras under the auspices of the Council of Scientific and Industrial Research. He was equally distinguished in the field of administration also, having held office both as Principal of Presidency College, Madras and Director of Public Instruction, Madras.

During the two years of his stay in the Institute, the research programme initiated under his direction has borne rich fruit in the shape of several processes whose industrial utility has been successfully proved in large laboratory scale or semi-pilot-plant scale trials. Special mention may be made, in this connection, of the processes for the production of electrolytic manganese from the low-grade ore, cuprous oxide from copper scrap, calcium gluconate from glucose and p-aminophenol from nitrobenzene. Gratifying progress has been made in the investigation of several other processes. The rapid strides made in the organisation of research and the completion of so many important investigations in so short a period bear witness to the yeoman service rendered by Dr. Dey

His sustained interest in the growth and development of this Institute found practical expression among other things in his donation of valuable sets of, back volumes of several scientific periodicals from his personal collection to the library of the Institute. Concern for the welfare of the staff was ever uppermost in his mind and he won the affection and esteem of all of them by the constructive efforts he made towards the provision of the various amenities needed in a place like Karaikudi.

The Advisory Board of the Institute at its last meeting in Madras in December, 1954 placed on record their deep sense of appreciation of the splendid work that had been done by Dr. Dey in carrying out the tasks of the Director of the Institute.

COMMITTEES AND CONFERENCES:

Shri B. A. Shenoy, Senior Scientific Assistant was deputed from the Institute to participate in the Indian Standards Institution Convention on "Engineering and Building Materials" at Calcutta from 11th to 14th December, 1954. Two papers were presented by him on the occasion, namely, "Anodic Oxidation of Aluminium and its Alloys for decorative and corrosion purposes" by A. Jogarao and B. A. Shenoy and "On setting up standards for Electro-plated Finishes for use in Buildings" by S. Ramachandran and S. R. Rajagopalan. Shri Shenoy also took this opportunity to visit several industrial establishments in Calcutta connected with the Aluminium and Metal Finishing Industries.

The Advisory Board of the Central Electrochemical Research Institute, Karaikudi met on the 20th December, 1954 at the Central Leather Research Institute, Madras under the chairmanship of Dr. R. M. Alagappa Chettiar.

Among those present were Dr. S. S. Bhatnagar, Dr. J. C. Ghosh and Dr. B. B. Dey, Member-Secretary. Dr. A. Jogarao, Assistant Director, C. E. C. R. I., Sri B. V. S. Iyengar, Architect, Shri B. M. Das, Director, C. L. R. I. and Shri K. G. Krishnamurthy, Assistant Secretary, C. S. I. R. attended the meeting by special invitation.

ADDRESSES AND LECTURES :

Shri S. Govindarajulu Naidu, Vice-Chancellor, Shri Venkateswara University, Tirupati, visited the Institute on 29-10-54 and addressed the members of the staff.

Shri B. M. Das, Director, Central Leather Research Institute, Madras and Shri Pyarelal Agarwal, Commissioner of Income-Tax visited the Institute on 29-12-54 and after going round the Institute, addressed the members of the staff.

Shri O. V. Alagesan, Deputy Minister for Railways, Government of India, visited the Institute on 10-1-55. He saw the work being carried out in the various departments of the Institute and later addressed a gathering of the members of the staff.

STAFF :

We welcome the following members who joined this Institute during the last quarter :-

1. Shri Baghavandas Office
Sharma Assistant 1-11-54
2. Shri R. Ganesan III Divi-
sion Clerk 14-12-54

We convey our congratulations to Shri M. Srinivasa Rao who has been promoted to the post of Laboratory Supervisor.

VISITORS :

1. Shri B. M. Das, Director, Central Leather Research Institute, Madras.
2. Shri S. Govindarajulu Naidu, Vice-Chancellor, Shri Venkateswara University, Tirupati.
3. Shri Pyarelal Agarwal, Commissioner of Income-Tax, Mysore.
4. Shri O. V. Alagesan, Deputy Minister for Railways, Government of India.
5. Lady Lokasundari Raman, Bangalore.
6. Prof. Eugene P. Link, State, University Teacher's College, New York.
7. Shri P. Mukherji, Commissioner of Income-Tax, Madras.

BOOK REVIEWS

New Instrumental Methods in Electrochemistry

By Paul Delahay.

(Interscience Publishers Inc., New York,
1954; Indian Agent: Asia Publishing House,
17, Gunbow Street, Bombay.)
437 pp, \$ 11.50.

Interscience publishers are to be congratulated on the publication of this book, the latest in the field of instrumental methods of analysis applied to electrochemistry. They seem to have a wonderful knack of persuading the right people to write books on specialised fields of scientific work. In a foreword to the book, Dr. Kolthoff states that "the aims and objectives of the present book are to offer the theoretical fundamentals of the newer methods of electrochemical analysis and the new techniques which have been used" and rightly points out that Dr. Delahay is "eminently qualified to fulfil these aims, having contributed so much to the theoretical developments himself."

This book is divided into four parts. Part one deals with voltammetric and related methods, comprising ten chapters covering more than two-thirds of the book. Part two is devoted to coulometry, electrolytic separations and related methods, about fifty pages being devoted to these topics. Some thirty pages comprise part three of the book in which Dr. C. N. Reilley has interpreted the analytical significance of high-frequency methods. Part four of the book contains four chapters on instrumentation and occupies nearly sixty pages. The remaining pages are devoted to two appendices and to the author and subject indexes.

A brief resumé of the electrochemical methods of analysis is given in the first chapter. An attempt has been made to point out the distinction between voltammetry and polarography and the

distinction is maintained with clarity throughout the book, perhaps for the first time. In the second chapter, the fundamentals connected with electrode potentials as well as the kinetics of electrochemical reactions are discussed, giving due importance to the mathematical derivation of the relevant formulae. The Nernst Equation has been and is still the starting point for the explanation of electrochemical reactions. This fact as well as the shortcomings of the Nernst Equation have been prominently indicated in the second chapter.

The theoretical background for voltammetry and polarography at constant voltage is incorporated in chapters three to six. It is complete with the formulation of differential equations and the solution of boundary value problems. The electrode reactions met with under varying conditions, in reversible and irreversible, kinetic and catalytic processes are explained. The mass transfer problems are solved with several assumptions which, though inevitable, are sometimes questionable. The inherent difficulties encountered in the solution of mass transfer problems by hydrodynamic principles and the recent work in this field have also been included.

The rest of the chapters in part one pertain to voltammetry and polarography at continuously or periodically changing potential, voltammetry at controlled current, phenomena in stirred solutions and voltammetric titrations. The limiting currents obtained with rotating or vibrating electrodes in stirred solutions are found to be proportional to the concentration of the oxidized or reduced substance and so enable one to apply those electrodes in analytical work. The application of voltammetric methods to find the end point of many titrations has been pointed out.

As mentioned earlier, the fundamental concepts of coulometry and electrolytic separations have been thoroughly discussed in part two. This is quite necessary in view of the increased attention bestowed nowadays on electrolysis at controlled potential and on coulometric titrations for practical purposes.

High frequency methods is a new branch of work in which interest is being evinced in recent times. In part three, Dr. Reilley has discussed the theories relating to "condenser" and "coil" type methods. The applications and instrumentation have also been discussed.

Part four in which the general principles of approach to instrumentation techniques have been exclusively discussed is extremely useful from the practical point of view.

The book is intended to be an interpretation of "theory, instrumentation and applications to analytical and physical chemistry" and would probably be a disappointment to those who expect the book to be a practical guide on "New Instrumental Methods," as the title might indicate at first glance. More than three-fourths of the book is devoted to a thorough and critical treatment of the theoretical developments enumerated above, giving characteristic mathematical analysis of the different topics and indicating potential applications wherever possible. Doubts therefore arise as to the suitability of the present title of the book.

The appendices included at the end of the book contain the special forms of the Nernst equation and the derivation of some of the other equations in the text.

The quality of the print and the get-up of the book needs no praise and is extremely satisfactory. A few errors which the reviewer has come across while reading through the book may be pointed out here. These are:

"agreement" for "agreement" in page 66, line 3; "occurring" for "occurring" on page 383, line 3 and "reservoir" for "reservoir" in line 12.

The book is of great value primarily for analytical chemists and theoretical electrochemists and should certainly prove to be an incentive to further work.

H. V. K. Udupa.

Ferromagnetic Domains

by K. H. Stewart

(Cambridge Monographs on Physics,
1954, pp 176, price 25 sh.)

This small monograph explains in brief and clear physical terms the theory of Ferromagnetism on the basis of "elementary domains" into which a ferromagnetic substance can be divided. This theory can be traced to Weiss who first formulated the idea to account for the ease with which elementary moments of a ferromagnetic can be aligned in comparison with those of a paramagnetic though the source of their magnetism is the same i. e., magnetic moments possessed by electrons due to spin or orbital momentum. While in paramagnetics, these moments are random in direction and hence microscopically unobservable, in ferro-magnetic substances there exist elementary domains in which the moments are correlated though the resultant moment of each domain is aligned at random with respect to the rest.

Stated thus, Weiss's idea seems to be strikingly simple but it was found necessary to develop it from a more detailed quantitative point of view. Today a consistent picture has been built up and the extensive bibliography given by the author illustrates the amount of work that has been done to place the theory on a sound footing. Experimental confirmation came from the Bitter patterns, i. e. magnetic powder patterns. The reader will find a large number of illustrations (photographs and diagrams) to facilitate understanding of the physical principles.

Of the seven chapters on Magneto-crystalline anisotropy, magnetostriction, domain arrangement, domain walls, hindrances to wall movements, time effects, and magnetic and thermal energy changes, special attention should be drawn to the first three as being fairly complete from the standpoint of the physicist. The chapter on time effects could have been more detailed but in making this comment the reviewer is probably influenced by his own interest in time dependent statistical phenomena.

Taken as a whole, the book serves the purpose expected of a monograph—to focus attention on particular aspects rather than give dilatory accounts attempting to cover wide fields. It is a necessary supplement to Bozorth's classic treatise on 'Ferromagnetism'.

Alladi Ramakrishnan.

*Survey of the Indian Chemical
and Pharmaceutical Industry-1954:*

by The Indian Chemical Manufacturers
Association.

The first survey of the Indian Chemical and Pharmaceutical Industry was published in 1951 by the Indian Chemical Manufacturers Association. The present survey covers the period of the first Five Year Plan (1951-55) and is the joint effort of several individuals. The industries dealt with are the acid industry, the alkali and ancillary industries, fertilizers, synthetic organic chemicals, pharmaceuticals and industrial chemicals. A separate chapter has been devoted to the consideration of some new industries like petroleum refining and petrochemicals, plastics, rubber, insecticides and fungicides and textile auxiliaries and chemicals.

Policies regarding railway freight, excise; tariff protection, labour and scientific and industrial research have been frankly discussed from the industrialists' point of view and the various ways in which Government can help the industries have been set forth. The final

chapter "Blue Print for the Chemical Industries" gives in a nutshell valuable information regarding the present state and future prospects of various industries.

The trouble that has been taken in bringing out this survey abounding in statistical information culled from various sources is commendable and the publication is to be welcomed as giving a clear picture of the achievements and the potentialities of the private sector which is expected to play a vital role in the development of India during the period of the Second Five Year Plan.

N. Subramanian.

Annual Review of Physical Chemistry,
Vol. 5 (1954): G. K. Rollefson, Editor &
R. E. Powell, Associate Editor.
(Annual Reviews, Inc. Stanford,
California, U. S. A.)

This volume which is the fifth of the series gives like the earlier ones a survey of the progress in the different branches of Physical Chemistry in the preceding year - in this case the survey generally covers the period up to December 1953.

Subjects like Thermochemistry and Thermodynamic Properties of Substances, Heterogenous Equilibria and Phase diagrams, Solutions of Electrolytes, Solutions of Non-electrolytes, Isotopes, Spectroscopy and others, have been brought under review every year. However, the choice of different scientists to survey the progress in these subjects in different years has provided an extensive coverage of literature. Discussions on topics like Ion Exchange, Crystallography, Solid State, Colloids, Properties of Macromolecules, etc., have been added from time to time when progress in that particular branch has been particularly active. Cryogenics has been a subject for review for the first time in this volume. The individual authors have made the essays very interesting by stating at the outset the particular aspect of the topic they

propose, to discuss and by providing necessary background information about the subject to enable the reader to follow the discussions without difficulty. They have also shown in which of the earlier volumes the other aspects of the problem have been discussed.

These volumes and others to follow will constitute a valuable addition to any library, for it places in the hands of active research workers a valuable set of references in allied fields, and in the collection of which they will otherwise have to spend a considerable time. Even for the beginners these volumes will be an invaluable asset for they show the latest trends in the different branches of physical chemistry, and also indicate where exactly the beginners can get a more exhaustive treatment of the particular aspect of the subject of interest to them.

The book has been excellently got up, and has a very good index; the only regret, as one closes the book, is that the contribution by Indian scientists to the progress of physical chemistry has not been extensive.

S. Ramachandran.

Titanium and Titanium Alloys

by John. L. Everhart.

(Reinhold Publishing Corporation, 1954.)

This small volume on a topic of very great present day interest contains in its 180 odd pages a wealth of information which will doubtless be valuable to those interested in the application of titanium and its alloys to various fields of designing and fabrication. The book, as stated by the author, will not prove as useful to those engaged in titanium research and less so to those concerned with the production of the metal.

The book is divided into ten chapters. The availability and occurrence of titanium ores, a brief account of the methods of production, melting of titanium sponge, statistics of production since 1948 and possible increase in the future, comparison of its present price with

those of some other materials of construction etc. are included in the first chapter.

The physical, mechanical, fatigue and corrosion properties of high purity titanium, commercial titanium in the form of bars, sheets and forgings and various commercial titanium alloys are dealt with in the next three chapters. A number of tables and graphs showing the comparative properties of various alloys, commercial titanium produced by different firms, effects of alloying elements etc., are given.

Chapters V, VI, VII and VIII deal with heat treatment, forming and fabricating, joining, and machining and grinding, respectively. Under heat treatment annealing, surface hardening, nitriding, carburizing, siliconizing and molybdenizing have been discussed.

Forming and fabricating with commercial titanium have been treated with reference to forging, cold and hot heading bending, deep drawing, spinning, dimpling, hydropress forming, drop hammer forming etc.; flaring, shearing, casting and lastly to powder metallurgy.

Joining of titanium by methods of arc, resistance, spot and seam, flashbutt and cold welding, brazing, adhesive bonding and mechanical fasteners are dealt with in Chapter VII.

In the next chapter the machining and grinding characteristics of titanium alloys with reference to turning, milling, drilling, tapping, thread cutting, reaming, sawing, broaching, flame cutting, grinding etc., are discussed.

Cleaning and finishing of titanium forms the subject matter of Chapter IX. Several conventional methods of cleaning and finishing are described in brief.

In the last chapter, the present uses of titanium and its alloys in various fields are given, specially in aircraft production. Possibilities of their use in various other fields in future when cheaper metal may be available are pointed out.

References to literature have been given at the end of each chapter. On the whole, the book should be very useful, in that it brings together under one cover much of the information required by those working with titanium and its alloys.

N. N. S. Siddhanta.

Rare Metals Hand Book

by Clifford A. Hampel, Editor.
(Reinhold Publishing Corporation, 1954)

Rare Metals Hand Book is a timely and valuable publication. It is an authoritative source book for the latest available data on more than 34 less-common metallic elements. The subject matter is very well arranged in twenty-nine chapters dealing with the production of metals from ores or other raw materials; production statistics; economics; physical and chemical properties; fabrication techniques, alloys and application of each element. The value of the book has been further enhanced by the inclusion of selected bibliographical references for a more detailed study and understanding of metals. Convincing reasons have been put forward for the inclusion of elements like boron and silicon along with less-common metals and it is also clearly pointed out that cost alone is the proper basis for regarding a given metal as rare or common.

While discussing the commercial attractiveness of ores or other raw materials as sources of metals, it is pointed out that for extraction of copper even 1% ore can be attractive whereas in the case of iron or aluminium it should be 30% or more. As one example at least of a truly dispersed natural raw material which is preferred to a more concentrated one as the source of a commercial product, experience is cited of plants using sea water containing only 0.13% magnesium for magnesium production which achieved lower production costs during war time, although vast deposits of ores containing 30% or more of magnesium were available. The author mentions several methods involving

ion-exchange, porous membrane, adsorption and electrochemical techniques for the utilisation of sea water as a source of metals and says that a most important and commercially attractive method would be the deliberate cultivation of specific marine organisms which concentrate one or more elements in their bodies by biological activity.

Interesting points are brought out in dealing with the production of some rare metals. The most important new commercial possibilities included are: (1) Selective extraction of particular metals from even a dilute solution containing several metals by the use of a mercury cathode, (2) Production of metals of extremely high purity using an anode of the amalgam containing several metals with an appropriate cathode in an electrolytic cell, (3) Production of certain metals by displacing the amalgam of a metal from solution through the use of zinc amalgam and subsequently treating the amalgam of the metal to get pure metal, (4) Production of titanium metal by thermal decomposition of titanium dichloride, (5) Electrolysis of fused salt to produce a sodium metal containing calcium and the subsequent crystallization of calcium, (6) Production of boron by the electrolysis of potassium fluoborate in a fused bath of potassium chloride and also by electrolysis of a molten mixture of potassium chloride, potassium fluoborate and boron oxide and (7) Separation from zirconium and production of a concentrate containing about 90% by weight of hafnium oxide from a feed material containing 2% by weight of hafnium oxide by the preferential adsorption of hafnium by silica gel from a methanol solution of the mixed tetrachloride available commercially.

Rare Metals Handbook is bound to be especially valuable to all chemists, metallurgists and engineers connected with the production, fabrication and application of the many less-common metals.

V. Aravamuthan.

Non-Ferrous Foundry Metallurgy

by A. J. Murphy (Editor). (Pergamon Press, London, 1954) 497 pp.

The publication under review is the co-operative effort of a number of specialists and covers a rather wide field in the science of melting and casting of non-ferrous metals and alloys. The book has a rational and scientific approach to the art of founding. As the editor himself points out in the preface, the technology of the non-ferrous industry has no longer to depend upon the development of operative skills and must be based on the understanding and application of scientific principles.

The first four chapters deal with aspects of physical metallurgy which are important from the point of view of foundry metallurgy and cover the properties of metals and alloys both in solid and liquid states, solution of gases in liquid metals and solidification of metals. The fifth chapter is devoted to foundry technology including industrial

melting of non-ferrous metals. The sixth chapter discusses the properties and testing of castings while the seventh chapter deals with casting individual non-ferrous alloys.

It is inevitable that there should be a certain amount of overlapping and repetition of the subject matter in a book of this nature, covering exhaustively the science and technology of founding, and with each chapter written by several experts. In fact this repetition may even be desirable so that each chapter when read at random can be cogently and intelligently followed.

Metallurgists and all others connected with non-ferrous foundry practice will find this book a useful guide. It should certainly find a place in any technical library concerned with metallurgy or foundry practice. The book is printed neatly on excellent paper and beautifully got up. It is amply illustrated with photomicrographs, photographs and drawings.

R. Mallikarjunan.

ABSTRACTS

Alternating current polarography of organic compounds I. General introduction and theory: Breyer, B., Bauer, H. H. and Hacobian, S., *Austral. J. Chem.*, **7**, 305-312 (1954)

The results of experiments conducted in aqueous buffered solutions are reported. The potential corresponding to the peak of the A. C. wave coincides generally with the half step potential of the D. C. wave. Other characteristics like the shape of the waves, adsorption effect, bulk concentration, height of mercury reservoir and presence of surface active substances have been studied.

A discussion of the theory underlying the process is given in addition to a schematic diagram of the electrode solution system.

Polarographic determination of free sulphur in petroleum fractions: Harrison, S. and Harvey D., *Analyst*, **79**, 640-43 (1954)

A method of estimating free sulphur in petroleum fractions is indicated. The supporting electrolyte is a 0.2 M solution of ammonium acetate in glacial acetic acid. Using a mercury pool anode, the half wave potential of the reduction wave is -0.39 V. Satisfactory results are obtained when the free sulphur concentration ranges between 0.5 to 10 P.P.M. There is no interference from other organic compounds.

Polarographic determination of zinc in gold: Deal, S. B., *Anal. Chem.*, **26**, 1459-60 (1954)

The method given is useful in the determination of concentrations of zinc (0.001% to 1%) in zinc-gold alloy. The first step is to separate gold by precipitation with aqueous sulphur-dioxide solution. After the removal of gold, zinc is determined in the solution polarographically with 4 M ammonia-4 M ammonium chloride supporting electrolyte. Potential values have not been corrected to standard potentials. Standardization graphs for zinc are given.

Polarographic determination of uranium: Legge, D. I., *Anal. Chem.*, **26**, 1617-21 (1954)

A procedure for uranium analysis in ores is described. Uranium is separated from the bulk of the other metallic impurities by eluting a nitric acid-ether solution through a short column of cellulose pulp. It is then estimated polarographically in oxalic and sulphuric acids media. Impurities present in small quantities have no effect on the polarographic determination. Greater accuracy is possible in analysis with low-grade samples than was previously possible. The cellulose column and the hot-box utilized are illustrated.

Polarographic determination of tin in rocks: Reichen, L. E., *Anal. Chem.*, **26**, 1302-04 (1954).

A more rapid method of estimation than the gravimetric one has been devised in which the supporting electrolyte is dilute hydrochloric acid containing tartarate ion. Measurement is both rapid and accurate. No precipitation of tin is necessary except that iron, if any, should be separated. Comparative data on the results obtained by polarographic and gravimetric methods are given. The

supporting electrolyte is 4.6 M HCl-0.1 M sodium tartarate and the half wave potentials of the reduction waves of tin are at -0.35 V and -0.68 V Vs S. C. E. respectively.

The behaviour of the lead dioxide electrode: Jones, P., Lind, R., and Wynne Jones, W. F. K., *Trans. Faraday Soc.* **50**, 972 (1954)

A new technique of measuring the oxygen overvoltage on lead peroxide anode in relation to current density under practically constant surface conditions is described. Results obtained appear to bear out the usefulness of the method.

The inorganic phosphates as polyelectrolytes Callis, C. F., Van Wazer, J. R., and Arvan, P. G., *Chem. Rev.*, **54**, 777 (1954)

A description is given of the various methods which have been used to characterize these completely inorganic, strongly ionized polyelectrolytes, which have been found to show degrees of polymerisation ranging from 2 to 2000 depending on the exact composition of the salt.

