



The William Blum Lectures

#15 - George Dubpernell - 1974



**The 15th William Blum Lecture
Presented at the 61st AES Annual Convention in Chicago, Illinois
June 17, 1974**

Electroplating, Electrochemistry and Electronics

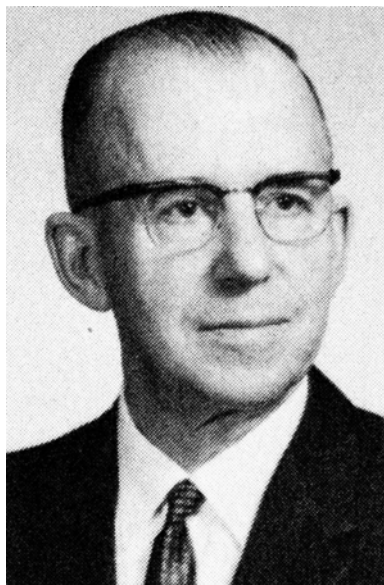
by

George Dubpernell

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Editor's Note: Originally published as *Plating & Surface Finishing*, **62** (4), 327-334 (1975), *Plating & Surface Finishing*, **62** (5), 436-442 (1975) and *Plating & Surface Finishing*, **62** (6), 573-580 (1975), this article is a re-publication of the 15th William Blum Lecture, presented at the 61st AES Annual Convention in Chicago, Illinois on June 17, 1974.

ABSTRACT

A brief review is given of the history of the electrodeposition of metals and of the formation of the American Electroplaters' Society. The extent of the commercial plating of different metals is discussed. A new point of view is given on the nature of electrode potentials, including some new experimental data and examples of the place of hydrogen overvoltage in metal deposition. It appears that "overvoltage" is probably an electronic property of the surface of the electrode, and may be intimately related to the "surface states" commonly postulated in electronics. If the suggested relationship is correct, overvoltage measurement may possibly provide a new tool for electronic studies of metal and probably also semiconductor surfaces. Some of the relatively close relationships which exist between electroplating, electrochemistry and electronics are pointed out.

Historical

Electroplating had its beginnings in 1800, as soon as Volta announced the discovery of the voltaic pile, or primary battery, as a source of power.^{1,2} Thus, plating was a battery powered industry for almost a century, and it was not until around 1880-1900 that direct current generators took over the major portion of the power supply. Following the introduction of commercial nickel plating in 1869-1870,³ it was not long before dynamo electric machines started to be used on a small scale.

Edward Weston was quick to seize this opportunity and to fill the need, particularly since he failed to break the patent monopoly on nickel.³ Abraham Van Winkle was one of his backers.⁴ Thus, the 1876 catalog of Condit, Hanson and Van Winkle featured the Weston Dynamo-Electric Machine in four sizes. The names of over 30 purchasers of the machines were listed, and in just a few years these numbered in the hundreds.

A Metal Polishers Union was formed in 1880 by Charles Ernest of the Michigan Stove Company, with Local No. 1 in Detroit, Michigan.⁵ This union was at first part of the Knights of Labor, but in 1889 became affiliated with the American Federation of Labor, and later on, probably in the 1930s, also with the C.I.O. It published a monthly *Metal Polishers Journal* beginning in 1890, and this magazine continues right down to the present under the title *Metal Polisher, Buffer and Plater*. However, this journal is confined almost entirely to union matters, with only an occasional technical article, generally a reprint from other sources.

The American Electroplaters' Society was formed by Charles H. Proctor and others to meet the needs of foreman platers for more knowledge of chemistry and electrochemistry. Mr. Proctor presented a paper on the electrodeposition of brass in 1907 at the first convention of the newly formed American Brass Founders' Association, a splinter organization of the American Foundrymen's Association, and suggested the formation of another sub-group, a Platers and Polishers Association.⁶ This suggestion was favorably received, but Mr. Proctor decided that it would be better to form an entirely independent organization, which he succeeded in doing in March and April, 1909, the National Electro-Platers' Association of the United States and Canada (NEPA).⁷

The American Foundrymen's Association dropped its activities directed to the formation of a platers sub-group as soon as the NEPA was successfully launched. The NEPA was converted to the American Electroplaters' Society as of June 1, 1913.⁸

The newly-formed National Electro-Platers' Association (NEPA) divorced itself completely from the Metal Polishers Union.⁹ The 30,000 member union tried to discourage the growth and activities of the new Society for several years, but the Society adhered firmly to its educational goals and maintained its separate existence. This situation explains why the early lists of Branch officers included a sergeant-at-arms who was posted at the door of the meeting place and checked to see that only bona fide members entered.

Another pre-AES publication was a little supply house magazine called *The Plate* and published monthly from January, 1909, to October, 1909, by the Dow Chemical Mfg. Co. of Mansfield, Ohio, unrelated to the Dow Chemical Mfg. Company of Midland, Michigan. This little magazine was edited to a considerable extent by Herbert J. Hawkins, but seems to have been discontinued when it became apparent that the new NEPA would soon be publishing a journal, something which actually came to pass about a year later, in the fall of 1910.

The Periodic Chart

A long-period chart of the elements, most suited for use in electroplating studies is reproduced here (Fig. 1) with the most recent changes and additions included. When this chart was first published by the writer in 1946,¹⁰ he had been using it regularly from 1926 on. In the meantime, similar charts were published by Ellingham^{11,12} and Blum.¹³ In discussing the writer's chart, Dr. Blum was kind enough to call it "the plater's road map," which indeed it is.

PERIODIC CHART FOR THE ELECTROPLATER

																		1	2												
																		H	He												
																		3	4	5	6	7	8	9	10						
																		Li	Be	B	C	N	O	F	Ne						
																		11	12	13	14	15	16	17	18						
																		Na	Mg	Al	Si	P	S	Cl	A						
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr														
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54														
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe														
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103															
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw															

METALS EASILY ELECTRODEPOSITED

Figure 1 - Periodic chart emphasizing the metals easily electroplated at high current efficiency from aqueous solution.

By means of this chart one can obtain some guidance as to the probable plating behavior of a given metal, and the best choice of solution composition for obtaining deposits of it. This is done primarily by analogy to the already known chemistry and physics



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of the neighboring elements.¹⁴ Similarly, elements close to each other in the chart are more likely to deposit together as an alloy from a mixed solution, than elements at a distance from each other.

It is interesting that it appears that the more newly-discovered elements give promise of being readily electrodeposited from aqueous solution. Thus, there was speculation on the possible discovery of element No. 112.¹⁵ If this is confirmed, the new element would occupy a position under mercury, No. 80, and presumably would be easy to isolate by electrodeposition.

The consumption of metals in electroplating

The various metals deposited commercially in the United States will be discussed in alphabetical order. While there are changes from time to time, these are generally slow in arriving, and on the whole the figures are remarkably stable from year to year. Some discussion of the electrolytic production of metals is included, but electrolytic refining is omitted.

The sources of information on the annual consumption of metals in electroplating are quite limited; frequently one is restricted to the personal estimates of individual experts having some knowledge. Even these may vary widely and merely serve to indicate the order of magnitude.

The chief sources of information are the annual report of the U.S. Bureau of Mines on the Mineral Industry in the *Minerals Yearbook* and the *Metal Statistics* published annually by the American Metal Market Company. These are useful for total metal production, and also have the consumption in electroplating in some instances. In some cases the % of the production used for electroplating is known approximately and can be used for an estimate.

An excellent review was given by F.T. Taylor in 1929.¹⁶ Dr. Blum gave a few figures in 1953.¹⁷ A more recent German review has some information.¹⁸ Sometimes an article will give information on an individual metal, but this is not common. The writer made surveys of United States consumption in 1953 and 1968 which form the basis for the summaries below.

Brass

An estimate of 1,000,000 to 1,200,000 lb./yr. was given for 1968 by the True Brite Chemical Products Company. This is used largely on such items as builders' hardware and light fixtures. Brass plating is an old industry dating back to the introduction of cyanide solutions, and a patent of von Ruolz in 1841. Currently, a white brass plate is also used as one of the undercoats for decorative chromium plating.¹⁹

Cadmium

The Udylite Corporation gave a figure of about 7,200,000 lb. of cadmium used for plating in 1968, and 6,871,000 lb. in 1953. The latter figure checks with a 1953 estimate from the U.S. Bureau of Mines of 6,500,000 to 7,000,000 lb. The stability of these figures reflects the fact that the cadmium available is mainly a by-product of zinc production, and thus limited. Cadmium is used as a silvery-appearing rustproof plate. Its use began about 1920, and Taylor gave a consumption of about 1,300,000 lb./yr. in 1929.¹⁶ Dr. Blum estimated about 4,000,000 lb./yr. in 1948.¹⁷

Chromium

M&T Chemicals Inc. indicated that about 35,000,000 lb./yr. of chromic acid was used for chromium plating in 1968, compared to a figure of about 20,000,000 lb./yr. in 1953 from the Mutual Chemical Company. A still more recent estimate is that about 40,000,000 to 42,000,000 lb. of chromic acid was used for chromium plating in 1971. This is based upon about 80-81% of the production being used in plating (90% for metal finishing and 90% of that for chromium plating). An annual production figure is given by the U.S. Department of Commerce.²⁰ The figure for 1972 would indicate roughly about 44,000,000 lb. of chromic acid used for plating in 1972.

Chromium plating started in 1924, and prior to that time only a few pounds per year of chromic acid were used, and it was imported at a high price. The growth in total chromic acid consumption has been almost linear since 1924, at an annual increase of about 1,000,000 lb./yr., with a tendency to a higher growth rate of more like 2,000,000 lb./yr. in the past ten years.²¹ Dr. Blum estimated about 15,000,000 lb./yr. of chromic acid consumed in plating in 1948.¹⁷



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Flake electrolytic chromium metal is also produced and used in the production of high-chromium alloys, and for the final adjustment of the composition of stainless steel. The process was developed by the U.S. Bureau of Mines and consists basically of the electrolysis of chromium ammonium sulfate solution with stainless steel cathodes, from which the electrolytic chromium is flaked off every three or four days. The Union Carbide Corporation started producing about 4,000,000 lb./yr. in 1954,²² and this was later increased to about 6,000,000 lb./yr. by increasing the size of the cathodes to make more complete use of the solution depth available. Some electrolytic flake chromium metal is produced similarly in Japan and Russia.

Cobalt

While the electrodeposition of cobalt and its alloys has been the subject of research for a long time, the commercial use was somewhat restricted by the cost, generally about double that of nickel. Usage has developed in magnetic coatings for memory devices, and to replace nickel during nickel shortages. The Cobalt Information Center reported the use of about 165,000 to 220,000 lb./yr. in 1968, plus about 55,000 to 66,000 lb./yr. for electroless plating.

Copper

Copper plating has been used from the beginning, but the various fields are very diverse and include electrotyping as well as electroplating, electroforming, electrolytic foil production for printed circuits and other purposes, and electrolytic powder production, and the total annual consumption is relatively unknown. Taylor¹⁶ estimated about 1,000,000 lb./yr. in 1929. This seems rather low as the yearbook of the American Bureau of Metal Statistics gave 14,000,000 lb./yr. in 1928 for "plated ware" of all types.

Dr. Blum estimated¹⁷ about 28,000,000 lb./yr. in 1948 (1% of total copper consumption), and this seems a valuable indication of the right order of magnitude. The American Brass Company estimated the use of copper for electroplating and electroforming in 1953 to be between 12,000,000 and 15,000,000 lb./yr. from their knowledge of copper anode sales.

Amax Copper, Inc., gave a total in 1962 of about 9,775,000 lb./yr. for alkaline copper plating, and 12,050,000 lb./yr. for acid copper deposition; a complete total of 21,825,000 lb./yr. for 1962. In 1968 this same source estimated 20,300,000 lb./yr. for various metal finishing uses, and a grand total of 38,600,000 lb./yr. including 6,200,000 lb./yr. for foil production, but not including electrolytic copper powder. The Copper Development Association, Inc., estimated 11,500,000 lb./yr. of copper for foil production in 1968. The electrolytic copper powder production was given as about 12,000,000 lb./yr. in 1957.

It is traditional in the copper industry to estimate about 1% of the annual production for electrodeposition purposes; on this basis about 40,000,000 lb./yr. would have been used in 1970 and 1971.

Gold

Technic Inc. estimated gold consumption in electroplating as about 20,000 lb./yr. in 1953, and about 170,000 lb./yr. in 1968. A report²³ of the National Materials Advisory Board gives an approximate indication of quantities of gold used by electroplating in various fields. From this we can estimate about 131,500 lb./yr. in 1967 and 137,000 lb./yr. in 1968. A forecast of about 190,000 lb./yr. is given for 1973.

Iron

The use of electrodeposited iron has varied considerably from time to time. There was formerly a substantial electrolytic iron powder production but this is now negligible and has been replaced by other methods. In 1968 the Van Der Horst Corporation of America were using about 100,000 lb./yr. of iron as an undercoat for hard chromium plate. The Bureau of Engraving and Printing in Washington, D.C., was using about 3500 lb./yr. for printing plates in 1968. The National Cash Register Company calculated that about 75 lb./yr. of iron was consumed in iron-nickel alloy plate in 1968 for computer memory devices and for plating over 30,000,000 ft./yr. of beryllium copper wire. Allied Research Products, Inc., reported about 1000 gal. of iron sulfamate solution in use in 1969. According to the SKC Corporation about 8,000,000 lb./yr. of electrolytic iron flake metal for the production of special alloys was used in 1968, but was largely imported, and domestic production was being dropped.



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Lead

According to the U.S. Bureau of Mines, the use of lead plating is decreasing. They gave a figure of about 1,974,000 lb./yr. in 1953, and 778,000, 812,000 and 534,000 lb./yr. in 1968, 1969 and 1970, respectively. In addition, a consumption of about 4,000,000 lb./yr. was estimated in 1953 in hot galvanizing, and about 6,400,000 lb./yr. in the production of terneplate. A major use at present is in lead-tin alloy plate for printed circuits.

In contrast to the above, Dr. Blum estimated lead plating in 1948 as 22,000,000 lb.¹⁷ The Lead Industries Association, Inc., gave a figure of 1,400,000 lb./yr. for 1968 for lead plating.

Manganese

Manganese has not found use in plating, but nearly all of the metal used to alloy with other metals is produced electrolytically. The U.S. Bureau of Mines reported that the consumption of such electrolytic flake manganese was about 51,406,000 lb./yr. in 1968.

Nickel

Figures for the consumption of nickel in electroplating from 1876 to 1958 were given previously.²⁴ This has grown constantly in spite of irregularities in the supply and increasing prices. The consumption was given as 50,866,000 lb./yr. in 1968 by the U.S. Bureau of Mines. The corresponding figure for 1972 was 57,844,000 lb./yr. The world consumption of nickel for electroplating in 1971 was about 131,000,000 lb./yr., about 16% of the total nickel production.²⁵ Originally, in 1869 practically all of the nickel produced was used for plating, and in 1890 this was still about 90%, but now the production of alloys such as stainless steel and other uses take the bulk of the nickel, although the % used for plating is increasing currently.

Palladium

Engelhard Minerals & Chemicals Corporation estimated that about 30 lb./yr. of palladium was used in 1968 on electrical contacts and as an electrode catalyst.

Platinum

In 1953, Baker & Company estimated that about 70.6 lb./yr. of platinum was used in plating. Engelhard Minerals & Chemicals Corporation estimated that about 125 lb./yr. of platinum was used for plating in 1968, mainly as an electrode catalyst.

Rhodium

Baker & Company estimated the use of rhodium for plating in 1953 as about 1000 lb./yr. In 1968, Engelhard Minerals & Chemicals Corporation gave a rhodium consumption of about 625 lb./yr. Rhodium plate has been used for jewelry and reflectors.

Silver

In 1929, Taylor¹⁶ stated that 17% of the silver sold for industrial uses was consumed in plating. Another source gave 15% of the consumption in 1929 for plating, or 282,000 lb./yr. On the same basis, 1,000,000 lb./yr. was estimated in 1951. Dr. Blum¹⁷ gave a figure of 700,000 lb./yr. for 1948. The American Bureau of Metal Statistics estimated 875,000 lb./yr. in 1953. The U.S. Bureau of Mines gave 1,050,000 lb./yr. as the consumption in 1968. Thus, it is apparent that the amount of silver plating has been steady at around 1,000,000 lb./yr. for several decades.

Tin

Taylor¹⁶ discussed the use of tin plating in 1929, but did not give a figure for the tonnage of tin consumed. Some idea of the extent of these miscellaneous uses of tin plating can be formed from the fact that the Tin Research Institute, Inc. estimated them roughly 3,500,000 lb./yr. in 1953.

The production of tinplate (strip steel sheet coated with tin) underwent a revolution in World War II days, beginning in the late 1930s. Previously only hot dip tin was used, but electroplating the strip in either acid or alkaline tin plating baths offered substantial economy in the use of tin. This is such a large industry, however, that the amount of tin used in electroplating increased radically, and, in fact, it became the largest single metal electroplate, even exceeding the annual consumption of nickel in electroplating.

Thus, Dr. Blum estimated about 27,000,000 lb./yr. of tin used in plating in 1948.¹⁷ The Tin Research Institute estimated about 33,400,000 lb./yr. used in the production of electrotinplate in 1953, plus about 3,500,000 lb./yr. for miscellaneous tin plating, giving a total of about 37,000,000 lb./yr. for tin plating in 1953. In 1968 the indication was for 66,414,000 lb./yr. of tin for tinplate, 4,200,000 lb./yr. miscellaneous uses, 1,400,000 lb./yr. in lead-tin alloy plate, and 200,000 lb./yr. in tin-nickel and tin-copper alloy plates, giving a final total of 72,214,000 lb./yr., not including chemicals used in making up plating baths.

