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THE ELECTROMOTIVE BEHAVIOR OF SINGLE ZINC CRYSTALS. THE EQUILIBRIUM POTENTIAL

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An examination of the electromotive characteristics of single metal crystals may be expected to contribute information touching four important problems. (1) It is the present practice in measuring the electrode potentials of the semi-rigid lattice metals, *e. g.*, zinc, cadmium and copper, to employ as a standard electrode a finely divided conglomerate of crystals prepared by rapid electrolysis under specified conditions and to assume that the potential of such an electrode, if reproducible, is uniquely characteristic of the element. The study of single crystal electrodes, if such electrodes be found capable of yielding constant and reproducible potentials, offers a means of more clearly defining the significance of measurements on crystal matrices and of studying the more generally important relation between surface structure and potential by connecting an observed potential with a structure definitely describable in the crystallographic sense. (2) It has heretofore been found impossible to prepare satisfactorily reproducible electrodes of the rigid lattice metals, *e. g.*, iron and nickel; the marked discrepancies in the measurements reported by various observers may be attributed, at least in part, to differences in physical structure conditioned by the arbitrary methods of preparation adopted and to unknown quantities of gas held in solution in the interstitial layers of the polycrystalline metal, difficulties which should be minimized by the use of single crystals. (3) The establishment of a reproducible potential for a single strain-free crystal would seem to furnish the only sound basis for the study of the relation between mechanical strain and electrode potential. (4) The coördination of electromotive and photoelectric data which is possible at present only for the soft alkali metals requires that both measurements be made upon comparable specimens of the metal. A finely divided matrix is not well adapted to photoelectric or contact potential measurement while the massive specimens generally employed in photoelectric determinations do not give reproducible potentials in electrolytes. It is an open question whether any two polycrystalline mosaics are strictly comparable and the influence of crystal orientation has to be considered.[2] It seems probable that the correlation of the electromotive, photoelectric, and vapor pressure characteristics of single metal crystals will throw light on the mechanism of the reaction

$$\text{M (atom in surface lattice)} \longrightarrow \text{M}^{n+} \text{ (in solution)} + nE \text{ (lattice)}$$

as well as on the various energy transitions involved in this reaction.

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[2] Linder, *Phys. Rev.*, **30**, 649 (1927), has obtained evidence for a 2:1 variation in the photoelectric work function between the basal and prismatic orientations of zinc.

The present paper reports measurements designed to appraise the electromotive behavior of a typical, easily prepared crystal, that of zinc, with especial reference to the constancy and reproducibility of the potential of the primary cleavage (0001) face. Some hundreds of measurements on air-free cells of the type

$$Zn, ZnCl_2 \text{ (aq.)}, HgCl, Hg$$

made on fifteen crystals prepared by three different methods have shown conclusively that a single zinc crystal is a reversible electrode capable of yielding potentials constant to a few hundredths of a millivolt and reproducible over dissimilarly prepared crystals to one or two-tenths of a millivolt.

Experimental

Materials and Equipment.—The zinc employed in the preparation of the electrolyte and matrix electrodes was Kahlbaum's analytical grade purified by two fractional distillations in vacuum and a final electrolytic precipitation. Analytical grade hydrochloric acid was redistilled twice. Water from the laboratory still was redistilled from alkaline permanganate and sulfuric acid. Mercury of good initial purity was washed in the usual tower, redistilled twice in an oxidizing atmosphere, and filtered through a small capillary. Calomel was prepared electrolytically from the purified mercury and hydrochloric acid, washed and dried in vacuum. A small quantity of the purified mercury was redistilled once again, partially converted to calomel, and used in one of two duplicate calomel electrodes in the first cell set up, checking the purity of the main stock. Tank nitrogen was freed from reactive gases by repeated passage over hot potassium in a reciprocating gasometer.