Methods of separating rare earth elements in quantity: Spedding, F. H. and Powell, J. E., *J. Metals*, **6**, 1131 (1954)

A review of the different methods developed at the Iowa State College, for the isolation of fairly large quantities of rare earth metals. Details of three processes involving ion exchange resins are given. These methods involve the elution of an adsorbed band of mixed rare earths down a cation exchange bed by means of a 5% citric acid solution, adjusted to a pH of 2.5-3.0 with ammonia or a 0.1% citric acid solution, adjusted to a pH of 5.0-8.0 with ammonia or an ammonium salt of ethylene diamine tetraacetic acid. The resin bed used was of commercial grade sulfonated styrene-divinylbenzene copolymer. Operations have been scaled up to a unit which utilizes 45 six-inch and 100 four-inch columns with beds 4 feet long. These columns are loaded with about 50 lbs. of mixed rare earths every 10 or 15 days. Eluant flows through the columns by gravity with very little attention and most of the effluent citric acid is recycled. Most of the rare earths are recovered in such a state that by some simple chemical procedure it is possible to obtain yields of 40-90% of individual rare earths of 99-99.99% purity. These methods, according to the author, hold out promise of application in the separation of quantities of rare earths of the order of a few hundred pounds in an extremely pure condition.

Contact rectifiers for electrolysis installations: Kralh, G., and Stritzl, P. F., *Ind. Chemist*, **30**, 472 (1954)

The authors describe the advantages of the A. E. G. contact rectifiers for a. c. - d. c. conversion and consider the principal problems inherent in the design. It is concluded that these rectifiers have proved their worth in the Chemical Industry where constant load at high efficiency is the chief consideration.

3-Ton arc furnace: *Metallurgia*, 50, 288 (1954)

A 3-ton modern arc furnace has been installed at Clyde Alloy Steel Co., Ltd. for producing high quality castings from mild steel scrap and turnings. The installation makes use of the hydraulic method of electrode regulation which is responsible for high efficiency. The average melting time for a 3 ton charge is 2.16 hours. The furnace, which is rated at 2000 kVA is fed from a 6.6 kV supply through a transformer of suitable capacity; the power consumption per ton of metal melted is 650 kWh. The electrodes are held in position by means of spring loaded clamps for easier working.

Carbon and Graphite Electrodes Evaluated for use in Ferro-alloy Furnaces: Hogue, R. S., Westlake, R. L. and Moga, G. M., *J. Metals*, 6, 1379 (1954).

The authors give a brief account of the electrode sizes, the method of their application and the relationships between electrode diameter and current density, temperature and thermal conductivity and temperature and electrical resistivity by means of graphs for both the carbon and graphite electrodes. They have also given the typical room temperature properties of carbon and graphite electrodes, and some electric furnace products with representative values for electrode consumption, voltages, current and current densities.

The Soderberg Self Baking Electrode: Sem, M. O., *J. Electrochem. Soc.* 101, 487 (1954).

The use of different materials in the electrode pastes for Soderberg electrodes is discussed. Optimum calcination temperature for the various types of cokes used are considered. Baking conditions in a self-baking electrode are described. Details of the electrode holder equipment for the different types of melting and smelting furnace are given.

A Cell for the Preparation of Small Quantities of Alkali Metals: Baker, P. S., Wells, G. F., and Rathkamp, W. R., *J. Chem. Educ.*, 31, 515 (1954).

A small cell for the fused electrolysis of alkali halides, particularly for making lithium is described. Information about the materials of construction, cell operation and storage of the product is also included.

The Place of Sodium in the New Metal Technology: Sittig M., *Chem., Eng. Progr.*, 50, 457 (1954).

The uses of sodium metal in various industries, specially in the production of titanium metal, are given.

Electrolytic Preparation of Molybdenum: Senderoff, S. and Brenner, A., *Chem & Process Eng.*, 36, 17 (1955).

Coarse powders of pure molybdenum were deposited on the cathode from a solution of K_2MoCl_6 in a 1:1 (w/w) mixture of sodium and potassium chlorides at a temperature of 90°C and current densities of 3 to 100 amp/sq. dm., the electrolysis being carried out in an argon atmosphere. The authors describe briefly a method of preparing K_2MoCl_6 .

Chemical Engineering Aspects of Titanium Metal Production: Powell, R. L., *Chem. Eng. Progr.*, 50, 578 (1954)

Production of $TiCl_4$ from rutile, its purification and production of titanium metal by reduction of $TiCl_4$ by the Kroll process, purification of the sponge metal etc., are described. Other methods of production of the metal are briefly mentioned. Diagrams of the equipment are given. Six references are cited.

The Oxidation of Titanium at High Temperatures in an Atmosphere of Pure Oxygen: Jenkins, A. E., *J. Inst. Metals*, 82, 213, (1954).

Oxidation of refined and commercial titanium has been investigated in the temperature range 600-925°C at 700 mm. O_2 pressure. The oxidation process was followed by the gain in weight of specimens at various intervals. Distribution of O_2 in the scale and the metal core was determined at temperatures where the scale could be stripped. The scales in such cases were examined and were found to be porous and the oxidation process was shown to occur at metal oxide/metal interface. A glancing angle X-ray diffraction technique was used to determine the nature of the scales and the surface layers of the metal core. The scales consisted of rutile modification of TiO_2 . The surface layers of the metal core consisted of $Ti-O_2$ solid solution, the oxygen concentration gradient being dependent on the oxidation temperature. A mechanism for oxidation of Ti at high temperature has been suggested.

Development of melting techniques for titanium and zirconium: Miller, G. L., *Ind. Chemist*, 30, 577 (1954).

The development of melting techniques for Ti and Zr has been traced. Various methods e.g. melting in vacuum arc furnace, in split graphite tube resistor furnace, induction furnace, consumable electrode arc melting, skull, float or levitation, drip and auto-crucible melting have been described with sketches of the furnaces and the advantages and disadvantages indicated in each case. The author holds that some of the techniques may be the answers for other melting problems. Seventeen references are cited.

Rare earths—not so rare: *Ind. Eng. Chem.* 46, No. 12, 15A (1954)

A brief review of the acid and alkaline processes for the decomposition of monazite and of the applications of the rare earth metals and their compounds

Rare earths in metallurgy: Evans, H., *Metal Ind.* 85, 365 (1954) and *Iron and Steel (London)* 27, 567 (1954)

Extracts from the Presidential Address to the Birmingham Metallurgical Society. The first article deals with the applications in non-ferrous metallurgy. In amounts of 0.02% to 0.2% Mischmetall is used to improve the high temperature life of Ni-Cr and Ni-Cr-Fe heater alloys. The beneficial effect of Mischmetall on the life of these alloys is attributed to the improved adhesion of the protective oxide scale to the wire. As alloying elements present in amounts of the order of 1-3%, the rare earth metals have been used to improve the fluidity, tensile strength and creep resistance of magnesium-base alloys which are used in the construction of certain parts of jet aeroengines.

In the field of ferrous metallurgy, dealt with in the second paper, Mischmetall, alone or with magnesium, has been used as a desulfurizer in the

production of cast irons having spheroidal graphite structures. Addition of Mischmetall or the compounds of rare earths like oxides and fluorides, improves the ductility, tensile strength and hot workability of steels. Possible theories about the mechanism of improvement of these properties by the use of Mischmetall are discussed.

The Electrolyses of Solutions of Rare Earth Metal Salts in Basic Solvents: Moeller, T., Zimmermann, P. A., *Science*, 120, 539 (1954).

Saturated solutions of anhydrous yttrium acetate, neodymium bromide, lanthanum nitrate, and impure neodymium iodide in anhydrous ethylene diamine and monoethanolamine were electrolyzed in a 60 c. c. cell, using bright platinum electrodes separated by a medium porosity glass disc. A potential difference of 110 V was employed. Small quantities of water were added in some cases to increase the conductivities. Low current densities were used which varied from 0.04-5.4 mA per sq. cm. Electrolysis was carried out for long durations extending upto 96 hours. The cathode after electrolysis was dipped in ether and dried in an atmosphere of nitrogen. Deposits were obtained only with diethyleneamine solutions. The maximum weight of deposit that could be obtained was 40 mg. All deposits were smooth and metallic in appearance. They were oxidized in air or in contact with water, and evolved hydrogen with HCl. Gravimetric analysis indicated an average rare earth content of about 50% in these deposits. The deposits showed none of the properties of hydrides. Microanalysis showed the presence of C, H, and N, which were probably from the trapped, or adsorbed organic solvent. X-ray diffraction established that the deposits were not rare earth metal compounds. Very high "d" spacings in the lattices of Y deposits were noted. Neodymium deposits were borderline between crystallinity and the amorphous state. Lanthanum deposits were amorphous in nature.

The Application of Cathodic Protection to Chemical Plant: Murphy, F. D., *Ind. Chemist*, 30, 483 (1954).

The basic principles of cathodic protection, various techniques, and economics are discussed.

Improved Anodes for Copper Plating: *Chem & Met. Eng.*, 61, 124, (1954)

American Brass Co. is reported to have discovered that incorporation of 0.2-0.3% phosphorus in pure electrolytic copper gives anodes that cause 10-15% more copper to deposit on the cathode per lb. of anode and which eliminate the formation of anode sludge and so render diaphragms unnecessary.

Electrodeposition of the Platinum Metals: Laister, E. H., *Metal Ind.*, 83, 427 (1954).

A discussion of the process and applications to the plating of Pt, Pd and Rh.

Battery Grade MnO_2 from Low Grade Ore: *Chem. & Met. Eng.*, 61, 122 (1954).

Low grade manganese ores (containing 5 to 20% Mn) are leached with diluted nitric acid and the manganese nitrate obtained is heated at controlled temperature to get battery grade MnO_2 .

Production of Electric Power From Fresh and Salt Water in the Hydrophilic Pile: Pattle, R. E., *Nature*, 174, 660 (1954).

If alternate layers of salt and fresh water are separated by alternate basic and acidic membranes and the membrane electromotive forces (each of the order of 30 mV) are effectively connected in series, an e. m. f. can be built up which is large compared with electrode polarization voltages. An apparatus giving a maximum e. m. f. of 3.1 V is reported to have been constructed.

New Atomic Battery (Heat Battery): *Chem. Eng. News*, 32, 4183 (1954).

Heat from radioactive polonium is converted into electrical energy by the use of a thermocouple in this new atomic battery, which has been developed in the Mound Lab., and operated by Monsanto Chemical for the U. S. Atomic Energy Commission. In the battery, 150 curies of polonium are sealed in a small capsule, the surface of which is in contact with the hot junctions of 40 thermocouples, but thermally insulated with silica-aerogel, positioned within a surrounding container. Cold junctions of the thermocouples are on the surface of the container. Between the hot and the cold junctions a temperature difference of 450°F is maintained.

The unit is small and weighs only 31 gms. Polonium is used as radioactive source for reasons of safety. The element is a source of pure α -particles (5.298 m. e. v. energy with a 138 day half life) which can be very easily shielded by a paper.

The life of the battery is dependent only upon the radio active material used. The voltage and the current ratings can be varied by choosing proper sizes of wires and the number of thermocouple junctions. The output is not affected by extreme fluctuations of temperature.

This type of battery may be used in instruments needing a battery with long life, light weight, capacity to withstand extreme temperature variations and known output:

From the Monsanto test unit using a polonium heater of 4.65 watts, a maximum electrical power of 9.4 milliwatts (0.2% efficiency) has been obtained. The unit has an internal resistance of 15 ohms, no load voltage 0.75 volt, and current power of 25 milliamperes.

Large scale production of this type of battery is not economical as the α -emitting radio-isotopes are routinely available only in relatively small quantities and their cost is high.

Polonium battery is one of the batteries developed within a year, the others being (i) solar battery of Bell Telephone Laboratory, (ii) & (iii) β -emitting units of RCA and Tracerlab. The RCA battery employs strontium-90, as its radioactive source and atomic energy is directly converted into electrical energy. The RCA battery is of high voltage, low current and high internal resistance.

The Tracerlab battery employs radioactive 'tritium' as the source of power. In this battery atomic energy is directly converted into electricity.

INSTRUCTIONS TO AUTHORS

1. All papers intended for publication in the Bulletin of the Central Electrochemical Research Institute should be addressed to the Editor, Central Electrochemical Research Institute, Alagappa College P. O., Karaikudi.

2. Communications which have appeared in any other journal will not be published in this journal, unless this course is specially approved by the Editorial Board

3. Articles should be in English and all papers should be carefully revised and be in the final form for printing. Papers should be submitted in typescript with double-line and marginal spacings.

4. Positions for figures in the text should be indicated, and all references verified.

5. Authors are solely responsible for the factual accuracy of the papers. The Bulletin authorities are not responsible for the views, opinions or results expressed by them.

6. Authors should enclose line-drawings of the diagrams in their papers drawn in Indian ink on smooth white Bristol Board.

7. Articles not accepted for publication will be returned to the contributors.

Telegrams : " OIL GAS "

Telephone : 55425

Consult :—

VIJAYAM BROS
ENGINEERS & CONTRACTORS
6, RAMASWAMY STREET,
MADRAS - 1.

**SPECIALISTS IN OIL GAS PLANT AND
LABORATORY EQUIPMENT**

For requirements of:

GAS PLANT, GAS & WATER PIPE INSTALLATIONS WITH FITMENTS OF
GAS & WATER TAPS, LABORATORY SINKS AND LABORATORY FURNITURES

For

***Universities, Colleges, Hospitals and
Research Laboratories***

**Advertisements will be accepted for publication
in the Bulletin at the following rates**

Position	One Insertion	Two Insertions	Four Insertions
	Rs.	Rs.	Rs.
Full Page	60	100	180
Half Page	35	60	110
Special positions :			
Inner Front Cover Page	70	120	210
Back Cover Page	80	150	280

Advertisements should be received with blocks, size not exceeding 8" × 5" for full page, and 4" × 5" or 8" × 2½" for half page. Advertisers are requested to state whether they are willing to accept less favoured positions if it is not found possible to allot special positions specified by them.

PROF. M. S. THACKER
OUR NEW DIRECTOR OF SCIENTIFIC
AND INDUSTRIAL RESEARCH (D. S. I. R.)

The happy news that Prof. M. S. Thacker will head the Council of Scientific and Industrial Research comprising all the 14 National Laboratories and all ancillary bodies has reached us at the time of going to Press. We hasten to offer our respectful and loyal greetings to Prof. Thacker. A sketch on Prof. Thacker's eminent contributions in the fields of Science and Engineering and the role he played in the country's technological development will be published in our next issue.

We crave the indulgence of our subscribers, contributors and those who have sent in advertisements for the delay which has occurred in bringing out this issue of the Bulletin, which became inevitable owing to the change of Printers.

“PURPOSIVENESS”

While it is true that, long before our country became free, a few far-sighted great men—scientists, industrialists and financiers—realise and did something substantial, in their own way, towards the establishment of a few major industries in the country, it is only after the attainment of India's Independence in the year 1947 that the motto “Industrialise or Perish” became, so to speak, the watch-word of both the Government and the people. The ebullient and resurgent spirit of the nation left her in no doubt in deciding upon *Industrialisation through Purposive Planning* as the only course open for rapidly raising the standard of living of the masses.

The launching upon the First and Second Five-Year Plans; the participation in various international programmes of technical assistance; the inviting of foreign experts and the sending our young men to other countries for higher technological training; the establishment of the chain of National Laboratories in different parts of the country; and every other conceivable step that one sees, being implemented, in all departments and walks of life; all these have at the back of them, the same great Purposiveness—economic regeneration of the country. This has generated an expectant psychological tempo which, one cannot fail to notice, pervades the length and breadth of the whole country. The air is fecund with ideas, hopes and aspirations of the people, as regards “Expansion and Modernising of existing Industries”, “Starting of New Industries”, “Improved Health”, “A Higher Living Standard and Greater Prosperity” etc., etc. This keen aliveness of the people, this emphasis on “PLANNING” in every sphere of activity, this burning desire to work hard for the realisation of the cherished objective, are a great promise to the country's well-being; and it is clearly a sin of one fails to get “excited”

about it. In this kind of dynamic atmosphere, with no room for compromise, vacillation or complacency on major and essential issues, it behoves all those who happen to be engaged in Research—Scientific and Industrial—directly or indirectly, to correctly understand and apprise themselves of the important and valuable role that the nation has assigned to them.

As far back as the year 1943, when the organisation of the National Research Council was under active consideration, it was clearly recognised by those intimately associated with the scheme that the National Research Council, besides carrying out its other functions,

- “(a) *shall plan the main lines of scientific work in accordance with national needs, formulate schemes for the above purpose, review and modify the same whenever necessary and recommend ways and means for implementing the results of accomplished researches,*
- “(b) *shall ensure balanced development of all branches of science and minimise overlapping,*
- “(c) *shall advise and help relevant authorities regarding the training and supply of scientific personnel for pure and applied research.”*

Research—Pure or Applied—always implies adequate financial support, as an essential pre-requisite for its successful pursuit, and it might be said that this was duly recognised by the Research Foundations, Trusts or other financing and administering bodies. During the past decade or two, however, a new task, has fallen on the leaders of science, all over the world, namely that of fully apprising and convincing those controlling the purse-strings, of the significant changes that have come about,

in the methods of present-day research—with all kinds of costly and specialised apparatus and equipment, laboratory services and other facilities and most important of all, *the team work* which has almost become indispensable in solving the complicated problems inherent in most modern Projects. In the United States, the U.K., the U.S.S.R., and other countries, it seems, the meaning of this is fully appreciated, as is evident from the very considerable sums allotted for research in their national budgets, every year.

The position in India is quite different. Till a few years ago, no importance was attached to expenditure on research in the annual budget. Thanks to the great fillip given by Prof. A. V. Hill, F.R.S., Secretary of the Royal Society, London, through his speeches and exhortations during the course of his sojourn in our country in the year 1943, asking the Government to ear-mark for Research at least 1 per cent of our Annual budget, prominent scientific bodies in India started pressing forth their demands more firmly than ever before. The inspiring Presidential address delivered at the National Institute of Sciences, the same year, reiterated the fervent his hope that the Government of India would “take courage and swim with the current of modern world’s enlightened opinion and not cling to cautious, wooden and antediluvian policies which will perpetuate Ignorance, Poverty and Disease in this land”. The same trend is noticeable in the recommendations of the Industrial Research Planning Committee made in the year 1945 under the Chairmanship of Dr. R. K. Shanmukham Chetty, in the recommendations of the Director, Scientific and Industrial Research year after year and in the recommendations of the first and second Reviewing Committees of the Council of Scientific and Industrial Research made in the years 1949 and 1954 under the chairmanship of Dr. Ardeshir Dalal and Sir Alfred C. Egerton, Kt., F. R. S. respectively.

The result of all these has been an increasing awareness, at governmental level, of the

advisability of allotting funds for research far more liberally than was ever contemplated in the pre-Independence era. Judging from the figures given in the First Five-Year Plan reports, while the total expenditure on research in India in relation to the national income is very much smaller than in the U.K., the U.S.S.R. and some other countries—it being only a small fraction of the 2.5% provided under the heading ‘Miscellaneous’ out of the total budget of over Rs. 2,000 crores — as rightly pointed out by the Egerton Committee, yet it cannot be denied that it is substantial enough, considering the present undeveloped state of affairs in most other spheres, including the industries themselves. As more industries come to be established and expanded and as more explorative and developmental work evolves, one can legitimately expect that the ‘Funds-position’ will also progressively improve and brighten up.

That being so, it is incumbent on all those engaged in research to show a sympathetic and responsible understanding of the Tax-payer’s occasional outburst of impatience, dissatisfaction and even disappointment at the “unproductive and wasteful expenditure” on research. For, in the ultimate analysis of things, it cannot be denied that the Tax-payer has a right to ask for “returns” commensurate with the “sacrifices” he is asked to undergo. It is therefore well, in their own interest and for the sake of steady human progress at large, that research workers realise the importance of carrying the Tax-payer along, by keeping him well-informed and fully convinced of the useful and fruitful nature of the results that emanate from the labours of scientists. There is no easier, lighter or pleasanter way for the technologists, engineers and all grades and categories of research workers to face this task than by continuing to work hard and labour intelligently in their respective laboratories and fields of work, which alone can help in securing the verdict of the nation in their favour.

The sooner research-men realise that what is expected of them is “RESULTS”, the

better—"CONCRETE RESULTS" tangible, substantial and *directly* useful to the establishment of a new kind of industry, or increasing the yields and cutting down the costs in existing industries, finding inexpensive and indigenous substitutes for materials which are relatively costly and rare, reducing the number of operations and eliminating processing difficulties, evolving newer and more efficient labour-saving devices or the like. As in the case of the big Engineering Industrial Projects, so in Research too, TARGETS must be set, PROGRAMMES must be chalked out in detail and TIME-SCHEDULES should be laid. In addition to doing these, it is of paramount importance that the active research workers themselves, no less than the sponsors of research, keep themselves alive to the same, so that there is a constant effort on the part of every one to adhere to the programmes and time-schedules, as much as possible, in order to attain the targets.

To the orthodox researcher of an earlier generation, or to one who *is* engaged in academic or "Pure" research, for its own sake, as an intellectual adventure or an exciting pastime, urged by no 'profane' or utilitarian motive but mere inquisitiveness and insatiable curiosity, almost verging on a "pathological thirst to penetrate the unknown, to uncover the secret, to find out what has not been found out before", all this "PURPOSIVENESS" in research will no doubt appear most unintelligible and will naturally lead him to the sour conclusion that "the value the world sets upon motives is often grossly unjust". Besides, it

is further often pointed out that "no matter how able the scientist may be, how well equipped the facilities, how diligent the staff, one can never guarantee results". This line of thought and this trend of argument are no doubt perfectly justified as long as one thinks of "Pure" Research, but they lose their force and validity the moment one comes to Applied Research which, it cannot be gainsaid, is always undertaken with a view towards stated objectives and hoped-for results in terms of "returns" several-fold the investments made. It is essential in this context to have a clear-cut conception of not only the frontiers of applied research but also the texture, if such a word may be used, and the "constitution" of applied research. Much that is spoken of as "basic research" and much that goes under the title "fundamental research", in reality, falls within the scope and purview of Applied research. One can find for oneself any number of illustrations to prove the veracity of this statement, if only one looks into the past fifty years' history of the developments in some of the prominent research foundations established in different countries. It is, therefore, important to note that under the pretext of "Applied" or "Industrial" research, fundamental or basic research is not precluded from playing its role. What matters and matters very much is that objectives must be clearly visualised, whether it is basic research or developmental research or pilot plan studies. It is this which lends that PURPOSIVENESS to research—scientific and industrial—so essential if "CONCRETE RESULTS" are to be produced.