The consumption of tin in tinplate production has been dropping, probably due to increasing use of tin-free steel (TFS) having a very thin chromium plate. Thus the Bureau of Mines figures have been 53,772,000; 50,254,000; 47,338,000; and 38,652,000 lb./yr. for 1969, 1970, 1971 and 1972 respectively.

Zinc

Taylor¹⁶ gave the amount of zinc used in zinc plating as certainly more than 20,000,000 lb. in 1929. Morral²⁶ gives a zinc consumption in plating during the 1930s varying from about 4,000,000 lb./yr. in 1933-1934 to over 12,000,000 lb./yr. in 1940. Dr. Blum¹⁷ gave a figure of 32,000,000 lb./yr. in 1948, 2% of the total zinc consumption. In 1953, the American Zinc Institute estimated 30,000,000 lb./yr., but Dr. Saltonstall considered this figure quite low. In 1968, the Zinc Institute, Inc. estimated the use of 10,000,000 lb./yr. of zinc for rustproofing various parts, but excluding the electrogalvanizing of steel sheet and wire. The Zinc Development Association estimated 60,000,000 to 80,000,000 lb./yr. of zinc used for plating in the entire world, from which one might estimate about half used in the United States or 30,000,000 to 40,000,000 lb./yr.

The difficulty with figures on zinc is that the amount used in plating steel sheet and wire is unknown. The amount of zinc used in hot-dip galvanizing has been approaching 1,000,000,000 lb./yr. in recent years, and thus completely dwarfs the amount of zinc applied by electrogalvanizing. The quantity of zinc used in electrogalvanizing is not recorded separately, and is merely included as an unknown fraction of the total used in both hot and electrogalvanizing for rust proofing purposes.

The double standard of electrode potentials - pH and reference electrodes

The pH scale

It is not commonly realized that the pH scale is primarily a scale of the potential of the platinized platinum hydrogen electrode in acid and alkaline solutions, and thus a second and separate scale of electrode potentials. The history of the creation of the pH scale has to be examined carefully to make this clear.²⁷

The behavior of platinized platinum in acids and alkalis was known in the 1800s. However, it was not until 1893-1894 that LeBlanc^{27a} and Smale^{27b} proposed its use as a reference electrode, and felt that they showed that it was reversible with reference to the solution and to the deposition of hydrogen. Nernst^{28,29} seems to be silent on this, although he was responsible for the acceptance of the normal hydrogen electrode as the zero of electrode potential,³⁰⁻³² instead of the calomel electrode as recommended by Ostwald.

The strength of various acids and bases was investigated in 1878-1894 by Ostwald, Arrhenius, and Nernst,²⁸ among others (reference 28, pages 606-609). In 1895, LeBlanc³³ gave a good summary of the situation (reference 33, pages 178-181). He

pointed out that the potential difference between two hydrogen electrodes, one in a normal solution of acid and the other in normal alkali, was 0.81V at 18°C and that the acid would be about 0.8 normal in hydrogen ion.

He calculated that the concentration of hydrogen ions in the alkali would be 0.8×10^{-14} , while that of the hydroxyl ions would be about 0.8 normal. From this he calculated further that pure water would be about 0.8×10^{-7} normal with regard to both hydrogen and hydroxyl ions.

Nernst (reference 28, pages 598-600) discusses the electrolytic dissociation of pure water, and points out that it was determined by a variety of methods by various workers in 1893-1896, and has a surprisingly high temperature coefficient. While the hydrogen ion concentration of water was about $0.7\text{-}0.8 \times 10^{-7}$ normal at 18°C, at 25°C it was found to be in the range 1.1 to 1.2×10^{-7} normal.

Thus, about 14 or 15 years before the introduction of the pH scale for acidity and alkalinity, the stage was set completely for Sorensen in 1909 to dub this in on the hydrogen electrode potentials of neutral solutions, and acid and alkali to 1N strength. Sorensen³⁴ did this in the midst of a 173-page study of the effect of hydrogen ion concentration on enzyme action (reference 34, pages 159-160; chart between pages 176-177). This paper was published simultaneously in Danish, French and German but, unfortunately, not in English. Even more unfortunately, the chart was published separately as a large wall chart, and not reprinted in later textbooks. Thus, W.M. Clark refers³⁵ vaguely to the "Sorensen-Michaelis Map" or later⁴⁴ to just the "Sorensen Map," without indicating explicitly that he means this chart.

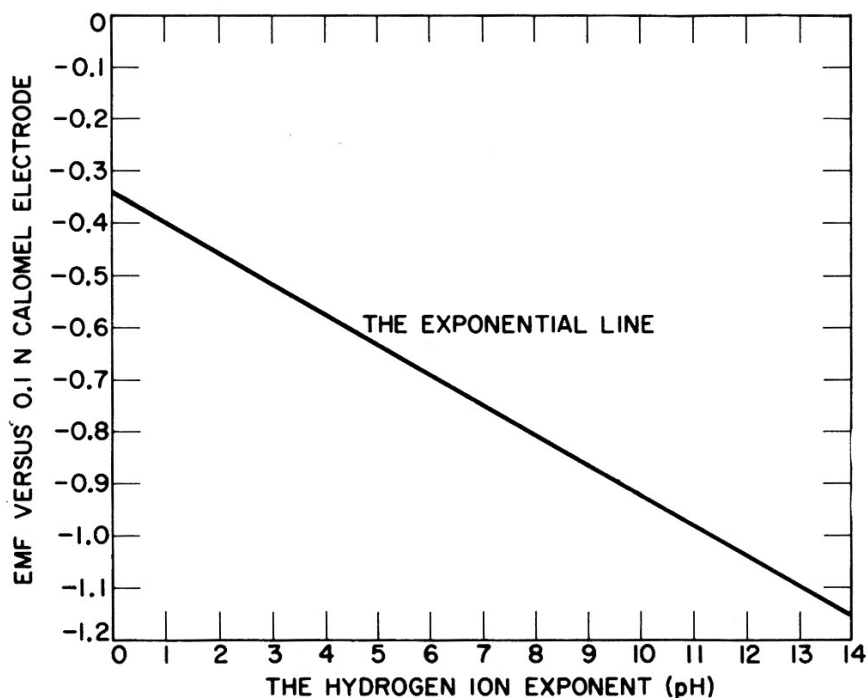


Figure 2 - Sorensen's original chart in 1909 of the pH scale applied to the potential of the hydrogen electrode, with the potentials reversed and buffer titrations eliminated.

The chart in question was also confusing in that titration curves of various buffers were superimposed upon the new pH scale. Figure 2 shows Sorensen's original chart of the proposed pH scale applied to the potential of the hydrogen electrode measured against the 0.1 normal calomel electrode, with the potentials reversed and the buffer curves eliminated. Sorensen mentioned in a footnote that the new pH scale gave positive numbers for the concentration of hydrogen ion, except for acids stronger than one normal, where the pH was negative.

The new pH scale was criticized at first as substituting unnecessary numbers for the potentials of the hydrogen electrode in various media, but during the 1920s it came to be widely adopted, and the primary position of the hydrogen electrode was lost sight of. It was easier to say that the acidity changed one pH unit, than that the potential of the hydrogen electrode was 0.059V higher or lower. Nevertheless, the primary meaning of a pH unit is that it corresponds to 0.059V change in hydrogen electrode potential.

Michaelis adopted the pH scale promptly, and published a book on hydrogen ion concentration in 1914,³⁶ with a second edition in 1922 followed by an English edition in 1926.³⁷ The second edition appeared in two parts, the second part having the title, *Oxidation - Reduction Potentials*.³⁸ The second part was translated into English,³⁹ and appeared in still another edition.⁴⁰ The outstanding American promotion of the use of the pH scale came in the book of W. Mansfield Clark on the *Determination of Hydrogen Ions*, which appeared in three editions in less than ten years.⁴¹⁻⁴³ However, Clark soon realized that the pH scale, while convenient, obscured the fundamental measurement, which was the potential of the hydrogen electrode. The shortcomings of the pH scale were discussed in the last edition of his book in 1928 (reference 43, pages 38-40, 545).

In his Nichols Medal address in 1936,³⁵ Clark said: "For a still distant date the author has contemplated a new edition of this book, written on a more consistent basis, and from it there might be eliminated the term 'pH'." However, the complete change which occurred in Clark's attitude towards the pH scale seems to have been lost in the flowery language of his address.³⁵

True to his word, Clark never did re-edit his book on *The Determination of Hydrogen Ions*. Following retirement from teaching at Johns Hopkins in 1952, he produced an outstanding work on *Oxidation - Reduction Potentials of Organic Systems*, published in 1960.⁴⁴ Clark was proud of his habit of writing as he pleased, but this last book appears to take a conventional attitude toward the use of the pH nomenclature. He describes the improbable or impossible concentrations or gas pressures resulting from the Nernst theory as "... mere calculation numbers" (reference 44, pages 24-26).

Clark seems to have succumbed to the heavy pressure of the circumstances, and says (reference 44, page 27): "An apparent exception to this will be our use of pH numbers for conditions such that their interpretation in the ordinary manner is of doubtful physical significance. We use pH numbers as a concession to custom and as a convenience while having noted in Section 4 that pH numbers could be replaced."

Clark discusses large negative pH numbers (reference 44, page 14), as having no physical meaning, but does not seem to offer any explanation or way out of the difficulty. Thus, Lewis and Randall in two editions,^{45,46} call attention to the fact that concentrated hydrochloric acid (16M) appears from emf measurements to have an activity coefficient of the hydrogen ion of about 43, or in other words it is more than 4000% dissociated! This is consistent with the experience of chromium plating workers that strong hydrochloric acid is about the only acid that will strip chromium plate all by itself, but points up the lack of meaning or inadequacy of our measurement system.

Clark (reference 44, page 14) concludes his discussion of pH numbers such as -4 or -10, etc. by saying: "It is quite obvious that it never was the intention to have 'pH = -10' interpreted as either an activity or a concentration of 10,000,000,000 ... Had there been used the standardized value of E_h , it could have been more easily interpreted as indicative of the availability of protons." (hydrogen ions).

On page 15 Clark says: "... we use the behavior of a hydrogen electrode as the operational basis, ..." The present writer takes this expression to mean that the behavior of the hydrogen electrode is the important experimental result, or the significant measurement.

Another of the most important proponents of the pH scale who ultimately seems to have become disillusioned with it was Holger Jorgensen of Copenhagen, a close associate of Sorensen himself. Jorgensen published an enthusiastic book on the value of pH measurements in 1935,⁴⁷ in which he lamented that the opportunity had been lost to designate the important new pH unit degrees Sorensen, °S, similar to °C for temperature.

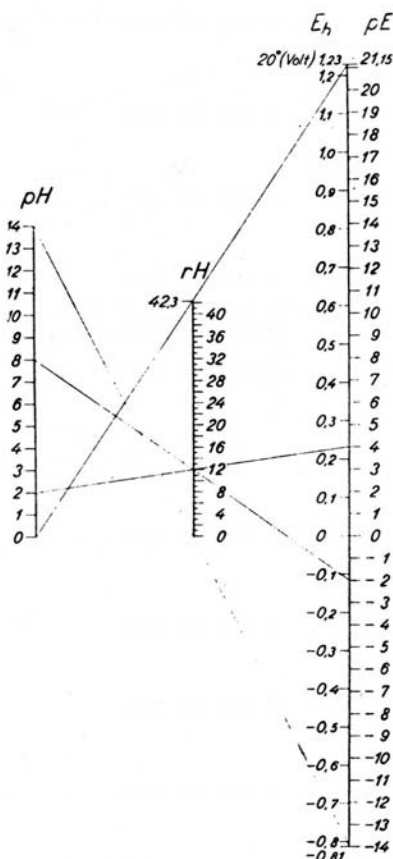


Figure 3 - Jorgensen's chart of the pH scale and his proposed substitute pE scale, and the relation of both to the potential of the hydrogen electrode (Potentials reversed compared to American practice). Reproduced with permission from Jul. Gjellerups Forlag a-s, Copenhagen.

Sorensen died in 1939. He may have passed on to Jorgensen some questions as to the value of the pH scale. At any rate, Jorgensen proposed the use of pE units instead of pH units in a little booklet in 1945,⁴⁸ but unfortunately this booklet is almost unknown and attracted almost no attention. Figure 3 taken from Jorgensen's book shows how he substitutes a pE scale for the pH scale, and the relation of each to the potential of the hydrogen electrode, E_h .

Luder and Zuffanti published an excellent book on *The Electronic Theory of Acids and Bases* in 1946,⁴⁹ but this book also seems to have had almost no effect on the use of the pH scale, even though it has had widespread acceptance. However, it did not extend its coverage to include the hydrogen electrode and the pH scale.

It is evident that the use of the pH scale has obscured its more important significance, the potential of the hydrogen electrode. One has to stop to think when reading the scientific literature, and particularly whenever results are plotted with varying pH; oh!, that means they vary with the voltage of the hydrogen electrode. Even if pH is determined with indicators or with a glass electrode, the real meaning of the resultant number is the voltage that the hydrogen electrode would have in the solution in question. This result is secured by calibration against known buffer solutions.

Reference electrodes

While electrochemists attempt to consider reference electrodes on a single scale of electrode potentials, such electrodes appear to be of two types, and to require two different potential scales. Perhaps it may be considered that clean metal surfaces have one scale of electrode potentials often known as the electromotive force series (reference 50, page 1134; reference 51, page

88), but metals coated with oxide, or equivalent surfaces, are sensitive to acid or alkali and show a different response requiring a different scale. Thus reference electrodes fall into two classes according to whether or not they respond to acid and alkali.

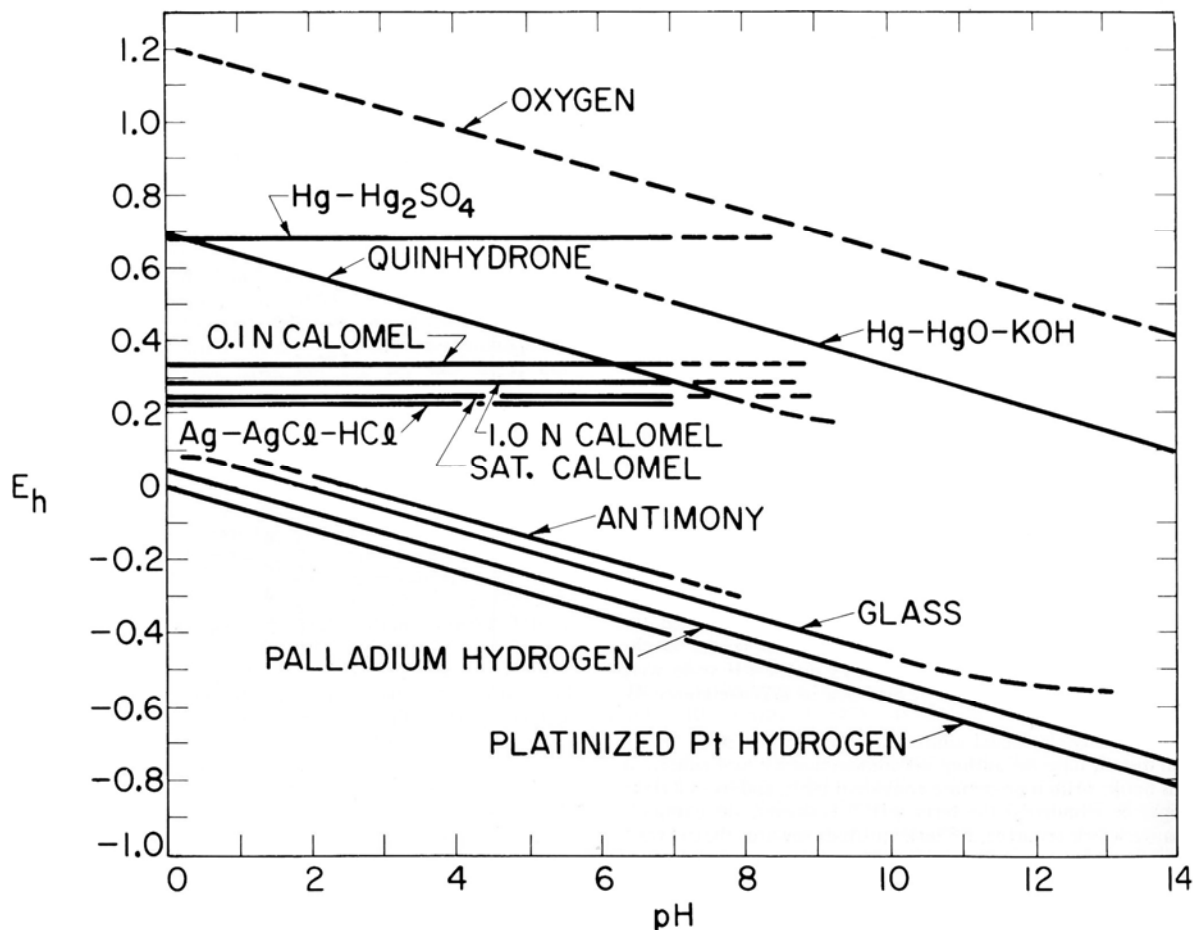


Figure 4 - Approximate potentials of common reference electrodes in solutions of varying pH.

Clark (reference 43, page 259; reference 44, page 264) diagrammed this difference between hydrogen and quinhydrone electrodes on the one hand, and calomel electrodes on the other, but confined his diagram to acid solutions in the range of pH 0-7. Extending the range from pH 0-14 and including data on some other common reference electrodes taken largely from Potter,⁵¹ the writer constructed the diagram shown in Fig. 4. While this is only of approximate accuracy, it shows the difficulty of conversions from one reference electrode to another, especially if these are of different types and used in solutions of varying pH.