The potentiometer and constant temperature installation were similar to those described in a previous paper[3] except that thermostatic regulation was effected without relays with a Thyratron grid-controlled mercury arc tube. Duplicate Weston cells, thermostated to 25.0° and frequently checked for consistency during the measurements, were calibrated against Bureau of Standards certificated cells immediately before the final measurements.

Preparation of Electrolyte.—Air-free zinc chloride electrolyte was prepared by treating an excess of purified finely divided zinc with purified hydrochloric acid in an all-glass storage flask, diluting with distilled water, boiling, evacuating quickly after closing the flask, and finally passing purified nitrogen during cooling. The storage flask was fitted with side stopcock and siphon delivery tube passing through a ground stopper. The delivery tube carried a glass wool filter, stopcock and junction ground to fit the cell described below. Some difficulty was encountered in obtaining an electrolyte which could be accepted as an equilibrium solution; dissolution of the zinc in the acid was extremely slow, requiring, with the assistance of platinum scraps and continuous warming, about four weeks to attain the approximate completion indicated by cessation of a noticeable evolution of hydrogen. On dilution and again on boiling the basic chloride precipitate appeared. The electrolyte was allowed to stand in contact with the mixture of metallic zinc and basic precipitate at the cell temperature for at least two months before introduction into the cell.

Analyses were carried out on the electrolyte taken from the cell after completion of a series of measurements. Quadruplicate samples were taken from a weight buret and analyzed gravimetrically as silver chloride. Analyses checked to within 0.1%.

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[3] Anderson, THIS JOURNAL, **48,** 2286 (1926).

Preparation of Matrix Electrodes.—The platinum spiral cathode usually employed in the preparation of finely divided metal electrodes by rapid electrolysis was replaced with a point cathode, a straight stiff platinum wire extending to within a few millimeters of the end of an open 6-mm. glass tube immersed in the electrolyte. The close current regulation necessary to obtain a deposit of the required character with the spiral cathode is unnecessary with the protected point cathode; beautiful trees of silver-white microcrystals are obtained without any current regulation whatever. When the point is first immersed the current remains of the order of a few milliamperes until the deposit passes the orifice of the tube, then increases rapidly to as much as three amperes as the tree grows without apparent alteration in the character of the deposit. The finely divided metal was washed with distilled water, stored under water and dried in a vacuum desiccator immediately before introduction into the cell.

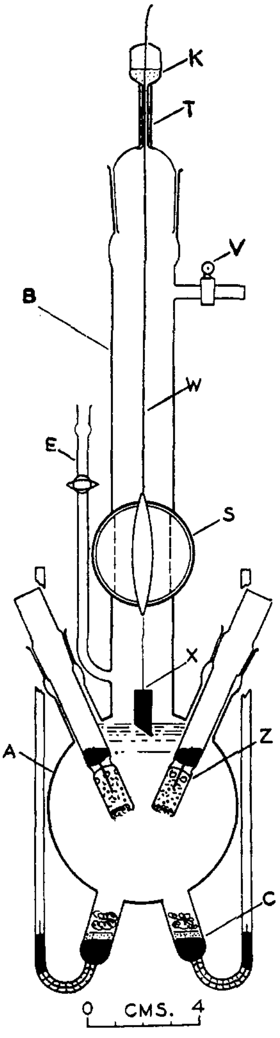

Fig. 1.

The Cell.—It was required that the cell permit of filling with exclusion of air and desirable that it permit of interchanging crystal electrodes without admission of air. The cell proper, A, Fig. 1, carrying duplicate calomel electrodes C and duplicate matrix electrodes Z, is separated from the chamber B by a stopcock of 20-mm. bore. The crystal X is tied to the platinum wire W, which makes a sliding fit in the capillary tube T; the lead wire passes out through sealing wax in the cup K. The matrix electrodes are of a new design allowing a free circulation of electrolyte through the mass of finely divided metal; the metal is packed between glass wool plugs around a stiff platinum wire which extends upward into a mercury cup as indicated.

