Summary

Accurate determinations of the activities of liquid zinc, cadmium, tin, lead and bismuth in five binary-alloy systems have been made at temperatures ranging from 400° to 600°.

With the single exception of the system, cadmium–bismuth, which gave a very complicated type of activity curve, all the alloy systems investigated showed escaping tendencies or activities greater than required by Raoult's law. In regard to departures from this ideal solution law, and also in regard to the heats of mixing, the results of this research furnish strong evidence for the validity of the internal-pressure theory as applied to liquid metal systems.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE EFFECT OF PRESSURE ON OVERVOLTAGE

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In 1919 MacInnes and Adler[1] published a theory of overvoltage based in part upon the theory of Möller[2] and in part upon the then unpublished work of Goodwin and Wilson. Since then the latter have published their data,[3] which indicate that overvoltage increases as the pressure is reduced, and with extreme rapidity at low pressure.

In 1914, Harkins and Adams[4] determined the effect of pressure on the hydrogen overvoltage of mercury. They state, "Keeping the current constant, the pressure in the hydrogen cell may be raised from one atmosphere to three and reduced to twenty millimeters, without producing any significant change in the potential between the cathode and the hydrogen electrode. In such a system the potential values are never absolutely constant. They may undergo a progressive gradual change or be subject to slight eccentric variations, but such changes can in no way be correlated with changes in pressure." Newbery found that oxygen overvoltage is practically constant in the range between 1 and 100 atmospheres.[5]

It will be noted that the conclusions reached by Goodwin and Wilson, and by Harkins and Adams are quite contradictory, but it is thought that the data and discussion herein contained, which are much more closely in agreement with the latter, indicate how both conclusions have been reached.

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[1] MacInnes and Adler, THIS JOURNAL, **41**, 194 (1919).

[2] Möller, *Z. physik. Chem.*, **65**, 226 (1909).

[3] Goodwin and Wilson, *Trans. Am. Electrochem. Soc.*, **11**, 172 (1921).

[4] Harkins and Adams, *Thesis,* Library of the University of Chicago, **1914.**

[5] Newbery, *J. Chem. Soc.*, **105**, 2419 (1914).

Both papers referred to above stress the necessity for expressing the overvoltage as a difference between the potential of the cathode and that of a reversible hydrogen electrode under the same conditions. Though this is the usual definition of overvoltage, the method of measuring such differences directly presents certain difficulties due to the non-reversibility of the hydrogen electrode at low pressures. An analysis of the experimental conditions employed by both Goodwin and Wilson, and Harkins and Adams suggested the possibility of studying certain factors individually without violation of any of the conditions inherent in the usual procedure. This analysis was undertaken after preliminary work upon the effect of pressure on the nickel cathode which appeared at first to agree with the conclusions of Goodwin and Wilson. This work was later found to be incorrect.

The effect of pressure on overvoltage as usually defined involves two distinct effects, that on the hydrogen electrode and that on the cathode potential. The practice of separating these effects when the influence of conditions other than pressure upon overvoltage is studied is quite general. It was therefore our purpose to study these effects separately and then to combine the numerical results.

In determining the effect of pressure on the hydrogen electrode potential, the hydrogen electrode and the mercurous sulfate electrode, used as a reference electrode, were in communication in the same pressure bottle. Sulfuric acid of 0.1 *N* concentration was used throughout and the hydrogen was prepared by the method of Cooke and Richards.[6] Connection between the two electrodes was made by a column of sulfuric acid sufficiently long to insure the absence of mercury ions in the hydrogen electrode vessel during the time required to make the measurements.