Thus, one cannot make measurements with the saturated calomel electrode in neutral solutions around pH 7 and then convert them to the hydrogen scale by subtracting 0.244 V, as is sometimes done. This conversion would only be correct at pH 0, and a further conversion to the potential of the hydrogen electrode at pH 7 is necessary if the results are really desired to be transposed to the hydrogen scale.

In a similar vein, there are many artifacts in the literature due to measuring potentials in solutions of widely different pH with a reference electrode of the calomel electrode type, instead of using a pH-sensitive reference electrode such as the hydrogen electrode or the glass electrode. A few examples may serve to illustrate the point.

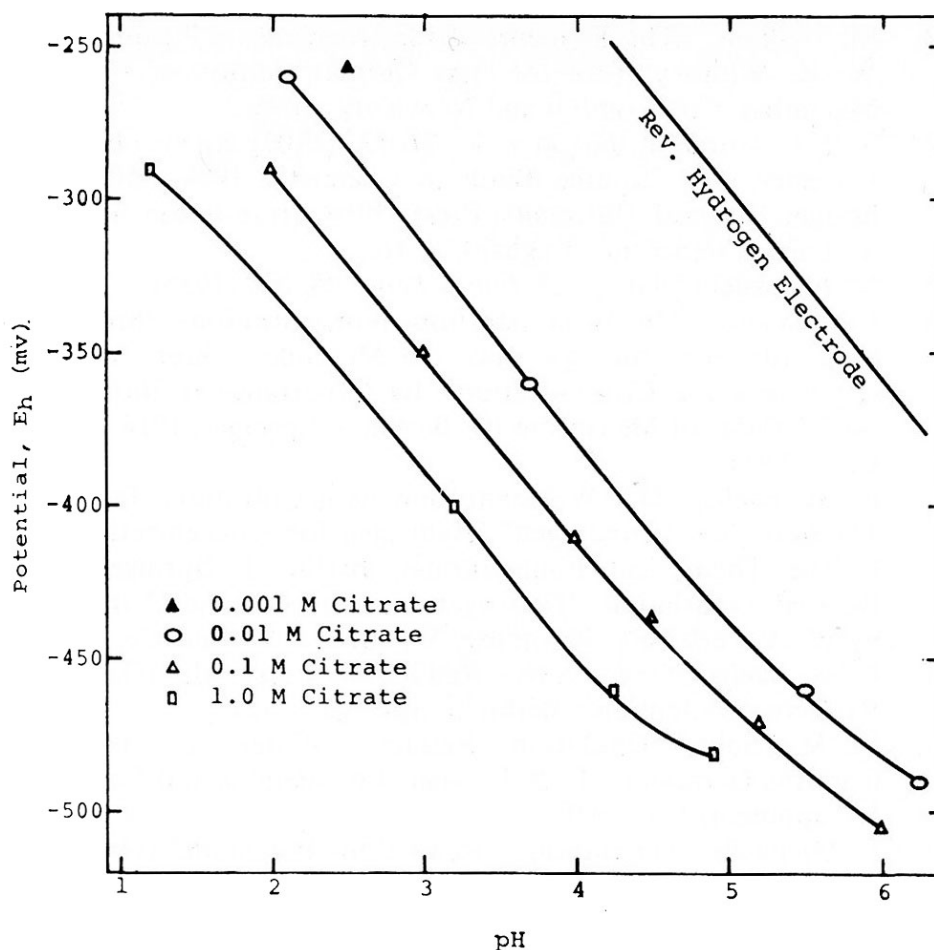


Figure 5 - Willey's measurements of the potentials of tin in solutions of varying pH. Reprinted with permission from *Brit. Corrosion J.*

Figure 5, taken from a paper by A.R. Willey⁵² shows that tin can exhibit an almost perfect "hydrogen electrode behavior" over certain ranges of pH. It is obvious that if the potentials had been measured against the hydrogen or a similar electrode as zero instead of the 0.1N calomel electrode, that they would be relatively constant for each condition, and most of the variation would be eliminated.

Figure 6 gives some curves of the potential of chromium in solutions of almost the entire pH range of zero to 14, measured against the calomel electrode, as reported by Knoedler and Heusler.⁵³ In this case, the chromium is exhibiting a hydrogen electrode behavior. The potential of a hydrogen electrode varies about 828 mV between pH zero and pH 14, and it is evident that if these measurements were to be made against a hydrogen or other pH-sensitive electrode as zero, most of the variation would be eliminated and the curves would tend to coalesce into a single line.

Figure 7 shows some measurements on platinum with a calomel electrode as reported by Carr and Hampson.⁵⁴ The two solutions used were about pH 1 and pH 13, about 0.7 V apart on the hydrogen scale, and, if the measurements were made with a hydrogen electrode as zero, the two curves would tend to slide together into a single curve.

These three examples should suffice to show the importance of using a pH-sensitive reference electrode when making measurements in solutions of varying pH, or else using the proper conversion from one scale to the other. At any rate, the very nature of the results obtained depends upon the type of reference electrode selected.

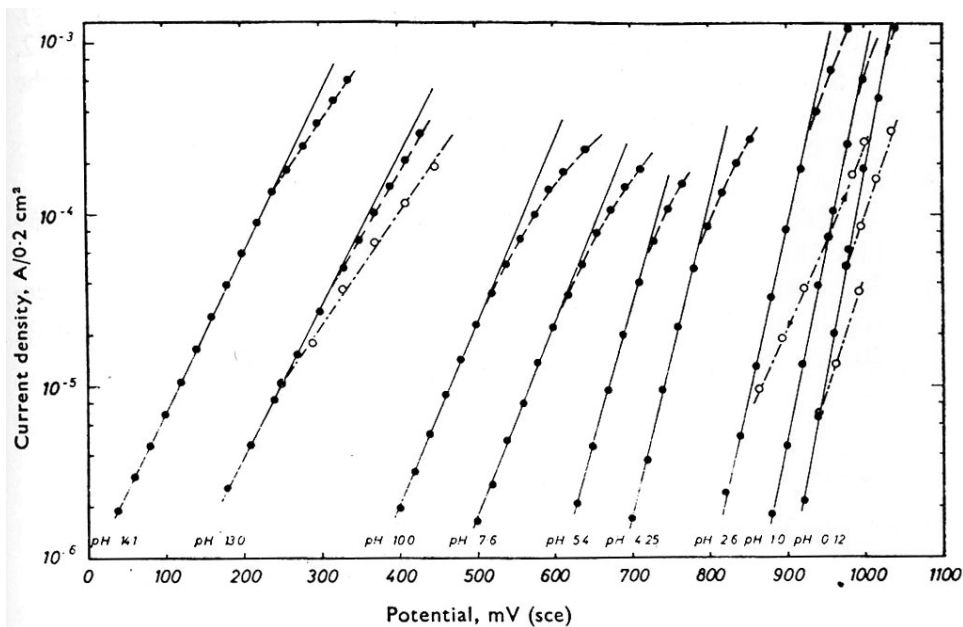


Figure 6 - Knoedler and Heusler's measurements of the potential of chromium against the saturated calomel electrode in solutions of varying pH. Reprinted with permission from Pergamon Press.

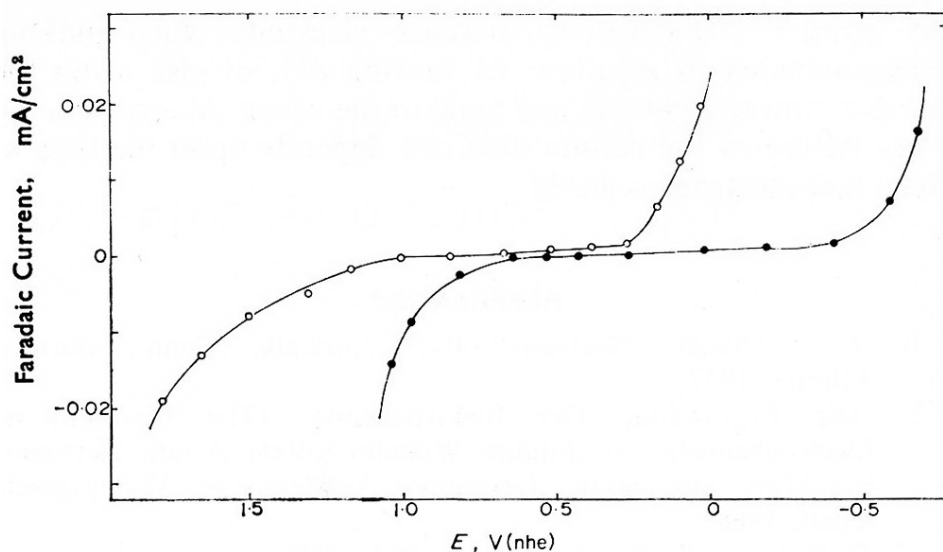


Figure 7 - Carr and Hampson's measurements of the potential of platinum against the calomel electrode in 0.13M H₂SO₄ (circles) and 0.19M NaOH (dots). Reprinted with permission from Pergamon Press.

On the nature of electrode potentials and hydrogen overvoltage

There has been much confusion and lack of progress in dealing with the question of the nature of electrode potentials and hydrogen overvoltage. Definitions of what is meant by "overvoltage" or "hydrogen overvoltage" have varied widely, and this has been a substantial part of the problem. Bockris titled an article in 1971, "Overpotential - A Lacuna In Scientific Knowledge."⁵⁵

There would seem to be no harm in going back to the publications of Nernst and his student Caspari in 1899 for the definition of overvoltage, since they appear to have coined the term and were about the first to clearly separate the quantity from the broader

term "polarization" used before that time. Kremann and Muller⁵⁶ give references to the earlier developments (reference 56, page 100, Part 2). Caspari's work was published in two papers,^{57,58} the first being presented by a colleague, A. Coehn. Caspari did not state a definition of "Ueberspannung" (overvoltage), but he used as his zero of potential or reference electrode the platinized platinum hydrogen electrode, whether it was in 1N H₂SO₄ or 1N NaOH, even though he knew its potential was actually more than 0.8V different in these two solutions.

Thus, Nernst's definition of overvoltage was given later as (reference 56, page 102, my translation): "... the potential of the cathode at which just visible hydrogen evolution appears, referred to a reversible hydrogen electrode in the same electrolyte through which no current is flowing, and under the same external conditions with reference to pressure and temperature."

Later workers extended the definition to include the overvoltage at a given current density of a working electrode, the reference hydrogen electrode remaining on open circuit and having no current flowing to it. Dr. Blum⁵⁹ stated (reference 59, page 366)" ... overvoltages for evolution of hydrogen should measure the departure of the cathode potential from that of a reversible hydrogen electrode in that solution."

While sometimes stated in different terms, this definition is still in use today. Thus, a tentative definition of the IUPAC circulated in November, 1972, stated:⁶⁰ "Overpotential (SI unit V) is the deviation of the potential of an electrode from its equilibrium value required to cause a given current through it."

Thus, we see that the definition of hydrogen overvoltage requires that it be measured against the potential of the hydrogen electrode in the same solution as zero, something which has not always been done. Since the potential of the hydrogen electrode is synonymous with pH, calling the hydrogen electrode zero automatically eliminates any possible effect of pH on hydrogen overvoltage. In a way this creates a new scale of electrode potentials, the vertical distance from the downward slanting line of the hydrogen electrode in Fig. 4 taken as zero, to any of the other electrodes.

Experimental

The writer first attempted⁶¹ to separate overvoltage into measurable component parts by the use of extremely thin platinum and palladium membranes, with hydrogen or oxygen being evolved on one side of the membrane only, and the potential of the other side checked for diffusion products of an electromotively active nature. No diffusion of electromotively active hydrogen or oxygen was detected. Instead, there appeared to be no diffusion whatsoever with the thicker membranes. When the membrane was made thin enough, some current penetrated solution in fine pores and charged the back side of the membrane.

In the discussion to Coehn's paper in 1899,⁵⁷ Ostwald suggested that possibly overvoltage was due to the formation of atomic hydrogen at the cathode, and Bredig described his work with Haber on the alloying of sodium with lead, tin and mercury, as a possible clue to the nature of overvoltage phenomena.

Since no electromotively active hydrogen was detected in the first experiments,⁶¹ the writer became imbued with the idea that the high negative potentials of cathodic overvoltage were due to the electrodeposition of small traces of electronegative metals such as lithium, sodium, potassium, calcium, etc. This was not a new idea; the writer adopted it particularly from a paper by F. P. Bowden.⁶² It was also mentioned in another paper in 1927 by Sand, Grant and Lloyd.⁶³

If this theory was correct, it appeared that a sufficiently pure solution of acid could be prepared containing no alkali or alkaline earth metals and that it would exhibit no overvoltage or a drastically reduced overvoltage, when the overvoltage was measured. An investigation was conducted to this end in 1950-1951 at the University of Connecticut using freshly distilled sulfuric acid in plastic containers.⁶⁴ No clear cut results were obtained in measurements on platinum electrodes, and it appeared that sulfuric acid could not be purified to any great extent in this way,⁶⁵ presumably because of the high boiling point of over 300°C.

The investigation was continued in 1967-1968 in the laboratory of Dr. D. J. Kenney at the University of Detroit. High purity sulfuric acid was synthesized by passing sulfur trioxide gas into doubly distilled water at temperatures around 40-50°C. A mercury cathode was used with a somewhat improved method of measuring the overvoltage, in that the solutions used were adjusted to the same conductivity, thus making the solution IR drop in comparative measurements at a given current density a constant factor, instead of trying to eliminate it.

It was found that when the pure sulfuric acid was used in the two-compartment measuring cell with the cathode compartment under a hydrogen atmosphere, the overvoltage hardly seemed to have been decreased at all. It was felt that some decrease in overvoltage must have been accomplished, so more careful measurements were made to determine the extent of the decrease, by comparison to the overvoltage in strong sodium sulfate solution. Neutral 1.5M Na₂SO₄ (pH 6.2) was used and compared to pure 0.2M H₂SO₄ having about the same conductivity (0.0966 mhos/cm vs. 0.0855 mhos/cm).

Surprisingly, the overvoltage plus IR drop was found to be identical in the two hydrogen-saturated solutions, within the limits of error of measurement, even though the cathode process was 100% hydrogen evolution in the sulfuric acid and 100% sodium deposition on the mercury cathode in the neutral sodium sulfate solution.

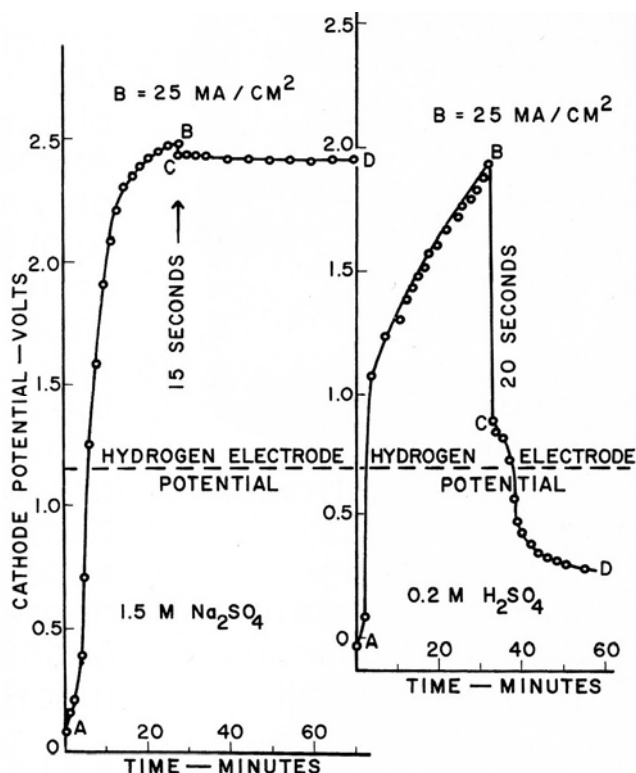


Figure 8 - Dubpernell and Kenney's measurements of cathode potentials on mercury with sodium deposition and with hydrogen evolution.

Overvoltage was found to increase almost linearly with current density at 25, 50, 100, 200 and 300 mA/cm², but at each current density appeared identical in each solution, whether 0.2M H₂SO₄ or 1.5M Na₂SO₄. Typical results at 25 mA/cm² (25 A/ft²) are given in Fig. 8. The investigation was reported in a paper at the 19th meeting of C.I.T.C.E. (Comite International de Thermodynamique et de Cinetique Electrochimiques) in September, 1968, but only the extended abstract has been published.⁶⁶

The two curves in Fig. 8 are shown with the hydrogen electrode potential as a common axis, since this is the zero point or equilibrium potential against which overvoltage is measured. The line AB in each case is the charging curve with gradually increasing current densities up to the maximum shown at B. The circuit is opened at B and the drop in potential followed manually as rapidly as possible from B to C, and then on to D. While with hydrogen evolution in 0.2M H₂SO₄ there is a sudden drop in potential of about one volt upon opening the circuit, in the case of sodium deposition from 1.5 M Na₂SO₄ the drop is only about 50 mV at 25 mA/cm², and the potential is then stable at the reversible sodium deposition potential on mercury. The small drop in potential of about 50 mV is probably largely a measure of the solution IR drop included in the measurement when the current is flowing.

It can readily be noted from Fig. 8 that the overvoltage appears to be identical in the two cases. It seems likely that more refined measurements would only establish the identity more accurately within closer limits. Thus the original idea of overvoltage being due to the electrodeposition of electronegative metal failed to be borne out, but overvoltage instead appears as an intrinsic reproducible property of the cathode metal, mercury in this instance.