In filling the cell the crystal was suspended in the vestibule B, the calomel electrodes charged dry through the side tubes, and the matrix electrodes sealed in with an exterior ring of sealing wax. The electrolyte reservoir was connected at E, V connected to vacuum and the nitrogen gasometer. With S and E open, the cell was evacuated up to the stopcock of the electrolyte reservoir, washed out with nitrogen, again evacuated and the required quantity of electrolyte drawn in. The pressure was then brought slightly above that of the atmosphere with nitrogen and the cell disconnected. The crystal electrodes could be lowered or withdrawn without admission of air by warming the sealing wax in K. Interchange of crystals was effected by drawing up the crystal to be discarded, closing S, and replacing the air in the vestibule by nitrogen after introducing the new crystal.

Preparation and Mounting of Crystal Electrodes.—The preparation of an isolated area of a cleavage surface as nearly strain-free and crystallographically perfect as possible is of fundamental importance and a large number of preliminary measurements were made for the purpose of determining the effect of various methods of handling upon potentials. The majority of the crystals measured were monocrystalline rods cast in pyrex tubes by the method of Bridgman.[4] The diameters of these rods varied between 4 and 20 mm.; 6–8 mm. rods were found especially convenient. The rods were removed from the tubing by carefully squeezing the tube in a vise with parallel jaws after cooling with liquid air and fixed in a miter box arrangement with molten sealing wax in such a way as to prevent distortion during cutting. A short section was cut off with a broad bladed jewelers' saw moving in guides and the cleavage located by trial and error on this section. The rod proper was then cooled in liquid air, without direct contact between the metal and liquid air, and split into sections with a sharp knife blade and one-ounce hammer. The liquid air cooling greatly facilitated the cleavage, favored the production of mirror-like planes without visible imperfections, and minimized distortion during cleavage. The crystal sections were heated for at least three hours under paraffin at 200–250° and left in the solidified paraffin until taken out for measurement. Annealing by heating to 400° in vacuum induced recrystallization, which started, apparently, from slightly strained regions. Immediately before introduction into the cell one end of the crystal was tied to the platinum lead wire and a small area in the center of the cleavage face to be measured was cleared of paraffin with a soft wood stylus. The crystal was suspended in the electrolyte in such a way that only this isolated area was exposed. A few crystals prepared by other methods and measured for purposes of comparison are given special consideration in the next section.

Electromotive-Force Measurements.—Table I, which is largely self-explanatory, presents measurements on six crystals made after preliminary work had indicated the approximate experimental conditions required; all measurements on the last six crystals prepared are given without selection of particularly favorable results. The crystals designated as X-1, X-2, X-4, were split Bridgman rods prepared by the method outlined above from zinc of exceptional purity.[5] X-3 was similarly prepared from Kahlbaum's analytical grade zinc without further purification. The crystal X-5, supplied to us by Mr. Cyr and obtained by him incidentally to the purification of zinc by slow distillation, contained an unusually perfect basal plane which had not been subjected to the slightest mechanical deformation. X-6 was a Bridgman rod of the "spectroscopically pure" zinc, with cleavage approximately perpendicular to the rod axis, which was suspended in the electrolyte without isolation of a section of the cleavage face; the electrolyte was in contact not only with the cleavage face but with the sharp edges and sides of the rod. The cells required approximately forty-eight hours to reach equilibrium after filling and readings were made at intervals of from one to eighteen hours thereafter over periods of from four to eight days. The duplicate calomel electrodes checked consistently to 0.01 millivolt. The potentials of four matrix electrodes measured simultaneously with the crystals are given to the nearest tenth millivolt in Table I; these potentials were constant within

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[4] Bridgman, *Proc. Am. Acad. Arts Sci.*, **60**, 307 (1925).

[5] Total impurity under 0.0001%. Supplied to us through the kindness of Mr. H. M. Cyr of the Research Laboratory of the New Jersey Zinc Company. Cyr has found that the ordinary properties of this zinc, *e. g.*, resistance to acid attack and behavior under mechanical working, are markedly different from those of ordinarily pure zinc.