From the data of Table I it is to be noted that the potential of the hydrogen electrode decreases as the pressure is reduced, and down to at least 100 mm. the decrease is quite close to that demanded by the Nernst formula. The accuracy of these values is well within the limits that Goodwin and Wilson, or Harkins and Adams, attained in measuring overvoltage. The greater difficulty experienced in maintaining steady potential values for the hydrogen electrode when the pressure is quite low is due to several factors. The rate at which the hydrogen is introduced and the size of the bubbles admitted tend to produce fluctuations in pressure. Any differences in the pressure of the hydrogen before and after it enters the cell would have a similar effect, because of volume changes. The greater tendency toward ebullition at the lower pressures may cause irregularities in the pressure due to irregular bubble emission. If the capacity of the hydrogen electrode is small or if it is not sufficiently well saturated with hydrogen it may cease to function as a hydrogen electrode entirely at low pressure. The potential under such conditions becomes quite positive—

[6] Cooke and Richards, *Am. Chem. J.*, **10**, 81 (1888).

about that of the single potential of platinum in sulfuric acid. In so far as the pressure conditions are favorable to equilibrium conditions the potential of the hydrogen electrode is a function of the partial pressure of the hydrogen.

In order to define certain terms and conditions, several factors will be discussed before dealing with the effect of pressure on the potential of the cathode.

The term *reduction in pressure* may be interpreted in either of two ways. It may refer to changes in the total pressure of the gases above the electrolyte irrespective of their nature or number, or to the change in the partial pressure of some one gas without a change in the total pressure of the gases in the system. The potential of the hydrogen electrode is assumed to be dependent only upon the partial pressure of the hydrogen, whether that is produced by a change in the total pressure of pure hydrogen or by varying the percentage of hydrogen in the mixture of gases present in the system. The methods used for the study of the effect of pressure on the potential of the cathode are such that both the partial pressure of the hydrogen and the total pressure in the system vary. This makes it necessary to determine the part that each of these two factors contributes to the potential changes noted. If, as in the case of the hydrogen electrode, the potential of the cathode is dependent upon the partial pressure of the hydrogen and is independent of the total pressure, and the overvoltage increases rapidly at low pressure as observed by Goodwin and Wilson, it should then be possible to increase the polarization of a cathode which exhibits a certain potential when operating in an atmosphere of pure hydrogen by replacing this gas with another gas such as nitrogen. Experience has not supported this conclusion. According to the Nernst equation the potential of the hydrogen electrode becomes more positive as the pressure is reduced, and the data of Goodwin and Wilson indicate that decreased pressure makes the cathode more negative. According to this it may be assumed that pressure need not change the cathode potential in the same direction as it affects the potential of a reversible hydrogen electrode.

The use of the hydrogen electrode as an *anode* in work at low pressures involves certain factors not involved in other work on overvoltage. At atmospheric pressure there is a limit to the amount of current which may be passed through a cell having a hydrogen electrode as an anode without polarizing the anode. It has already been mentioned that the hydrogen electrode itself may become less stable at low pressures. It is therefore concluded that if a hydrogen electrode is used as the anode at low pressure the possibility of polarization is much greater. This makes it advisable to use an electrode with large hydrogen capacity so that the oxygen liberated per unit area will be small. The area of the platinum base is not the only factor which determines the capacity of the electrode for the sorption of hydrogen. The nature of the platinum black deposit is also important. The capacity of electrodes may be compared by noting the time it takes for bubbles to appear if the electrolyzing circuit in which they are serving as electrodes is reversed.

The use of hydrogen anodes of large capacities makes the time required for the establishment of the equilibrium potential after a change in pressure much longer. With the added danger of oxygen polarization when the electrode serves as an anode it is impractical to use the anode to determine the reversible hydrogen electrode potentials at low pressure Although such hydrogen anodes are more sluggish in attaining the reversible hydrogen electrode potential, their potentials are much steadier and consequently the current is much more constant than could be obtained with anodes of other types.

The *design* of the *cathode* is important in the investigation of overvoltage, and certain requirements are worthy of discussion. The danger of polarizing the anode has led some investigators to use a small cathode. There are two errors which attend this use of very small electrodes. The first has its origin in the close relation of overvoltage to surface tension. In some investigations the electrodes have been discs of metal surrounded by glass, shellac, or other supporting and insulating materials. Now it is known that with a mercury electrode the bubbles tend to form between the glass and the mercury, so it is logical to assume that with other metals also the potential may be affected by the presence of a second phase with a different surface energy. There is a second error involved and this may be greatest when a study of the effect of pressure is made. The use of a cathode so small that a bubble is large compared with the size of the cathode may introduce a condition quite foreign to that met with in ordinary large electrodes. The lead cathode used by Goodwin and Wilson[7] had an area of 0.0033 sq. cm., which is small compared to the size of bubbles which may be liberated. This is especially true at low pressures where the volume of the gas is great.[8] It is better to use a very large anode than to introduce uncertainty of conditions by the use of small cathodes.