—A. JOGARAO.

ELECTROCHEMICAL BEHAVIOUR OF ION-EXCHANGING SUBSTANCES

X. Further Potential Measurements in NaCl and KCl Solutions.

by

D. MacGillavry and H. J. C. Tendeloo,

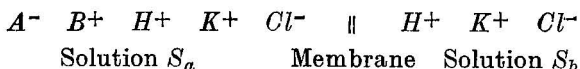
(Laboratory for Physical and Colloid Chemistry, Agricultural University, Wageningen, The Netherlands)

Potentials of young plant roots in KCl solutions have been investigated in this laboratory for a number of years.¹⁻⁹

Measurements have been reported for several plant species. Recently, a more extensive investigation was started of potentials of Lucerne clover, *medicago sativa*, Northern France variety.

The observed shifts of potential with KCl and HCl concentration show characteristic trends. Analogous trends might be expected for Donnan membrane potentials of various systems. A model, representing conditions at the root wall, was proposed by Vervelde and Tendeloo^{6,7} and discussed further by MacGillavry and Tendeloo. This type of system containing a single membrane is represented in diagram I.

Diagram I



The non-permeating anions A^- and cations B^+ are supposed to derive from a mixture of weakly ionizing substances.

As far as this analogy goes one should expect similar behaviour in NaCl and in KCl solutions. Biologically, however, Na^+ and K^+ are not similar. Hence, it was thought of interest to compare root potentials in NaCl and in KCl solutions.

It is implicit in this approach that electrolytes can diffuse into and out of certain sections of a root without much hindrance. This space is lined on the outside by the root wall, or a membrane just within the root wall, and on the inside by membranes showing

definite physiological activity and selectivity. Hope and Stevens¹⁰ consider that the greater portion of this "apparent free space" contains protoplasm having a spatial arrangement of negative immobile ions. According to the extended theory of Donnan equilibria the concentration of immobile ions— anions and cations—will vary with the pH. (See ref. 6).

It is recognized by plant physiologists that on purely physio-chemical grounds sodium and potassium may show a somewhat different behaviour. Even the equilibrium distributions of potassium through the protoplasm, Butler¹¹ points out, might be different from the equilibrium distributions for sodium because of the smaller radius of the hydrated potassium ion. This difference in ionic volume already offers a possible explanation of the observed differences between the steady potentials for the two ions.

Another explanation, admittedly less probable, would be selective permeability of the root wall for potassium and sodium; sodium should not be able to penetrate in measurable amounts within the time of measurements. On account of the comparable lengths of time required for establishing NaCl and KCl potentials, this explanation appears less satisfactory.

The authors mentioned above and also Robertson, Wilkins and Weeks¹², it may be added, showed that the initial uptake of KCl by various plant roots at first is rapid and then becomes slower until after about 20 minutes a steady metabolic rate is established. As a rule steady potentials are established within a few minutes, 4-10 minutes, sometimes a longer time is required. This time lapse is of the same order of magnitude, and it can hardly be doubted that a steady metabolic rate is accom-

panied by a stationary root potential as observed with usual techniques.

Since Donnan systems of the type indicated can account for the observed shifts of potential (see earlier publications), they are primarily due to the conditions at the outside membrane.

Experimental results and variance analysis :

The electric chain as now used is shown in Figure I. It was originally developed by Tendeloo, Vervelde and Zwart Voorspuy. AgCl/Ag and also HgCl/Hg electrodes have

been used. Other minor modifications were adopted from time to time. Further experimental details are given in (1) and (9).

A first series of measurements was reported on in publication (8). A root was measured first in a set of NaCl solutions and then in the corresponding set of KCl solutions. All solutions contained 5×10^{-6} N HCl. It was noted that apparently stationary potentials could be established also in the NaCl solutions, usually after a few minutes, as was the case in the KCl solutions. Such a behaviour is indicative of a quick adjustment of the roots to these changes

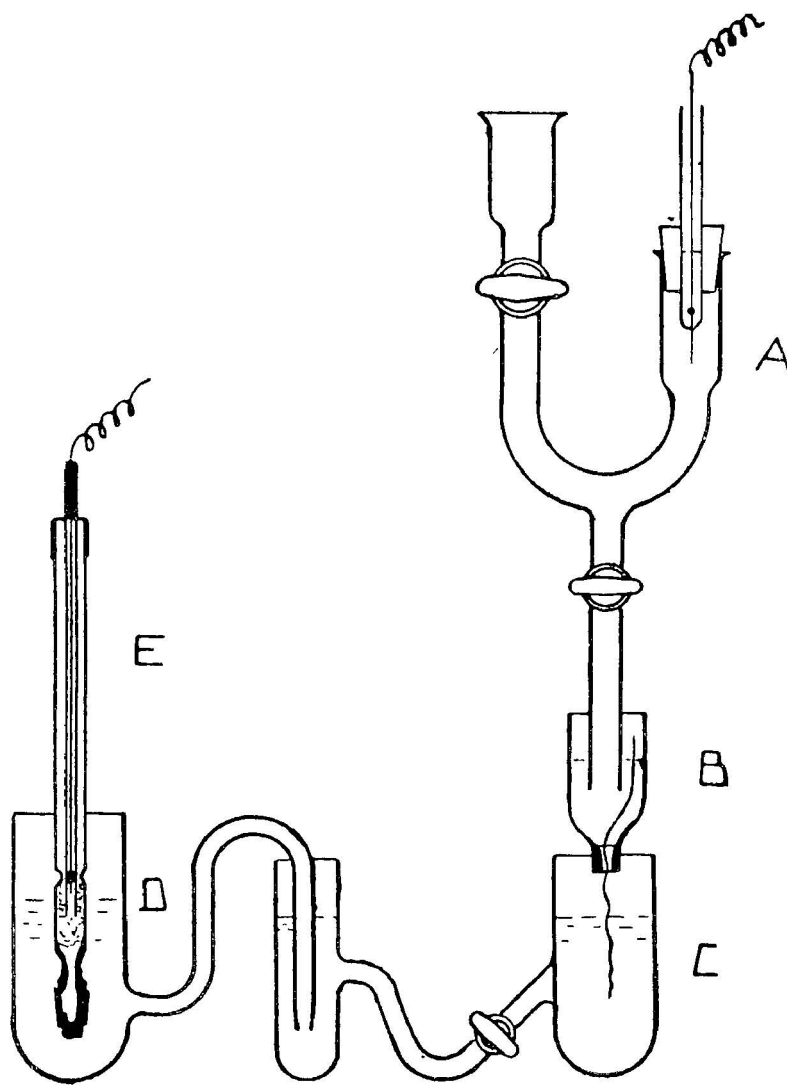


Fig. 1.

of medium and concentration. A quick adjustment would be expected also for a Donnan system with small inner volume (solution S_a in Diagram I).

The new series of measurements was done under slightly modified conditions, as it was noticed that especially the potentials in the most dilute KCl solutions of the first series might show a peculiar ambiguity. A potential fitting the normal pattern might be found and at times also an abnormal less negative potential. To forego, if possible, this ambiguity of steady potential, the range of concentrations was narrowed down. Also, as in the series of KCl solutions described in ⁽⁹⁾ and as well in all previous work (excepting ⁸), no HCl was added to the 10^{-2} M KCl solution in the electrode holder A. In the first series of measurements in NaCl and KCl, the solution in A contained 10^{-4} N HCl + 10^{-2} M KCl. Finally, in the present series potentials were measured first in KCl and then in NaCl.

Of the different AgCl/Ag electrodes used some showed a somewhat different potential in 10^{-2} M KCl against the saturated HgCl/Hg electrodes. Thus, the mean of the potentials in all solutions for each root would be the combined result of the true root level and the electrode level. Since an effect due to root level is not studied at this time, the measured mean potential was deducted from all potentials measured for the root. The values so obtained are listed in Table I.

The potential averages are listed in Table II.

TABLE II

Potential averages.

Molarity	10^{-4}	5×10^{-4}	2×10^{-3}	10^{-2}
KCl	-29	-10.5	+9.5	+35.5
NaCl	-21	-12.5	+2	+26.5

By this method, it will be seen from the variance analysis (Table III), the apparent root effect has been eliminated. The other variance estimates are not affected by this procedure. This is true also for the interaction of concentration and medium, which is of special interest as will become clear from the following.

TABLE III

Variance Analysis

Source of variation	Sum of squares	Dimension	Variance estimate	F	Critical F values
Concentration	21,201.2	3	7,067.1	2.84	4.13
Medium	72.5	1	72.5		
Roots	0.3	5	0.1		
Interaction				7.62	2.88
cxm	540.2	3	180.1		
Residual	889.2	35	25.4		
	22,703.4	47			

TABLE I

Potentials of Lucerne clover.

Molarity KCl*

Molarity NaCl*

Root	10^{-4}	5×10^{-4}	2×10^{-3}	10^{-2}	10^{-4}	5×10^{-4}	2×10^{-3}	10^{-2}
1	-19	-10	+12	+39	-21	-13	-6	+19
2	-36	-16	+8	+37	-26	-6	+10	+29
4	-36.5	-10.5	+9.5	+37.5	-18.5	-11.5	+4.5	+26.5
12	-23	-5	+13	+26	-18	-12	-1	+22
5	-30	-14	+9	+38	-24	-16	+5	+33
17	-30.5	-8.5	+5.5	+36.5	-18.5	-15.5	+0.5	+30.5

*All solutions contained 5×10^{-5} N HCl.

The variance analysis did not indicate an effect due to the medium, NaCl or KCl, but did show an interaction of medium and concentration. The averaged potentials in Table II already show that the potentials in KCl-HCl vary more than in NaCl-HCl. This was found also for series I (Ref. No. 8.)

Since there is interaction of medium and concentration, independent empirical equations may be derived for the two media. For the chosen concentrations the successive logarithms do not differ by a constant amount. This makes the question as to significance of linear and higher components harder to settle. As the range of concentrations is rather short it is improbable that the coefficients of the quadratic and the cubic terms, apart from significance, can be known with any certainty. Thus, we will merely indicate for the two media the slopes between the lowest and the highest concentrations, resp. 10^{-4} and 10^{-2} M. These slopes are

$$\text{for KCl } \frac{29+35.5}{2} \text{ 32mV/log M unit.}$$

$$\text{and for NaCl } \frac{21+26.5}{2} \text{ 24mV/log M unit.}$$

In comparison, figures reported by Hope¹³ are for KCl 32mV/log M unit and for NaCl 28mV/log M unit. The slopes are of the same order of magnitude, but the difference is less marked.

The interpretation in terms of Donnan equilibria will be treated further in forthcoming publications.

In conclusion it may be said that the patterns of root potentials of Lucerne clover in NaCl-HCl and KCl-HCl solutions appear to be different and may not be considered identical. It is noteworthy that a difference became evident even in the fairly narrow range of concentrations selected this time.

SUMMARY

Comparison of root potentials of Lucerne clover in NaCl-HCl and KCl-HCl solutions was extended. A difference in behaviour was indicated also in the narrower range of concentrations of a new series of measurements. The shifts of potential are primarily due to the variations of the Donnan equilibria across the root wall membranes.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Dr. N. H. Kuiper and Ir L. C. A. Corsten of the Department of Mathematics for advice about questions of variance analysis.

REFERENCES:

1. Tendeloo, H. J. C., Vervelde, G. J., and Zwart Voorspuy, A. J., *Rec. trav. chim.*, **63**, 97 (1944)
2. Tendeloo, H. J. C., Vervelde, G. J., and Zwart Voorspuy A. J., *ibid*, **65**, 539 (1946).
3. Tendeloo, H. J. C., Vervelde, G. J., and Zwart Voorspuy, A. J., *Versl. Konink. Ned. Akad. v. Wetenschappen*, **53**, 169 (1944).
4. van der Molen, W. H., and Tendeloo, H. J. C., *Versl. Konink. Ned. Akad. v. Wetenschappen*, **50**, 763 (1947).
5. Vervelde, G. J., *Proc. Konink. Ned. Akad. v. Wetenschappen*, **51**, 308 (1948).
6. Vervelde, G. J., and Tendeloo, H. J. C., *Rec. trav. chim.* **72**, 62 (1953)
7. MacGillavry, D., and Tendeloo, H. J. C. *Rec. trav. Chim.* **73**, 15 (1954).
8. Tendeloo, H. J. C., and MacGillavry, D. *Proc. Konink. Ned. Akad. v. Wetenschappen*, **57**, 509 (1954).
9. MacGillavry, D., and Tendeloo, H. J. C., *Proc. Konink. Ned. Akad. v. Wetenschappen*, **57**, 513 (1954).
10. Hope, A. B., and Stevens, P. G., *Australian J. Sci. Res.* **B5**, 335 (1952).
11. Butler, G. W., *Physiologia Plantarum*, **6**, 617 (1953).
12. Robertson, R. N., Wilkins, M., and Weeks, D. C., *Australian J. Sci. Res.* **B4**, 248 (1951).
13. Hope, A. B., *Australian J. Sci. Res.* **B4**, 265 (1951).

ELECTROLYSIS OF SODIUM SULPHATE SOLUTIONS

by

P. S. Desikan and V. Aravamudan

(Central Electrochemical Research Institute, Karaikudi)

Sodium sulphate is obtained in India from two main sources, (1) from the salt lakes at Didwana and Sambhar (Rajputana), and (2) as a bye-product in the viscose rayon industry.

According to the estimates of the Salt Experts Committee (1950), an annual recovery of 50,000 tons of sodium sulphate of 92% purity can be realised from the lake bitters in Rajputana¹.

In the viscose rayon industry, sodium sulphate is thrown out as a bye-product, when cellulose xanthate is neutralised with sulphuric acid in the spinning baths. The total daily production of sodium sulphate in the three rayon factories in India is about 12 tons on a moisture-free basis.

Only 1/5th of the total production of sodium sulphate is consumed in India at present in Kraft paper, glass and other chemical industries. The utilisation of the surplus sodium sulphate by developing suitable electrolytic or other processes to produce caustic soda is one of the recommendations of the Planning Commission, in connection with the development of the Alkali Industries².

Sulphuric acid is manufactured in India at present mainly from imported sulphur. So a suitable process to electrolyse sodium sulphate would be useful both for supplying to a great extent our requirements of sulphuric acid and for stepping up the production of caustic alkali.

Moreover, production of sulphuric acid and alkali from sodium sulphate will mean much to the viscose rayon industry, as it will make the industry almost self-sufficient with respect to these two important raw materials. The problem here becomes much simpler because there is no need for the concentration of the product from the electrolytic cells as the dilute liquors can be recycled.

With these aims in view, investigations on the electrolysis of sodium sulphate were taken up in this Institute.

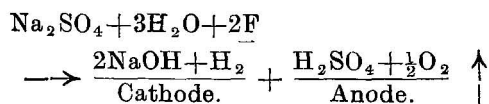
The electrolysis of sodium sulphate can be conducted in two ways: (i) by using two diaphragms with two solid electrodes, (ii) by using a mercury cathode with only one diaphragm. Investigations on both the processes have been conducted in Europe³⁻⁸ and large-scale mercury cells were worked out in Germany during the war.⁷⁻⁸

A. EXPERIMENTS WITH TWO-DIAPHRAGM CELLS.

For our investigations, the two-diaphragm process was taken up first and work was concentrated on the selection of proper diaphragms, cathode and anode materials and fixing up the optimum operating conditions.

A rectangular cell of teakwood, of 12" × 4" × 6" size coated inside with bituminous paint was made. Two grooves through which the diaphragm and the electrodes could be slid were provided at a distance of 2" from the middle of the cells on either side. The two diaphragms thus divided the cells into three compartments. An iron cathode of 6" × 3" size with 25% perforations and a lead anode of identical dimensions were placed at the farther side of each diaphragm. A 28% solution of pure Na₂SO₄ was used as the electrolyte.⁶

The reaction occurring as a result of electrolysis is represented as follows:



Diaphragms: The diaphragms used to prevent the catholyte and anolyte from mixing should withstand the action of mild acid and alkali, should be mechanically strong, and the permeability should not be too high or too low. They should be of reproducible quality and easily obtainable in India. To satisfy these conditions a number of materials were tried.

Two ordinary asbestos sheets were first used at both electrodes as diaphragms. The electrolysis was started at room temperature with 28% Na₂SO₄ in the central compartment

and distilled water in the end compartments. A current density of 8.95 amps/sq. dm. was employed. At the end of 7 hours a concentration of 0.608 N H_2SO_4 and 0.6 N NaOH was reached in the end chambers. After 7 hours, the diaphragms began to peel off and the electrolysis could not be continued. The overall current efficiency was only 50%. The cell voltage was 5.7.

In an attempt to make the asbestos more stable, it was impregnated with deposited silica, by dipping sheets in sodium silicate and then in 30% sulphuric acid on the lines indicated by Stender and co-workers.⁹ These asbestos-silicate diaphragms were stable on the acid side and not on the alkaline side, and offered high resistance, the cell voltage being 9.6 for the same current density.

Other diaphragms which were tried without success include diaphragms made by mixing cement and magnetite and wooden battery separators. The former offered enormous resistance while the latter was very brittle.

Porcelain diaphragms were tried next. Two porous pots of high porous alumic variety were placed 2" apart in the wooden cell with a spiral lead anode and iron cathode, to cover the diaphragm on all sides. They were filled with distilled water and the wooden cell was filled with a solution of sodium sulphate. Preliminary runs showed that the diaphragms were quite stable though the resistance offered was rather high. The current efficiency at room temperature was only 55%.

Effect of Temperature: In an attempt to reduce the voltage and increase the current efficiency, electrolysis at higher temperatures was tried by heating the electrolyte with a steam coil. It was found that at a temperature of 80°–85° C the current efficiency increased to 90–92% and the voltage was reduced from 9.5 to 7.5. When the porous pots were kept closer together with 0.5" gap, the voltage was further reduced to 6.4.

Anode and cathode materials: When a part of the mild steel cathode is exposed to the atmosphere, there is formation of ferric hydroxide. So, stainless steel cathodes were later employed. In the anode chamber, lead peroxide is formed and crumbles to powder, resulting in the loss of anode material and impure anolyte. A lead-silver alloy with 5% silver was employed and considerable reduction in PbO_2 formation was realised.

With all the above modifications, namely porcelain diaphragms, stainless steel cathode lead-silver alloy anode, and a temperature of 80 to 85°C, a run was made for 10 hours to get 200 c.c. of 4 N NaOH and 340 c.c. of 4N acid with an overall current efficiency of 92.5%. At this stage, it was possible to set up continuous operation by feeding Na_2SO_4 continuously withdrawing acid and alkali at the same rate by employing slight suction at the cathode and anode chambers (Fig. 1).

The anolyte and catholyte contain in addition to acid and alkali, sodium sulphate diffused through the diaphragm. A 12% NaOH solution contained 3.44% Na_2SO_4 and the corresponding anolyte contained 14.6% H_2SO_4 mixed with 19.6% Na_2SO_4 .

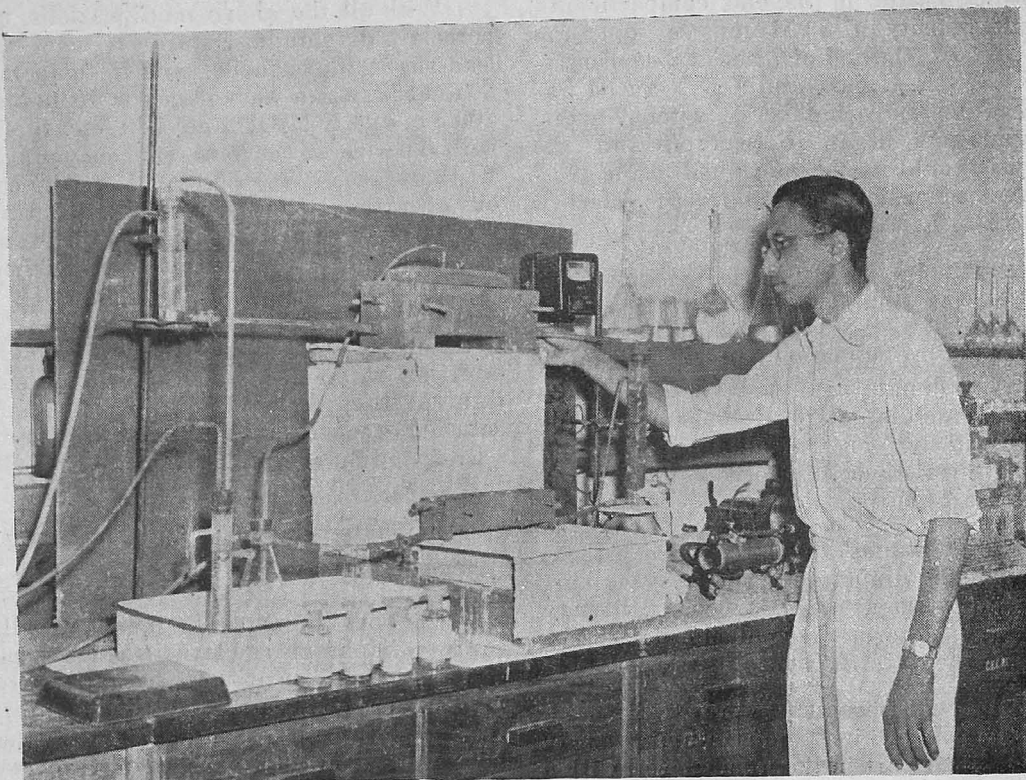
B. EXPERIMENTS WITH FLOWING MERCURY CATHODE CELLS

The advantages of the mercury cells over the two-diaphragm cells are (i) the direct production of high purity concentrated sodium hydroxide, and (ii) a lower cell voltage owing to the use of only one diaphragm. The method has been worked out by various research workers^{6, 7, 8} and the I. G. Farben Industrie worked out a pilot-plant horizontal cell of 10,000 amp. capacity before the war.⁷

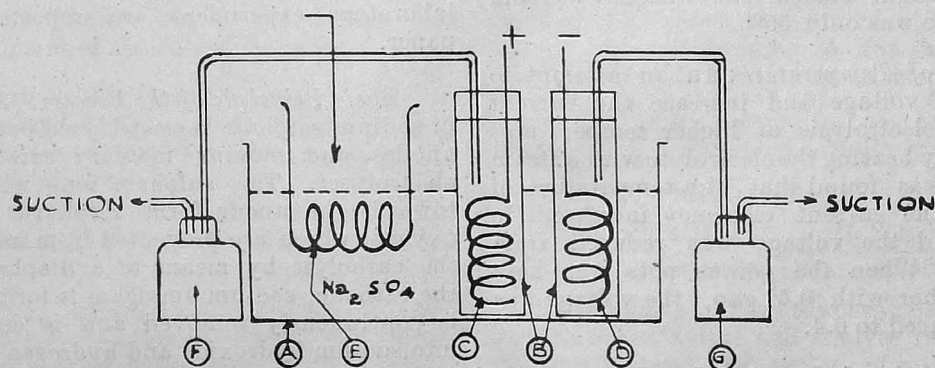
The work on the mercury cells was taken up by us with a view to adopt the process under Indian conditions, and the results of our laboratory experiment are reported in this paper.