±0.05 mv. The measurements indicated by asterisks were made two minutes after shaking the cell and show a negligible sensitivity.

TABLE I

OBSERVED POTENTIALS IN VOLTS FOR THE (0001) FACES OF SIX SINGLE ZINC CRYSTALS AT 25°

Electrolyte: 0.4496 *M* $ZnCl_2$(aq.). Elapsed time for each series at least ninety-six hours. Interval between successive readings, one to eighteen hours.

X-1	X-2	X-3	X-4	X-5	X-6
1.07794	1.07786	1.07790	1.07800	1.07801	1.07795
98	83	88	801	800	790
95	82	89	799	802	795
95	85	89	801	803	795
95	82	87	800	802	796
94	84	88*	800	802	796
95	83	88	801	802	797
95*	85*	1.07790	801	802	796
94	84		802	804	799
95	84		801	803*	791
93	84		800	800	790
95	86		801	801	791
97	86		800	800	800
96	85		802	802	1.07797
95	90		1.07801	802	
95	88			802*	
96	90			802	
1.07795	90			801	
	86			802	
	87			1.07803	
	1.07790				

POTENTIALS OF SIMULTANEOUSLY MEASURED MATRIX ELECTRODES

I	II	III	IV
1.0776	1.0778	1.0775	1.0779

From the point of view of the theory of crystal growth and crystal surface energies, the stability of the potential of a crystal face during prolonged contact with the electrolyte and the closely related effect of etching are of importance. In two cases crystals were allowed to stand in contact with the electrolyte for two months; potentials measured at the end of this period checked the original equilibrium potential to within 0.05 mv. in both cases. Etching by immersion of the crystal in dilute hydrochloric acid until the mirror-like cleavage surface had become dull was found to accelerate the rate at which the face attained the equilibrium potential but did not alter this potential within the limits of reproducibility for initially unetched crystals. Similarly a crystal which had attained the equilibrium potential by immersion for twenty-four to forty-eight hours in the electrolyte and then been withdrawn into the cell vestibule required less than an hour to reach the equilibrium value after re-immersion. Initial potentials observed immediately after introduction of an unetched cleavage surface into the electrolyte were consistently lower than the equilibrium potential and rose slowly, the more slowly the more dilute the electrolyte, until the equilibrium value was attained.

Discussion of Results

The conclusion of primary importance to be drawn from this work is that of the constancy and reproducibility of the equilibrium potential of single zinc crystals when an isolated area of a (0001) face is presented to the electrolyte, a result essential to further work bearing on the question of the variation of potential with orientation and on the study of the surface structure of crystals by measurement of non-equilibrium potentials. A further conclusion is that this equilibrium potential is very nearly equal, if not identical, to that of electrolytically prepared matrix electrodes. A comparison of the measurements on crystal X-5 with those on X-3 indicates that the potential is relatively insensitive to the presence of impurities in the zinc from which a crystal is made—a result to be anticipated from the known fact that during the growth of a single crystal impurities are thrown out at the crystal boundaries—and comparison of X-5 with all the other crystals indicates that the potential is not affected by the slight mechanical deformation attending the cleaving process. Finally, the measurements on crystal X-6 show that a rod which is a cylindrical section of a crystal parallel to its major axis and which contains along with the (0001) face sharp edges and orientations other than the (0001) gives the same equilibrium potential as the isolated basal plane.