In the present work the effect of pressure on the potential of the cathode has been studied at two current densities at least for each of the metals used by Goodwin and Wilson. The cathodes used included mercury, the metal investigated by Harkins and Adams. For reasons given in a previous paper the current densities were selected without reference to the number of bubbles being liberated per second. For each metal in Tables

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[7] Ref. 3, p. 173.

[8] It is important to note the fact that overvoltage is peculiarly sensitive to variations in the experimental conditions, so certain properties or relations are often cited as characteristic of overvoltage even though they have been found only by the use of highly specialized conditions.

II, III and IV a description of the cathode is given together with data on current density, the cathode potential and the overvoltage. The overvoltage values were obtained by subtracting the potential of the reversible hydrogen electrode at the given pressure from the cathode potential at the same pressure.

The cathode potentials are practically constant at all pressures studied except for temporary fluctuations. These fluctuations will be discussed in considering the conclusions reached by Harkins and Adams. The overvoltage shows a slight increase paralleled by a decrease in the potential of the reference electrode. The order of magnitude of these changes in overvoltage is about 50 millivolts for a change from atmospheric pressure to a partial pressure of 11 mm. According to Goodwin and Wilson, correspond-

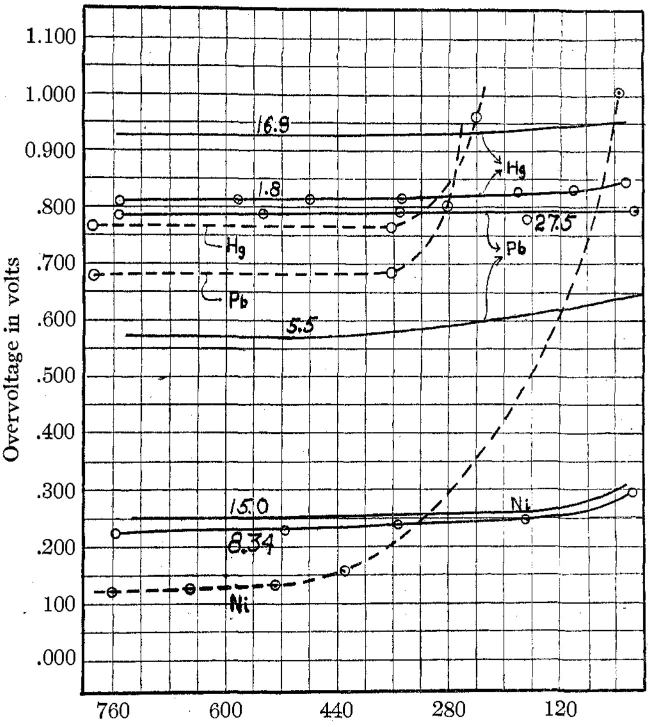

Fig. 1.—Relation of the hydrogen overvoltage to pressures of one atmosphere or less. The dotted lines represent the data of Goodwin and Wilson, the full lines, the data of the present paper. Two full lines are given for each metal; the higher line represents the higher current density. The two lines for nickel are close together, which indicates that at 20° an increase of current density is much less effective in increasing the overvoltage of nickel than in the case of the other two metals. The current densities for the respective lines are given in the figure except that the numbers for mercury give the currents instead of current densities

ing changes produce at least 850 millivolts' difference in overvoltage. For comparison, the values of Goodwin and Wilson are plotted in Fig. 1 by lines represented by dashes while the data of the present paper are represented by continuous lines.