The above investigation was checked and extended in 1969-1970 by Kuo-Ming Wu at the University of Detroit⁶⁷ using the same method and overvoltage on mercury at a given current density appears to be the same whether the cathode process is the deposition of metal from a salt solution or hydrogen evolution from sulfuric acid.

Two main series of measurements were made with two different conductivities of the solutions. The conductivity measurements in each series are shown in Fig. 9, and it is to be noted how closely the conductivities were adjusted.

The first series in Fig. 10 shows the overvoltages at 200 mA/cm² (200 A/ft²) with cesium, potassium or lithium deposition on the mercury cathode, compared to hydrogen evolution from sulfuric acid. The overvoltages (including IR drop) are essentially identical in each case.

The second series in Fig. 11 shows the overvoltage at 200 mA/cm² (200 A/ft²) in solutions of sodium, barium, and magnesium perchlorate, compared to sulfuric acid of the same conductivity. The sodium and barium deposited with 100% current efficiency with no visible hydrogen evolution; magnesium only deposited at very low efficiency or not at all, but this did not affect the overvoltage measurement. Again the overvoltage (including IR drop) appeared identical in the solutions of the same conductivity, regardless of the exact cathode reaction. The time scale in Figs. 10 and 11 is marked negative during charging, zero at the point of current interruption, and positive when following the decay of potential.

Figures 10 and 11 show typical results; measurements were generally made at 20, 50, 100, 200 and 300 mA/cm². Over this rather limited range, overvoltage (including IR drop) appeared to vary almost linearly with current density, with the greatest deviation at the lowest current densities. Higher current densities could readily be investigated if the mercury cathode is agitated a little.

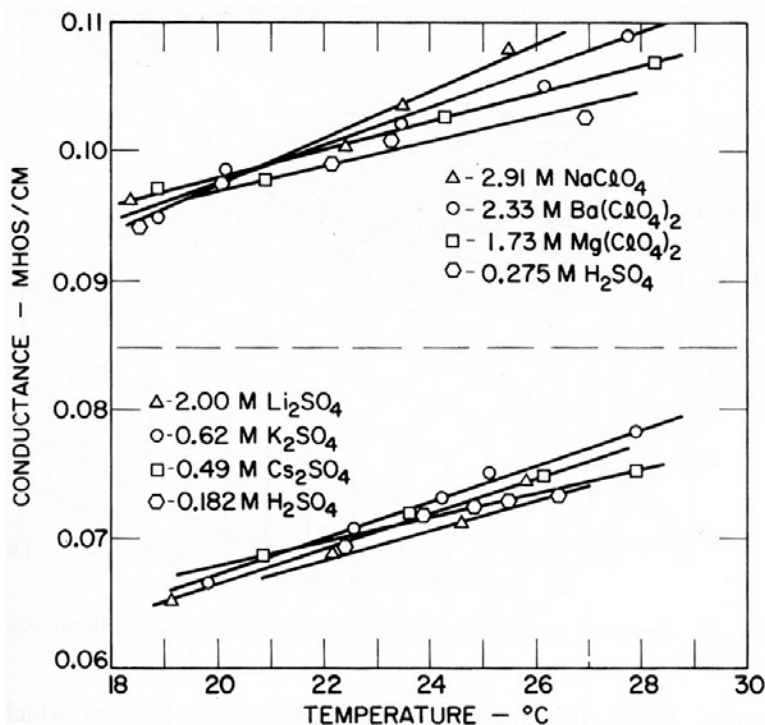


Figure 9 - Kuo Ming Wu's measurements of the conductivity of solutions.

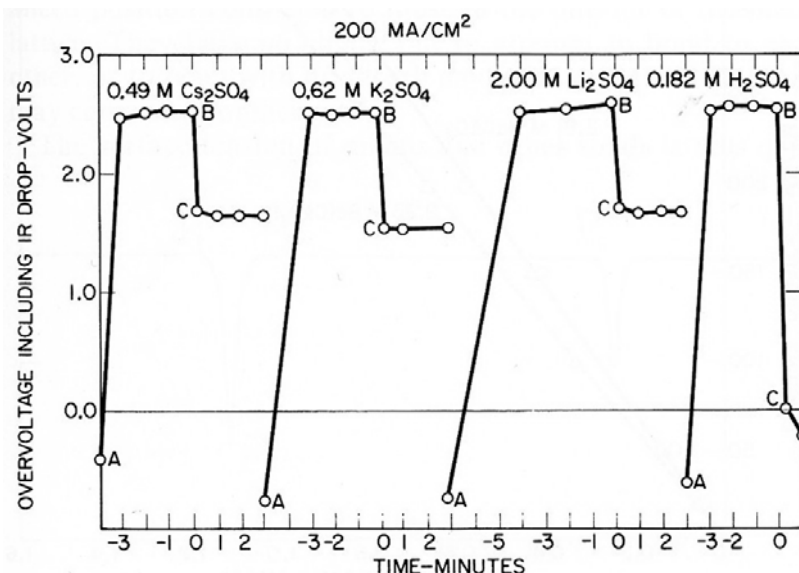


Figure 10 - Kuo Ming Wu's measurements of overvoltage plus IR drop on mercury at 200 mA/cm².

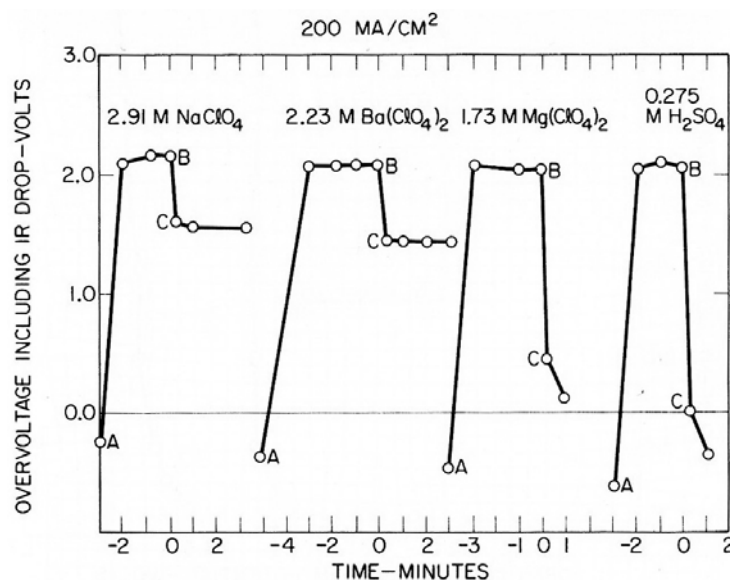


Figure 11 - Another series of measurements by Kuo Ming Wu of overvoltage plus IR drop on mercury at 200 mA/cm².

The deposition potentials or amalgam potentials of the various metals recorded on open circuit are shown in Figs. 12 and 13, and it is noteworthy that they are quite reproducible and show little variation with current density, considering the fact that the measurements were not of great accuracy and were made more for qualitative than quantitative purposes. The results with magnesium perchlorate are given in Fig. 14, since they also indicate a small open circuit potential due to magnesium deposition.

Some of the indicated IR drops due to the fall in potential on opening the circuit are given in Figs. 15 and 16. Here again, the accuracy of measurement appears to be sufficient for indicative purposes. It was originally thought that only the IR drop through a fixed part of the solution in the cathode chamber would be shown, and that this would be substantially identical in each instance. However, this no longer appears to be the case. Rough calculations indicate that a resistive fall in potential is measured that is substantially larger than would be expected in the cathode chamber solution alone, and the IR drop is greater in the case of solutions giving lower amalgam potentials.

The measurements thus indicate that we are dealing with a closed system including its own set of adjustments and balances. There appears to be a powerful force present which regulates the total voltage of open circuit potential and IR drops to a constant amount at a given current density. This is especially evident with the measurements with sulfuric acid solutions, which give a lower total voltage at lower current densities, but which finally increase to match the others as the current density is increased.

It would appear that probably a cell could be designed in which the IR drop in the solution would be accurately known, and thus permit the estimation of any other resistances included in the measurements such as the metallic surface resistance postulated in the present paper.

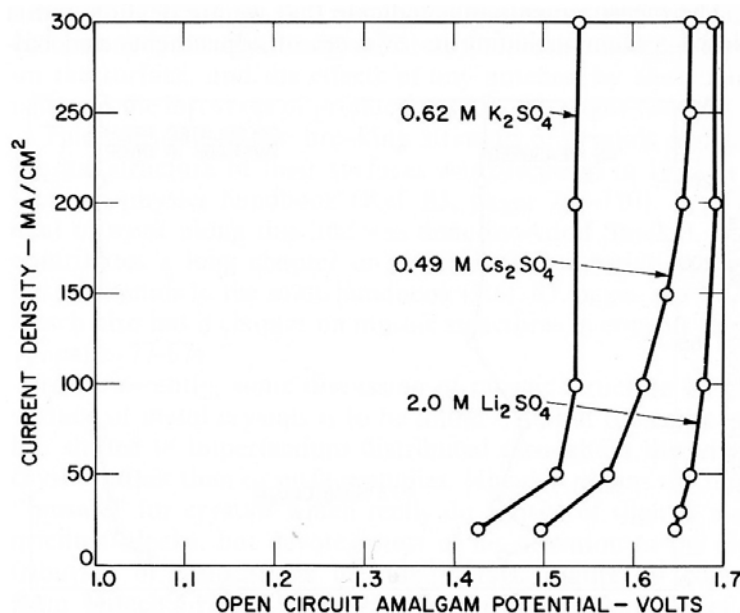


Figure 12 - Open circuit amalgam potentials of lithium, potassium and cesium (Kuo Ming Wu).

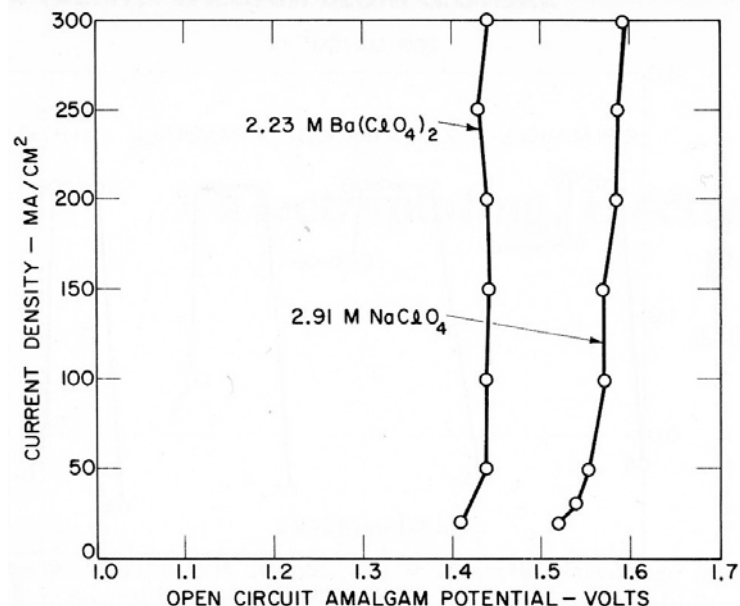


Figure 13 - Open circuit amalgam potentials of sodium and barium (Kuo Ming Wu).

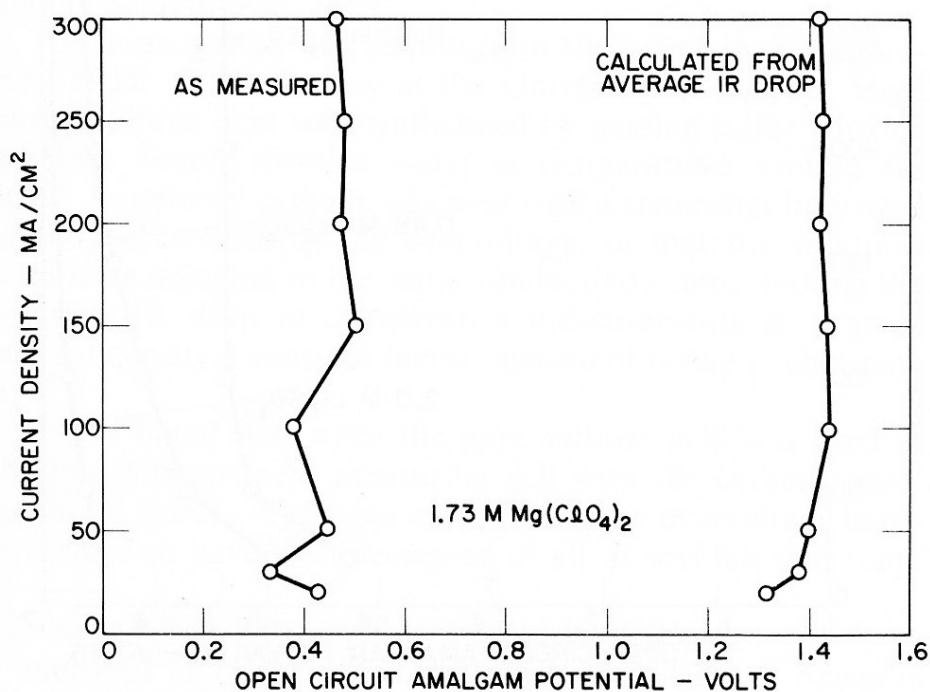


Figure 14 - Open circuit amalgam potentials of magnesium (Kuo Ming Wu).

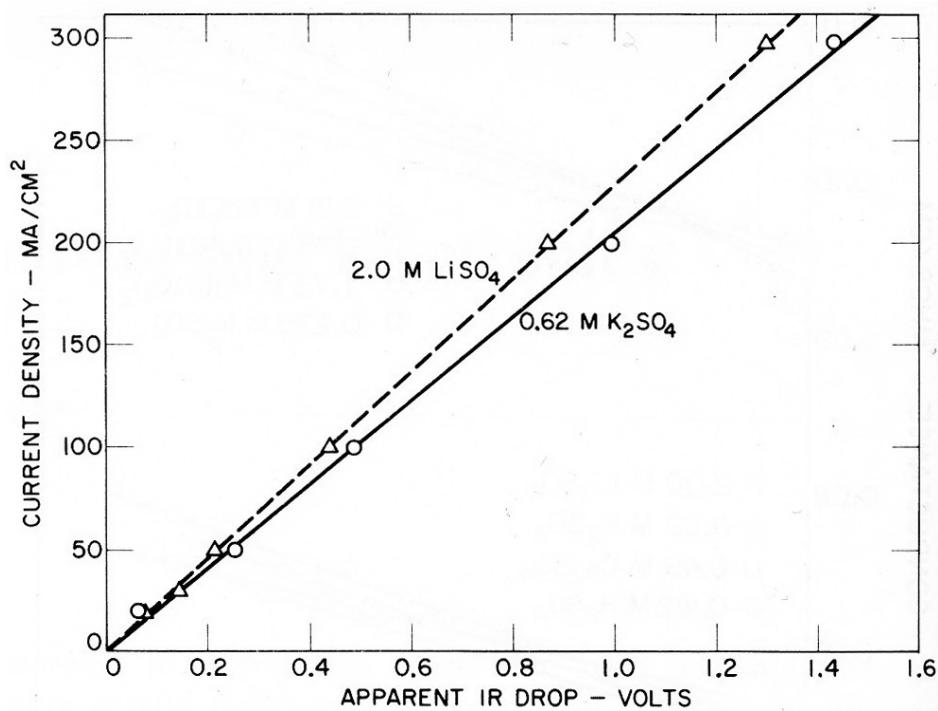


Figure 15 - Apparent total IR drop with potassium and lithium sulfates (Kuo Ming Wu).

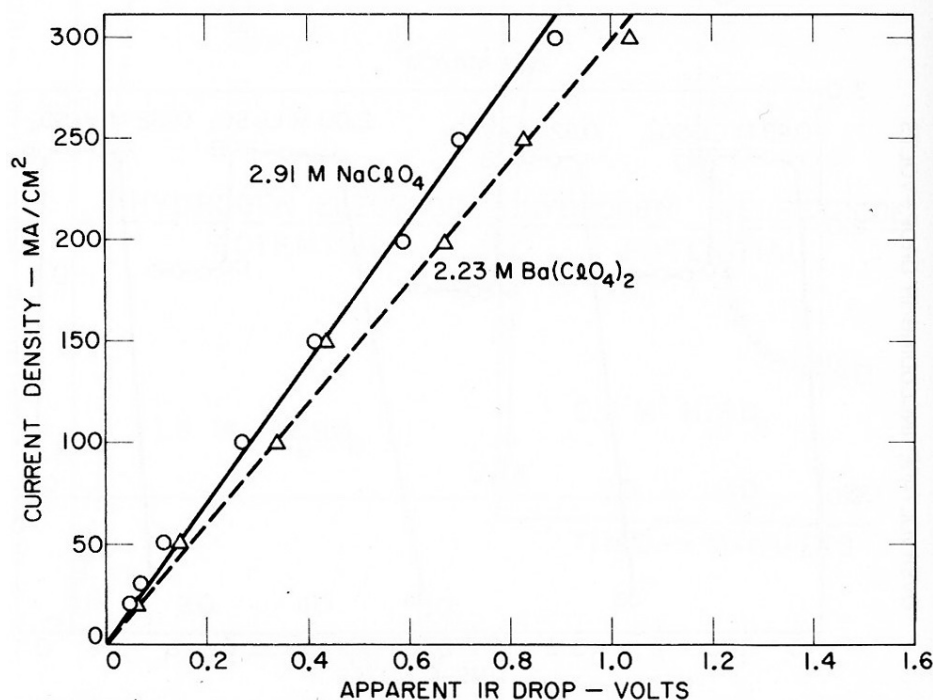


Figure 16 - Apparent total IR drop with sodium and barium perchlorates (Kuo Ming Wu).

