

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE FURMAN CHEMICAL LABORATORY OF VANDERBILT UNIVERSITY]

TWO TYPES OF OVERVOLTAGE AND THE TEMPERATURE EFFECT¹

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RECEIVED AUGUST 20, 1923

PUBLISHED DECEMBER 13, 1924

Two Types of Overvoltage

Results obtained from a study of the effect of temperature on overvoltage have indicated a generalization which, though it extends into almost every phase of this subject, has been largely ignored in previous work. The overvoltage at any hydrogen electrode is usually defined as the difference between its potential and that of a reversible hydrogen electrode at the same temperature and partial pressure of hydrogen. If the electrode is more negative than the reversible hydrogen electrode, the overvoltage is considered as positive. Negative overvoltages are commonly designated as undervoltages. The overvoltages considered in this paper are in all cases those determined while the circuit is closed, that is, while a current is flowing through the surface of the electrode (cathode). The overvoltage as thus defined may owe its characteristic value either to a cathodically produced potential which will be designated as overvoltage of Type A, or to the single potential of the cathode material, in which case it has a positive temperature coefficient and in this paper will be designated as overvoltage of Type B. The former type is less dominant in active metals at low current densities and has a negative temperature coefficient.

In the use of metals above hydrogen in the electromotive series as cathodes for the electrolysis of acids there is a certain minimum potential, below that of the hydrogen electrode, which must be applied in order that these metals shall function as cathodes. This potential is the single potential of the metal when in contact with the electrolyte and is a measure of the back e.m.f. which opposes electrolysis when the cell consists of an active metal cathode and a reversible hydrogen electrode anode. *These single potential values persist as the cathode potential in many instances even though the electrolyzing current densities are quite high.*² Other investigators have chosen to call such potentials overvoltage, since they are obtained when the current is flowing and we shall continue to do so, but prefer to designate such cathode potentials as of a different type

¹ Presented at the Milwaukee Meeting of the American Chemical Society, September, 1923.

² MacInnes [THIS JOURNAL, 42, 2233 (1920)] discusses the counter electromotive force of open circuits in relation to overvoltage but does not mention the fact that values close to the single potential may be obtained with active metals in a closed circuit in which the current is flowing continuously.

because of inherent characteristics which distinguish them from overvoltage of the more common type.

Overvoltages of Type A have values distinct from those of the single potential of the cathode materials and are cathode potentials which represent the polarization produced by the electrolyzing current. With metals below hydrogen in the electromotive series such potentials build up when the slightest current densities are applied. For those metals above hydrogen, the magnitude of the current density necessary to bring overvoltage of Type A into play varies between the widest limits depending on several factors. In this connection it is of interest to note a definite instance. The data given by Rideal³ for the cathode potentials of zinc indicate that the overvoltage of this metal remains almost constant as the temperature rises. The overvoltage obtained by him at 1.6 milliamperes' current density and 18° is 655 millivolts or practically the same as the single potential of zinc in 0.1 *N* sulfuric acid. Even at a very high current density, 16 milliamperes per sq. cm., his value for the overvoltage at 18° is increased above this value by only 25 millivolts. These results indicate that Rideal's experiments on this metal relate almost entirely to overvoltage of Type B. The confusion which results when data relative to overvoltages of both types are compared without discrimination, calls for a study of the conditions which favor one or the other of the two types and a comparison of their characteristics.

Overvoltages of Type B are much more stable toward disturbing influences than those of Type A and are not subject to the effects usually associated with overvoltage—such as a decrease in magnitude with stirring, the adherence to a linear relation toward the logarithm of the current density, etc. The overvoltage of Type B serves to set a lower limit beyond which any disturbing influence upon the overvoltage of Type A cannot exert its usual lowering effect. In the case of inactive metals used as cathodes this limit is the potential of the hydrogen electrode. Consequently those conditions which favor overvoltage of Type B are small current density on smooth cathodes; rough cathode surfaces which, because of their large specific surfaces give, with large, even currents, current densities that are actually small; high temperature; disturbances which cause stirring of the electrolyte; and impurities of the electrode which favor solution in the electrolyte.