Basic Principle of the Process: A solution of sodium sulphate is electrolysed between lead anodes and moving mercury cathode in an electrolyser. The sulphate ions which move towards the anode form sulphuric acid and oxygen, which are prevented from mixing with the catholyte by means of a diaphragm. At the cathode, sodium amalgam is formed which is continuously removed and is decomposed into sodium hydroxide and hydrogen by means of pure water in the presence of graphite.

The selection of proper electrolysing vessels, anodes and diaphragms are all dealt with by various workers^{6, 7, 8}. Lead-silver (10%) alloy anode has been selected as the best by the workers of I. G. Farbenindustrie⁷. For the diaphragms, various materials were tried and 'mipore' was used successfully in Germany. We have conducted our experiments



Experimental Arrangement for the Study of Flowing Mercury Cathode Cells



- | | |
|------------------------------------|----------------------------------|
| A. OUTER VESSEL | D. STAINLESS STEEL CATHODE |
| B. DIAPHRAGMS | E. HEATING COIL |
| C. LEAD SILVER (5%) ANODE | F. COLLECTING VESSEL FOR ANOLYTE |
| G. COLLECTING VESSEL FOR CATHOLYTE | |

DRG. NO. ECR.1/M/226/55

Fig 1. Diaphragm Cell Assembly

with aluminic variety porous porcelain diaphragms indigenously available and found them to give comparatively good performance, a fact supported by the data given in this paper. Experiments conducted with imported 'microporous rubber' diaphragms proved the possibilities of conducting the electrolysis at a lower cell voltage. The electrolysing vessel was made of rubber lined steel in the German pilot plant. We have made use of a concrete vessel, which can be more easily fabricated than good quality rubber lining which requires specially skilled labour.

The variable operating characteristics in the process are the current density, concentration of the feed electrolyte and the rate of flow of the electrolyte through the diaphragm. The minimum current density for the formation of sodium amalgam is 10 amps/sq. dm.¹⁰. The effect of concentration of Na_2SO_4 feed has been studied by Grube and Stainoff⁶ who have reported 30% Na_2SO_4 as the best. The effect of current efficiency on the concentration of the anolyte, which in turn depends on the rate of flow of the electrolyte through the diaphragm, has been studied by us.

Description of the Laboratory set-up: (Fig. 2). The electrolyser is a rectangular channel (B) 12" x 3" x 2" (inside dimensions)

made of concrete. The inside of the cell is coated with chlorinated rubber paint. Mercury flows through the cell from the reservoir (A) and comes out of the cell to pass through two amalgam-decomposers. In order to prevent the electrolyte from going out with the mercury, two mercury-seals (C) are provided at the ends. There are two amalgam decomposers one vertical (D) and the other horizontal (E). The vertical decomposer is made of glass (1½" diam. and 8" high) and is provided with baffles. It is packed with graphite pieces of ¼" cubes. The horizontal decomposer which is connected in series with the vertical one, is made of mild steel in rectangular channel form and is also filled with graphite pieces. The mercury, coming out of the horizontal decomposer is collected in a narrow, tall reservoir (F) from where it is pumped to the reservoir A. The pumping of mercury continuously is effected in a much simpler, less cumbersome and efficient way than in the method adopted by Grube and Stainoff⁶. The arrangement is as described below : (Fig. 3).

Water under pressure is sent through the tube (a) of Fig. 3 which ends in a perforated nozzle (n). The nozzle is covered with a bell shaped tube which forms the bottom part of the delivery tube (b). Water while escaping through (b) under pressure, carries particles of

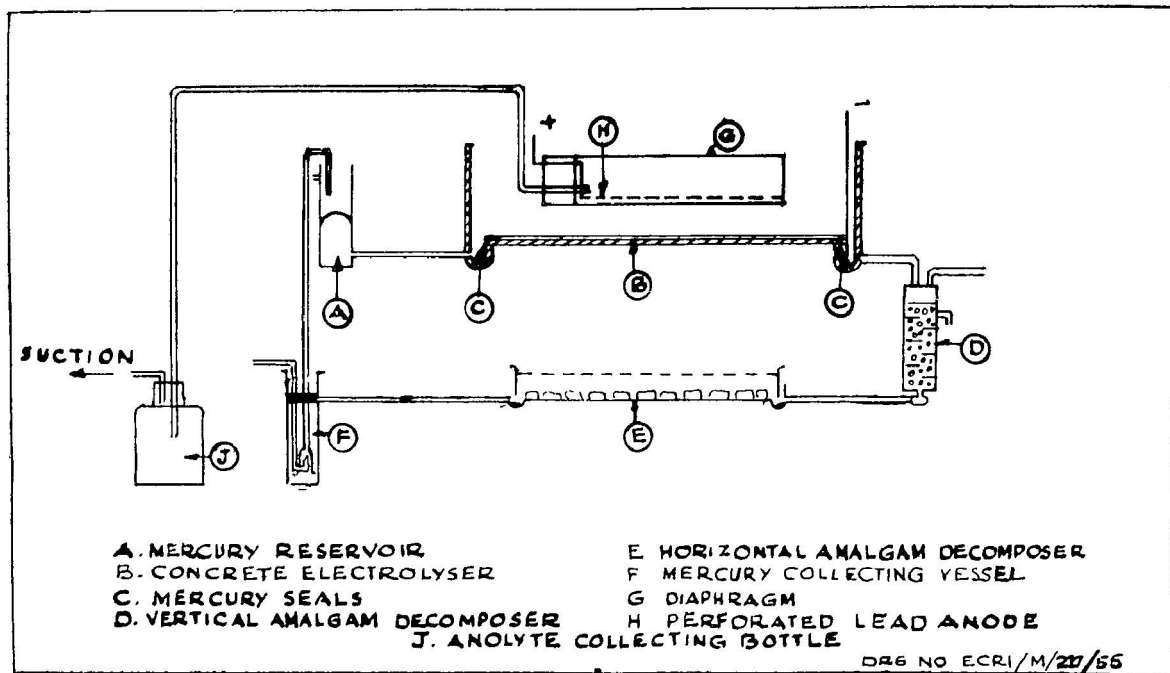


Fig. 2. Flowing Mercury Cathode Cell Assembly.

mercury from the bottom reservoir. The mercury and water collect at the reservoir (A) and while the latter overflow through the tube (x) mercury falls to the bottom and flows through the cell. The level of mercury at the bottom reservoir is maintained by the inflow of mercury from the amalgam decomposer. In order that no water enters the cell, the mercury level is always kept higher at the reservoir (A) than at the cell. This system of ejecter pump using water is able to pump the mercury at a rate of 100 cc. per minute and this can be adjusted by controlling the pumping water. As there is no moving part in this simple pumping system, no manual attention is required.

The anode chamber of the cell consists of a porous porcelain diaphragm (G) (aluminic variety) of $1\frac{1}{2}$ " diam. and 6" long (Fig. 2) inside which a perforated lead sheet (H) of $6" \times 3"$ size with 25% perforations is kept. The diaphragm is closed with a rubber stopper with holes to make electrical connections and for an outlet to take off the anolyte, which is a mixture of sulphuric acid and sodium sulphate. This outlet is connected to suction through a bottle (J) where the acid collects. The porous pot is suspended in the cell by means of plastic coated metal wires $\frac{1}{4}"$ above the mercury layer in the cell. The current lead from mercury layer is taken by dipping a wire through a glass tube in the mercury seal.

A 30% solution of Na_2SO_4 , prepared from commercial Rajputana salt is fed from a reservoir into the cell. A part of it is sucked through the diaphragm while the rest goes out to collect in a vessel at the bottom.

A measured volume of pure distilled water is kept at the two decomposers before starting each experiment.

A steady D. C. supply of 10 amperes is passed through the cell. The suction pump (a laboratory filter pump) to remove the anolyte liquor is operated and the rate of suction is adjusted by a stop-cock arrangement and a byepass.

Experiments were conducted to verify the current efficiency of the cell with respect to the alkali at conditions already arrived at by previous workers¹, i.e., a cathode current density of 10 amps./sq.dm., sodium sulphate concentration of 300 gms. per litre (sp. gr. 1.23) and cell temperature of 40°C .

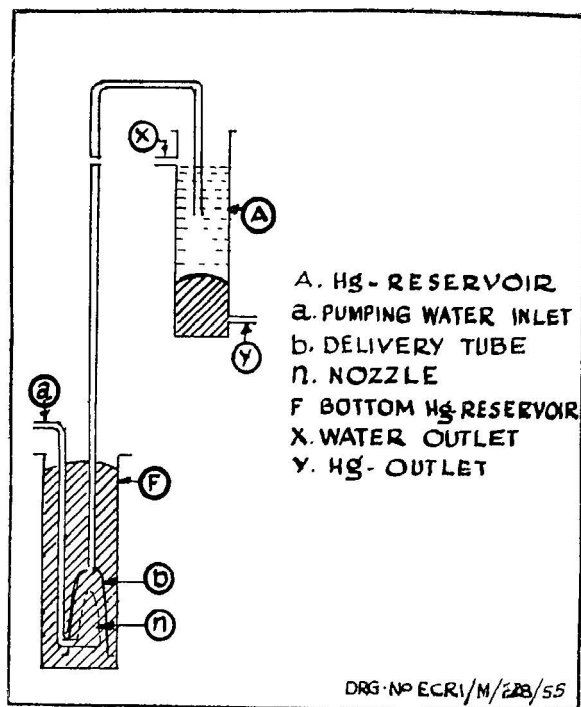


Fig 3. Ejecter Pump System using Water for Pumping Mercury.

The rate of flow of mercury was 40 c. c. per minute. Under the above conditions, the cell was run and the concentration of the alkali formed was measured every hour by titrating with standard acid. The current efficiency was calculated. The results of a typical set of such experiments are given in Table I.

By repeating the above experiments, it is seen that the concentration of the alkali can go upto 18 N (i.e. 720 gpl) and that the cell voltage for a current density of 10.5 amps./sq.dm. is 6 V as against 8.6 V obtained by Grube and Stainoff². The current efficiency which is 95% at the cathode and 92.8% at the anode when the average anolyte concentration is 1.635 N (i.e. 8% acid) is found to decrease with increase in the anolyte acid concentration. This in turn is dependent upon the rate at which the anolyte is removed.

Effect of acid concentration on current efficiency:

To study the effect of the concentration of acid on current efficiency, a series of experi-

TABLE I

Time in hours.	Cathode current density amps./sq. dm.	Cell voltage.	Concentration of alkali.		Gms. of NaOH produced,		Cathode current efficiency. (%)
			Vertical decomposer (N)	Horizontal decomposer (N)	Total	In one hour.	
-	10	6.8	1.22	0.595	14.32	—	—
1	10	6.3	6.05	0.765	39.3	14.98	95.0
2	10	5.8	10.28	1.06	44.02	14.72	93.6
3	10.5	6.0	13.25	1.482	57.7	13.68	91.5
4½	10.5	6.0	17.7	2.248	77.3	19.6	94.2
5	10.5	6.0	18.0	2.77	87.2	9.9	94.9

Average acid concentration in the anolyte

... 1.635 N

Current efficiency at the anodes.

... 92.8%

ments was conducted each lasting for 5 hours at various rates of suction (adjusted by the stop cock in the bypass and measured by a manometer connected to the suction line), and the current efficiency of the acid formation was calculated. The results are tabulated below (table II) and a graph has been drawn showing the relation between the concentration of acid and current efficiency (fig. 4).

TABLE II

No.	Vacuum applied (Manometer reading cm. of Hg).	Rate of flow through the diaphragm (cc. per hr).	Concentration of acid. (gms. per litre)	Current efficiency at the anodes.
1	27	240	62	94.5%
2	23	170	80.5	92.8%
3	20	120	99	91.5%
4	15-17	80	150	89%
5	8-10	70	170	85.2%
6	5-6	50	200	75%

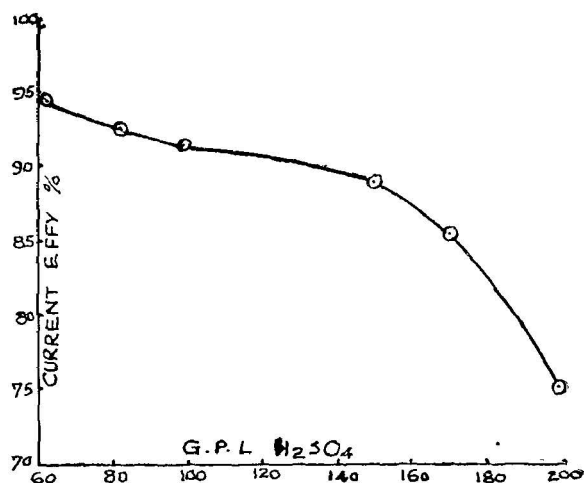


Fig. 4. Relation between Current Efficiency and Acid Concentration.

It is seen that the current efficiency falls gradually up to a concentration of 150 g. p. l. when the efficiency is 89%, but further increase in the concentration results in a deep fall of current efficiency. Thus at a concentration of 170 g. p. l the efficiency is 85% while at a concentration of 200 g p. l., it is only 75%. So, building up the acid to an optimum concentration of 15 to 16% where the current efficiency is 89% will be economical.

Experiments with microporous rubber diaphragms:

Some experiments were conducted by substituting microporous rubber sheets obtained from M/s. American Hard Rubber Company as diaphragms instead of indigenous porous porcelain pots. To support these sheets and the anode, a wooden anode box was made (Fig. 5 a). Grooves were provided at the bottom to slide the diaphragm and the anode. The top lid was made removable by unscrewing. Two small holes

position of sodium amalgam in the electrolyser itself began to accumulate under the diaphragm with the result that there was an increase in the voltage and decrease in current efficiency. This could be instantaneously rectified by tilting the anode box a little to allow the escape of hydrogen bubbles when the voltage comes down. Hence constant attention was required for frequent tilting and even then the performance was not satisfactory. A set of readings under such conditions is given in Table III A.

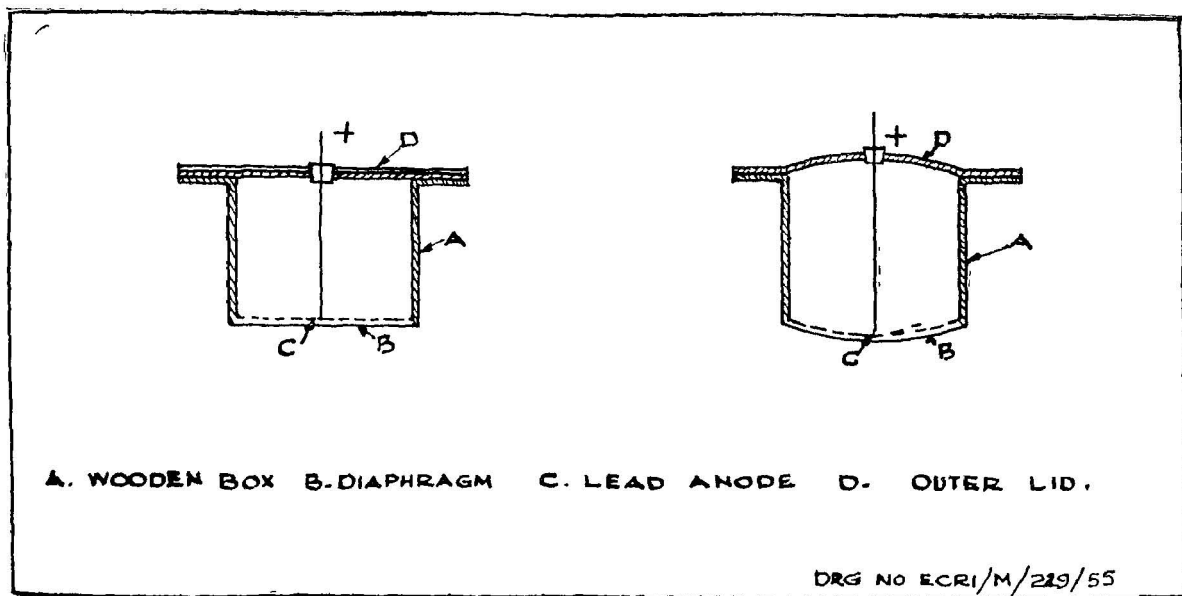


Fig. 5 a and 5 b. Section of Flat Diaphragm and Curved Diaphragm.

closed with one holed rubber stoppers were provided, one-for taking out the current lead and the other to fit in a glass outlet tube connected to suction through a bottle for removing the acid. The whole wooden box was coated with chlorinated rubber paint. This anode box was placed in the concrete cell in the place of porous pot in Fig. 2, $\frac{1}{4}$ " above the mercury layer.

In the original design (Fig. 5-a), the diaphragm and the anode were stretched flat. The experiments conducted with this arrangement were unsuccessful owing to the following reasons: the small amount of hydrogen evolved by partial decom-

The defect was permanently overcome by changing the design of the anode box as indicated in Fig. 5 b. Here the diaphragm and anode were stretched in a curved form as shown. The top-lid was also made curved, in order that it might not bend and give way due to heat.

Experiments conducted with this arrangement are recorded in Table III B. The cell voltage was steady at 5.3 which is lower than that with porous porcelain. The current efficiency was as high as 100% at a concentration of 97.5 g. p. l. acid and 87% at a concentration of 150 g. p. l.

TABLE III

A. With Flat Microporous Rubber Sheet.

No.	Cathode Current density amp./sq. dm.	Cell voltage.	Amp. hours passed.	Gms. of acid produced	Concentration gm/litre.	Anode current efficiency
1.	10	6-10 (unsteady)	27.8	47.8	45.5	95.6%
2.	10	6-10 (unsteady)	15.7	20.8	83	74%
3.	10	6-10 (unsteady)	17.4	18.8	112.5	60%

B. With curved Microporous Rubber Sheet.

No.	Cathode Current density amp./sq. dm.	Cell Voltage.	Amp. hours passed	Gms. of acid produced	Concentration gms/litre.	Current efficiency	
						Anode	Cathode
1.	10	5.5	39.7	71.5	37.6	100%	94%
2.	10	5.3	47.8	86.0	97.5	100%	92%
3.	9.5	5.3	29.1	45.5	150.0	87%	87%

The above constructional and other details have been incorporated in a large-scale unit of 100 amp. capacity.

Effect of impurities in the electrolyte: Iron in the sodium sulphate even in very small quantities affects the formation of sodium amalgam in the cell. This could be seen by the evolution of hydrogen in the electrolyser itself, with little decomposition in the vertical and horizontal decomposers.

Organic impurities, especially tannins, alkaloids and the like with which sodium sulphate liquor from cinchona factory wastes is contaminated was found to affect the electrolysis even when they were present to an extent of 0.01%. The best way of purification of the salt was found to be concentration and crystallisation of the Glauber's salt.

CONCLUSIONS. From the results of our laboratory experiments, it can be concluded

that the electrolysis of sodium sulphate can be successfully conducted by a flowing mercury cathode process in a concrete electrolyser coated with chlorinated rubber. Alumic variety porcelain diaphragms made in India or better still microporous rubber sheet diaphragms fixed in a closed wooden anode box as described in this paper are quite suitable. The cell voltage is 5.8 to 6 in the case of porcelain diaphragms and 5.3 in the case of microporous rubber diaphragms at a current density of 10 amps./sq. dm.

The process yields pure concentrated sodium hydroxide of 50% strength and sulphuric acid of 15 to 17% concentration mixed with an equal quantity of sodium sulphate. A current efficiency of 90% is realised. The process can be advantageously employed in the Viscose Rayon industry, in the cinchona alkaloid industry etc., where sodium sulphate is got as a bye-product and where pure caustic soda and 15 to 17% sulphuric acid mixed with sodium sulphate can be directly used.

REFERENCES :

1. *Chemical Age (India)*, October, 1952, pp. 22-28.
2. "Programmes of Industrial Development (1951-56)", Planning Commission, Government of India, P 144.
3. Watson, E. R., *J. Soc. Chem. Ind (London)* **42**, 251, (1923).
4. Atwell, H. V., and Fuwa, E, *Ind. Eng. Chem.* **15**, 617 (1923).
5. Stender, W. W., and Seerak, I. J., *Trans. Electrochem. Soc.* **68**, 493 (1935).
6. Grube, G., and St. Stainoff, *Z. Elektrochem.* **44**, 640 (1938).
7. FIAT, Final Report No. 831.
8. FIAT, Final Report No. 432.
9. Stender, W. W., Jonitsky, J., & Sabo, B. O., *Trans. Electrochem. Soc.* **71**, 568 (1939).
10. Thomas, L. R. *Ind. Chemist* **29**, 489 (1953).

COMMERCIAL POSSIBILITY OF PRODUCING ELECTROLYTIC CALCIUM GLUCONATE IN INDIA

by

B. B. Dey, H. V. K. Udupa and V. Sarada Menon

(Central Electrochemical Research Institute, Karaikudi)

Calcium gluconate, being soluble, practically tasteless and non-irritating to tissues, is being increasingly used in medicine. It may be administered by mouth or by subcutaneous injection. Its usefulness in the medical treatment of calcium deficiency is widely recognized. It is an oral antidote for fluorine and oxalic acid poisoning. It can replace fruit acids with advantage in fruit jelly manufacture and in baking powders¹. The gluconate is also useful in the preparation of homogeneous pastes such as dentifrices and polishing agents for metals². Ferrous gluconate containing 12 per cent iron is readily made from calcium gluconate and is used in the treatment of iron deficiency anaemias and also as an elixir, because it is reported to produce less gastrointestinal disturbance than ferrous sulphate³. Incidentally it may be mentioned that aluminium gluconate has potential use as a tanning agent.