Discussion

It was first thought^{66,67} that the apparently reproducible cathode potential called overvoltage was perhaps due to the production of a fixed quantity of hydrated electrons in the solution at the interface corresponding to the current density used. The hydrated electron had been produced and identified by Hart and Boag in 1962,⁶⁹ by means of pulse radiolysis. This led to a good deal of further investigation of the generation and properties of such hydrated electrons, which culminated in the publication of a separate book on the subject.⁷⁰

Hydrated electrons, or more broadly, solvated electrons, have an intense blue color and their presence or absence can readily be shown by optical means. It was noted as far back as 1878⁷¹ that the electrolysis of liquid ammonia turned it blue, but that the liquid became colorless when the current was discontinued. Cady reported in 1897⁷² that the electrolysis of sodium or potassium salts dissolved in liquid ammonia gave a stable blue color which formed at the cathode, and that the resultant solution of sodium, for example, conducted like a metal.

Walker⁷³⁻⁷⁶ felt that he detected the formation of hydrated electrons at the cathode in aqueous electrolysis with platinum and silver cathodes by both chemical and optical means, but his results have thus far not been confirmed by more recent work.⁷⁷

The hydrated electron is a very short-lived species in aqueous solutions, although it is reported to be stable for several milliseconds in alkaline media. In strongly acid solutions it decomposes quite rapidly, and such acid solutions are used as "scavengers" for hydrated electrons.

Since overvoltage (including IR drop) was found to be identical in both acid and in neutral or slightly alkaline solutions, it was concluded that it could not be due to hydrated electrons in contact with the solution at the cathode, and must be located within the metal of the cathode where it would be unaffected by the composition of the solution. This is a startling conclusion requiring extensive revision of one's thinking, but appears to be the only conclusion that fits the facts.

While metal surfaces are commonly considered "homogeneous" right up the final layer of atoms as shown in Fig. 17,⁷⁸ the surface atoms are obviously stranded in an unbalanced position compared to those in the interior of the metal lattice. They have no choice but to attempt to bond to each other, or to react with or adsorb any gases or liquids that they may come into contact with.

The surface tension of metals and other solids is thus quite high, ranging roughly from 10 to 100 times that of aqueous solutions containing various concentrations of wetting agent.^{79,80}

Desch⁷⁹ gives the surface tension of ordinary salt, NaCl, as 3000 dynes/cm. Zwicky⁸¹ reviews the necessity of microscopic cracks in the surface of even the most perfect crystals, such as NaCl crystals, for example. The lattice spacing on the surface of such NaCl crystals is about 6% smaller than the spacing in the solid crystal, resulting in a tendency for the surface to contract. Zwicky's drawing of the probable cross section of the surface of an NaCl crystal is shown in Fig. 18. He considers that the surface is probably broken up into blocks consisting of about 10,000 atoms each.

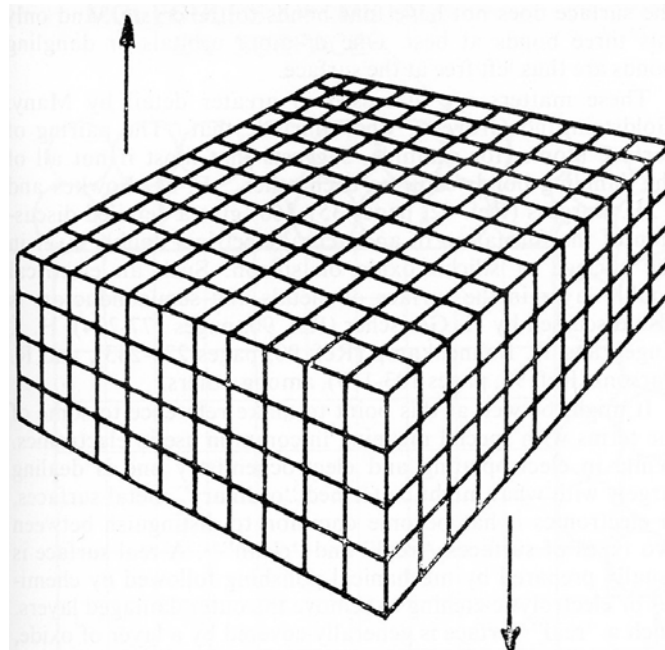
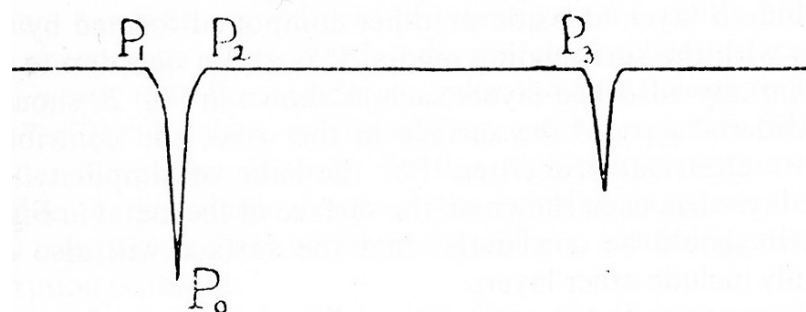


Figure 17 - Rogers' hypothetical crystal of metal containing no dislocations. Reproduced by permission from *The Nature of Metals*, American Society for Metals, 1964.



$$P_1P_2 \sim 8\text{\AA} \quad P_2P_3 \sim 100\text{\AA} \quad P_0P_1 \sim 50\text{\AA}.$$

Figure 18 - Zwicky's concept of the surface structure of a crystal of sodium chloride.

These considerations are borne out by the low breaking strength of NaCl crystals, about 50 kg/cm². If the surface is wetted, however, it will stand stresses as high as 16,000 kg/cm², near the theoretical value.

Such behavior is not uncommon. Thus chromium is a brittle metal, and much effort has been expended to produce it in ductile form.⁸² The writer at one time received a sample of Bureau of Mines' chromium wire the size of an ordinary paper clip when opened out. This chromium wire was stronger than the steel wire in bending, and could withstand almost any amount of bending. An important feature of making such chromium is the final removal of any air contaminated layer on the surface, and the effects of any notches, by electropolishing as the last stage of production (Ref. 82, pages 138-162).

This question of the breaking strength of crystals and the mosaic structure of their surfaces was discussed in 1933 in a German physics handbook (Ref. 83, pages 765-770). A good deal of work along this line was done by Adolf Smekal, who contributes a long chapter on the structure-sensitive properties of crystals to the same handbook (Ref. 83, pages 795-922). Desch also has a chapter on mosaic structures in crystals (Ref. 79, pages 77-87).

More recently, some discussion of mosaic structure on the surface of metal crystals is to be found,^{84,85} but the emphasis has shifted to imperfections distributed throughout the whole crystal rather than to surface studies. Hirsch⁸⁵ retains the term "mosaic" for crystals which really do consist of slightly misoriented blocks, but devotes most of his attention to the distribution of dislocations in bulk metals. Figure 19 copied from Hirsch's review shows a theoretical cross-section of a block of metal from Buerger,⁸⁶ showing the way he considers metal crystals to grow into what he calls a "lineage" structure, but without particular reference to the final structure of the surface of the metal.

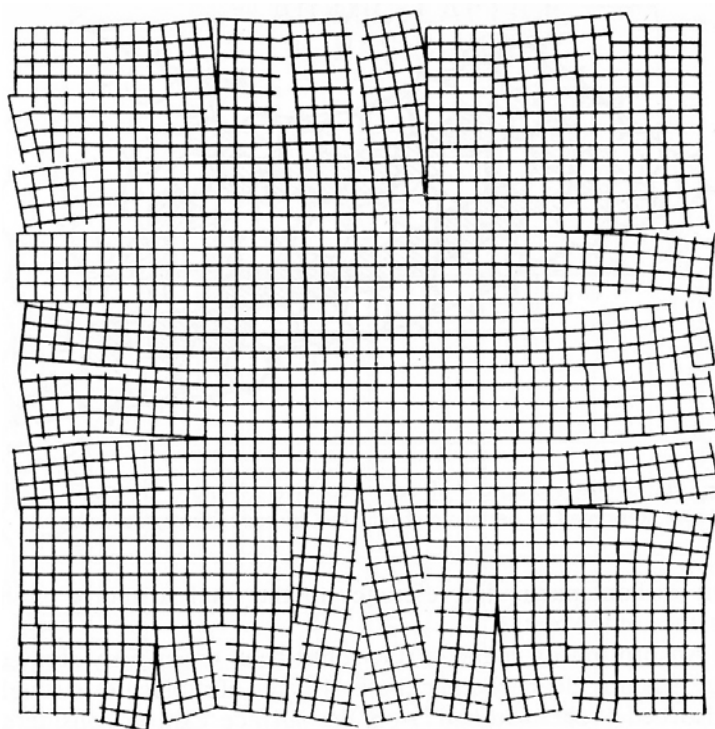


Figure 19 - Buerger's concept of a "lineage" structure of the cross section of a metal crystal. Reprinted with permission from Pergamon Press Ltd.

Adsorption on metal surfaces has been extensively studied, but it is not clear whether the first layer of molecules strongly adsorbed ("chemisorbed") on the surface can be considered to be part of the solid, or whether they still have some association with the solution, de Boer⁸⁷ found that the heat of adsorption is higher in capillaries than on flat surfaces, and that adsorption in such pockets, holes and cavities accounts for the experimentally known values of the heat of adsorption. Figure 20 is his sketch of adsorption within a capillary extending from right to left (Ref. 87, page 212). The line SS is the surface of the solid with the

actual surface atoms indicated. The row of molecules aa is the first layer adsorbed, bb is the second, cc the third and dd the beginning of a fourth layer. Adsorption has sometimes been used to estimate the true area of a metal surface, since it is to a considerable extent a reversible process.

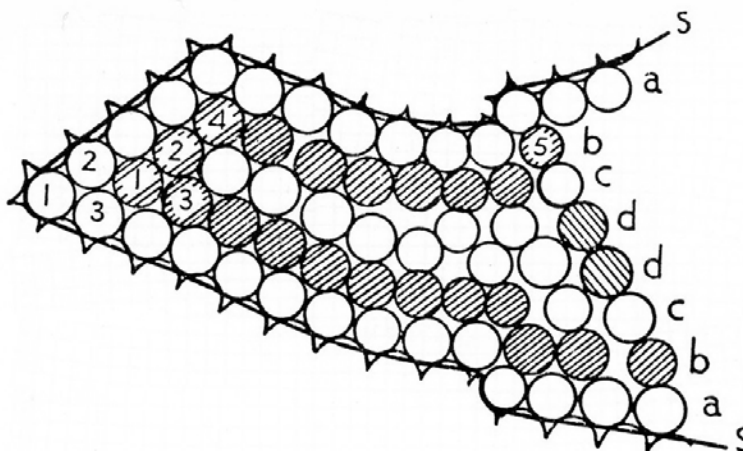


Figure 20 - deBoer's diagram of adsorbed layers filling a crevice in a solid surface. Reprinted by permission from The Clarendon Press, Oxford.

The surfaces of semiconductors such as germanium and silicon have been studied extensively in recent years in view of their use in device technology. There seems little reason to suppose that metal surfaces are radically different, and much of what is learned regarding semiconductor surfaces should also apply to metals. In fact, metals are ordinarily exposed to air and aqueous solutions and ordinarily have a surface layer of oxide on them which is in itself usually a semi-conductor.

Thus, bright metallic chromium was found by Andreeva⁸⁸ to form a "natural" oxide film on its surface 10-20 Å thick as soon as it was exposed to air at 25°C, and this oxide film thickened to 25-35 Å within 24-48 hr, after which it remained constant. This oxide film is normally invisible. Bright chromium plate is deposited with a varying thickness of oxide on it, sometimes so thick that it is visible. Holliday and Frankenthal⁸⁹ found about a 10 Å thick chromium oxide layer on a 50 Å thick chromium plate by chemical analysis.

D. R. Turner (Ref. 90, pages 285-310) considers that electrochemical reactions on metals may be characterized by phenomena occurring in the solution, but that if the electrode is a semiconductor, the rate determining process may also include phenomena that take place inside the surface of the electrode. In the study of germanium, he considers that each surface atom is covalently bonded on the average to two underlying germanium atoms. Current multiplication results are assumed to be associated with the "dangling-bond" electrons that remain on the underlying germanium atoms after the surface atom goes into solution during anodic action.

The electrical properties of the surfaces of semiconductors are also well reviewed by P. Handler (Ref. 90, pages 54-68). Handler considers that the surface region may consist of only the first layer of atoms or perhaps the first few layers of atoms. The existence of "surface states" equal to the number of surface atoms is discussed, and it is felt that these surface states may extend to the subsurface atoms. A germanium atom at the surface does not have four bonds to the crystal, and only has three bonds at best. One or more orbitals or dangling bonds are thus left free at the surface.

These matters are discussed in greater detail by Many, Goldstein and Grover,⁹¹ who conclude that "The pairing of surface atoms, for example, suggests that most if not all of the dangling bonds saturate each other." F. M. Fowkes and T. E. Burgess (Ref. 92, pages 351-360) give a detailed discussion of the formation of an internal electrical double layer in the surface of silicon oxide on silicon. Such an electrical double layer in the surface of metals and semiconductors is also discussed by H. Gerischer (Ref. 90, pages 177-204), H. J. Engell and K. Bohnenkamp (Ref. 90, pages 225-243), and R. Parsons (Ref. 93, pages 103-179), among others.

It might be well at this point to make reference to some of the terms with special meaning in common use in electronics. While in electroplating and electrochemistry one is dealing largely with what might be termed "ordinary" metal surfaces, in electronics it has become common to distinguish between two types of surfaces, "real" and "clean."⁹⁴ A real surface is usually prepared by mechanical polishing followed by chemical or electrolytic etching to remove the outer damaged layers. Such a "real" surface is generally covered by a layer of oxide, and also by other molecules adsorbed from the surrounding media. The "real" surface is not particularly different from a surface prepared for plating, but the operations are more precise and clearly defined, and carried out with greater care.

"Clean" surfaces are produced and maintained in an ultrahigh vacuum (10^{-10} to 10^{-8} mm Hg), by cleavage, by ion bombardment, or by heating at a high temperature in the vacuum. In this way surfaces are obtained and maintained that have something of a theoretical quality and are free of foreign adsorbed matter to better than a few per cent of an atomic monolayer. Nevertheless, such "clean" surfaces are said⁹⁴ to commonly exhibit lattice spacings twice as large as those in the bulk, and more complex structures are also observed.

Conduction in semiconductors is considered to be of two types, n-type (negative) and p-type (positive). Certain impurities (donors) give rise to n-type conduction, in which the electrons are the majority carriers and holes (positive, and otherwise similar to an electron) are the minority carriers. Other impurities (acceptors) result in p-type conduction in which the holes are the majority carriers and the electrons the minority carriers. We might say that there are two types of electricity, positive and negative, holes and electrons.

On the basis of these discussions it is proposed that metal surfaces are covered by a higher resistance layer of molecules of metal, probably at least several molecules thick, as shown in Fig. 21, or some equivalent. The presence of such a layer seems necessary to account for the potential difference called overvoltage, which seems to be located in the surface of the metal and to be a property of the metal itself. This overvoltage could not vary with current density if the metal was a uniform good conductor right up to and including its surface atoms.

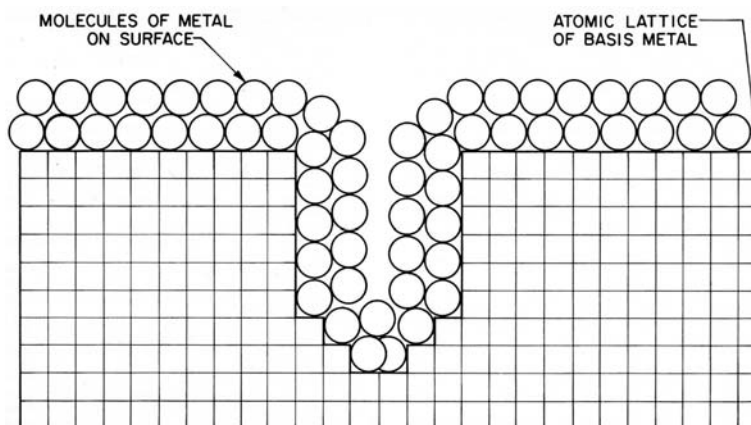


Figure 21 - Suggested diagram of the cross-section of metal showing the proposed layer of "molecular metal" on the surfaces.

Such a surface layer of "molecular metal" could hardly be expected to exist by itself under ordinary circumstances; and in contact with air and water, for example, would also have to include a layer of oxide or other compound formed by reaction with the surrounding media. It is also a question to what extent any adsorbed layers such as shown in Fig. 20 should be considered part of the surface of the solid, and contributing to its electrical properties. For the sake of simplicity, only one layer has been shown on the surface of the metal in Fig. 21, but it should be considered that the surface will also commonly include other layers.

It was thought that some clue to the magnitude of such surface layers on metals could be found in the extensive studies which have been made of thin films. This should be true particularly of gold, which has outstanding surface properties. Unfortunately, this does not work out in the investigations made to date, since the thin films have to be deposited on a substrate by electrodeposition, by evaporation, or by cathode sputtering in a vacuum, and the substrate seems to control the nature of the first few layers of atoms deposited.

Figure 22 (Ref. 94, pages 373-381, chapter by K. L. Chopra and L. C. Bobb on "Electrical Conduction In Thin Epitaxially Grown Gold Films") shows that even the most carefully sputtered gold films tend to have a high resistivity when the thickness goes below 200 Å. This is confirmed by Prostak, Mark and Hansen,⁹⁵ who state that a gold film thinner than about 200 Å evaporated onto glass is a very high resistance deposit which has a bluish color in transmitted light. These workers were able to obtain gold films of medium resistance by other means down to a thickness of about 50 Å, but thinner films had an extremely high electrical resistance. A comprehensive review of size-dependent electrical conduction in thin metal films and wires by D. C. Larson is available (Ref. 96, pages 81-149).