Previous to the discussion of the experiments on the effect of temperature upon these two types of overvoltage it is thought best to stress a point suggested in the previous paragraph which may be the cause of the confusion when experimental data relative to overvoltage are compared, namely, the nature of the cathode surface. With rough cathode surfaces it is almost impossible to know what the current density is because of

³ Rideal, *THIS JOURNAL*, 42, 94 (1920).

lack of information as to the specific surface of the electrode. Related to this is the fact that with either active or inactive metals it is the *actual* current density which determines the extent to which overvoltages of Type A are in effect and consequently the extent to which any conditions which could lower overvoltage *can* be effective. With a copper cathode and operating at a current density of 1.6 milliamperes per sq. cm., Tartar and Keyes⁴ find the overvoltage of copper to be 518 millivolts while, at about the same current density, Rideal^{3,5} determines the value as 103 millivolts. The discrepancy lies in the methods by which the electrodes were prepared, but the vital point is the extent to which *conclusions* drawn from the behavior of these two copper electrodes may be at variance.

Earlier Work on the Effect of Temperature

Tafel⁶ studied the effect of temperature upon the potential of the cathode measured against a mercurous sulfate electrode. Möller⁷ determined the potentials when hydrogen was liberated at a certain rate on different cathodes at temperatures from 0° to 10°, while Sacerdoti⁸ obtained the cathode potentials in sodium hydroxide solutions. Lewis and Jackson⁹ came to the conclusion that temperature has little effect on overvoltage and that at higher temperatures there is a tendency for the current to decrease which would probably imply an increase in overvoltage. With a view of securing accurate data as to the effect of temperature on overvoltage measured against a reversible hydrogen electrode operating under the same conditions, Harkins and Adams¹⁰ studied very carefully the effect of temperature on the overvoltage of mercury. Their data show *a decrease in overvoltage of about two millivolts per degree rise in temperature* and they point out the possible relation of this change in potential to the effect of temperature on the surface tension of the electrolyte. On the other hand, data presented by Rideal³ for a zinc cathode operating under a current density of 1.6 milliamperes per sq. cm. indicate that there is *no* change in overvoltage greater than the experimental error in making the measurements. His work leads to the conclusion that an increase in temperature of 40° produces only 2% variation in the overvoltage of a cathode of high overpotential. From this review of the information available as to the effect of temperature the unsatisfactory state of affairs is apparent.

Experimental Part

Apparatus.—The cell in each case consisted of the metal cathode in pure 0.1 *N* sulfuric acid solution together with a platinized-platinum wire gauze electrode of large area, which served as the anode, and another platinized-platinum electrode which served as the reference electrode. To maintain these platinum electrodes as hydrogen electrodes a stream of pure hydrogen prepared by the method of Cooke and Richards was bubbled through the cell. A sufficient length of time was allowed to free the cell from

⁴ Tartar and Keyes, *THIS JOURNAL*, **44**, 557 (1922). (Electrode polished with sand-paper.)

⁵ Film of metal deposited electrolytically.

⁶ Tafel, *Z. physik. Chem.*, **50**, 641 (1905).

⁷ Möller, *ibid.*, **65**, 641 (1908).

⁸ Sacerdoti, *Z. Elektrochem.*, **17**, 473 (1911).

⁹ Lewis and Jackson, *Z. physik. Chem.*, **56**, 193 (1906).

¹⁰ Adams, *Thesis*, 1914; Library of the University of Chicago.

oxygen before measurements were made. With metals other than mercury 48 hours was allowed. During this time a small current was passed through the cell.

In measuring the potentials a high sensitivity Leeds and Northrup galvanometer was used together with a potentiometer made by the same manufacturers. The current flowing through the system was measured¹¹ by the fall of potential through a resistance of 100,000 ohms in series with the electrolyzing circuit. The cathode potential was measured both against the hydrogen anode and the hydrogen electrode to be sure that no polarization of the anode occurs within the range of current densities used or as the temperature was changed. The thermostat was accurately controllable and could be quickly changed from one temperature to another. The temperature was read from a thermometer introduced into the cell.