Calcium gluconate should pass the B. P. test in order that it may be used for oral administration as tablets and in other forms. Pharmacological tests are necessary for testing the suitability of the product for intravenous injections. As a rule the calcium gluconate of B. P. quality marketed by most foreign firms is not suitable for parenteral use. Calcium gluconate of specially pure quality is required for this purpose.

Published reports about the requirements of calcium gluconate in India show considerable divergence. Thus, according to the Wealth of India¹ report, the annual demand for calcium gluconate is of the order of 90,000 lbs. of which a major part is imported into the country. The same source reports an indigenous production of only about 500 lbs. However, according to the Survey of Indian Chemical and Pharmaceutical Industry published by the Indian Chemical Manufacturers' Association⁴, the estimated demand for

calcium gluconate in India is about 56,000 lbs. and the production is roughly about 26,000 lbs. annually.

The Survey of the Indian Chemical and Pharmaceutical Industry⁴ referred to above reports that the installed capacity is at present 40,320 lbs. but is expected to rise to 60,000 lbs. From figures made available by the Government, it would appear that the installed capacity is nearly 111,000 lbs. per annum and that calcium gluconate is being manufactured by the electrolytic oxidation of glucose. The production during the years 1952, 1953 and 1954 (January-June) are also reported to be 14,300 lbs, 24,400 lbs and 10,400 lbs. respectively. The gap between the installed capacity and actual production may be due either to technical difficulties in working the existing process or to high production costs rendering competition with the imported material uneconomical. In either case, the situation can be remedied only by improvements in the technique of manufacture which would ensure uninterrupted operation and bring down the production costs. The investigations carried out in these laboratories were undertaken with precisely this end in view and have now succeeded in effecting valuable technical improvements in the electrolytic process of manufacture leading to a significant lowering of the production costs.

Several processes have been suggested for the regulated oxidation of glucose to gluconic acid but very few of them have been successfully commercialised. A number of chemical methods are available using different oxidizing agents like chlorine, bromine, iodine, nitric acid, mercuric oxide and potassium ferricyanide. Various fermentation processes using cheap raw materials like molasses, gur or cane sugar have been used with moderate success. Recently, a process has been developed⁵ in which the enzyme prepared from the fungus

mat of *Aspergillus Niger* obtained as a waste product in the fermentation process for citric acid manufacture is used to oxidize glucose. Because of its advantage of simplicity, both of operation and control, the electrolytic process is the only one which seems to have appealed to the Indian Industry so far. The process consists in oxidizing glucose in a 2 percent sodium bromide solution with iron or graphite cathodes and graphite anodes at a suitable temperature and current density. In the original process of Fink and Summers⁶ bromine loss was minimised by changing the direction of rectified A. C. every fifteen minutes. A current efficiency of nearly 90 per cent is claimed for the process. Recently, attempts have been made to use inverted cane sugar but the process⁷ has its own inherent drawbacks.

The process developed in the Central Electrochemical Research Institute⁸ conforms in details to the process originally developed by Fink and Summers except that rotating anodes are used in our process. The necessity of stirring the added calcium carbonate is met by the rotating anode which serves this purpose admirably and hence no external stirrer is used in this set-up. Conditions of electrolysis are the same as those used by Fink and Summers. A two per cent sodium bromide solution containing 20 per cent glucose dissolved in it is electrolyzed between graphite plate cathodes and rotating graphite anode (peripheral velocity of the anode surface 120-250 metres/min) for the theoretical period of time at a temperature of 30 °C. A weighed amount of calcium carbonate is added during the electrolysis and any excess filtered off at the end. Current efficiency has been calculated on the basis of glucose oxidized and the bromine loss has also been estimated. Calcium gluconate in solution has been estimated by determining the dissolved calcium as oxalate. Most of the calcium gluconate crystallizes out on cooling in a refrigerator and is then centrifuged, washed and dried. The mother liquor is recycled after making up the bromide and the glucose.

Fink and Summers⁶ passed nearly 10 per cent excess current in order to get nearly complete oxidation of glucose even though the current density used by them was as low as 1 to 2 amps./dm². When rotating anodes are used oxidation is almost quantitative even at very high current densities (28 amps./dm²).

Bromine loss which was of the order of 25-per cent in the experiments of Fink and Summers unless an alternator was used, has been brought down to as low as 2 to 5 per cent in our experiments using rotating anodes. The inter-electrode distance of 2 to 2.5 cms. suggested by Fink and Summers and by other authors to prevent shorting of the circuit due to crystals of calcium gluconate forming on the electrodes, can be reduced to one centimeter or less without any disadvantage. Because of this, for the same current density the cell-voltage would be lower in the rotating anode cell than in the usual cell with stationary anodes. The use of high current density reduces initial investment on graphite also. The consequent high current concentration may be expected to increase cell-capacity and thereby lower the floor-space requirements. The possibility of using a wide range of current density and cell-voltage also permits operation at higher voltages during off-peak hours.

The process has been thoroughly investigated on the laboratory scale using a wide range of current densities. A small sized unit capable of producing nearly 18 to 20 lbs. of calcium gluconate per day has been set up and successfully operated at a suitable current density. The matter of erecting a much larger unit is also engaging our attention.

The yield of calcium gluconate obtained by this technique has consistently been 95 per cent and above. The energy consumption per pound of calcium gluconate varies from 0.5 to 1.8 kw-hr (D.C.) depending on the current density employed for oxidation.

Samples of calcium gluconate prepared in this laboratory have been tested by several pharmaceutical firms. On the basis of chemical tests carried out by them they have all reported that the samples are satisfactory and conform to B. P. specifications. They have thus unanimously approved of its suitability for oral administration. Attempts are being made to purify the product further and render it suitable for parenteral use also.

The cost of production of calcium gluconate is worked out below assuming that a plant is installed and operated with a through-put of 90 lbs. per day. It is also assumed that the plant is run for 24 hours a day and 300 days in a year.

	<i>Rupees</i>
A. Cost of land and building ...	15,000
B. Cost of Equipments (M. G. Set, basket centrifuge, shelf-drier tanks, cell set-up, etc.)	33,000
C. Raw materials costs per year	
(i) Glucose: Rupee 1/- per lb.	22,500
Sodium bromide Rs. 4/- per lb.	2,400
Calcium Carbonate As. 9/- per lb.	4,200
Other chemicals.	3,000
(ii) Power, fuel, etc.	3,300
Total	35,400
D. Cost of labour and supervision per year.	14,400
E. Fixed charges (Insurance, 0.5 per cent of A plus B and depreciation, 10% of A plus B)	5,040
Total capital investment	1,02,840

Annual Operating Costs :

Raw Materials	35,400
Labour and supervision	14,400
Maintenance (5% of A and B)	2,400
Fixed charges, interest on capital, management, distribution and other overheads	9,280
Total	61,480
Profit 21%	12,770
	74,250
Annual Production :	27,000 lbs.
Cost per lb. of calcium gluconate = Rs. 2-12-0.	

The cost of glucose (dextrose C. P. granular, drums) prevailing in the United States as on Dec., 1954 ⁽⁹⁾ is 14 cents/lb. (Rs. 0-10-6/1lb.). The cost of calcium gluconate U. S. P. powder in drums is 60 5 to 63 cents (Rs. 2-14-0 to Rs. 3-0-0/lb.) and U. S. P. granular in drums of 20—2000 lbs. is 65 to 74 cents (Rs. 3-1-6 to Rs. 3-8-3/lb.). These cost figures are given for comparison with the cost calculated above.

REFERENCES :

1. "The Wealth of India—Industrial Products" (Council of Scientific & Industrial Research, Delhi, 1951) Part II, p. 9.
2. Thorpe J. F. and Whiteley, M. A. : "Thorpe's Dictionary of Applied Chemistry" (Longmans, London, 1946) Volume II, p. 297.
3. Kirk, R. E. and Othmer, D. F. (Ed.) "Encyclopedia of Chemical Technology," (Interscience Encyclopedia, New York, 1952) Volume VIII, p. 65.
4. "Indian Chemical and Pharmaceutical Industry" Survey by Indian Chemical Manufacturers' Association, 1954, p. 108.
5. Indian Patent No. 39,441 (1948).
6. Fink C. G. and Summers D. B., *Trans. Electrochem. Soc.* 74, p. 625 (1938).
7. Balasundaram, S., Hirani R. K., and Subramanian V., *J. Sci. & Ind. Research (India)*, 10B, p. 22 (1951).
8. Menon, V. S., Udupa, H. V. K., and Dey, B. B., *J. Sci. & Ind. Research (India)* 13B, p. 746 (1950); Indian Patent 51,189 (1955).
9. *Chem. & Eng. News.* 32, p. 5129-46 (1954)

COMMERCIAL POSSIBILITY OF PRODUCING ELECTROLYTIC PARA-AMINOPHENOL IN INDIA.

by

B. B. Dey, H. V. K. Udupa and G. S. Krishnamurthy

(Central Electrochemical Research Institute, Karaikudi)

Para-aminophenol and its derivatives find wide commercial application for a variety of purposes, their most important use being as developers for photographic negatives. A concentrated solution of p-aminophenol is a very good developer which is rapid, soft-working and suitable for tropical climates. For photographic purposes, it is usually marketed as its hydrochloride or stabilised with sodium sulfite under the tradenames¹ of Rodinal, Unal, Kodolan, Citol, Paranol, Perinol and Azol. It is an intermediate in the production of several other important derivatives like 'Metol' (N-methyl p-aminophenol sulfate) and "Glycine" (N-p-hydroxyphenyl-amino-acetic acid) which are also very useful as photographic developers.

Para-aminophenol is also used in the preparation of a large number of dyestuffs, particularly azo and sulfur colours. Among them may be mentioned ¹Chrome Deep Brown 3R, Supranol Yellow RA, Pyrogene Direct Blue RLCE, Hydron Blue BG, Immedial Black, Immedial Green, Katigen Red Brown 6 RN. Under the trade name of Ursol P, it is used as a fur, hair and feather dye, which dyes a deep brown by after-oxidation. In the field of pharmaceuticals it is an intermediate for the preparation of phenacetin (p-ethoxy acetanilide) and methacetin (p-methoxy acetanilide) which possess excellent antipyretic and analgesic properties.

There are two grades of p-aminophenol available in the market. The photographic grade is in the form of white crystalline leaflets melting at 185-186° C. Since the free base oxidises very rapidly in air, the commercial product is generally light-tan to dark-brown in shade. Usually the free base is not marketed as such for photographic developers but is sold in the form of its salts usually the hydrochloride or the sulfate and stabilised with sodium sulfite.

Import figures are not available for this product mainly because it is normally used in admixture with other derivatives. Information received from a private firm indicates that there is a potential demand of at least 15,000 lbs. per annum. India is the second largest consumer in the world of raw cinematographic films and of sensitised materials, and with the growth of the dyestuff industry, it is to be hoped that the consumption of this chemical will increase considerably. In this connection it is interesting to note that in 1945 the United States produced 857,000 lbs. of p-aminophenol and its salts¹.

The raw materials required for the production of p-aminophenol, are nitrobenzene, sulfuric acid and soda ash. Nitrobenzene is at present entirely imported from other countries as there is not much demand for it. The Tariff Commission in its report on the dyestuffs industries in India has estimated the annual requirements of nitrobenzene at 595 tons². Nitrobenzene is obtained by the nitration of benzene with a mixture of nitric and sulfuric acids. There is no plant in India at present which refines crude benzol to pure benzene, toluene etc., because of inadequate demand. All the 1.5 million gallons of crude benzol obtained from coal are at present used up as motor fuel². With the steady building up of the dyestuff industry there is bound to be a ready outlet for the disposal of benzene etc., in large quantities so that the growth of a stable dyestuff industry would stimulate production of the coal tar primaries on a large-scale.

Nitric acid and sulfuric acid required for the nitration of benzene are produced in adequate quantities to meet the demand. Soda ash is also being manufactured by two plants and the total production is expected to reach 80,000 tons per year². It is thus seen

that our country can be self-sufficient with respect to the raw materials for the manufacture of p-aminophenol. Therefore the process presents attractive possibilities for commercial exploitation.

Para-aminophenol is not at present being manufactured in India and our requirements of this material are met by imports from abroad.

Various chemical methods have been developed for the preparation of p-aminophenol ever since it was prepared by Bayer & Co., in 1874 by reducing p-nitrophenol with tin and hydrochloric acid. These methods suffer from the drawback that they involve the use of costly intermediates like p-nitrophenol, p-azophenol etc., which have themselves to be prepared first by a series of operations from coal tar primaries. The electrolytic method first developed by Gattermann³ attracted immediate attention because it makes use of the cheap and abundantly available nitrobenzene and can be carried out in a single step to give p-aminophenol directly. Several authors have described methods in which acids of varying strengths have been used and the reduction carried out at different metals with or without addition agents. During World War I, the Eastman Kodak Co., adopted Thatcher's modification of Gattermann's, and McDaniel et al⁴ have given a detailed description of the process. This process was abandoned after some years in favour of the chemical process because of the use of strong sulphuric acid which is a serious handicap in operation on a commercial scale and the use of platinum electrodes which entailed heavy capital expenditure.

The advantages of using dilute sulphuric acid and cheap materials like Cu, Ni, Pb etc., were first emphasised by Hale⁵ and Imray⁶ and this process was further developed by Dey and co-workers⁷ who describe the use of 20 percent sulphuric acid as the electrolyte and amalgamated monel or copper as the cathodes. Later Wilson and Udupa⁸ made some preliminary studies on the use of rotating cathodes in the reduction of organic nitro-compounds and found that higher current densities can be safely employed without any decrease in the current efficiency or the yield of aminophenol.

Work was taken up in these laboratories to study the process further and to work out an

economic process using the rotating electrode. Rotating disc-type cathodes of amalgamated copper or monel have been used for this purpose and current densities of the order of 20 amps. per dm² have been used. Several successful runs have been made both on the laboratory and semipilot-plant scales and yields of 65-73% have been consistently obtained⁹.

Sulphuric acid of 30% strength is used as the catholyte in a divided cell made of glazed porcelain. The catholyte is separated from the anolyte (40% sulphuric acid) by porous diaphragms. The cathode is of amalgamated copper or monel and the anode of sheet lead. Electrolysis is carried out at 80-85°C at a current density of 20 amps./dm² until all the nitrobenzene gets reduced. The operating cell-voltage is between 3.8 to 4.6 volts and the energy consumption (D. C.) is 3.0 kwh /lb. of free base.

After the electrolysis the unreacted nitrobenzene is distilled off in steam, the tarry impurities removed by filtration and the filtrate decolorised by animal charcoal. The electrolyte is then neutralised with sodium carbonate until the pH is about 6.6. This is again steam-distilled to remove aniline and the residue is cooled to 0°C to recover the p-aminophenol crystallising out. It is then filtered off, washed with cold water, stabilised and dried. An alternative procedure of isolation has been developed which consists in concentrating the electrolyte under reduced pressure and isolating the p-aminophenol as sulfate. The spent acid can then be used over again for further electrolysis, making the process more economical. After 4 or 5 runs the electrolyte becomes fouled due to the building up of aniline when it becomes necessary to neutralise the electrolyte with either lime or soda ash and then recover the p-aminophenol as the base.

The application of high current densities of the order of 20 amps./dm² using amalgamated, rotating disc-type cathode and the isolation of the p-aminophenol as the sulfate in order to conserve the sulphuric acid are claimed as the novel features of the process.

The cost of production of p-aminophenol has been worked out below assuming that a plant is installed and operated with a throughput of 50 lbs. per working day of 24 hours for 300 days in a year.

Rupees

A. Land and building costs	...	15,000
B. Equipment costs: Motor Generator set, glass-lined vacuum-distillation set-up, refrigerator unit, drier, boiler, cell set-up etc.	...	50,000
C. Raw material costs per year:		
(i) Nitrobenzene, 86.8 lbs/day at Rs. 1/4/-per lb.	...	32,550
Sulphuric acid (98%) 54 lbs/day at Rs. 0-3-0 per lb.	...	3,038
Soda ash, 58 lbs/day, at Rs 20 per cwt.	...	3,107
Other chemicals	...	1,000
(ii) Power, fuel etc., at Rs 30/day	...	9,000
Total debits		<u>48,695</u>
(iii) Credit side:		
Cost of aniline, 6.51 lbs/day at Rs. 2/lb.	...	3,906
Cost of sodium sulphate at Rs. 12/100 lbs.	...	2,800
Total credits.		<u>6,706</u>
∴ Total raw materials costs		<u>41,989</u>
D. Cost of labour, supervision etc., at Rs. 30/day		10,800
E. Fixed charges (insurance at 0.5% on A plus B, Depreciation at 10% on A plus B		6,825
Total investment		<u>1,24,614</u>

Annual Operating costs:

1. Raw materials	...	41,989
2. Labour and supervision	...	10,800
3. Maintenance (5% of A plus B)	...	3,250
4. Fixed charges (interest on capital, management, distribution and other overheads)	...	12,500
Total operating costs	Rs.	<u>68,539</u>

Total annual production of p-aminophenol free base ... 15,000 lbs.
 ∴ Cost of production per lb of base Rs. 4 9 0 (approx.)

Assuming selling price of p-aminophenol at Rs. 5-12-0 per lb. the total turnover per year would be Rs. 86,250 thereby assuring a profit of nearly 26%.

The price of p-aminophenol is ultimately dependent more on the cost of nitrobenzene than on anything else. If the supply of cheap nitrobenzene is assured, the process will be highly economical making commercial production more attractive. The cost of nitrobenzene in the U.S.A. as on December 1954, in car load quantities was 12 to 13 cents/lb (0-9-1 to Rs. 0-9-10 lb) and that of p-aminophenol in drums of 200 lbs. was 97 to 99 cents/lb. (Rs. 4-9-3 to 4-11-3/lb.) These cost figures are given here for comparison with the cost calculated above.

REFERENCES:

1. Kirk, R.E., and Othmer, D.F. (Ed.), "Encyclopedia of Chemical Technology", (Interscience Encyclopedia, New York, 1947) Vol. I, p. 740.
2. Indian Chemical and Pharmaceutical Industry, Survey by Indian Chemical Manufacturers' Association, (1954), p. 29; 76; 86.
3. Gattermann, L., and Koppert, K., *Chem. Ztg.*, 17, 210 (1893); *Ber.*, 26, 1847 (1893).
4. McDaniel, A.S., Schneider, L., and Ballard A., *Trans. Electrochem. Soc.*, 39, 441 (1924)
5. Hale, A. J., The Application of Electrolysis in Chemical Industry, (1919), p. 52
6. Imray, O., *B.P. 18081*, (1915)
7. Dey, B.B., Govindachari, T.R., and Rajagopalan, S. C., *J. Sci. Ind. Research (India)*, 4, 574 (1946)
8. Wilson, C L., and Udupa, H. V. K., *J. Electrochem. Soc.* 99, 289, 1952
9. *Indian Patent 53, 195*, Application filed, Nov. 23, 1954.

THEORETICAL ASPECTS OF THE ELECTROLYTIC METHOD OF PREPARING HEAVY WATER

by

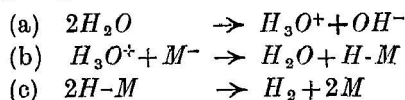
G. S. Subramanian

(Central Electrochemical Research Institute, Karaikudi)

The discovery of Urey and Washburn¹ that water from an old electrolytic cell is heavier than ordinary water led them to the identification of a "heavy" hydrogen and ever since that time various investigations have been directed to find out the exact cause of this isotopic fractionation during electrolysis. Urey and Rittenberg,² by the application of statistical mechanics and from the known molecular spectrum of H_2 and its compounds determined the different thermodynamic properties of deuterium and its compounds. They estimated the electrode potential differences from the free energy differences for hydrogen-hydrogen halide reactions and found the electrode potential differences between the two isotopes at 298.1°K to be 0.00886 Volts for the hydrogen chloride reaction and 0.00195 Volts for the hydrogen iodide reaction. These values are so small that no separation of the hydrogen isotopes can be expected by fractional electrolysis in so far as this fractionation depends on the differences of electrode potentials. The enrichment may be due to other causes than the electrode potential differences, perhaps the rates of diffusion to the electrode surface or the rates of recombination of hydrogen atoms on the electrodes. By thermodynamic reasoning, appreciable differences in other properties of these two hydrogen isotopes have been established and these differences as well as the differences in reaction velocities of which the electrolytic fractionation of the hydrogen isotopes is probably an example are very great indeed for the two isotopes.

The separation of hydrogen isotopes by electrolysis of solutions of electrolytes in water depends essentially upon the removal of hydrogen from water molecules. The only change in the nature of electrolyte during electrolysis is the increase in the electrolyte concentration and the change in the relative number of hydrogen and deuterium atoms. In evolving a theory of electrolytic separation, Topley and Eyring³ assume that the solution surrounding the cathode is in thermodynamic equilibrium with

the bulk of the solution and that the mole fractions of all ionic species are small compared with the atomic fractions of both H and D. The evolution of hydrogen takes place in the following stages:



Stage (b) is the neutralisation of a hydrated hydrogen ion by the negatively charged metal M with the formation of a hydrogen atom attached in some way to the surface atom M. Stage (c) represents the desorption of hydrogen in the molecular form from the metal surface. It is assumed that (a) and (b) are reversible and in equilibrium and also that stage (c) represents a slow reaction. Topley and Eyring³ support their assumptions by the theories of over-voltage due to Gurney¹ and others. As such, stage (c) represents the cause for isotopic separations and the difference in the rate of this reaction is responsible for the isotopic enrichment. On the basis of this theory, the authors are able to derive an expression for the electrolytic separation coefficient at different metallic cathodes.