These results when considered in conjunction with the probable potential energies associated with the various possible positions of atoms on the surface of a zinc lattice permit us to draw certain tentative conclusions regarding the significance of the equilibrium potential. Kossel,[6] with a view to explaining the mechanism of crystal growth, has recently calculated for the cubic ionic lattice of sodium chloride the potential energy changes attending the addition or removal of an ion at the surfaces, edges and corners of this crystal. Similar calculations cannot be carried out at present for an atomic metal lattice but it seems probable that the relation of potential energy to lattice position in such lattices will be found to parallel that in the ionic lattice. If this parallelism be assumed, we may draw up a table of the relative energies required to remove an atom of zinc as a function of the position of the atom in the region of the (0001) lattice face. Position 1 requires the maximum, (7) the minimum energy for removal of an atom

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[6] (a) Kossel, *Gött. Nach.*, 135 (1927); (b) *Metallwirtschaft*, **36**, 877 (1929); also (c) Stranski, *Jahrb. d. Univ. Sofia*, **24**, 297 (1927–1928); (d) *Z. physik. Chem.*, **136**, 259 (1928).

(1) Unbroken (0001) surface layer
(2) Edge of perfect crystal
(3) Corner of perfect crystal
(4) Surface layer broken to depth of one atom layer; the "repeatable step" corresponding to the lattice energy
(5) Isolated atom projecting from a corner
(6) Isolated atom projecting from an edge
(7) Isolated atom projecting from an unbroken (0001) surface layer

The hexagonal symmetry of the zinc lattice would be expected to alter the absolute values for the edge and corner energies calculated for a cubic lattice but probably would not affect relative positions in this series.

The relation of this result to the free energies measurable by electrode potentials may be obtained by thermodynamic analysis of the electrode reaction into four primary reactions representing the elementary processes involved

$$\begin{array}{rlr}
\text{Zn (lattice)} \longrightarrow & \text{Zn (gas)} + \Delta H_1 & (1)\\
\text{Zn (gas)} \longrightarrow & \text{Zn}^{++}\text{ (gas)} + 2\text{E (gas)} + \Delta H_2 & (2)\\
\text{Zn}^{++}\text{ (gas)} \longrightarrow & \text{Zn}^{++}\text{ (solution)} - \Delta H_3 & (3)\\
2\text{E (gas)} \longrightarrow & 2\text{E (lattice)} - \Delta H_4 & (4)\\
\hline
\text{Zn (lattice)} \longrightarrow & \text{Zn}^{++}\text{ (solution)} + 2\text{E (lattice)} + \Delta H_5 & (5)
\end{array}$$

$$(-\Delta H_5) = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 = (-\Delta F_5) + T\,\mathrm{d}\Delta F_5/\mathrm{d}\,T$$

Reactions 2 and 3 representing, respectively, the ionization of zinc vapor and the solution of gaseous zinc ion are independent of the electrode structure. ΔH_1, the heat of sublimation, would be expected to vary with atomic position in accordance with the postulated energy series provided a sufficient number of similarly situated atoms are present to insure the validity of statistical laws. The evaluation of ΔF_5 involves the absolute potential of the hydrogen electrode, which is not definitely known, but this difficulty does not arise in considering the variations in ΔF_5. The correlation of variations in ΔF_5 with atomic position with the corresponding variations in ΔH_1 requires a knowledge of the variation of the heat of the single electrode reaction 5 and of the variation of the heat of condensation of electrons with the arrangement of atoms on a crystal face, neither of which can be evaluated at present; we may, however, as a working hypothesis tentatively assume that the variations in the potential energy of atomic position are paralleled by variations in ΔF_5, a relatively low value of the potential energy—or high energy of removal—corresponding to a high ΔH_1, a numerically low $(-\Delta F_5)$, and a low electrode potential. On this basis it would be predicted that the potential of the unbroken (0001) face of a single zinc crystal should be a minimum and the potential of isolated atoms of zinc "adsorbed" on this surface a maximum, while the potential corresponding to the stepwise growth or disintegration of the crystal should be intermediate between these extreme values. It would be predicted that in contact with an electrolyte isolated atoms with a high potential energy should rapidly disappear and we might be led to expect that final equilibrium would be established when the crystal presents an unbroken (0001) face to the electrolyte, in accord with the principle of minimum energy developed in particular by Stranski.[6d] It would seem probable, on the other hand, that in the purest crystal and electrolyte which can be prepared, there must still be present traces of impurities sufficient to prevent the formation of the ideal surface structure.[7] Our experimental results are consistent in indicating that the surface structure of crystals which have attained the equilibrium potential is broken rather than regular. The effect of etching in accelerating the rate of attainment of equilibrium, the fact that a crystal in attaining the equilibrium potential seems invariably to lose its mirror-like appearance, the stability of potential of these etched surfaces over long periods of time, and the results for crystal sections all seem to point, furthermore, to the conclusion that the equilibrium potential must be identified with the process of stepwise growth of the crystal, that it measures the energy of the "repeatable step." This energy is independent of orientation and the equilibrium potential cannot, therefore, be assigned to any crystal face.