The first experiments were conducted with the view of testing the effect of temperature upon the overvoltage of other electrodes. The data for gold and copper are represented in Fig. 1, and those for tin at the higher current density, Fig. 2, may be considered with this group. In all these cases there is a decrease in overvoltage with increase in temperature. The data show that the decrease in overvoltage is about 2 mv. per degree as found by Harkins and Adams in the case of mercury. This indicates that the decrease is to a considerable extent independent of the cathode material, which further links overvoltage with a property of the electrolyte. Curves obtained with more rapid changes in temperature are less regular, since the current tends to increase automatically as the temperature is raised. Such variations in current are due to decreased cathode polarization and demand a close watch over the current in order to maintain this factor constant.

After a determination of the effect of temperature on the overvoltage

¹¹ In all experiments the current flowing through the cell is specified but the point of bubble appearance has been omitted because of lack of definiteness of any such point. To illustrate the uncertainty of overvoltage so defined for nickel the following observations are submitted.

Experimenter	Value	Point defined
Caspari ¹²	0.21	First bubbles
Goodwin and Wilson ¹³1265	2 bubbles per minute, 77 micro-amp.
Tartar and Keyes ⁴ (commutator).....	.224	First perceptible current
(direct).....	.278	1300 micro-amperes per sq. cm.
A. Coehn ¹⁴14	First perceptible large current
Harkins ¹⁵15	Bubble method
Rideal ³03 0.21	

It will be noted that some of the values are less than the single potential of nickel and that they vary from 50 to 100% among themselves.

¹² Caspari, *Z. Elektrochem.*, **6**, 37 (1899).

¹³ Goodwin and Wilson, *Trans. Am. Electrochem. Soc.*, **40**, 173 (1921).

¹⁴ Coehn, *Z. physik. Chem.*, **38**, 609 (1901).

¹⁵ Harkins, *THIS JOURNAL*, **32**, 518 (1910).

of inactive metals, tin, as a representative of the more active metals, was used as a cathode. Attention has already been called to the similarity of the behavior of the overvoltage of tin when the current density is

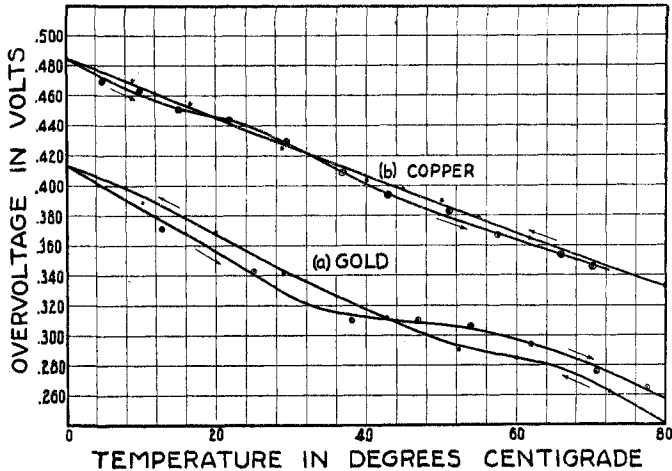


Fig. 1.—The effect of temperature on overvoltage. Current density 147 micro-amperes per sq. cm.

large. Curve b of Fig. 2 indicates the complete reversal of the effect of temperature when the current density is so small that the cathode potential but slightly exceeds the single potential of the cathode material.

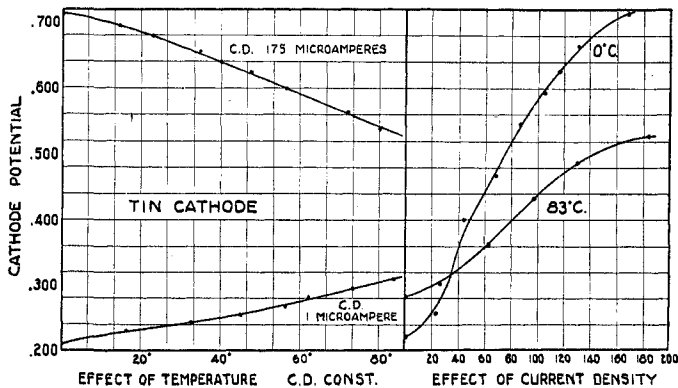


Fig. 2.—Effect of temperature on the overvoltage of tin at a low and at a high current density and the effect of current density on overvoltage at a low and at a high temperature.