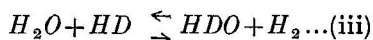
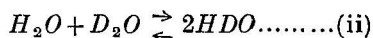
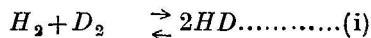
R. P. Bell⁶ considers that the separation is due to the differences in behaviour of the two isotopes at one or more of the following stages in the process of electrolysis:

- (a) The mobility of hydrogen and diplogen (deuterium) ion
- (b) The rate of neutralisation of the two ions by electrons
- (c) The rate of combination of hydrogen and diplogen atoms on the electrodes.

According to him (a) cannot be an important factor in the separation since it can be carried out equally well in acid or in alkaline solutions. It is more difficult to decide between (b) and (c). Topley and Eyring³ and Bell and Wolfenden⁷ observed that the efficiency of separation is substantially the same for a number of different cathode materials, which makes

it very improbable that the observed phenomena are due to the rate of combination of atoms on the electrode surface. Stage (b) seems to be more probable for bringing about the electrolytic enrichment.

Farkas and Farkas⁸ on the other hand consider that the following reactions are operative in all processes where hydrogen is evolved from aqueous solutions:



These equations define the D content of the hydrogen evolved from a solution of given D content under equilibrium condition. In a number of processes where hydrogen is evolved from aqueous solutions it could actually be observed that the establishment of these equilibria does in fact occur and is in these cases the only cause for the separation of hydrogen isotopes.

In cases where the establishment of the equilibria (1), (2) and (3), especially that of (3), is not attained, as for instance in electrolysis in general or in the dissolution of metals in water or in acids, the exchange reaction $H_2O + HD \rightarrow HOD + H_2$ may be operative to a certain extent, thus modifying the primary separation of the hydrogen isotopes caused e.g., in the electrolysis by the different rate of discharge of H^+ and D^+ ions or by the different rate of recombination of the H and D atoms.

That the separation of isotopes of hydrogen is due to the different rates of recombination of gaseous atoms on the electrode is also the view supported by Halpern⁹. It is this recombination process which determines the rate of separation of hydrogen isotopes. On the basis of this hypothesis Halpern establishes a relationship which expresses the separation coefficient as a function of well-known thermodynamic constants of H and D compounds and of frequencies with which the atoms carry out their thermal oscillation on the electrode. His equation gives a certain range for the value of the separation coefficient which is in good agreement with the observed values.

The mechanism of overvoltage is also responsible for the difference in the rates of evolution of H_2 and D_2 . Eyring, Glasstone and Laidler¹⁰ have suggested a mechanism based on the theory of overvoltage. This theory is based upon the absolute reaction rate theory

of chemical reactions and relates the current density I at an electrode to the overvoltage V by means of the expression $I = I_0 \cdot \exp \left(\frac{\infty VF}{RT} \right)$

where I_0 is a constant for a given electrode representing the current passing in each direction at the reversible potential and ∞ is the fraction of the added potential V operating between the initial state and the activated state of the system. The examination of I_0 in terms of the heat and entropy changes of the activation processes suggests that the slow process may consist in the transfer a proton from a molecule of water in the solution to another water molecule attached to the electrode surface. This theory explains satisfactorily the magnitude of the separation factor and its variation with electrode material and temperature.

Separation Coefficient: The separation of the isotopes during electrolysis is defined by the coefficient ∞ , called the separation coefficient. ∞ is generally defined as $\infty = \left(\frac{H_g}{D_g} \right) / \frac{H_{liq}}{D_{liq}}$

where H_g is the mole fraction of hydrogen in the gaseous phase, H_{liq} is the mole fractions in the liquid phase and D_g and D_{liq} have the same significance for deuterium. The best way to study the electrolytic separation of hydrogen isotopes is the determination of this separation coefficient under various conditions.

Nature of Electrodes and the efficiency of separation: Electrodes of different metals give different separation efficiencies. The following data from the work of Topley and Eyring (loc. cit.) illustrate the factor.

Separation factors for various conditions of electrolysis.

Electrode	Electrolyte.	Separation factor.
Lead	0.5 N KOH	7.2—7.4
Platinum	"	6.5—7.6
Platinum	0.5 NH_4SO_4	5.7
Iron	0.5 N KOH	6.9—7.6
Nickel	"	5.5
Copper	"	6.8
Silver	"	5.3—5.8

The data refer mainly to massive electrodes at current densities of the order of 1 amp./sq. cm.

Edwards and co-workers¹¹ feel that one of the characteristic features of the electrolytic separation of the hydrogen isotopes is its lack of reproducibility, which is also reflected in the

frequent discrepancies between the results of different investigators. They conducted experiments using electrolytes of 2% solution of sodium hydroxide containing 0.5–1% D_2O and cathodes of different metals. C. D. of cathode was 0.25 amp./cm², the temperature of the electrolyte being 25° to 30°C. Loss by evaporation and spray was minimised by fitting each cell with an effective condenser and measured by placing each group of cells in series with a voltammeter consisting of an electrolytic cell fitted with drying tubes so that the loss of weight of the cell was due to electrolysis only. Results for α are given below:

Cathode.	Electrolytic separation co-efficient.	Mean.
Nickel	(i) 4.3, 4.0 (ii) 4.8, 4.3, 5.5, 6.2, 6.4	5.1
Copper	5.9, 6.3, 5.7, 7.0, 5.1, 6.65, 5.8, 7.0	6.2
Arc carbon	6.85, 6.3, 4.85, 5.2, 5.7	5.8
Iron	10.1, 9.6, 9.2, 8.6, 11.0, 10.2, 10.9	9.9
Nickel coated with sulphide	6.3, 6.3, 7.2, 6.7, 6.0, 5.9	6.4
Iron coated with sulphide	8.9, 8.4, 10.9	9.4
Graphite	3.1, 8.9, 4.7, 8.7, 4.7, 3.6	6.7

The variations in α are in every case greater than the most unfavourable estimate of the experimental errors. It seems that in protracted electrolysis under favourable conditions, serious fluctuations in the separation co-efficient cannot be eliminated. The contrast between iron and the other cathode materials, the extreme variability of α at a graphite cathode, and the effect of a sulphide film on Ni are of interest.

Walton and Wolfenden¹² determined the influence of temperature and current density on the electrolytic separation of hydrogen isotopes at different cathode materials; current densities of the order of 1 milliamp per sq. cm. were used. The metals investigated fall into two groups viz., silver, platinum, nickel with separation factor of 5 to 7 which falls considerably with rise in temperature and mercury and tin with separation factor about 3 where the effect is not so predominant. Generally with low separation factors, the temperature co-efficient is small but with large separation factors there is a large negative temperature

co-efficient in each case. Eucken and Bractzler¹³ have made comprehensive investigations on the influence of the cathode material, special attention being given to the previous history of the material. They concluded that there was no parallelism between the actual overvoltage and the separation factor which later was increased by previous anodic treatment of the electrode. Poisons such as α -naphtha quinoline decreased the separation factor.

Influences of other factors on the separation: Regarding the influence of temperature on the electrolytic separation of hydrogen isotopes, Walton and Wolfenden¹⁴ measured the same between 15° to 98° at mercury and silver cathodes. The electrolyte was 0.5 N HCl (with 0.5 N KCl added in the experiment with Hg). The anode consisted of the same material as the cathode. The separation co-efficient can be expressed as:—

$$L_n \alpha = \Delta \frac{E}{RT}$$

where E is the activation energy. α falls at the silver electrode with rising temperature, whereas at mercury it remains constant. Addition of a catalyst poison lowers the separation co-efficient considerably and alters the sign of its temperature co-efficient. On the basis of detailed experiments it is reported¹⁵ that under certain conditions of electrolysis, the current density has no effect on the separation coefficient. This is further confirmed by T. Naguchii¹⁶ who electrolysed 20% NaOH solution at 18° with nickel electrodes using a C. D. of 0.05–1.0 amp./sq. cm. under constant volume and concentration of NaOH maintained through continuous supply of water free from NaOH. He found that the separation co-efficient is not greatly affected by current density. For the same electrodes the separation factors are different with different electrolytes. A. I. Brodskii¹⁷ and co-workers report that the separation factor determined by electrolysis 100 cc. of 0.2N salt solution in 0.1% D_2O between platinum electrodes and measuring the concentration of D_2O in the residual liquid (12.5 cc.) increases from 5.6 for KOH through H_2SO_4 , KCl, NaCl and K_2CO_3 to 10.6 for Li_2SO_4 . The effect of other ions like nitrate ions and ammonia on the electrolytic separation of H_2 – D_2 isotopes was investigated by Hojman¹⁸. The presence of NO_3^- in the electrolyte did not change the separation factor whereas it was increased by the electrochemical oxidation of NH_3 .

Different types of cells for electrolytic preparation of heavy water are described in literature and need not be repeated here. Certain important considerations that are to be looked into in the design of the cells for electrolysis may be mentioned. In the process of electrolysis, the concentration of hydrogen in the neighbourhood of the cathode decreases while that of deuterium increases owing to the preferential electrolysis of the hydrogen. It is therefore evident that as electrolysis proceeds the local concentration of deuterium hydroxide in the neighbourhood of the cathode becomes much greater than that in the bulk of the solution; such local concentration not only in itself increases the proportion of deuterium liberated as gas, but also favours the exchange reaction by which the electrolytic separation is opposed.

Applebey and Ogden¹⁹ in stressing these points recommend the following principles in the design of cells for the production of heavy water: (a) the metal used for the electrode material must be a poor catalyst for the exchange reactions, (b) the evolved hydrogen gas must be removed as rapidly as possible from the electrode surface, (c) local concentration of deuterium hydroxide at the electrode surface must be avoided. The last two conditions can be attained by efficient stirring of the electrolyte either mechanically or by the gas evolution itself, the efficiency then depending largely on the correct design of electrodes.

REFERENCES:

1. Urey, H. C., and Washburn, E. W., *Proc. Nat. Acad. Sci., U. S.*, **18**, 496-98 (1932).
2. Urey, H. C., and Ritterberg, D., *J. Chem. Phys.* **1**, 137 (1933).
3. Topley, B., and Eyring, H., *J. Chem. Phys.* **2**, (1934) 217.
4. Gurney, R. W., *Proc. Roy. Soc.*, **A134**, 137 (1932).
5. Bell, R. P., *J. Chem. Phys.*, **2**, 164 (1934).
6. Topley, B., and Eyring, H., *J. Amer. Chem. Soc.* **55**, 5058 (1933).
7. Bell, R. P., and Wolfenden, J. H., *Nature* **133**, 25 (1934).
8. Farkas, A., and Farkas, L., *J. Chem. Phys.*, **2**, 468 (1934).
9. Halpern, O., *J. Chem. Phys.*, **3**, 452 (1935).
10. Eyring, H., Glasstone, S., and Laidler, K. J., *J. Chem. Phys.*, **7**, 1053 (1939).
11. Edwards, A. J., Walton, H. F., Bell, R. P., and Wolfenden, J. H., *J. Chem. Soc.* 286 (1936).
12. Walton, H. F., and Wolfenden, J. H., *Trans. Farad. Soc.*, **34**, 436-49 (1938).
13. Eucken, A., and Bractzler, K., *Treatise on Physical Chemistry* by Taylor and Glasstone (Van Nostrand, New York, 1947), vol. I, p. 67.
14. Walton, H. F., and Wolfenden, J. H., *Nature* **138**, 468 (1936).
15. Anon, *J. Electrochem. Soc. (Japan)*, **3** 388 (1935).
16. T. Noguchii, *J. Electrochem. Soc. (Japan)*, **3**, 305-10 (1935).
17. Brodskii, A. I., and Skrinnikova, N. P., *Chem. Abstr.*, **30**, 5485 (1936).
18. Hojman, J. M., *Chem. Abstr.*, **48**, 1852 (1954).
19. Applebey, M. P., and Ogden, G., *J. Chem. Soc.*, 163 (1936).

NOTES AND NEWS

COMMITTEES AND CONFERENCES :

Dr. H. V. K. Udupa, Senior Scientific Officer and Shri A. Sreenivas, Junior Scientific Assistant were deputed to attend the 42nd session of the Indian Science Congress held at Baroda during January 1955. They presented papers on "A New Technique in Electrolytic Practice" by H. V. K. Udupa and B. B. Dey and "Utilization of South Arcot Lignite for the Production of Calcium Carbide" by A. Jogarao and A. Sreenivas.

On the invitation of the Commerce & Industries Ministry, Government of India, Dr. A. Jogarao, Assistant Director (Plg.) attended the first meeting of the Development Council for Heavy Chemicals (Alkalies) Industry in New Delhi on the 22nd and 23rd April, 1955 convened for the purpose of formulating the development programmes and fixing the targets for certain Heavy Chemicals, e. g. Caustic Soda and Chlorine, Soda ash, Calcium Carbide, Potassium Chlorate, Sodium Hydrosulphite etc., for the Second Five-Year plan period.

A scheme of Discussion Groups in the Central Electrochemical Research Institute was inaugurated at the instance of Dr. A. Jogarao, Assistant Director (Plg.) on 2nd April, 1955 by Prof. M. S. Thacker, Director, Indian Institute of Science, Bangalore. The object of the Discussion Groups was explained to be to stimulate informal and frank discussions amongst a limited number only of the specialists engaged in research on the particular subject, who constituted that group. It was pointed out that in the usual monthly colloquia, where all the members of the Institute could be present, such a free and frank discussion at the level of a specialist was not feasible. Hence this scheme of Discussion Groups was inaugurated.

Prof. Thacker expressed his great pleasure and appreciated the idea of constituting the existing members of the scientific staff of the Institute into a number of specialist groups, so that each could have detailed and specialist discussions concerning the group they belong to.

Keeping in view the work of the Institute now in progress, 8 groups were constituted, viz. Electrothermics, Electrolytic Oxidation and Reduction, Batteries, Electrowinning of metals, Electrodeposition and Metal Finishes,

Reaction Kinetics under Electric Discharges, Electro-Analysis and Electrode Kinetics and Corrosion.

There are not more than a dozen research workers in any one of these Groups, so that it became easy to have the discussions in a thorough-going manner, without irrelevant considerations or digressions, disturbing the atmosphere.

ADDRESSES AND LECTURES :

A scheme of "Annual Address" covering a topic of scientific and research interest to be held annually has been initiated during the current year. Dr. H. L. Wallden of the Swedish Mission delivered the annual address on "Colloidal Chemistry and its applications to surgery" on 14th March, 1955. Shri S. K. Patil, M. P. presided over the function.

Shri O. V. Alagesan, Union Deputy Minister for Railways visited the Institute on Monday, the 10th January 1955. After going round the Institute, he addressed a gathering of the members of the staff.

Shri K. Kamaraj Nadar, Chief Minister of Madras visited the Institute on 5th February 1955. He was shown round the Institute and the problems under investigation were explained to him. Later he addressed the members of the staff.

Dr. C. S. Piggot, U. S. Technical Commissioner, National Academy of Sciences, Washington D. C. visited the Institute on 8th February 1955 to discuss matters relating to the technical aid to be extended to C. E. C. R. I. under the T. C. A. Plan. He addressed the members of the staff, prior to his departure.

Sir S. Varadachari, Retired Judge, Madras High Court visited the Institute on 19th February, 1955. He was shown round the various departments of the Institute and later he addressed the members of the staff.

Shri N. D. Sundaravadivelu, Director of Public Instruction, Madras visited the Institute on 9th March, 1955. After going round the Institute, he addressed the members of the staff.

Mr. H. R. Mills, Scientific Adviser to U. K. High Commission, Colombo, Ceylon visited the Institute to discuss matters relating

to technical aid for the Institute under the Colombo Plan. He addressed the members of the staff prior to his departure.

STAFF :

Dr. B. B. Dey, Director, C. E. C. R. I. retired from office with effect from 10th February 1955 on expiry of his terminal leave.

We convey our congratulations to the following members of the staff, who have been promoted to the posts mentioned against their names :

1. Shri M. Srinivasa Rao, Laboratory Supervisor.
2. Shri N. Balasubramanian, Senior Laboratory Assistant.
3. Shri K. S. R. Naidu, Storekeeper (Workshop)
4. Shri C. Swaminathan, Gas Mistry.
5. Shri R. Satyamoorthi, III Division Clerk.
6. Shri P. Chiranjilal, Gestetner Operator.

PERSONAL :

We record with deep regret the sudden and untimely death of Sri C. Subbiah, Gasman, C. E. C. R. I. from snake-bite.

SOCIAL :

Republic Day was celebrated on 26-1-1955. Dr. RM. Alagappa Chettiar, Chairman of the Advisory Board of the Institute hoisted the flag and addressed the gathering of members of the staff and their families. Sports were conducted for the children who were present, and prizes and sweets were distributed. In the evening, the Institute buildings and grounds were illuminated, and there was a film-show organised by the Staff Club.

Dr. A. Ramaswami Mudaliar, Vice-Chancellor of the Travancore University unveiled the portrait of the late Dr. Shanti Swarup Bhatnagar on the 6th February 1955. At the function got up in this connection, Dr. RM. Alagappa Chettiar and Dr. A. Jogarao, Assistant Director (Plg.) made speeches paying tributes to Dr. Bhatnagar and his great work. In the course of an interesting reminiscence of his early association with Dr. Bhatnagar, Dr. Ramaswami Mudaliar pointed out how much the Council owed to the untiring zeal and dynamism of Dr. Bhatnagar.

The Annual Day of the Staff Club was celebrated on 14th March, 1955 under the presidentship of Shri S. K. Patil, M. P., and in the immediate presence of Dr. RM. Alagappa Chettiar. The annual day address was delivered by Dr. H. L. Wallden and the prizes to the winners in the various sports items were given away by Miss H. Erickson, both of the Swedish Mission, Tiruppattur. The celebrations concluded with a variety entertainment got up by the members of the staff, followed by a dinner at which several distinguished guests were present.

Mrs. M. S. Thacker declared open on the evening of the 2nd April, 1955 one of the garden parks in the Institute's campus, named "Shanti Square". Prof. M. S. Thacker and Dr. RM. Alagappa Chettiar were also present at the pleasant function got up in this connection.

A film club has been organised under the auspices of the staff club and a monthly film-show is being regularly arranged. The Staff Club has also built up a nucleus library of general and recreational books for the use of the members. Donations for this were received in the form of books and money from the members themselves and from organizations like the U.S.I.S.

VISITORS :

1. Shri O. V. Alagesan, Deputy Minister for Railways, Government of India. 10-1-1955.
2. Lady Lokasundari Raman, Bangalore. 25-1-1955.
3. Prof. Eugene P. Link, State University Teachers College, New York, U.S.A. 25-1-1955.
4. Mr. P. Mukherji, Commissioner of Income-Tax, Madras. 27-1-1955.
5. Shri K. Kamaraj Nadar, Chief Minister, Madras. 5-2-1955.
6. Sir A. Ramaswami Mudaliar, Vice-Chancellor, Travancore University, T.C. 6-2-1955.
7. Dr. C. S. Piggot, U. S. Technical Commissioner, National Academy of Sciences, Washington D.C. 8-2-1955.
8. Sir S. Varadachari, Madras. 19-2-1955.
9. Shri N. D. Sundaravadivelu, Director of Public Instruction, Madras. 9-3-1955.
10. Shri S. K. Patil, M. P., Bombay. 14-3-1955.
11. Mr. H. R. Mills, Scientific Adviser to U.K. High Commission, Colombo, Ceylon. 31-3-1955.

BOOK REVIEWS:

MODERN ASPECTS OF ELECTRO-CHEMISTRY.

Edited by J. O. M. Bockris, Pp. X + 344.
(Butterworths Scientific Publications, London, 1954). 40 s.

This book contains five chapters written by experts in the line. The subject matter is very well arranged and numerous very useful references are given at the end of each chapter.

The first chapter deals with different types of poly-electrolytes, the principles involved in their preparation, their properties, theories about them and their applications. It contains a very good summary of the theoretical and experimental work of recent years in the field of synthetic polyelectrolytes. Ionic solvation forms the subject of chapter 2. Because of the importance of a knowledge of the configurations and properties of the solvation sheath for the development of an equation of state for concentrated solutions and because of its applications to certain properties of dilute solutions such as solubility, heat capacity, kinetics of ionic reaction etc., the structural aspects of the theory are discussed in full. "Equilibrium properties of electrified inter-phases" is the subject matter of the third chapter. The discussion pertains only to inter-phases for which the radius of curvature is large compared to the thickness of the interfacial region. The significance of potentials of real phases, the effect of adsorbed layers, the thermodynamics of the ideal polarized electrode, ionic distribution in the double layer, specific adsorption of ions etc., are all covered. The mechanism of activation-controlled phenomena in electrode kinetics is discussed in chapter four. A good treatment is given of the hydrogen evolution reaction, the oxygen evolution, mechanisms in redox reactions, sonic electrode kinetics, separation of isotopes etc. The electrochemical properties of nerve and muscle cells are fully described in Chapter V.

A thorough grasp of the fundamentals of electrochemistry and a good knowledge of mathematics are essential to appreciate and derive the full benefit from this book.* This book is a good supplement to advanced text books in Electrochemistry.

V. ARAVAMUTHAN.

ELECTROPLATING ENGINEERING HANDBOOK

Edited by A. Kenneth Graham. Pp. XX + 650.
(Reinhold Publishing Corporation, New York, 1955) \$10.

Electroplating Engineering Handbook is the first and the only book of its kind on the subject of electroplating. Though this subject is of very great commercial importance, the data regarding the practical processes connected with electroplating have so far remained scattered through the literature and no attempt had been made to collect all the essential information on the subject under one cover. The present volume will fill a very conspicuous gap in the literature on the subject of electroplating and allied subjects.

The thirty-six chapters contained in the volume, each dealing with a particular branch of practical electroplating, have been contributed by more than forty well-known experts in the field. The book has been divided into two parts. Part one, on general processing data, includes articles on design for plating, metal surface preparation and cleaning, processing and operating sequences, bath compositions and operating conditions, plating standards and specifications, analysis of baths, testing of electrodeposits, cost, water, waste disposal, industrial hygiene, metallurgy for electroplater, surface protection and finishing treatment including phosphate coating, chromate conversion coating, anodizing of light metals etc., as well as some tables of data. Certain chapters e. g. cleaning, electropolishing, water, waste and metal surface treatment contain also related engineering data.

In the second part, under the heading "Engineering Fundamentals and Practice", articles on engineering of plating installations, e. g., plant location and layout, floors, tanks, linings, heating and cooling practice and equipment, racks, barrels, automatic plating machines, anode and cathode rod and bus system, anodes and cathodes, D. C. generators, rectifiers, periodic reverse current plating, rinsing, drying, filtering and general maintenance are included.