The conclusion reached by Harkins and Adams that pressure has no effect on overvoltage, except for eccentric variations which they could not correlate with pressure, is probably due to the relatively small variations that do occur compared to the unsteadiness otherwise associated with overvoltage potentials. We have been able to correlate many such fluctuations with the changes of *total* pressure. In discussing the use of the hydrogen electrode as the anode we have indicated reasons for the nonreversibility of the hydrogen anode when used under the conditions peculiar to work on the pressure effect.

TABLE I

EFFECT OF PRESSURE ON THE POTENTIAL OF THE HYDROGEN ELECTRODE

Cell: $H_2 \mid 0.1\ N\ H_2SO_4 \mid Hg_2SO_4 \mid Hg$. Temperature, 0°

Time H. M.	Pressure total	Partial pressure of hydrogen	Potential obs.	Potential calc.
11:50	757	753	0.7552	
12:37			.7554	
2:00			.7555	
2:33			.7556	0.7554
5:25	375	371	.7487	
6:00			.7480	
6:25			.7479	
7:10			.7479	0.7468
9:00	104	100	.7322	
9:15			.7324	
9:25			.7324	
10:05			.7324	0.7313
10:58	9	4.5	.6795	
11:15			.6770	
11:30			.6759	
11:37			.6755	
12:00			.6755	0.6952

The data of the present paper show fluctuations at any one pressure which might be termed eccentric. It was often observed that as the pressure was being reduced, the cathode potential would increase and then later decrease. However, more careful observation shows that *such increases are due to the rapid expansion and later escape of a bubble already on the cathode*. (See Table II.) Such changes are more noticeable when only one bubble is present on the cathode, particularly in the case of mercury. Here the small bubbles which form around the edge later gather to form a large bubble at the top of the meniscus. The variation of the potential during the growth and escape of one of these bubbles is several millivolts.

The cathode potential becomes more negative as the bubble grows until it is large enough to roll upon the surface as the small bubbles unite with it.

TABLE II

EFFECT OF PRESSURE ON THE POTENTIAL AND THE OVERVOLTAGE OF A MERCURY CATHODE

(The data for cathodes of lead and nickel are given in Fig. 1)

Area of cross section of containing tube: 0.1452 sq. cm. Measurements at the stated currents in microamperes.

16.89			1.775		
Pressure Mm.	Cathode potential	Over-voltage	Pressure Mm.	Cathode potential	Over-voltage
750.5	1.6810		750.3	1.5652	
	1.6817	0.9263		1.5652	0.811
599.5	1.6817		581.3	1.5652	
	1.6790	.9263		1.5652	
				1.5652	.812
473.0	1.6791				
	1.6798	.9295	459.0	1.5652	
				1.5650	
366	1.6796			1.5652	.815
	1.6800	.9338			
			348	1.5653	
245	1.6798			1.5653	.819
	1.6782	.939			
			183.5	1.5645	
109	1.6757			1.5657	.830
	1.6767				
	1.6740[a]		103	1.5640	
	1.6751	.947		1.5590[a]	
				1.5589	.834
20	1.6633				
	1.6500		19	1.5430	
	1.6595	.954		1.5400	
				1.5420	
				1.5440	
				1.5480	
				1.5480	.843

[a] A large bubble was observed to leave just *before* the reading was taken. Note the *lowering of the potential* which this caused.

When this occurs the potential decreases slightly at first and then very rapidly as the bubble escapes. The galvanometer deflections indicate the tendency for the bubble to escape several seconds before the bubble leaves the cathode. These observations as to the effect of bubble size on overvoltage do not seem at first to be in agreement with the effects of bubble size on overvoltage as observed by MacInnes and Adler.[1] However, the conditions of the two experiments are quite different so that differences are to be expected. It is planned to extend the work connected with bubbles on mercury and discuss the subject in a later paper.