Therefore, with active metals the sign of the effect of temperature depends on the type of overvoltage exhibited by the cathode.

The right-hand section of Fig. 2 illustrates the marked influence tempera-

ture may have on the relation of overvoltage to *current density*. It will be observed that if the temperature is low the cathode potentials start at much lower values and rise much higher with the current density than do the corresponding values when the temperature is higher. This indicates that temperature is an important factor in the effect of current density on overvoltage, particularly in the region of small current density.

The overvoltage cycle for tin drawn in Fig. 3 emphasizes the interrelation of the temperature effect upon, and the current density relation to, overvoltage. Path A-B indicates the change in overvoltage due to increasing temperature at a constant low current density, B-C the change due to

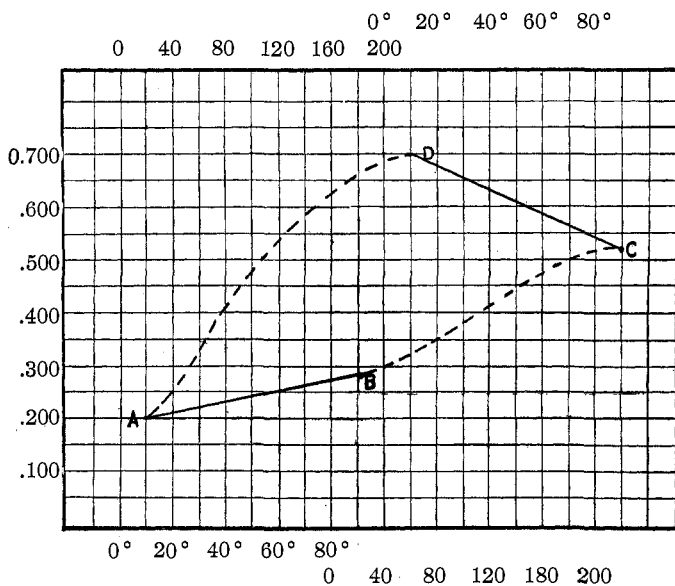


Fig. 3.—Overvoltage cycle for tin as constructed from the curves of Fig. 2. Lower straight line obtained at 1 and upper at 175 micro-amperes per sq. cm.

increasing current density at a constant high temperature, C-D the effect of temperature at a constant high current density and D-A the reduction of the overvoltage to the initial value as the current density is decreased at a constant low temperature.

The third part of the experimental work was undertaken in order to ascertain the mode of establishment of the Type A overvoltage as the current density is increased by small increments at different temperatures. It was thought that by using metals from different parts of the electromotive series a comparison of the sets of curves thus obtained could be made to indicate differences due to the nature of the cathode material. The metals selected were bismuth, lead and zinc. The cathodes were first molded in

Pyrex glass and the zinc and bismuth cathodes were finally polished. In each case the relation of the overvoltage to current density was determined first at 80° and then at 70° and so on until 0° was reached. This procedure augments the temperature effect somewhat on account of the time effect,

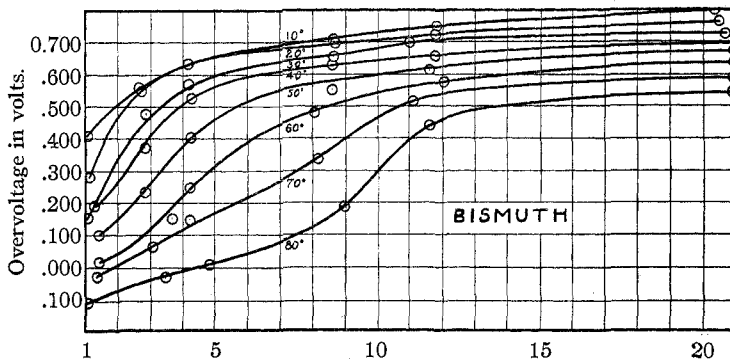


Fig. 4.—Current density in micro-amperes.

but it brings out sharply the relative importance of the two types of overvoltage in metals below hydrogen in the electromotive series as compared to their relative importance in cathodes of the active metals. The series of