In all the chapters due consideration has been given to the important factors. Within

the limited space allotted, enough information has been packed without sacrificing the clarity of presentation.

At the beginning of part one, a glossary of some technical terms with their definitions is provided. Tables of requisite data are given wherever necessary. The numerous sketches and diagrams included in the book will go a long way in driving the meaning of the text home easily.

The book is devoted mainly to a practical consideration of the subject; however, reference has been made at the end of every chapter to other literature on the particular subject which should enable the interested reader to pursue the more theoretical aspects of the subject.

The language of the book, in spite of the articles being contributed by different authors, is more or less uniform.

This volume should prove quite useful not only to the designer, manufacturer, supplier and purchaser of electroplating and related equipment, but also to all others interested in the subject of electroplating.

N. N. S. SIDDHANTA.

ELECTROMETRIC pH DETERMINATIONS: THEORY AND PRACTICE—By Roger G. Bates, pp. XIII + 331. (John Wiley and Sons, New York, 1954). \$ 7.50

pH measurements play a vital role in research, industrial and clinical laboratories; and there are pH measuring instruments designed to suit the special needs of different types of investigations. Therefore, it is necessary to have a very clear idea of the basic principles involved in the measurement of pH and the various units that make up a good pH meter.

Dr. Bates has, within the compass of a small volume, provided with considerable success the necessary details for a thorough understanding of the subject—both theory and practice.

The book is divided into two parts, the first part made up of the first six chapters entitled Ch. I. Fundamental Principles and Conventions; Ch. II. Definition of pH scales; Ch. III. Liquid Junction Potentials and Ionic Activities; Ch. IV. Establishment of pH Standards; Ch. V. Buffer Solutions; Ch. VI.

Quantitative Aspects of Acidity and Basicity in Non-aqueous Solutions. These chapters deal with the theoretical aspects of the subject. The basic principles involved in the measurement of electrode potentials, the need for an agreed convention for assigning the sign to the electrode potential, the necessity for introducing the "activity" concept in the place of "concentration" to fit in with the modern developments in regard to theories of solution, the liquid junction potentials, the method of calculating and eliminating them, the establishment of pH standards, and the reasons for preferring pH reference solutions to standard potentials are discussed. Further, buffer solutions, their characteristic properties, and the method of preparing, storing and preserving them are given in considerable detail. And even though pH unit is limited to dilute water solution, the acidity and basicity of non-aqueous solutions have been discussed in view of the important data that have been collected in the field. The scope for further research in the various aspects of the subject are shown from time to time.

The second part of the book is made up of the last four chapters Ch. VII. Cells, Electrodes and Techniques; Ch. VIII. Properties of Glass Electrodes; Ch. IX. Measurement of Electromotive Force—the pH meter; and Ch. X. Automatic pH Control. These chapters cover in great detail many experimental aspects of pH determinations. The preparation of the hydrogen, calomel and silver—silver chloride electrodes are given; the antimony electrode receives a passing mention. A separate chapter is exclusively devoted to the widely used glass electrode. Electrodes made of glass with good hygroscopicity and chemical durability are stated to give good pH response. The sources of error in using glass electrodes and the care that has to be bestowed on them are also discussed. The different American and British types of pH meters, the important units that enter into their assembly, the different adjustments and minor repairs that could be attended to are shown. The progress of instrumentation has advanced sufficiently to enable automatic control of pH. The key elements in such controls are indicated to be the electrode assembly, the amplifier, the recorder, the controller, and the reagent valve.

A number of useful tables and graphs add to the value of the book; references to current literature, and the index are fairly exhaustive.

Even a casual reader can note the earnestness and thoroughness of the treatment of the subject. The anxiety to co-ordinate, within limits, the theoretical developments in the subject with actual practice is quite patent. A compact and self-sufficient hand-book for electrometric pH determination has been given by Dr. Bates to workers in research laboratories and industries, and the book must be made readily available to them.

S. RAMACHANDRAN.

THE PROCEEDINGS OF THE CONFERENCE ON OXIDATION PROCESSES, AMSTERDAM, MAY 6TH TO 8TH, 1954. CHEMICAL ENGINEERING SCIENCE (Special Supplement), Pp. 135. (Pergamon Press Ltd., London).

This special supplement contains eleven papers, on an important group of chemical processes indicated by the name of "Oxidation" which were discussed at the conference held in Amsterdam, Netherlands. The Conference was mainly attended by chemists and chemical engineers from U. S. A., U. K., and the continent of Europe. The papers presented at the conference relate mostly to controlled oxidation reactions of special types which have been thoroughly studied in recent years. Some of them even disclose new methods recently discovered for the manufacture of chemicals by oxidation processes.

In keeping with the ever-growing developments in the oil industry, it is but natural that the oxidation of hydrocarbons should feature so prominently in this volume. Normally a number of hydrocarbons are not oxidized directly but through intermediates formed by chlorination, sulphonation etc., by replacing the groups introduced by the hydroxyl groups. Studies reported here have now shown it possible to prepare chemicals by direct oxidation with molecular oxygen. A free radical chain mechanism has been applied by G. H. Twigg in explaining the liquid phase oxidation of paraffin hydrocarbons. This is followed by a paper on the manufacture of synthetic fatty acids by oxidation of paraffinic hydrocarbons by molecular oxygen.

The paper on the "Air oxidation of mixtures of benzene and cyclohexane to phenol" is interesting from a theoretical point of view in so far as the yield of phenol seem to be dependent on cyclohexane concentration.

Three other papers discuss the direct oxidation of benzene derivatives. Two of them relate to the direct use of molecular oxygen and the other to the use of nitric acid for oxidation. The manufacture of p-tertiary-butyl benzoic acid by blowing air through liquid p-tertiary-butyl benzene using cobalt catalyst is a process developed by Shell Development Company, California, and has been presented as a paper containing all aspects of the chemical engineering details of the process. The other paper relates to "the preparation of cumene hydroperoxide" by the liquid phase oxidation of cumene with molecular oxygen. "Nitric acid oxidation design in the manufacture of adipic acid from cyclohexanol and cyclohexanone" to give more than 90 per cent yields is a very important contribution, in which even the corrosion problems have been thoroughly discussed.

Some of the other interesting papers presented were "Oxidations carried out by means of vanadium pentoxide catalysts", "Oxygen processes in the steel industry", "The provision of oxygen for industrial processes" and "The use of oxygen in gasification". Special mention may be made of the important new process of B. A. S. F. for the production of acetylene by partial oxidation of gaseous hydrocarbons. Professor Bartholome has designed a special type of burner in which the speed of the gas at any place is higher than the flame velocity of the gas mixture. The oxidation is simply used here for the production of heat to support the formation of acetylene from methane. Further decomposition of acetylene to the elements is prevented by an instantaneous cooling of the products.

It is unnecessary to point out the value of the proceedings of such an important symposium on the specialised field of oxidation processes. Not only have new reactions evolved in recent years been published, but also valuable discussions of both theoretical and practical interest, which are included at the end of each paper. These discussions and papers shed much light on the characteristics of high temperature catalytic reactions and this should certainly prove helpful for those engaged in work on similar problems. Most of the papers discuss in elaborate detail the process, the equipments and their designs along with other chemical engineering considerations. There is no doubt that this special supplement should encourage a more adventurous and masterly approach to oxidation processes for

the manufacture of chemicals with due emphasis on their technological aspects.

H. V. K. UDUPA.

FERROUS PROCESS METALLURGY

By John L. Bray. Pp. X + 414. (John Wiley & Sons, Inc., New York, 1954), 6.50\$.

The first edition of "Ferrous Process Metallurgy" appeared in 1942 and ever since then it has been a popular textbook with the students and teachers of metallurgy at the University level and above. The book under review is a revised edition and is certainly an improvement over the previous edition. John L. Bray, late professor of Metallurgical Engineering, Purdue University and author of the book has made a memorial for himself in this book.

The present edition contains eight chapters while the previous edition contained 14. The subject matter deals mainly with American practice. The first chapter starts with a survey of world deposits of iron ore and covers beneficiation of iron ore with a bias towards heavy media separation and agglomeration, and emphasis on the sintering process. The first chapter also deals with fuels, fluxes, limestone and air very succinctly. 117 pages are devoted to blast furnace. The historical references are American. The chapter gives an adequate description of blast furnace and blast furnace practice including carbon refractories, blast furnace stoves, cleaning of blast furnace

gas and the chemistry of the blast furnace. Some recent trends in iron production like high-pressure operation of blast furnaces, oxygen enriched blast, the Wiberg Soderfors Process, Krupp-Renn Process etc., are very interestingly dealt with.

The chapter on basic open hearth occupies 100 pages and covers all aspects of basic open hearth steel manufacture. This chapter contains an interesting paragraph on the uses of radio-active tracers in metallurgy. Figure 72 in the previous edition "The basic open hearth process" summarizing the process need not have been omitted in the present edition. The chapters on Wrought iron, Bessemer process, Electric Furnaces and Ingots and Ingot moulds are very well written. An interesting description of continuous casting process is included in the chapter on ingots and ingot moulds. The chapters in the previous edition dealing with History, The metal iron, Cementation and crucible process, Scrap, Ferro alloys and Iron & Steel Industry in United States are omitted in the present one, but the more important topics of some of these chapters are incorporated in suitable places. Those familiar with the previous editions would however miss the bibliographies given at the end of each chapter.

The author rightly prefers simple line drawings to actual photographs for illustrating the various processes. Both students and teachers interested in ferrous process metallurgy will find a good friend in this book.

R. MALLIKARJUNAN,

ABSTRACTS

Catalytic Decomposition of Hypochlorite Solution by Iridium Compounds I. The pH-Time Relationship: Ayres G. H., and Booth M. H., *J. Am. Chem. Soc.*, **77**, 825 (1955).

The decomposition of sodium hypochlorite catalysed by iridium compounds has been studied with reference to the pH of the solution and the various possible reactions of hypochlorite have been discussed.

Catalytic Decomposition of Hypochlorite Solution by Iridium Compounds II. Kinetic Studies: Ayres G. H., and Booth M. H., *J. Am. Chem. Soc.*, **77**, 828 (1955).

The decomposition of hypochlorite was found to be a first order reaction and the reaction rate was approximately found to be doubled by a 10° rise in temperature in the range 20-40 C.

Ionization in Solutions of Nitrogen Dioxide in Nitric Acid from Optical Absorbance Measurements: Lynn S., Mason, D M., and Coreoran W. H., *J. Phys. Chem.*, **59**, 238 (1955).

Data obtained by measuring the optical absorbance of solutions of nitrogen dioxide in nitric acid at 0°C and 1 atmosphere have been applied to the study of ionization occurring in these solutions. In nitric acid solutions containing less than 1 formal weight per cent of nitrogen dioxide the nitrogen dioxide is said to be 70% ionized into nitrosonium (NO^+) ions, whereas the nitric acid is said to be 5% ionized with nitronium (NO_2^+) ions.

The Dissociation of Fluoborate Ion in Anhydrous Hydrofluoric Acid: Kilpatrick M., and Luborsky F. E., *J. Am. Chem. Soc.*, **76**, 5863 (1954)

The results of conductance studies on potassium fluoride and potassium fluoborate in anhydrous hydrogen fluoride are given to confirm the existence of the equilibrium $F^- + BF_3 \rightleftharpoons BF_4^-$.

Electrochemical Behaviour of Cation Exchange membranes in Liquid Ammonia: Bergin M. J., and Heyn H.A., *J. Am. Chem. Soc.*, **76**, 4765 (1954).

The applicability of cation exchange membranes in calculating cationic concentrations and also for determining the activity coefficients of salts in liquid ammonia, alcohol or water solutions has been indicated.

The pH in Chlorine-Caustic Electrolysis by the Mercury Cell: Barr L., *J. Electrochem. Soc.*, **101**, 497 (1954).

The influence of pH of the feed-brine on the reactions in a chlor-alkali cell of the mercury type is discussed and the range of pH suitable for the best efficiency is indicated.

Hydrogen Overvoltage on Bright Platinum: Schudinger S., *J. Electrochem. Soc.*, **101**, 426 (1954).

The influence of pH and salt effects on the hydrogen overvoltage on bright platinum was investigated. The rates of hydrogen-producing reactions at low current densities were determined. The mechanisms of overvoltage are discussed.

The Conductances of Some Potassium and Sodium Salts in Dimethylformamide at 25°: Ames D. P., and Sears P. G., *J. Phys. Chem.*, **59**, 16 (1955).

The conductance of dilute solutions of ten potassium and sodium salts in dimethyl formamide have been measured at 25°.

Electrical Conductance and Density of Molten Salt Systems. $KCl-LiCl$, $KCl-NaCl$ and $KCl-KI$: Van Artsdalen E. R., and Yaffe I. S., *J. Phys. Chem.*, **59**, 118 (1955)

Apparatus and the methods employed in the measurement of the electrical conductance and the density of the molten salt systems, $KCl-LiCl$, $KCl-NaCl$ and $KCl-KI$ are described. Observations on specific conductance, molar volumes and equivalent conductance isotherms are given. Heat of activation and entropy of activation have also been calculated.

Electrolyte-Solvent Interaction IV: Tetra-butylammonium Bromide in Methanol-Carbon Tetrachloride and Methanol-Heptane Mixtures: Sadek H. and Fuoss R. M., *J. Am. Chem. Soc.*, **76**, 5897 (1954).

Conductance measurements designed to bring out the effects of factors like density, dielectric constant, viscosity and index of refraction have been made. When another solvent is added to methanol the degree of association of the electrolyte decreases despite the accompanying decrease in dielectric constant. However, association increases when the dielectric constant drops below 25.

Electrolyte-Solvent Interaction V: Tetra-butylammonium Bromide in Ethanol-Carbon Tetrachloride Mixtures: Sadek, H. and Fuoss, R. M., *J. Am. Chem. Soc.*, **76**, 5902 (1954).

Behaviour opposite to that found in CH_3 , OH CCl_4 .

Electrolyte-Solvent Interaction VI: Tetra-butylammonium Bromide in Nitrobenzene-Carbon Tetrachloride Mixtures: Sadek, H. and Fuoss, R. M., *J. Am. Chem. Soc.*, **76**, 5905 (1954).

A more realistic model than the sphere in continuum is proposed so as to get a constant value for the size of the ion.

The Constitution of Ionic Liquids: The Electrical Conductivity and Viscosity of Molten Salt Systems: Harrap, B. S., and Heymann, E., *Trans. Faraday Soc.*, **51**, 259 (1955).

The systems $AgCl+AgBr$, $PbCl_2+PbBr_2$, $AgCl+PbCl_2$, $AgCl+KCl$ and $AgBr+KBr$ have

been studied with reference to temperature and molar composition. These systems do not show any compound formation in the solid state. The deviation of the equivalent conductivity isotherm from additivity is found to vary with the difference in both size and charge of the replacing ions.

Transference Numbers of Potassium Ion in Methanol and Ethanol Solutions: Smisko, J. and Dawson L. R., *J. Phys. Chem.*, **59**, 84 (1955).

Cation transference numbers have been determined at 25° in solutions of potassium bromide in methanol and of potassium thiocyanate in methanol and in ethanol from 0.0015 to 0.01 *N*. It is concluded that the solvation of the cation is greater in methanol than in ethanol or water.

Transference Numbers of Electrolytes under Pressure: Wall F. T. and Gill S. J., *J. Phys. Chem.*, **59**, 278 (1955).

A method of determining transference numbers of simple electrolytes under high pressures is described. It is an adaptation of the usual moving boundary method, the movement of the ions being followed by resistance measurements using probe electrodes.

Electrode Potentials in Fused Systems I. Sodium Hydroxide, Stern K. H., and Carlton J. K., *J. Phys. Chem.*, **58**, 965 (1954).

Potentials of silver, copper, nickel, cobalt and tungsten in fused sodium hydroxide were measured in the range 340-600°C using gold as reference electrode and potential-time curves were obtained. Potential changes are related to reactions occurring at the electrodes.

The Standard Potential of Silver-Silver Chloride Electrode in Methanol: Mukherjee, L. M., *J. Phys., Chem.*, **58**, 1042 (1954).

The standard potential of silver-silver chloride electrode in spectroscopically pure and dry ethanol has been measured by means of two types of cells without junction. The value +0.00977 volt differs in magnitude and sign from those reported by previous workers.

Solvents Having High Dielectric Constants I: Conductimetric Studies of Solutions of Hydrogen Chloride and Potassium Chloride in Formamide: Dawson L. R., Newell T. M., and McGreary W. J., *J. Am. Chem. Soc.*, **76**, 6024 (1954).

The conductances of hydrogen chloride and potassium chloride dissolved individually in formamide at various concentrations are reported.

Explosive Limits of Hydrogen-Chlorine Mixtures: Umland A. W., *J. Electrochem. Soc.*, **101**, 626 (1954).

Mixtures of gases typical of chlorine made by the electrolysis of salt were exploded to find the lower explosive limit for the concentration of hydrogen at pressures from 0 to 135 psi. It varied from 3.1 to about 8.1% hydrogen, depending on pressure and chlorine concentration.

Electronic Configuration in Electrodeposition from Aqueous Solutions: Lyons, E. H., Bailar J. C., and Laitinen H. A., *J. Electrochem. Soc.*, **101**, 410 (1954).

Metal deposition from complex ions of cobalt, nickel, copper and zinc was investigated. Deposits were obtained only from 'outer orbital' ions but not from ions supposed to have hybridized orbitals involving the penultimate electron shell.

Ion-Exchange Membranes I. Membrane Potentials: Graydon W. F., and Stewart R. J., *J. Phys. Chem.*, **59**, 86 (1955).

A method of preparing homogeneous ion-exchange membranes of the polystyrene sulphonate type is described. The membrane potentials have been measured and deviations from the ideal values are discussed.

Potentiometric Studies on Sodium Acetate-Sodium Perchlorate Systems in Acetic Acid: Higuchi T., Danguilan M. L., and Cooper A. D., *J. Phys. Chem.*, **58**, 1167, (1954).

The possible influence of salts having a common ion on the dissociation behaviour of a base such as sodium acetate in acetic acid has been studied. From the results obtained with sodium perchlorate as the added salt, it is conjectured that the sodium perchlorate undergoes greater dissociation than sodium acetate. It is also concluded that the practice of estimating pK values of acids and bases in water by determining the pH of half neutralised solutions cannot be applied to certain non-aqueous systems.

Conductance of Salts in 1 : 2 Ethylenediamine-Methanol Solutions: Dawson L. R., and Keely W. M., *J. Phys. Chem.*, **58**, 1066 (1954)

Conductances of silver nitrate, strontium bromide, potassium, silver and strontium iodides and magnesium, strontium and barium chlorides in the temperature range -20 to 20°C have been measured.

Tracer Electrophoresis II. The Mobility of the Micelle of Sodium Lauryl Sulfate and its Interpretation in Terms of Zeta Potential and Charge: Stigter D., and Mysels K. J., *J. Phys. Chem.*, **59**, 45 (1955).

The electrophoretic mobility of micelles of sodium lauryl sulphate in water and salt solution at finite concentration of micelle has been measured and the values extrapolated to infinite dilution. Corresponding zeta potentials and charges at the shear surface have been calculated. A roughness of the surface has been postulated to account for the discrepancy in the values of the zeta potential obtained this way and calculated from the charge of the micelle with a diffuse double layer.

The Behaviour of the Silver-Silver Chloride and the Mercury-Mercurous Chloride Electrodes at High Temperatures: Lietzke M. H., and Vaughn J. V., *J. Am. Chem. Soc.*, **77**, 876, (1955).

The performance of the above electrodes at temperatures from 25 to 263° is described. Evidence for the hydrolysis of calomel at low acid concentrations and high temperatures has been presented.

Thermodynamic Interpretation of Polarization Curves: Pourbaix M., *J. Electrochem. Soc.*, **101**, 217C (1954).

Several principles of the thermodynamic interpretations of polarization are enumerated and some applications are given.

Studies on the Anodic Polarization of Zirconium and its Alloys: Maraghini M., Adams G. B., and Van Rysselberghe P., *J. Electrochem. Soc.* **101**, 400 (1954).

Several aqueous electrolytes were employed in studying the anodic polarization of zirconium and its alloys. In chloride solutions, corrosion potentials were found to be below that of oxygen evolution. The formation of the oxide film was studied in detail.

The Electrochemical Polarization of zirconium: Hackerman N. and Cecil O. B., *J. Electrochem. Soc.*, **101**, 419 (1954).

Cathodic and anodic polarizations of zirconium in neutral sodium chloride solution have been studied at constant current densities of 3.5×10^{-8} to 3.5×10^{-3} amp/cm². In neutral sulphate solutions zirconium was passive under anodic treatment.

Application of Constant Potential Electrolysis to Organic Compounds: Part II—Preparation of Theophyllin by electrolytic reduction at constant cathode potential.

Urabe, N. and Yasukochi, K., *J. Electrochem. Soc. (Japan)*, **22**, 525 (1954).

8-chloro theophyllin has been reduced electrolytically at a constant cathode potential. The control circuit is made up of a 3-stage vacuum tube amplifier and a d. c. circuit with several 2A3 tubes. The constant cathode potential electrolysis was performed in a caustic soda solution with platinum anode and mercury cathode. Various cathode potentials viz., -0.3 v, -0.5 v, -1.2 v and -1.5 v. (ref. std. calomel half cell) were employed. The electrolysis at -0.3 and -0.5 v gave theophyllin. At -1.2 v, a reduction product having M. P. 165°C which is probably 6-oxy-desoxy theophyllin was obtained, which was also obtainable by reducing the -CO- group at the 6th position of 8-chlorotheophyllin. The electrolysis at -1.5v gave desoxytheophyllin.

The Effect of Ultrasonic Waves on the Electrodeposition of Copper: Wolfe, W. R., Chessin H., Yeager E. and Havorka F., *J. Electrochem. Soc.*, **101**, 590 (1954).

Polarization measurements indicate that ultrasonic waves produce a marked decrease in polarization, while x-ray diffraction studies show that they favour preferred orientation.

Influence of Impurities in the Electrolyte in Chlorine Caustic Electrolysis by the Mercury Cell Process: Angel G., Lunden T., Dahleuss, S. and Brannland, E., *J. Electrochem. Soc.*, **102**, 124 (1955).