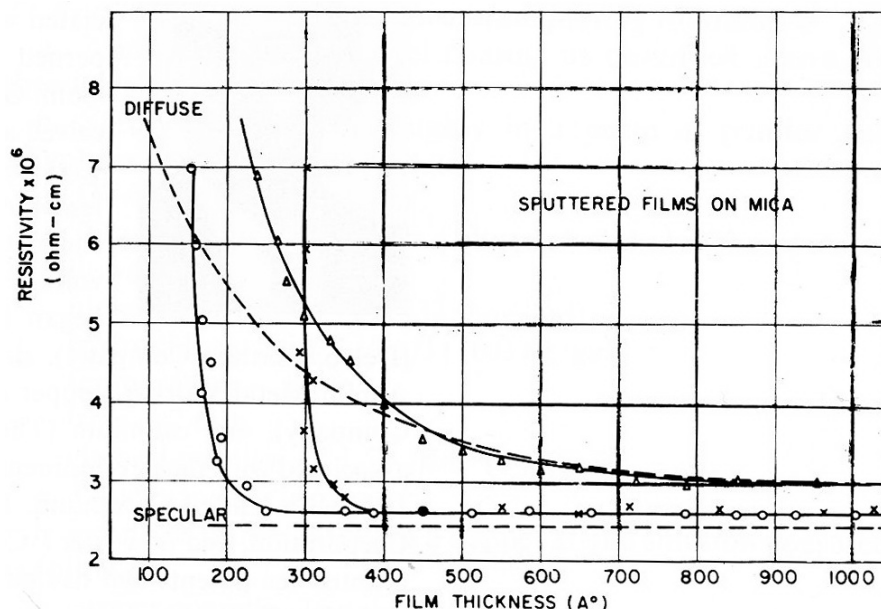


Figure 22 - Chopra and Bobb's measurements of the resistivity of sputtered polycrystalline and single-crystal (left hand curve) gold films on mica. Reprinted with permission from Pergamon Press Ltd.

Chopra⁹⁷ showed very clearly by means of transmission electron micrographs, the exact manner in which the thinner gold films less than 100 Å thick are made up of islands, and not a continuous film at all. As the film thickens or is heat treated, electrical continuity is attained at a critical thickness, and coalescence of the islands is also seen to occur as would be expected.

A current review⁹⁸ of the surface structure of gold indicates that the anomalous nature of the first two or three atomic layers is still incompletely understood.

There has been a good deal of investigation recently of optical phenomena at electrodes during electrochemical reactions, which may be considered under the title "electroreflectance" (ER). Kuwana published⁹⁹ an extensive review which includes the comment that: "In the double layer region, the ER due to the solution side of the interface appears to be small compared to ER of the metal surface, assuming specific adsorption is absent."

Another area which will benefit from the theory proposed here is that of the cathodic electrolytic heating of metal surfaces. There is a long bibliography on this subject extending all the way back to Sir Humphry Davy in 1808. Briefly, if a metal surface is made cathode at a high current density such as 3 to 5 A/cm² using 100 to 300 V_{dc} and a solution such as 5 to 10% sodium carbonate, there is arcing at the surface, which is heated red hot and even to melting. Iron and small platinum wires can be melted in this way. The process has been used commercially for case hardening in half a dozen countries, but does not seem to have achieved a noteworthy industrial importance. It is an excellent means of heating a metal surface, and it is helpful to think of the heat being generated in the surface of the metal directly, as well as in an arc against the solution. Reference is made to a book by Yasnogorodski¹⁰⁰ and to three German articles by Eichhorn.¹⁰¹⁻¹⁰³

Hydrogen overvoltage in electroplating

The hydrogen overvoltage of the basis metal being plated is often a dominant factor in plating from both acid and alkaline solutions, and may even determine whether or not any plate at all is obtained. For example, cast iron, malleable iron, or high carbon steel surfaces may become difficult or impossible to plate after cleaning and pickling in preparation for plating, due to the low hydrogen overvoltage of the resultant surface. Such surfaces of pickled or acid dipped cast iron or high carbon steel rival the surface of platinized platinum used for the hydrogen electrode in having a low hydrogen overvoltage, making it so easy to evolve hydrogen at a low potential that it is difficult to deposit many metals.

Alkaline cyanide zinc solutions often could not be used for plating cast iron or malleable iron parts, as only hydrogen evolution was obtained, or at best the coverage was poor.^{104,105} One solution to the problem was to introduce a little mercury into the bath, or to dip the part in an acid mercury-containing dip prior to plating in order to increase the overvoltage of the surface, and this procedure was patented.¹⁰⁶⁻¹⁰⁸ It was also found that treating such surfaces in boiling hot, concentrated cyanide solution for 5 to 30 min would increase their overvoltage and permit them to be zinc plated.¹⁰⁹ Sometimes the only remedy is to grind or polish off the low-overvoltage surface, or to plate over it with a heavy undercoating of another metal such as copper or cadmium. Two more recent references show that this type of behavior is still a problem.^{110,111}

Chromium plating utilizes very strongly acid baths, and is only possible on bright, dense, highly-polished surfaces in general (which have a relatively high hydrogen overvoltage). This was clearly recognized by Haring and Barrows in 1927.¹¹² If nickel surfaces are "passive," it may be impossible to chromium plate them. This can happen in a number of ways. Anodic alkaline cleaning tends to oxidize nickel and make it "passive," and should be avoided. Poorly-covered zinc die castings may have dull, streaky, dark nickel deposits in the recesses which are difficult to cover with chromium and even tend to prevent coverage on surrounding areas. The use of black nickel plate to produce low overvoltage electrodes has been patented.¹¹³

Bright nickel plate from solutions containing excessive amounts of brightener may be "passive" and impossible to chromium plate even though it appears satisfactory. Probably very small invisible amounts of nickel compounds on the surface are sufficient to give a low overvoltage condition, under the reducing conditions at the cathode. Similarly, Raney nickel powder is a catalyst used for hydrogenation, and very small quantities are effective.

The theory of the electrodeposition of chromium itself is probably very closely tied up with the theory of hydrogen overvoltage. A black, powdery coating of chromium probably has a low overvoltage and tends to inhibit further chromium deposition and promote hydrogen evolution. The success of the hexavalent chromium plating solution may be due to the ability of chromate to complex or otherwise render harmless such impurities as iron, copper, zinc, nickel, lead, etc.

This type of impurity is difficult to control in trivalent chromium baths. The removal of lead is a definite step in the operation of chromium ammonium sulfate baths used for the electrowinning of the metal,^{114,115} and, if such baths are shut down for more than a few minutes, a low overvoltage condition results on the cathode chromium surface which may take many hours of electrolysis to overcome. This period of electrolysis is probably in the nature of an electrolytic purification, and is also required in breaking in a new bath before the current efficiency can be brought up to the normal level of around 50% or more.

The current efficiency in chromium deposition is closely related to the hydrogen overvoltage of the surface and simultaneous hydrogen evolution, although 10 or 20% or more may also be lost in side reactions such as reduction of hexavalent to trivalent chromium, or of trivalent to bivalent. If the temperature of the solution is increased, the current efficiency is generally affected quite strongly.

Figure 23 from a report by N.E. Ryan¹¹⁶ shows typical behavior of 300 g/L chromic acid solutions catalyzed with sulfate and with fluoride additions, and electrolyzed at over 1000 A/ft² for chromium production. It seems likely that the low current efficiency for heavy deposits in boiling hot solutions with sulfate is due to a low overvoltage condition, whereas in fluoride-catalyzed solutions a cleaner, more oxide-free surface is maintained which probably has a higher overvoltage and gives a higher current efficiency. Shluger and Mikhailova¹¹⁷ have shown that the oxide film on sulfate-catalyzed chromium deposits contains even more sulfate proportionately than is present in the solution, while Shluger and Osbenkova¹¹⁸ felt that there was no oxide film at all on fluoride-catalyzed chromium deposits.

Low overvoltage is not necessarily a problem or a hardship in all cases in chromium plating. Thus, Bedi¹¹⁹ used immersion deposits of platinum or palladium on steel to secure a low overvoltage condition for etch prevention at low current density areas in fluoride-catalyzed baths, and Bedi and Dubpernell¹²⁰ used the same surface treatment or even etched cast iron¹²¹ to prevent chromium deposition at high current densities for stop-off purposes. Glover¹²² reported an investigation of chromium plating on cast iron in which he found that high phosphorus seemed more important than the carbon in making cast iron difficult to plate.

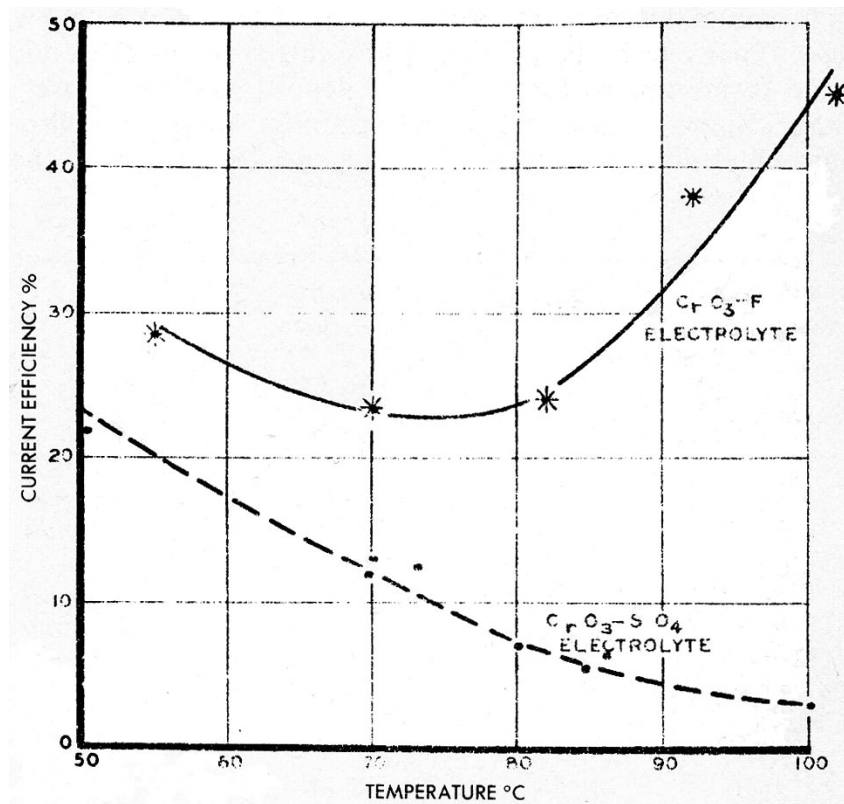


Figure 23 - Ryan's curves of current efficiency of chromium deposition at high temperatures with sulfate catalyst and with fluoride catalyst. Reprinted by permission from the Commonwealth of Australia, Aeronautical Research Laboratories, Melbourne.

In trivalent solutions, Jangg and Burger¹²³ obtained current efficiencies as high as 68% on a mercury cathode in chromium ammonium sulfate solution at pH 3.2. However, in many tests they obtained low current efficiencies due to the formation of black, spongy deposits with low overvoltage. Some of their results for chromium sulfate and chromium chloride are given in Figs. 24 and 25, and show the rather unusual result of decreasing current efficiency with increasing concentration. This should presumably be explained as due to impurities that cause lower overvoltage deposits in more concentrated solutions, but have less effect in more dilute baths.

J.E. Bride and co-workers have obtained a number of patents on chromium plating from trivalent solutions which give some indication of the dominant effect of impurities and overvoltage in these solutions, particularly if the plating speed results reported are recalculated as current efficiencies. Some of these results from one of the patents¹²⁴ are given in Fig. 26, and show the lack of reproducibility of three supposedly identical solutions tested at slightly different temperatures and made up at different times. This is presumably due to varying impurity effects and resultant varying overvoltage, as is also the falling off of current efficiency with current density. Another way of saying it might be to say that probably injurious impurities are complexed to a varying extent according to the details of the procedure and the exact organic additive used.

The William Blum Lectures

#15 - George Dubpernell - 1974

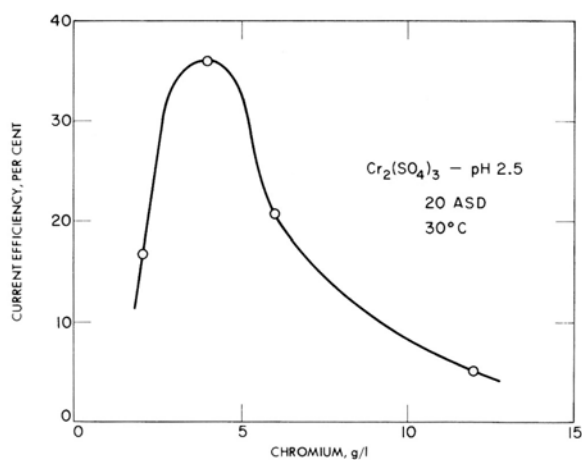


Figure 24 - Jangg and Burger's measurements of the current efficiency of chromium deposition on a mercury cathode from chromium sulfate solution. Plotted with permission from Pergamon Press.

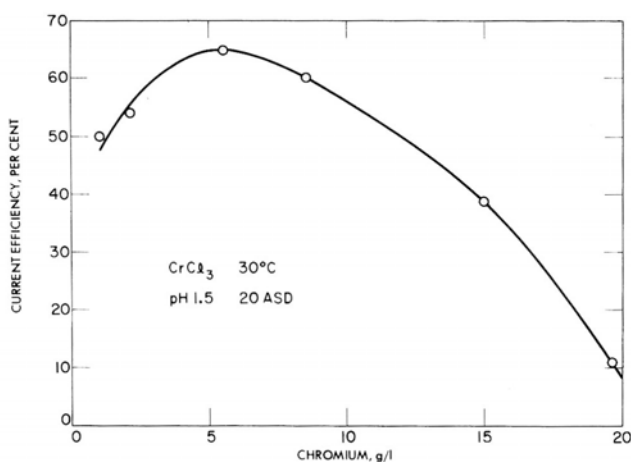


Figure 25 - Jangg and Burger's measurements of the current efficiency of chromium deposition on a mercury cathode from chromium chloride solution. Reprinted with permission from Pergamon Press.

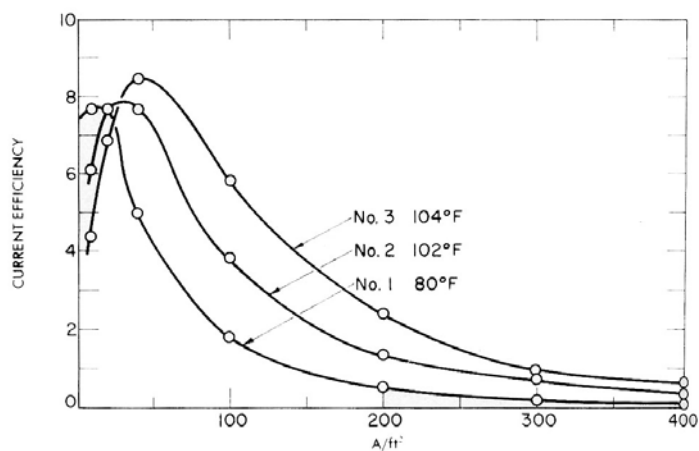


Figure 26 - Huba and Bride's measurements of the current efficiency of chromium deposition in three newly made up identical trivalent chromium plating baths at different temperatures.

Contact potential - Volta potential - Electrostatic surface potential

A continuous controversy has been going on under the name "contact potential" from the time of Volta right down to the present day, something like 180 years. Patai and Pomerantz¹²⁵ and Langmuir¹²⁶ state that Volta first discovered and measured the effect in 1797. When Volta disclosed the voltaic pile in 1800 (Ref. 1, p. 42), the title of his paper was "On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds." Volta hoped that he had discovered a means of perpetual motion, but time has not borne him out. It appears from another source (Ref. 127, pp. 133-134) that both Volta and Pfaff had worked out the first tables of the elements in the order of their ability to excite electricity, in 1793.

The name "contact potential" seems something of a misnomer, since the metals are first placed in contact but then separated for measurement of the contact potential or Volta potential across a thin, dry gas space, or in a vacuum. For this reason, the name "electrostatic surface potential" has been included above as being more descriptive. It was employed by W.A. Zisman, and seems worthy of future use (Ref. 128, pp. 1-9, "The Solid/Liquid Interface - An Essential and Active Frontier of Science").

Some of the confusion connected with contact potentials is related to their magnitude. This is often thought of as being in the range of μV , or at most a few mV, and thus unimportant in most work. That this is not true is easily evident from Fig. 27, showing the change in mercury surface potential in dry nitrogen upon addition of 2 ppm zinc (Ref. 92, pp. 219-226, paper by A.H. Ellison, G.A. Lyerly and E.W. Otto on "The Effect of Impurities upon the Surface Potential and the Spreading of Liquids on Mercury"). Within about a minute, the zinc appears at the surface of the mercury and changes the surface potential with reference to gold by about 0.80V. When the surface of the mercury is swept, it wrinkles up, and purification by removal of a surface film appears to result, as the surface potential changes considerably in the direction toward clean mercury.

Contact potentials are fairly reproducible in a number of dry gases and in a vacuum, and the exact distance between the electrodes is not critical. Generally, they are spaced 0.5 mm (0.0156 in.) apart at first, and moved further apart during the measurements. There is a great similarity to measuring a single electrode potential against a reference electrode, with the electrolyte in between replaced by a dry gas or a vacuum.