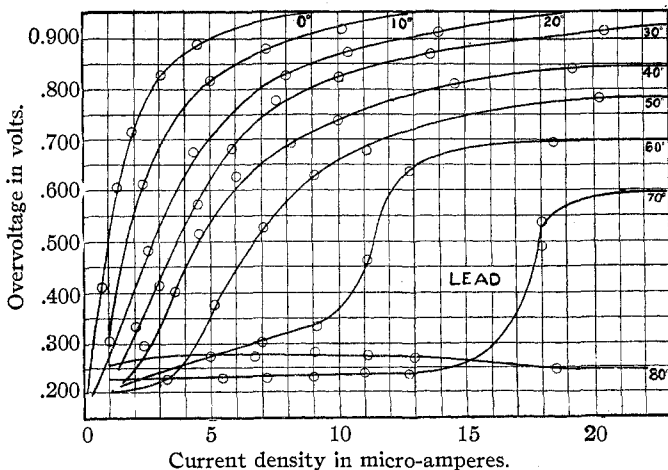


Fig. 5.—Relation of the overvoltage of lead to the current density at several temperatures. Note particularly the peculiar changes in the form of the curves between 50° and 80°; these seem to indicate a change in the nature of the surface of the lead.

curves given in Figs. 4, 5 and 6 indicates the influence of temperature on the overvoltage-current density relation and illustrates the relative dominance of the two types of overvoltage in cathodes of the different types of metals studied. The curves show that with both active and inactive metals the

overtoltage curves rise much less rapidly at the higher temperatures than they do at the lower temperatures. This indicates that increased temperature favors overtoltage of Type B. There is a marked difference, however, in the series of curves obtained with inactive metals as compared with those for the active metals, in that with inactive metals much smaller current densities are capable of establishing overtoltages of Type A even at the higher temperatures. In the curves for both lead and zinc the influence of Type B overtoltage in retarding the establishment of the former type of overtoltage is quite evident. With even the lower temperatures the curves for zinc show the dominating influence of the Type B overtoltage in the depression of the cathode potentials.

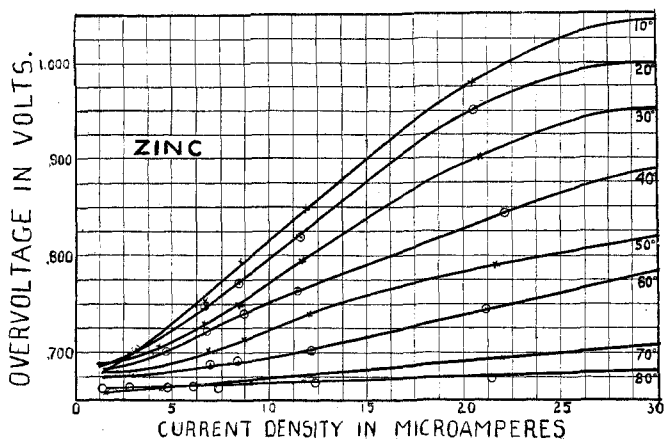


Fig. 6.—Relation of the overtoltage of zinc to the current density at several temperatures.

Relation of the Two Types of Overtoltage to the Two Methods of Measuring Overtoltage

Fig. 7 plots the values obtained by Tartar and Keyes⁴ using the commutator method of measuring overtoltage. These authors used copper, nickel and iron electrodes in 0.5 *N* sulfuric acid to which 15 g. per liter of zinc sulfate was added. Their work is discussed here on account of the striking illustration it presents of the tendency of active metals to give Type B overtoltage when the commutator method is used. The rapid increase in the overtoltage of copper, shown in Curve A, which is the least active of the metals, indicates that it gives overtoltages of Type A at much lower current densities and thus permits the deposition of zinc. Under such conditions nickel and iron, shown in Curves B and C, respectively, in accord with their greater activity, retain values close to their single potentials over correspondingly greater ranges of current density. The reduction in the effect of the current inherent in the use of the commutator

favors Type B overvoltage values when active metals are used as cathodes. The data of the same table show also that if the cathode is a very active metal like zinc, even the direct or continuous current method indicates the dominance of Type B overvoltage. Since the commutator method often gives overvoltage potentials characteristic of a stable, minimal potential of the cathode material, determinations of the effect of stirring, temperature, etc., upon overvoltage as measured by this method should not be expected to yield results similar to those obtained by the direct method.