An electrolytic cell for laboratory use with circulating brine and mercury was constructed to investigate the influence of metals on the cathodic current efficiency. Vanadium, molybdenum, chromium and titanium proved to be most harmful.

Electrolytic Reduction of Isobutyraldehyde in Acid Solutions: Sherlock Swann Jr., Onslott, E. I., and Baastad, F. H., *J. Electrochem. Soc.*, **102**, 113, (1955).

Reduction of aliphatic aldehydes having a branched chain in the α -position has been investigated. The effect of various cathode materials like cadmium, zinc, mercury and lead and of the physical condition of

the cathode on the reduction of isobutyraldehyde has been studied. In common with other straight chain aldehydes, isobutyl alcohol is the major products. Isobutane and isobutene are also formed in various proportions depending upon the physical factors

Polarography, Part I, Principles of Polarography: Baker, R. W. R., *Laboratory Practice*, **4**, 11-14 (1955).

The fundamental principles of polarographic analysis are described along with a simple circuit for conducting the same. Among the topics discussed are the proportionality maintained by the polarographic wave height to the concentration of electroactive ions in solution, the concepts of half wave potential and maxima, the significance of the Ilkovic equation, the formation of catalytic waves and the nature of the waves of organic compounds. A simple treatment of the anodic waves and the discharge of hydrogen ions at the dropping mercury electrode is also included.

Versatile Polarographic Cell: Pecsok R. L., and Juret, R. S., *J. Anal. Chem.*, **27**, 165-6 (1955).

When strongly basic or acidic solutions are analysed in conventional H-cells with agar plug, difficulties are encountered due to mixing. To tackle the same, a modification of the cell is described. There is a central compartment containing saturated potassium chloride solution, which is replenished from a reservoir with a stopcock arrangement. One of the limbs contains the calomel electrode with the usual agar plug and the other limb is connected with the central compartment by a sintered glass disc. An outlet for potassium chloride in the middle compartment has been provided. In this set-up, the diffusion of chloride ions is greatly minimised.

Polarographic Investigation of Organic and Inorganic Compounds in an Ammonia-Ammonium Nitrate Solvent: Leonard G. W., (Jr.) and Sellers D. E., *J. Electrochem. Soc.*, **102**, 95-97 (1955).

The utility of ammonia-ammonium nitrate as a non-aqueous solvent to study the polarographic behaviour of many substances is explained. The chief advantage is that a supporting electrolyte is not necessary. A shift in the half wave potentials is noted and yet the values are reproducible to ± 0.003 V. Well-developed polarographic waves conforming to the basic principles are obtained with substances like cadmium sulphate, lead monoxide, azobenzene, thiourea etc.

Polarographic Determination of Cadmium and Zinc in Zinc Sulphide-Cadmium Sulphide Phosphors, Deal S. B., *Anal. Chem.*, **27**, 118-20 (1955).

An easy polarographic method is described to estimate cadmium and zinc in a single determination. The diffusion currents of cadmium and zinc are measured in relation to the diffusion current of lead ion used as an internal standard. The base solution is 0.1 N potassium chloride and the maxima suppressor 0.005% methyl red and bromocresol green. Calibration graphs are obtained on performing experiments with the known standard solutions of cadmium, zinc and lead.

Analytical Applications of Barker Square wave Polarograph: Ferrot J., and Miliner, G.W.C., *Analyst*, **80**, 132-40 (1955).

A number of analytical problems tackled by using Barker Square wave polarograph and the advantages derived therefrom are given. Derivative type polarograms with the peaks indicating the constituents are obtained. The uses of this polarograph in alloy analysis and other special problems are indicated.

Potentiometric Titrations in Liquid Ammonia: Watt G. W., and Sonards D. M., *J. Electrochem. Soc.*, **102**, 46 (1955)

The titration of ammonium bromide with potassium and with potassium amide in liquid ammonia has been studied potentiometrically, with a view to finding out the optimum conditions for the use of the "Difference-Indicator" type electrode.

Colorimetric Determination of Manganese: Oxidation with Bromate in H_2SO_4 Medium: Purdy W. C., and Hume D. N., *Anal. Chem.*, **27**, 256 (1955).

A method for the colorimetric determination of Mn. in the centigram range is given. The authors first tried the method of Tomula and Aho in which manganous ion in a sulphuric acid solution is oxidized with bromate to the tripositive state, which was stabilized by complexation with syrupy phosphoric acid. But only the complex had an absorption peak at 500 μ . However, they found that Mn could be determined as the trivalent sulphate complex in strong H_2SO_4 . Manganous ion is oxidized to a trivalent sulphate complex with potassium bromate in 8M H_2SO_4 solution. The bromine produced both by the oxidation of Mn. and by the decomposition of bromate in strongly acid medium is discharged by the addition of cyanide to form cyanogen bromide, which otherwise causes an interfering colour. The complex measured at 500 μ in the spectrophotometer obeyed Beer's law over the range of 2 to 70 mg. of Mn per 100 ml. of the solution. The colour was stable for one week. Chromic ion which is difficult to remove shows 0.4% interference. Ions forming insoluble sulphates can be removed by filtration.

Determination of Hydrogen in Titanium: McKinley, T. D., *J. Electrochem. Soc.*, **102**, 117 (1955).

Construction, calibration and operation of an apparatus for a simple, rapid and precise method of determination of hydrogen in titanium and titanium alloys have been described. The method is based on the measurement of equilibrium pressure of the gas over the metal in a closed system. The theoretical range of the method is described as 0.0003 to 0.33% H, which can be extended to lower concentrations upto 0.00001% H_2 , with suitable alterations in the apparatus. Measurement has been made between 0.001% to 0.33% H, with a probable error of about 5.0%. The physical form of the sample is unimportant. Twenty analyses can be made in 8 hours.

Heavy Water from Geothermal Springs: *Overseas Engineer*, **28**, 309 (1955).

The U. K. Atomic Energy Commission has announced the formation of a new company called the Geothermal Development Ltd., in collaboration with the New Zealand Government for the production of heavy water from steam from the geothermal springs which abound in the Wairakei District of the North Island, New Zealand. The cost of the plant is £ 2-million and the electric power equipment will cost approximately £ 4 millions.

It is learnt that dry saturated steam at about 0.5 p.s.i. will drive three low pressure turbo alternators of approximately 11 MW each subsequently exhausting into jet condensers. Some of the power generated will be used to drive auxiliary steam compressors and cooling water pumps; the remainder will be supplied to the New Zealand grid. The output conditions of the turbo alternators will be 11,000 volts 3 phase 50. cycles. In addition, two back pressure sets of about 6 MW. rating will operate on dry saturated geothermal steam at inlet conditions of 180 p.s.i. and exhaust pressures of order of 50 p.s.i.

This steam will subsequently pass to the distillation unit which is designed by Head Wrightson Process Ltd., for the production of heavy water. Distillation unit will consist of 10 columns all approximately 200 ft. high and fabricated from $\frac{1}{2}$ " to $\frac{3}{4}$ " in M. S. plate. The largest column will be 13 ft. in diameter. The columns will be lagged and filled with expanded metal packing.

Production is expected to begin late in 1957. Artist's impression of the heavy water factory is given in the form of a good drawing showing the ten-column distillation unit and the probable outline of the first stage of construction.

Vapour Pressure Studies Involving Solutions In Light And Heavy Water: The Apparatus and the Determination of Vapour Pressures at 30° of Solutions of Sodium and Potassium Chlorides in Ordinary Water: Smith H.A., Combs R.L., and Googin J.M., *J. Phys. Chem.*, **58**, 997-99 (1954)

A description of the apparatus for the determination of the vapour pressures of solutions of NaCl and KCl relative to the vapour pressure of water is given. The gas saturation method is employed. A stream of nitrogen is passed through two efficient gas saturators and absorbers, each saturator containing 4 glass drum. of 25 mm. diam. which dip into the saturating liquid contained in 4 cells made of 38 mm. pyrex tubing each 7" long. The drums are rotated at a speed of 300-400 rpm. by a nickel plated rotating alnico magnet outside the saturator. The glass rotor exposes a film of solution to the gas stream. Efficiency is approximately 99%. The drying tubes or absorbers are fashioned from thin wall Pyrex tubing with Drierite covered with a layer of Anhydron. Nitrogen is passed through the apparatus, at a rate of 25 to 30 litres per hour. The drying tubes are weighed to ± 0.0004 gms. Gravimetric analysis of the salt solutions is carried out before and after each run. The vapour pressure of the salt solutions is calculated from the relation:

$$\frac{p_0 - p_1}{p_0} = \frac{m_0 (B + \Delta p_0) + p_0 (m_1 - m_0) - m_1 (B + \Delta p_1)}{m_0 (B + \Delta p_0) + p_0 (m_1 - m_0)}$$

where p_0 = saturated vapour pressure of pure water at the temperature of the thermostat, p_1 = vapour pressure of liquid in the solvents, m_0 = weight-gain of the

drying tube after the water saturator, M_1 = weight gain after the solution saturator; Δp_0 and Δp_1 are the pressure drops across the saturator-absorber combination for the pure water and the solution due almost entirely to the absorber. According to Raoult's law, a plot of $\frac{p_0 - p_1}{p_0}$ against mole fraction should give

a line which is essentially straight. The results show that this apparatus gives excellent agreement with the best data in literature.

Vapour pressure Studies Involving Solutions in Light and Heavy Water II: The Vapour Pressure of Heavy Water and the Separation Factor of the Mixed Waters: Combs, R. L., Googin, J. M., and Smith, H. A., *J. Phys. Chem.*, **58**, 1000-1001 (1954)

The gas saturation method as described above is used to measure the vapour pressure of pure deuterium oxide at 10 to 55° C. One of the two saturation is filled with distilled water and the other with D₂O. For measurement of the separation coefficient ∞ one of the saturators is filled with distilled water and the other with a mixture of the two waters. The analysis of the deuterium content of the water is done by the falling drop method.

Russia's New Caustic Soda Process: *Chem. & Process Eng.*, **36**, 151 (1955)

A competitive method for the production of caustic soda has been developed in Russia starting from sodium sulphate and pyrolusite. Sodium sulphide obtained by reduction, is treated with pyrolusite under certain conditions to obtain nearly 12% caustic soda.

The production of Beryllium and the Sheer Kormann Process: *J. Four Elec.* (1955)—No. 1, pp 16-17.

This article, after giving a brief summary of the various processes for the production of beryllium like Vivian's process, describes what is known as the "Sheer Kormann High Intensity Arc Process" for the production of beryllium metal.

Beryllium in the ores, is volatilised at the very high temperature of the arc of nearly 8000–11000° C as beryllium chloride by making it react with chlorine under pressure. The pure beryllium chloride thus obtained is electrolysed to get pure beryllium metal and the anodic chlorine evolved is recycled for chlorination.

The Preparation of Samarium Metal with Calcium: Onstott E. I., *J. Am. Chem. Soc.*, **77**, 812 (1955).

High purity Sa metal was prepared by reducing the oxide of the metal with an excess of calcium in a tantalum vessel under vacuum or in an atmosphere of argon at 1000° C. The samarium and excess calcium were co-distilled in a vacuum of less than 1μ at 1050–1100° C for 30–40 min. High purity Sa was obtained in 40% yield.

Chlorination of Travancore Monazite—Part II —Separation of Thorium from Rare Earths with Urotropine: Sarma, B., and Gupta J., *J. Sci. Ind. Research (India)*, **14B**, 82 (1955).

An investigation was made of the suitability of a urotropine-hydrochloric acid buffer for the separation

of thorium from the rare earths in the product obtained by the chlorination of monazite. Thorium hydroxide begins to precipitate from the solution at a pH as low as 2 at a 0.1M concentration of urotropine. The rare earths except tetravalent cerium do not undergo hydrolysis in these buffer mixtures upto pH 5. The precipitated thorium hydroxide was free from the rare earths, but contained uranium which however could be easily removed either by digesting the precipitate with a hot solution of ammonium carbonate or by reprecipitating thorium with oxalic acid from an acid solution. An overall efficiency of 85% for thorium recovery and 95% for the rare earths was obtained.

Metallic Rectifiers Approach Infinite Life: Rockett, F., *Electronics*, Vol. 28, No. 3, p. 162 (1955).

The developments in selenium, silicon, germanium and titanium-dioxide rectifiers are described. New designs give high temperature operation, reduced size and efficiencies upto 98% at normal ratings.

Electrodeposition of Cellulose: Mantell C. L., and Cozzarolli, F., *J. Electrochem. Soc.*, **102**, 110 (1955).

The aqueous plating bath suggested consists of 0.5–2.5% cellulosic material dissolved in a solvent mixture of NaOH (7 to 15%) ZnO (2% to saturation) and urea (6–10%). Chemicals like cyanamide, guanidine and guanylurea, which hydrolyse with alkali or zincates to form urea are mentioned as substitutes for urea. The authors have reported that cellulose could be plated from this bath (at room temperature) on a copper, bronze, or lead anode at an optimum c.d. (anode) of 0.137–1.11 amp./ft² and cell voltage of 1.10–1.28 V. At higher c.d. zinc was found to get deposited at the cathode. Increasing the cellulose concentration improved the current efficiency which decreased as the c. d. increased. The average c. e. obtained was 1.99–3.30%. The deposit of cellulose after stripping resembled a soft tissue paper about 0.006" thick and fragile. The suggested applications are wire insulation or coating of wire mesh, preparation of thin paper etc.

Anodising of Aluminium—Recent Advances: *Light Metals*, **18**, 91–93 (1955).

Two papers presented at a meeting of the London Section of the Institute of Metal Finishing held on January 17, namely "Some aspects of Sulphuric acid Anodising to DTD 910C" by V. F. Henley and "Some Recent Advances on Anodising" by A. W. Brace are discussed in brief.

Choice of electrolyte, importance of agitation difficulties connected with black anodised finishes and dimension changes on anodising are given. The process for bright anodised finishes is briefly described. Characteristics of anodic films and factors affecting the coating ratio are discussed.

It is suggested that anodic oxidation in sulphuric acid should be carried out at a higher voltage, say 20 V and using a more dilute solution, than at the conventional voltage of 12. Another suggestion made is that the possibility of producing enamel like finishes by using the chromic acid process should be exhaustively studied.

Heavy Oxide Coating for Aluminium: Dickinson, T. A., *Materials & Methods*, Vol. 41, No. 2, pp. 132–133 (1955).

This paper deals briefly with the method developed by Sanford Process Co., Inc., Los Angeles, to get hard oxide films on aluminium which are useful for high wear and corrosion resistance. The new process is said to give thicker films in a shorter time. These films are particularly useful in pistons, valves, cans, abrasion strips etc. The coating produced by Sanford Process have a measured Rockwell hardness ranging from C50 to C58, and a Mohs scratch hardness of about 8. Thick coatings can withstand upto 4000 V.

The details of the process are not disclosed as yet. The process uses a mixed electrolyte, a mineral acid and organic acid. Bath temperature is 0–15° F. Voltage ranges from 15–150 d. c. and the c. d. used is 12–15 amp / sq. ft.

The Plating of Powder-Metallurgy Bronze Parts: Raymond, E. V., Folly, R. T., and Chu, W. L., *Plating*, **42**, 150–151 (1955)

The various difficulties experienced in plating powder-metallurgy compacts are described. A brief review of the literature in regard to avoiding the absorption of cleaning and plating solutions and subsequent "spotting out" is given. For plating powder-metal bronze compacts with tin, impregnation with silicone, volatilization of residual salts and choking of the pores by immersion tin plating before electroplating with tin failed. Mechanical closure of the pores by cold working has been judged to be too expensive. The authors have found the oil impregnation method to be quite satisfactory. The sequence is given as follows.

After removing objectionable surface films by grit blasting with a fine abrasive, oil is impregnated by immersion in lubricating oil at 100°C. the time of immersion being not critical. Then the oil is cooled artificially to room temperature and the work withdrawn from it. The external oil is removed by agitation in a mild soap solution at 50°C and subsequently plated with tin from a conventional sodium stannate bath when an adherent porous plate which does not show "spotting-out" is obtained. 6 references, 2 photo-micrographs.

An Apparatus for Electropolishing Specimens for Metallographic Examination: Synkes, E. C., Hardrell, V. J., Haines, H. R., and Molt, B. W., *J. Inst. Metals*, **83**, 166–168, (1954–55).

The microstructure of uranium can be accurately interpreted by examination under polarised light after electropolishing. The electropolishing of uranium necessitates the continuous removal of the anodic layer during the process. If not, flow patterns are formed on the surface of the specimen due to the flow of gas. Many methods of removing the anodic layer have been tried and the machine with which this has been successfully carried out is described. In this apparatus the anodic layer is removed by injecting the electrolyte, through a horizontal nozzle inserted just above the uranium cathode, with the help of a centrifugal pump made of polyethylene. A schematic diagram of this unit is given. Compositions of four electrolytes useful for the electropolishing of uranium are given. 6 references.

Metal Cleaning with ultrasonics: Morris, M., *Metal Finishing*, Vol. 53, No. 2, pp. 63–64 (1955).

Ultrasonic sound waves are produced by instruments called transducers. These are brought into action by the influence of electricity. The favourite transducers are magnetostriction vibrators, quartz crystals and polarised poly-crystalline ceramics notably barium titanate. Of these polarised barium titanate has been found to be the most economical and most efficient type of transducer to use, both from the standpoint of construction cost and operation. When the transducer is brought into action it propels sonic energy with tremendous force in liquid layers and thereby set-up pressure fluctuations of considerable magnitude. Under such condition the liquid (trichlorethylene, perchlorethylene or alkali solution) is torn apart, bubbles of empty space come into being and subsequently the cavities collapse violently. This process is called cavitation. Cavitation gives the metal parts a scrubbing action and removes tripolis, rouges and other contamination which is relatively thick. A diagram is given illustrating the sequence of ultrasonic cleaning. The cleaning cycle is given as, precleaning by immersion, spray, vapour or any combination thereof; then subjecting to ultrasonic action to remove the last vestige of contamination either on the surface or in the recesses followed vapour degreasing.

Electrolytic Regeneration of Spent Pickling Solutions: Bramer, H. C., and Coull, J., *Ind. Eng. Chem.* **47**, 67 (1955).

The results of the laboratory investigation of a process for the electrolytic regeneration of spent sulphate pickling solutions are presented. The process makes use of selectively ion permeable membranes to separate the solution from the recovered acid so that ion deposition can occur in a low acid environment. The important operating variables are discussed.

The Role of Electric arc Furnace in Utilizing some Strategic Off-Grade Ores: Banning, L. H., *J. Electrochem. Soc.*, **101**, 613–621 (1954).

A clear analysis of the advantages of arc furnace smelting for the treatment of low grade ores is discussed with special reference to low grade, chromium, manganese, nickel and aluminium ores. Operating details for the 3-phase arc furnace for treating these ores are given. 10 references.

Electrolytic Preparation of Molybdenum from Fused salts: Senderoff, S., and Labrie, R. J., *J. Electrochem. Soc.*, **102**, 77–80 (1955).

This is the fourth paper in the series on the electrometallurgy of molybdenum. A scheme is presented, for the production of molybdenum metal from the ores. Molybdenum pentachloride, obtained by the chlorination of molybdenite, is reduced in the next stage to trichloride by paraffin-hydrocarbon-reduction. This is electrolysed in the fused state to obtain the metal. 4 References.

Extraction Metallurgy of Zirconium by Electrolysis of Fused Salts: III—Expanded Scale Process Development of the Electrolytic Production of Zirconium from K_2ZrF_6 : Raynes, B. C., Thellmann, E. L., Steinberg, M. A.

and Wainer, E., *J. Electrochem. Soc.*, **102**, 137 (1955).

Successful large scale operation of the electrolysis of K_2ZrF_6 in an electrolyte of fused $NaCl$ to produce Zr , in a cell producing 3-4 lbs. of the metal per run, followed by that of another producing 30-40 lbs. of Zr per run, has been described. Zr powder of high purity capable of giving, on consolidation, metal having fabrication properties comparable to those of Kroll Process Zr , has been reproducibly obtained at commercially acceptable current efficiencies. Further expansion to larger scale operation has been envisaged.

Bottom-Pour Furnace for Casting Titanium: Simmons O. W., et al, *Light Metals*, **18**, 11-12 (1955).

After explaining the chief disadvantages and difficulties in melting and casting of titanium, with other types of furnaces, the authors describe at length an arc furnace for this purpose with sketches. The inert atmosphere is maintained with a mixture of argon and helium (1:8). Operating details are given.—8 References.

Heat Treatment of Titanium alloys: Jaffe, L. D., *Metal Progress*, Vol. 67, No. 2, p. 101 (1955).

Titanium and its alloys were at first generally regarded as not amenable to heat treatment. Recent work has shown that this is not the case. This article makes an attempt to correlate the changes in properties and phase changes that take place on heat treatment.

Zirconium: Miller G. L., *Iron and Steel (London)*, **28**, 19-25 (1955).

The various methods for the production of the metal like the iodide process, the Kroll process etc., are reviewed with sketches of the equipments employed. Methods of melting and working with the metal

are outlined. Various applications of the metal are summed up with a brief account of its chemical and physical properties—32 references.

Germanium & Silicon for Electronic Devices: Rugare A. S., *Metal Progress* II, **67**, 87-91 (1955).

Several details about the two important semi-conductors germanium and silicon are described in this article. A good account is given of their extraction, processing of the impure metal by the latest technique of "Zone refining" (illustrated), to obtain hyperpure metals and crystallisation. Finally, a critical and comparative study of these two semi-conductors is made with special reference to their applications like transistors and solar batteries.

Carbon—A Neglected Metallurgical Tool: Swartz, C. E., *Metal Progress*, Vol. 67, No. 2, pp. 77-81 (1955).

Various applications of carbon and graphite in metallurgy are discussed. After surveying the sources and method for the manufacture of graphite an account is given of bonding and bonding materials for graphite. Several metallurgical operations employing graphite are mentioned. By far the most promising application of graphite is its use as moderator and reflector in nuclear reactors owing to its low thermal-neutron absorption.

The Production of Uranium at Spring Fields: *Ind Chemist*, **31**, 193-194 (1955).

Abstract of a paper given by Sir Christopher Hinton at a meeting of the Institute of Chemical Engineers in Manchester. The various stages in the extraction of uranium, viz. the dissolution of the ore, peroxide precipitation, conversion into the ammonium-di-uranate and finally into uranium fluoride are all described. The metal is obtained from the fluoride by reduction with calcium metal.