Lord Kelvin in 1897-1898¹²⁹ reviewed the previous controversies, pointed out that measurements of contact potentials as high as almost 4 V had been made, and described a dependable method of measurement. Figure 28 taken from Zisman¹³⁰ shows the type of apparatus employed. If A is moved away from B, it causes a deflection of the quadrant electrometer. If a potential is applied to counterbalance the contact potential, a point is reached where moving A away from B no longer gives a deflection of the electrometer, and thus gives a determination of the contact potential of A measured against B as a reference electrode.

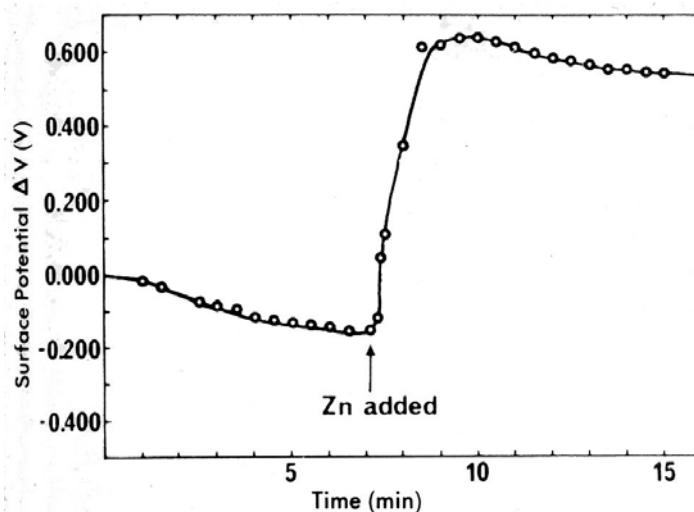


Figure 27 - Ellison, Lyerly and Otto's measurements of the change in mercury surface potential upon addition of two ppm zinc. Reprinted with permission from Marcel Dekker, Inc.

A good recent review of contact potential measurements is given by A. Dravnieks (Ref. 131, pp. 236-239). Dravnieks discusses the difficulties of these measurements and the choice of reference electrodes. He gives an interesting table of values based upon Michaelson's¹³² tabulation of work function measurements. This is reproduced in Table 1 with the work functions in a vacuum from which it was derived, and with the values for sodium and potassium from the same source added. The contact potentials are calculated using gold as the best available reference electrode, and by subtracting the work function of gold from that of each of the other metals. The familiar electromotive series is given for comparison. It is difficult to avoid the conclusion that these are merely two different methods of measuring the same quantity. Using gold as the reference electrode for the contact potentials tilts the noble metal end of the scale by about a volt or more, but the close relationship is still obvious.

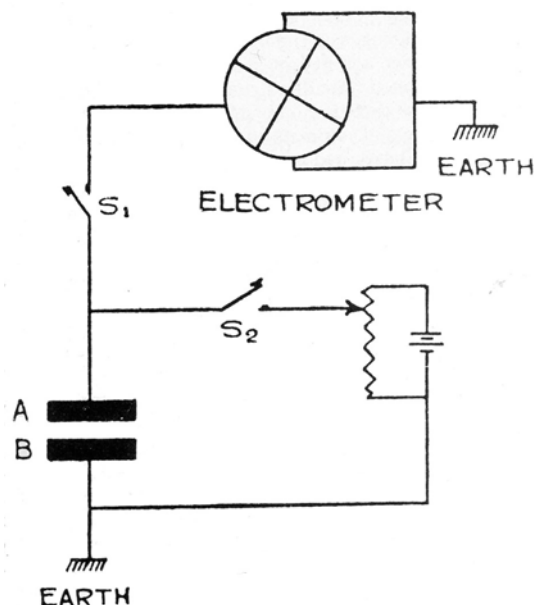


Figure 28 - Zisman's diagram of the most commonly used method of measuring contact potential differences. Reprinted by permission from the *Review of Scientific Instruments*.

Table 1

Metal	Average electronic work function in vacuum—electron V	"Contact Potential" in vacuum vs gold-V	Electromotive Series-V
Potassium	2.15	-2.43	-2.92
Sodium	2.27	-2.31	-2.713
Magnesium	3.46	-1.12	-2.38
Aluminum	3.74	-0.84	-1.66
Zinc	3.74	-0.84	-0.763
Iron	4.36	-0.22	-0.44
Cadmium	3.92	-0.66	-0.402
Tin	4.11	-0.47	-0.140
Lead	4.02	-0.56	-0.126
Hydrogen	—	—	0.000
Copper	4.47	-0.11	+0.34
Silver	4.28	-0.30	+0.799
Mercury	4.52	-0.06	+0.854
Palladium	4.82	+0.24	+0.987
Platinum	5.29	+0.71	+1.2
Gold	4.58	0.00	+1.42

While the contact potential measurements are not ordinarily of great accuracy and reproducibility, the potentials of the electromotive series have a somewhat similar background and are largely calculated from the thermodynamic properties of materials rather than being measured values (Ref. 51, p. 88; Ref. 68). Contact potentials or electrostatic surface potentials are quite sensitive to adsorbed layers on clean metallic surfaces, and this property has led to their use in studies of adsorption, such as those by Zisman and his collaborators¹²⁸ for example.

Instead of using a vacuum or a dry gas, Fort and Wells¹³³ found that steady, easily reproduced contact potential difference measurements could be made in a saturated nonpolar organic liquid environment such as cyclohexane or benzene. Using electrodes submerged in such media they were able to study the effect of the distance of separation of the electrode from the gold reference electrode. They found that contact potentials could be measured to a precision of ± 0.001 V in organic liquids.

An even greater accuracy of ± 0.000001 V useful in semiconductor work was found by Steinrisser and Hetrick,¹³⁴ using a low voltage electron beam technique to determine the photovoltage or photoelectric emission of cadmium sulfide exposed to an intermittent beam of light in a high vacuum.

Langmuir¹²⁶ was convinced that contact potentials and the electromotive series were intimately related, and stated "The Volta series of the elements is determined by the magnitude of ϕ , the electron affinity" (electronic work function). On the basis of the limited data available to him in 1916, he concluded that "... contact electromotive forces can account for only about half of the observed electromotive forces of cells." One might say that the more recent measurements given in Table 1 indicate an even better correlation.

A number of subsequent workers have studied this inter-relationship, but invariably appear unable to conclude that the two types of potentials are an identical property of the elements arrived at by different methods of measurement or calculation. Gurney¹³⁵ in 1932 showed the parallelism between the electrochemical series and the Volta contact potential series on the basis of general theoretical and mathematical considerations, and concluded that interface potentials are due to the electrons at the metal-metal junction, and that the Nernst theory of solution pressure of the metals is incorrect. He continues these same views in a later book (Ref. 136, pp. 33-38, 192-200).

Klein and Lange¹³⁷⁻¹³⁹ made their own measurements of Volta potentials of the elements against mercury as a reference electrode, in an argon atmosphere. However, they do not seem to compare these measurements with the electromotive series, and instead devote their attention to contact potential measurements between mercury and aqueous solutions. Even in a book in 1962,¹⁴⁰ a chapter is devoted to the Volta potential without discussing any possible relationship to the electromotive series.

Butler¹⁴¹ makes a comparison in 1951 on the basis of zinc as the zero reference electrode, and concludes that the metal contact potential difference is a large part of the electromotive force of the cell. He does not quite seem to consider these forces identical, but "... the electromotive forces generally show a fairly close parallelism with the contact potentials."

On the basis of the theory developed in the present paper, it appears that "contact potentials" or electrostatic surface potentials are largely eliminated when pieces of metal are pressed together in good electrical contact in the external circuit. All of the pieces of metal in the exterior circuit are combined as if consisting of a single piece of metal; the conduction electrons of each piece of metal are free to circulate among all of the pieces of metal and establish their own equilibrium. Now only the exterior surfaces of each piece of metal are free to exhibit the intrinsic "contact potential" of that metal, and it would seem best to regard this "contact potential" as having been largely eliminated at or near the points where the pieces of metal are pressed together. At or near these latter points where the pieces of metal are pressed together, only smaller differences of potential remain such as the contact resistance (IR drop), thermoelectromotive force, etc.

The high electrical conductivity of metals apparently does not mean that all points in a given piece of metal are at the same potential. It is a common observation that a piece of metal which is being chromium-plated may only plate on the projecting parts, and the low current density areas may receive no chromium plate at all. This means that during the flow of current, at least, the projecting areas were at a higher cathode potential, and the recesses at a lower cathode potential, simultaneously.

It is not good practice to plate articles made up of a number of pieces of different metals stamped or welded together. If this has to be done, the first effort is to find a solution, perhaps cyanide copper, which will cover all of the metals in the assemblage with a

good coating of a single metal, such as copper. Thereafter, the piece can be plated easily as a single piece of metal. Failing this, one expects difficulty around seams and welds between the different metals, or part of the assembly may plate readily and other parts not at all.

The so-called hydrogen electrode

It appears that any metal coated with its oxide exhibits an electrode potential behavior sensitive to acid and alkali that can be used to measure acidity and alkalinity over certain ranges of pH. Such responses have already been indicated in Figs. 5, 6, and 7 for tin, chromium and platinum. Others are shown in Fig. 4. Antimony and palladium are sometimes used. The glass electrode can possibly be considered a silicon oxide electrode. Mercury-mercury oxide electrodes are used for accurate pH measurement in alkaline solutions.

Bates (Ref. 142, pp. 304-306) describes a number of other "hydrogen ion electrodes," including tungsten, tellurium, bismuth, iridium, rhenium, osmium, ruthenium, and manganese dioxide. Ives and Janz (Ref. 143, pp. 116-117) also discuss hydrogen electrodes based on other metals, and include gold, rhodium, nickel and selenium, in addition to many of the above. New hydrogen electrodes are patented from time to time. One recent patent described uranium oxide,¹⁴⁴ and another palladium oxide.¹⁴⁵

A number of electrodes are quite far removed from the hydrogen electrode and yet give good responses to acidity and alkalinity. The mercury-mercury oxide electrode and the silver-silver oxide electrode are 0.926 and 1.17 V, respectively, above the hydrogen electrode, and are useful in alkaline solutions (Ref. 143, pp. 334-335). Cahoon¹⁴⁶ found the manganese dioxide electrode to be about 1.07 V above the hydrogen electrode, and to give an accurate pH response from pH zero to pH 11.5 with the apparent possibility that it could be used beyond this range. Cahoon has also contributed a good practical article on the use of reference electrodes.¹⁴⁷

While a hydrogen atmosphere is generally employed in the operation of the platinized platinum hydrogen electrodes and a few similar electrodes, most of the other metal-metal oxide reference electrodes mentioned above are used in air and have no special requirement.

Two notable investigations containing a great deal of information on the above matters were published in 1928 by French and Kahlenberg¹⁴⁸ and Closs and Kahlenberg.¹⁴⁹ In the first paper, French and Kahlenberg¹⁴⁸ report the changes in electrode potentials of 24 metals and graphite, starting with air-saturated normal potassium chloride solution in each case, when oxygen, nitrogen or hydrogen was bubbled through the solution. Nitrogen and hydrogen generally had similar effects, and air and oxygen were often similar. Other gases studied in some cases were carbon monoxide, methane and helium. The effect of stirring and complete submersion was also examined. In general, the gases had very pronounced effects on the potentials of the metals.

In the second paper, Closs and Kahlenberg¹⁴⁹ showed that a number of metals could be used instead of the hydrogen electrode for the potentiometric titration of acids and bases, particularly molybdenum, tungsten, arsenic, antimony and bismuth, but also tin and aluminum. While the metals have different potentials at the start, they all give the same end-point in an acid-base titration followed potentiometrically. In the discussion to this paper Professor Kahlenberg said: "I think that the other electrodes here mentioned are just as reproducible as the hydrogen electrode. They can be calibrated and used, any of them, particularly those that are not attacked. I do not believe we need a hydrogen electrode at all; ..."

The writer would conclude from the widely varying potentials in the above work that the so-called hydrogen electrode is only one example of a number of electrodes displaying similar behavior, and that its potential does not seem to have been shown to be that of hydrogen at all.

Dr. Blum characterized Kahlenberg's work in one of the above discussions very well when he said (Ref. 148, p. 194) "Dr. Kahlenberg has a faculty - I do not know whether I would call it a happy faculty or not - of developing a lot of facts which cannot be explained. I am not going to try to explain them."

The Nernst theory of the electromotive activity of the ions

Arrhenius proposed the theory of electrolytic dissociation in 1883-1887, and Nernst the theory of the electromotive activity of the ions in 1889.¹⁵⁰ Both of these theories seem to have been rather highly overworked, and it would appear to be time for serious reconsideration and re-evaluation. The objections would seem to have most commonly been ignored, brushed aside, and lost sight of.

Glasstone (Ref. 151, pp. 18-20, 321-322) gives a brief review of some of the objections to the theory of electrolytic dissociation. There was also a well-timed and fairly comprehensive symposium on the subject in September, 1903, at the fourth meeting of the American Electrochemical Society in Niagara Falls, New York. The situation was well summarized by Bancroft,^{151a} and an extensive discussion followed.

One of the strongest opponents was Professor Louis Kahlenberg (1870-1941) of the University of Wisconsin. Strangely enough, Kahlenberg studied in Ostwald's laboratory in Leipzig where he received his Ph.D. in 1895. He was at first an enthusiastic supporter of these new theories until he found that they did not agree with many experimental facts, and vigorously opposed them from about 1900 on.¹⁵²

A comprehensive bibliography of the publications of Kahlenberg and his associates is available.¹⁵³ In a few years, Kahlenberg's position became clear and was stated in four articles in 1901-1905,¹⁵⁴⁻¹⁵⁷ in addition to many research reports. One remarkable feature of his research reports was that many of them were published in the *Journal of Physical Chemistry*, even though its editor, W.D. Bancroft (1867-1953) was devoted to the theory of electrolytic dissociation. Lincoln¹⁵² quotes Bancroft as writing to Kahlenberg: "You are right, Kahlenberg, but you will find that you cannot convince people with facts."

Apparently this proved to be true. On the occasion of the 25th anniversary of the theory of electrolytic dissociation, G.N. Lewis¹⁵⁸ discussed many of the facts showing what a poor basis the theory had, and yet concluded in favor of the theory on the basis of its "serviceability."

Kahlenberg practiced what he preached. He wrote a text book of general chemistry¹⁵⁹ which made no use of the ionic theory and replaced it instead with the concept that solutions were merely chemical compounds having variable proportions. His textbook was popular and was used for quite a period of time, and passed through several editions. Kahlenberg established an enviable reputation as an excellent teacher.

However, Kahlenberg's opposition to the electrolytic dissociation theory was largely to no avail at the time. Lewis⁴⁵ promoted the activity coefficient which made some allowance for the behavior of individual ions, but was not adequate for much improvement, as has already been discussed (sometimes called a waste-basket factor, in that it included many errors and variables). The Debye-Huckel interionic attraction theory was introduced in the 1920s to extend the range of concentration covered by the theory of electrolytic dissociation, but did not extend to high concentrations or make an extensive alteration of the circumstances. Kahlenberg said despairingly in the discussion to LaMer's paper in 1927: "The trouble is, we don't take our Epsom salts seriously enough!" Unfortunately, this expressive comment was toned down in the printed discussion.¹⁶⁰

The same volume of the *Electrochemical Society Transactions* included a paper by Bancroft¹⁶¹ which reviewed some of the difficulties with the Nernst and Arrhenius theories. Outstanding is his comment that the measured pH of a solution does not necessarily show anything about the actual concentration of the hydrogen ion. Bancroft gives an example of the addition of enough sodium chloride to 0.1N HCl making the apparent hydrogen ion concentration equivalent to 0.5N HCl, and that this would correspond to a dissociation of 300% or more, which is, of course, absurd. This type of effect is still under study.^{162,163}

One might say at this point, what about the burgeoning field of ion selective electrodes, as described by Frant,¹⁶⁴ for example? In general, these electrodes do not serve to determine a given ion directly in the plating bath. Commonly, the desired ion is diluted very extensively in a medium of constant background composition and pH, and the desired ion may itself be altered in the process. Great skill and remarkable manipulative variations have been used to seek out "Nernstian" conditions and responses in this area of development, but it is obvious that electrode potentials are more often than not non-Nernstian. European workers¹⁶⁵ have expressed a preference for the term "ion sensitive" rather than "ion specific" or "ion selective."

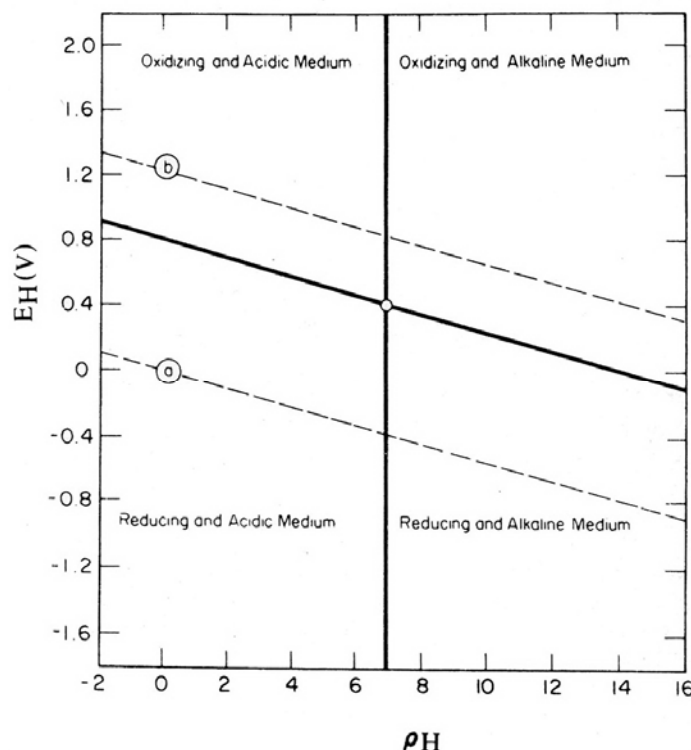


Figure 29 - Pourbaix diagram of electrochemical equilibria in water containing acid, alkaline, oxidizing and reducing media. Reprinted with permission from Plenum Publishing Corp.