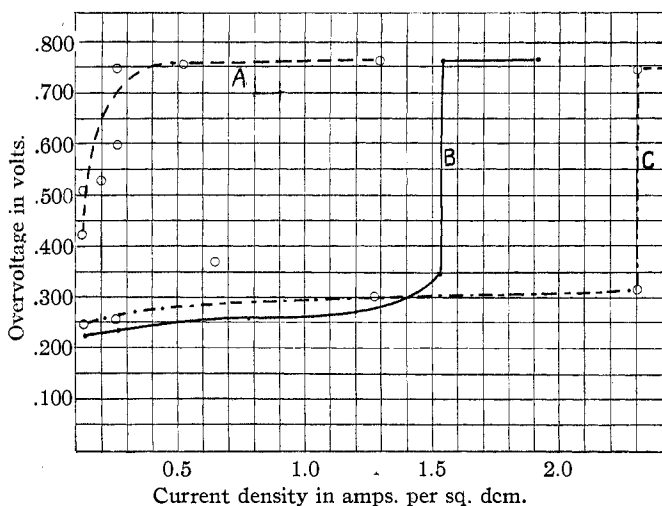


Fig. 7.—Current density required to establish an overvoltage of Type A upon cathodes of three metals, indicating a relation of the current density required to the position of the metals in the electromotive series. Copper A, nickel B and iron C.

Summary

1. The existence of two types of overvoltage has been demonstrated, and to differentiate them they have been designated overvoltage of Type A and overvoltage of Type B.
2. Type A overvoltage is a cathodically produced potential, is less stable toward a number of influences and has a negative temperature coefficient.
3. Overvoltage of Type B is the more stable. It is peculiar to active metals, has a positive temperature coefficient and corresponds closely to the single potential of the metal.
4. If metals above hydrogen in the electromotive series are used as cathodes the direct method of measuring overvoltage may give values characteristic of Type B, provided the current is small, the cathode is rough, the metal is soluble in the electrolyte, stirring of the electrolyte

occurs or if the temperature is high. With one or several of these factors operating the cathode potential may be distinctly of Type B *although a comparatively large current is flowing through the cell.*

5. The factors which favor Type B potentials retard the establishment of Type A overvoltage. Overvoltage values obtained by the commutator method at low current densities are commonly of Type B if the metal is active even though the ordinary method would, under similar conditions, give values characteristic of Type A.

6. It has been shown that at a current density of 175 micro-amperes per sq. cm., the decrease per degree rise in temperature of overvoltage of Type A is the same (2 mv. per degree) for several metals, thus indicating that this is not a property of the cathode material.

7. Progress in the study of the phenomenon of overvoltage has been much retarded by a failure to appreciate that the laws which have been proposed are usually intended for overvoltage of Type A, and in some cases investigators have failed to recognize in their experiments the factors which favor Type A or Type B overvoltage. They have classified all of the cathode potentials as overvoltage and, without subsequent discrimination, have used data peculiar to one of the two types *in the criticism or substantiation of a theory concerning the other.*

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THE REACTION BETWEEN POTASSIUM AMIDE AND CERTAIN SALTS OF COBALT AND IRON IN LIQUID AMMONIA

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RECEIVED FEBRUARY 5, 1924

PUBLISHED DECEMBER 13, 1924

Introduction

During investigations carried on in this Laboratory for the purpose of preparing amides, imides, nitrides and ammono salts of a number of representative metals, Dr. Franklin, E. W. Scott and later the author studied the action of potassium amide on a few salts of iron with rather discouraging results. An excess of potassium amide, for instance, was found to react with ferrous bromide and iodide hexammonates to form black products of variable and very indefinite composition.² The present work was undertaken primarily with the view of clearing up this anomalous reaction. It was thought that study of the behavior of cobalt salts toward potassium amide might afford some clue as to the conduct of salts of iron.

¹ National Research Fellow.

² (a) Franklin and Scott, unpublished work. (b) Bergstrom, *THIS JOURNAL*, **46**, 1558 (1924).