The significance of the fact that the initial potential measured when a crystal is brought into contact with the electrolyte is consistently lower than the equilibrium value is not clear; the most obvious explanation that this effect is due to gases dissolved in the crystal surface which slowly diffuse into the electrolyte is met by the difficulty that crystals which have once come to equilibrium with the electrolyte attain this equilibrium again in a relatively short time, in some cases within a few minutes, after they have been taken out into the air and then re-immersed in the electrolyte. Electrolytic crystals which have been exposed to hydrogen as well as to air exhibit similarly low initial potentials. Other possible explanations involve a re-arrangement of the crystal surface layer in favor of the stepwise structure or the formation of stable layers of adsorbed ions or a combination of these processes leading to final equilibrium at the interfaces of the system basic crystal lattice–surface region of lattice–adsorbed ion layer–homogeneous electrolyte. It may be pointed out, in any case, that if our interpretation of the electrode potential is valid, the estimation of the potentials of individual crystal faces, if possible at all, must be obtained from a study of these initial, non-equilibrium potentials. Measurements of this nature now in progress indicate that the initial potential observed when an unetched (0001) face is brought into contact with an electrolyte of 0.02 *M* zinc chloride in a nitrogen atmosphere is reproducible to within a few millivolts or within 10% of the difference between the initial and equilibrium

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[7] The conclusion of Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 253 (1929), that even the ideal crystal surface contains regularly spaced sub-microscopic crevices is of interest in this connection.

potentials. It should be of particular interest to determine the initial potentials for one or more naturally developed faces other than the (0001). Attempts to obtain prismatic or pyramidal faces by cleavage at liquid-air temperature have failed and measurements on mechanically cut sections have been abandoned as inconsistent; annealing sufficiently thorough to remove the effects of deformation during the cutting apparently induces recrystallization in the surface layer, the equilibrium potential is found to be identical to that of the (0001) face, and the initial potentials though showing some regularity are not sufficiently reproducible to allow of drawing any reliable conclusions regarding a variation of potential with orientation. In the light of our interpretation of the significance of the equilibrium potential, it appears probable that the measurements of Straumanis,[8] which are presumably for the equilibrium state, are without significance as regards the orientation–potential question. It seems essential that a method of growing, single metal crystals with naturally developed faces be devised and work on this problem is in progress.

I should like to record my great obligation to Professor P. W. Bridgman for his interest and advice during the course of this work.

Summary

1. Examination of the electromotive characteristics of single metal crystals is suggested as a means of determining the relation of potentials to definitely describable surface structures and of contributing thereby to the study of the mechanism of electrode reactions and of the complementary problem of metallic surface structure.

2. Single zinc crystals are found to behave as reversible electrodes; the (0001) cleavage face measured in air-free cells of type: Zn, $ZnCl_2$ (0.5 *M*), HgCl, Hg is capable of yielding potentials constant to ± 0.02 millivolt and reproducible over dissimilarly prepared crystals to ± 0.1 millivolt.

3. The significance of the equilibrium potential is considered in the light of Kossel's calculation of the potential energy of atoms at the various possible positions on a crystal surface. It is concluded that this potential is to be assigned to the "repeatable step" in the growth or disintegration of the crystal.

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[8] Straumanis, *Nature*, July 13, 1929; *cf.* Anderson, *ibid.*, January 12, 1929.