The Pourbaix potential-pH diagrams¹⁶⁶ provide a useful means of studying and recording thermodynamic data. If one considers that ions in solution are not electromotively active or potential-determining, but, at most, merely modify the pre-existing electrode potential, which is an intrinsic property of the electrode material, then it is of interest to examine the significance of the most general type of potential-pH diagram. Figure 29 is such a diagram (Ref. 167, p. 112; also Ref. 166, p. 100, and Ref. 168, p. 36). The line "a" is the potential of the hydrogen electrode, which also is the basis of the pH scale (Figs. 2 and 3), and the line "b" is the oxygen electrode. Potentials above the line "b" correspond to anode reactions and potentials below the line "a" correspond to cathode reactions. These reactions can be produced chemically as well as electrolytically, as by using hexavalent chromium, permanganate, hydrogen peroxide, fluorine, or other oxidizing agents to get oxidation or an anodic effect; and bivalent chromium, hydrosulfite, hypophosphite, metallic sodium or other reducing agents to get reduction or a cathodic effect.

Electrophysiology

Electrochemistry appears at least partly as an outgrowth of electrophysiological studies, and electrochemists have always been fascinated by the obvious importance of electrical phenomena inherent in living organisms. According to Motte-lay (Ref. 169, pp. 298-300) studies of electric fishes and eels were made in the 16th, 17th and 18th centuries prior to Galvani's work on "animal electricity" which was first published in 1791.^{1,170} John Hunter, a distinguished Scottish surgeon, received the Copley Medal of the Royal Society in 1775 for his work on the dissection of electric fish.¹⁷¹ Hunter found as many as 1182 "columns" or separate layers ("electroplaques" or "electroplates" in French) in each of the two electric organs of a very large fish 1.3 m (4.5 ft) long and weighing 33 kg (73 lb.) (Ref. 169, pp. 240-241).

It was the background of Galvani's work, and also that of Ritter,² that stimulated Volta to discover the voltaic pile or battery. Volta did not like ascribing an animal origin to electricity, and showed that it could be generated by metals in contact with salt solutions.

The electric eels of the Amazon River are said to be capable of delivering shocks of up to 600 V and one A or more, sustained for several milliseconds, in the course of killing or stunning their prey¹⁷²⁻¹⁷⁴ (also, Ref. 175, p. 157). The source and handling of this much electric power in nature does not seem to have received adequate explanation.

Beutner^{176,177} proposed a theory based upon the contact potential differences of the two sides of the biological membrane which appears to have merit. Grundfest (Ref. 175, pp. 141-166) considers the source of bioelectric potentials to lie within the membrane itself.

Dr. G. W. Crile (1864-1943) was a pioneer surgeon who devoted much attention to the electrical nature of life. With his associates, he was said to have dissected some 3734 animals of all sizes and varieties.¹⁷⁸ He published many books and articles, but the titles of two seem particularly suggestive.^{179,180}

A great deal has been published in this general area, and a comprehensive review is not possible in the present article. Several additional titles seem particularly noteworthy.^{181,182}

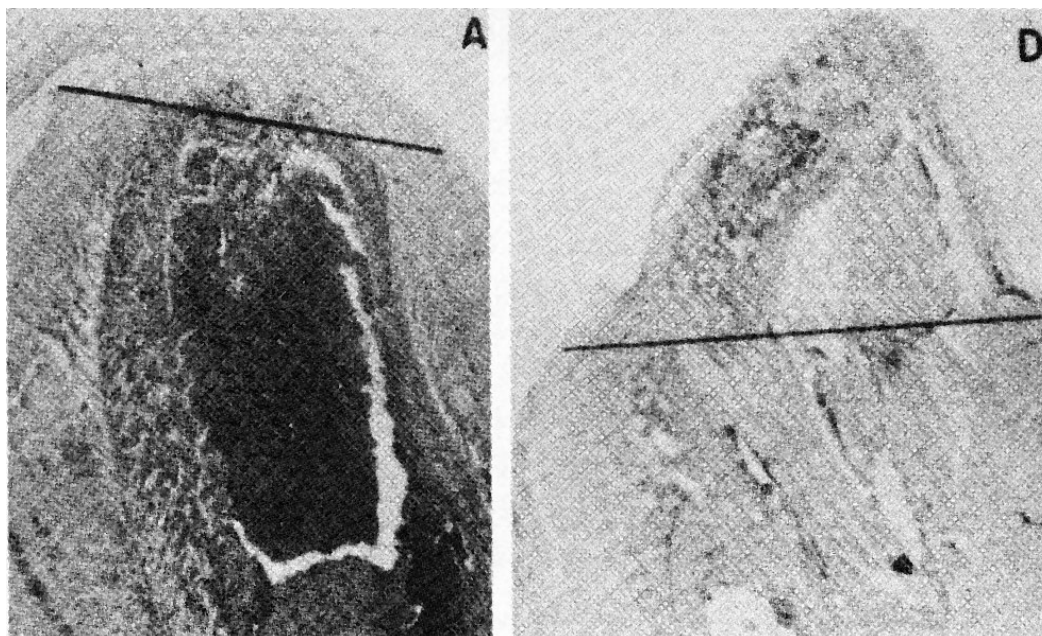


Figure 30 - Becker's results on the stimulation of bone growth of amputated rat's legs after seven days. The line shows the approximate level of original amputation. A is the control, D shows growth due to stimulation of extremely low current density as cathode. Reprinted with permission from Macmillan Journals Limited.

The Electrochemical Society, Inc. has continued activity in this field with the publication of a recent symposium.¹⁸³ The first article in this symposium is a noteworthy review of electrochemical events in tissue growth and repair by A.A. Pilla (Ref. 183, pp. 1-16). Pilla calls attention to the remarkable work of R.O. Becker on the stimulation of bone growth by extremely low current density cathodic treatment similar to plating except for the very low current density.¹⁸⁴ Figure 30 shows the result of Dr. Becker's tests over a seven day period.

Relationships to electronics

Many relationships to electronics have already been made evident. In 1796, (Ref. 185, p. 4) Volta named all dry conductors, conductors of the first class, and all wet conductors or liquid conductors, conductors of the second class. He had apparently originated this terminology a few years earlier (Ref. 127, pp. 132-133) in connection with the description of the table of metals and other conductors of the first class, in the order of their ability to excite electricity.

The first use of the term "semiconductor" is of special interest. In 1792, (Ref. 127, p. 5) in repeating Galvani's frog leg experiments, Volta was sensitive to the loss of charge to the ground through various nominally nonconducting materials, such as ice, a damp wooden or marble table top, a person, or damp wall hangings, and called these "semiconducting." In 1805, (Ref. 186, p. 79) Ritter credits Volta as using the term "semiconductor" for materials such as the above. However, further on (Ref. 186, pp. 225-239) in a more realistic discussion of semiconduction, Ritter states that Volta called such substances "semi-insulators", but that he prefers to call them "semiconductors." He did not have many examples, but mentions alcohol, ether, naphthene and metal oxides and their compounds.

The classification of conduction as "electrolytic" if electrode reactions are observed does not seem called for. Once the current has crossed the anode or cathode interface by means of an electron transfer reaction, the conduction through the medium is indistinguishable from metallic conduction, and Ohm's law is obeyed. This view, that there is fundamentally no difference between electrolytic and electronic conduction, has been expressed by a number of electrochemists, but their views have attracted little attention.

Thus, J.W. Richards¹⁸⁷ reviewed earlier work by Marvin on induced currents in electrolytic conductors showing that they behaved in exactly the same manner as a metallic conductor of the same resistance. Richards concludes from this and his own experiments that solutions are simple conductors of the same nature as metallic conductors.

Kahlenberg¹⁸⁸ reviewed the matter and favored the view that conduction in electrolytes is simple conduction the same as in metal, and that the reactions at electrodes are secondary phenomena.

Lukens¹⁸⁹ made a laborious study of current distribution in metal and in solutions by means of equipotential lines, and concluded that the lines are identical in every respect in the solutions as in the case of the metallic conductor.

Brenner¹⁹⁰ experimented with the induction of current in an electrolyte containing a dye, and without using electrodes, compared to electrolysis with electrodes. The difficulties of this type of experimentation are evident. Brenner concludes in favor of the migration of ions in the electrolyte, but this conclusion seems to represent his convictions more than clear cut results of the experiments.

Rosenberg and Postow (Ref. 191, pp. 161-190, an article on "Semiconduction in Proteins and Lipids") report electronic conduction in hemoglobin up to a hydration of about 20% and electrolysis and ionic conduction in the presence of more water.

The interpretation of these and other facts may be helped by placing the most important information available on the resistivity of different materials and media in a single chart for reference. This has been done in Fig. 31, which shows resistivities ranging from those of the best insulators such as polystyrene and mica to superconductors near the absolute zero of temperature. It is interesting that fused salts have such a narrow range of resistivity.

This is one of the longest scales in existence for any single property. A defect is that it tends to disregard the effect of temperature variation. Thus, a metal may appear as a superconductor on the right hand end of the scale at zero degrees Kelvin, but move up to the middle of the scale into the range shown for metals, as the temperature increases to room temperature.

Semiconductors, on the other hand, move in the opposite direction as the temperature is increased, and exhibit a decreasing resistivity. The same is true of aqueous solutions with which we are largely concerned - the resistivity decreases as the solution is heated. From this point of view, solutions can be looked upon as liquid semiconductors, and there seems no reason for not considering them as such. Their resistivity is in the middle of the semiconductor range. The occurrence of barrier layers and electrolytic rectification at the electrodes is a commonplace. The occurrence of electrode reactions at the electrodes is perhaps evidence that this is the only means by which the current is able to cross the interface.

The study of "amorphous" or liquid semiconductors has developed into an extensive area of investigation. Gubanov¹⁹² does not discuss the problems of ionic conduction in liquid electrolytes, but does conclude that there is no basic difference between liquid and crystalline electronic conductors, and that the mechanism of electron motion in liquids and crystals is of the same nature.

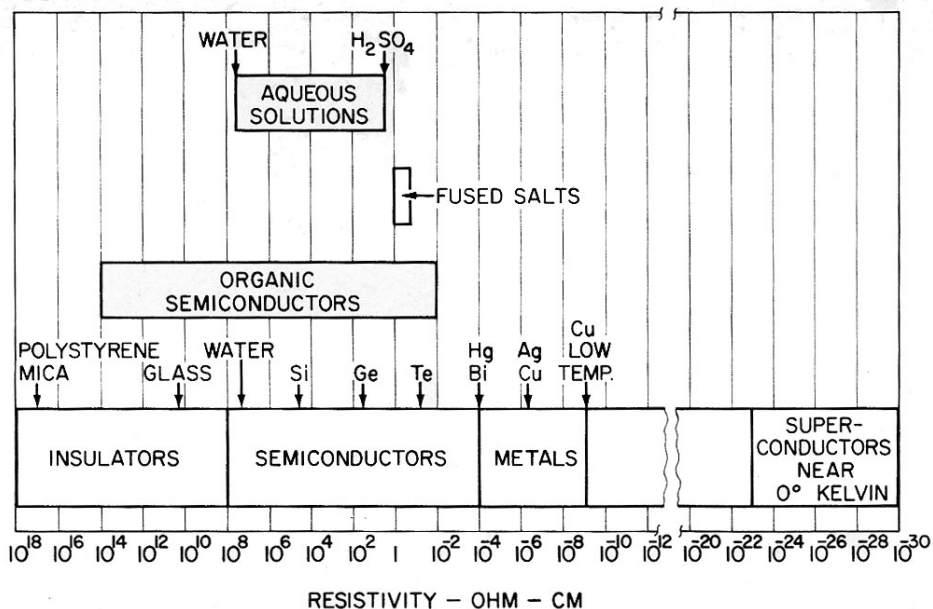


Figure 31 - Chart of the electrical resistivity of various media and materials at various temperatures.

The electronic properties of metal surfaces are of concern to solid state physicists. A noteworthy review is that of H.J. Juretschke (Ref. 90, pp. 38-53) who calls attention to a proposal of C. Herring¹⁹³ of a fictitious or artificial metal called "jellium metal." Jellium metal might be considered to be a positive jelly or a uniform positively-charged medium against which the electrons move. These considerations are apparently helpful in discussing the nature of metal surfaces. The most recent review by Boudreaux and Juretschke¹⁹⁴ is not available to the writer.

Bogenschütz (Ref. 195, pp. 319-368) gives an outstanding review of electronic devices based upon an electrochemical foundation, of which there are a surprising number. Some of this material also appeared earlier in several magazines.¹⁹⁶ There are coulometers and microcoulometers, and electrochemical timers. Eleven pages are devoted to electrolytic information storage cells. Devices based on redox reactions include an electrolytic analog transistor, the Solion and a vibrating transducer. Conductivity cells appear in several devices. Electrolytic rectifiers and condensers are, of course, old and well-established pieces of equipment. Other devices mentioned are a gastrointestinal sender, an electrolytic respirometer, and a stabilization cell. Dry batteries, storage cells, fuel cells, and thermogalvanic cells are also briefly described.

It is, thus, apparent that the electronic industry already has close ties with electroplating and electrochemistry, and uses these freely in its device technology. It should be mentioned that the book by Vijn¹⁹⁷ has also been helpful.

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About the author

Excepting the last sentence, this piece was written at the time Dr. Dubpernell was announced as the recipient of the 1973 Scientific Achievement Award:



Dr. George Dubpernell, a pioneer researcher in chromium plating and a world renowned expert in the history of electroplating, was chosen by the AES Scientific Achievement Award Selection Committee as the 1973 recipient. The announcement was made at the opening session of the 60th Annual Technical Conference of the American Electroplaters' Society.

Previously, Dr. Dubpernell was made a national honorary member of the Society at the National Convention in 1966. He has twice received the chromium plating award from the Society, first in 1960 and again in 1970, for outstanding papers on chromium plating. His earliest technical talk before an AES group was on chromium plating before the Detroit Branch in September, 1924. He became a member of the AES in 1925. He is the only U.S. charter member of the Institute of Metal Finishing, which he joined in 1926.

Dr. Dubpernell was active consultant for M&T Chemicals Inc. since his retirement in 1966 after 33 years of continuous service in the plating research department. From 1944 to 1955, he was manager of the Waterbury laboratories.



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Dr. Dubpernell's contributions to industry include the insoluble ball anode basket in the late 1920s, and the first detailed investigation of chromate conversion coatings on cadmium and zinc in the early 1930s. Both studies resulted in important patents. His work on chromium plating with Dr. Colin G. Fink at Columbia University in 1925-1927 included the establishment of bright plating ranges for large numbers of chromium bath compositions. He is perhaps most noted for publications on chromium plating in many editions of the *Metal Finishing Guidebook* and the Electrochemical Society's *Modern Electroplating*. The test he originated for revealing the crack patterns in chromium deposits is widely used and is known as the "Dubpernell test."

With United Chromium, Incorporated in Waterbury, Connecticut, from 1933 on, Dr. Dubpernell worked out successful conditions and equipment for barrel chromium plating which are still widely used. The barrel chromium plating work led to intensive development of insulating coatings for use in chromium plating baths. These included the formulation of stop-off lacquers and waxes, and rack coating compositions. This business grew into what is now M&T's Organic Coatings Division.

Born in Detroit, Michigan, May 30, 1901, Dr. Dubpernell became imbued with the desire to become a scientist while still in elementary school, and as a result attended Cass Technical High School where he graduated in January, 1919. Two years of experience as a lead plater at the Detroit Battery Company followed and was combined with two years of pre-engineering college training at Detroit Junior College (now Wayne State University). Dr. Dubpernell then worked as a zinc plater with the Harris Zinc Process Company of Hamtramck, Michigan.

Entering the University of Michigan in September, 1922, Dr. Dubpernell graduated in June, 1924 with the degree of B.Sc. in Ch.E. Here he studied under both Professor A.L. Ferguson and Professor E.M. Baker. He was employed in the laboratories of Dr. Colin G. Fink at Columbia University for two years, 1925-1927. During this time he also attended classes, and received an A.M. degree in Ch.E. from Columbia in 1927.

Returning to the University of Michigan in September, 1927, Dr. Dubpernell continued his studies towards a Ph.D. degree in chemistry under Professor A.L. Ferguson and was awarded this degree in August, 1933, for work on hydrogen overvoltage and the diffusion of hydrogen through platinum and palladium. During this period he commuted to Detroit, Michigan, where he was employed by the General Chromium Corporation and then by the Udylyte Process Company.

Dr. Dubpernell married Grace Greenville Hossack of Jersey City, New Jersey, May 28, 1927. The Dubpernell's have three daughters, all married, and nine grandchildren. In the course of keeping in touch with the progress of their children and grandchildren, Dr. Dubpernell and his wife traveled in all 50 states. Travel is also something of a family hobby, and after retirement, they took two cruises around the world and the North Cape cruise into the Arctic.

After he retired in 1966, Dr. Dubpernell did research work at the University of Detroit continuing his earlier investigations into the nature of hydrogen overvoltage.

Dr. Dubpernell's major hobby was book collecting, and he amassed what is probably the most complete private library of electroplating books and magazines. He served the AES Detroit Branch energetically as Branch historian. He has passed through various stages as a gardener, and took most pleasure from gratifying a youthful desire to raise apples.

Dr. Dubpernell passed away on June 16, 1992.