Two conditions may produce apparent increases in overvoltage of considerable magnitude. There is a possibility that the reference hydrogen electrode may cease to function reversibly and may thus revert to a platinum electrode. A second possibility is that a large fraction of the cathode may become covered with hydrogen bubbles at the lower pressures. This may cause an apparent increase in overvoltage in two ways. First, this layer of hydrogen gas would introduce a resistance in the electrolyzing circuit. Second, if the bubble merely insulates *part* of the cathode area the overvoltage would increase because of the increased current density. Such variations would be quite apparent if the cathode area were small compared with that of one bubble.

Summary

1. The effect of pressure on the *potential* of a cathode at which hydrogen is being liberated is in general very small at pressures between 760 mm. and 11 mm. The slight changes which occur are due to bubble expansion and consequent shielding of the cathode, and to increased stirring caused by the more rapid bubble liberation at low pressure.

2. Overvoltage defined with reference to a reversible hydrogen electrode increases as the pressure is decreased. This increase is paralleled entirely by a decrease in potential of the hydrogen electrode. Between 760 mm. and 11 mm. the range of variation of the overvoltage is about 50 millivolts.

3. The data of the present paper are of interest in connection with the theory of overvoltage presented by MacInnes and Adler.[1] According to them the overvoltage (E) is given by the equation, $E = (3RT/2pr).\gamma$ in which p is the pressure in the bubbles, r their radius, and γ the surface tension of the liquid. They reach the conclusion that the bubble radius is practically constant with variation of pressure, so the overvoltage should vary inversely as the pressure and thus increase very rapidly as low pressures are approached. The present work indicates that the overvoltage increases with decrease of pressure only to the extent that the hydrogen electrode potential decreases, that is, as the logarithm of the pressure. On the other hand, in earlier work in this Laboratory the overvoltage of a number of inactive metals was found to have the same temperature coefficient, and to decrease 2 mv. per degree in 0.1 N sulfuric acid. This seems to point to the surface tension of the liquid as an important factor in overvoltage. The above facts, taken together, seem to indicate that the theory of MacInnes and Adler is a partial rather than a complete theory of overvoltage.

4. Care was taken to avoid stirring of the liquid around the cathode, so the smallness of the increase of overvoltage with decrease of pressure cannot be due to the effect of stirring. The considerable lowering of overvoltage of the ordinary type produced by stirring was pointed out by Harkins and Adams[4] in 1914.

5. The overvoltage at a mercury meniscus in dil. sulfuric acid was found to *increase* as the large bubble at the top of the meniscus becomes larger, and to *decrease* suddenly when the bubble escapes.

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

THE INDIVIDUAL THERMODYNAMIC PROPERTIES OF IONS

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The Principle of the Specific Interaction of Ions

The available information regarding the thermodynamic properties of salt solutions, as manifested through electrometric and freezing-point measurements and particularly through the measurement of the solubilities of sparingly soluble salts in salt solutions, leaves no doubt that these properties even at high dilution are largely dependent upon the nature of the solution considered. It is not a question here of the typical deviations depending upon the valence type of the various solutes, but of deviations shown by isotypic ions in dependency of their individual nature. In spite of the fact that these peculiarities have, at first sight, a rather random character, a closer examination has shown that an important simplicity prevails, which has been formulated by the writer as the *principle of the specific interaction of ions*.

The basis and the applicability of this principle have been elaborately presented in a previous article,[1] where emphasis was laid upon the possibility of splitting the activity coefficient into two factors, a coefficient of interaction and a salting-out coefficient, the latter of which should be a function of the solvent only. This devision is valuable in cases where the possibility exists of determining separately the ratio of the two factors such as was shown in the previous article when salts of different valence type are used for saturating salts in solubility measurements. The calculation of these ratios requires a high degree of accuracy in the experimental determinations and but very slight deviations from the underlying principles because the equations for the calculations have such a form as to be highly sensitive towards such deviations.

The contents of the principles in question may, however, be expressed more simply without the above-mentioned division of the activity coefficient into its two factors. Let A_1B and A_2B represent two solvent salts with an anion (B) in common, and having the same equivalent concentration. Let X be an arbitrary cation and Y an arbitrary anion, present

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[1] Brönsted, THIS JOURNAL, **44**, 877 (1922).