were found to be positive and to increase with total salt concentration, with the numerical value of the ratio of sodium to potassium salt in the mixture, but to decrease generally as one goes from chlorides to iodides.

4. In general the results can be explained on the basis of complex formation, though at present no explanation is offered for the seeming decrease in complex formation proceeding from chlorides to iodides.

5. Tables of specific gravities of the solutions studied, and the relative viscosities of certain of these solutions are given.

It is a pleasure to acknowledge my thanks to Dr. George Shannon Forbes for helpful comments on certain of the results.

COLUMBIA, MISSOURI

THE EFFECT OF CHANGING HYDROGEN-ION CONCENTRATION ON THE POTENTIAL OF THE ZINC ELECTRODE

BY THEODORE W. RICHARDS AND THEODORE DUNHAM, JR.

When a metal of weak basic character (such as gallium) is studied with regard to its single electrode potential, the salt solutions in which the metal is immersed must be acidified to prevent hydrolysis. The possible effect on the potential of such acidification has not been adequately ascertained.[1] Accordingly, this paper recounts a brief study of the effect of adding acid to the salt solution around a typical easily and exactly reproducible metal electrode, in order to demonstrate experimentally the sign and magnitude of the potential difference thus caused. Zinc was chosen for the purpose. The results were merely preliminary, and were inevitably not very conclusive. Nevertheless, when, as here, theory is incomplete, even tentative experimental results may be of value.

Earlier papers on this subject are as follows. Broughton[2] studied the decomposition voltage of zinc sulfate solutions in the presence of acid, but since he made his measurements with a flowing current, the *fall* of potential which he observed was due (as he saw) to the decrease of resistance of the solution. For the present purpose these results have no significance. A. Siemens[3] measured the potential of zinc in an acid solution, but not in pure zinc sulfate. Details are lacking, moreover, as to salt-bridges and other particulars, so that these results also have little signifi-

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[1] Since the completion of our experimental work a general but rather vague theoretical discussion of this matter by A. Smits has been published in "Die Theorie der Allotropie," (Barth, Leipzig, 1921), especially on pp. 176 and 399. Apparently our results are not inconsistent with his conclusions.

[2] Broughton, *Met. Chem. Eng.*, **20**, 155 (1919).

[3] Siemens, *Z. anorg. Chem.*, **41**, 249 (1904).

cance. Kistiakowsky[4] and Horsch[5] made accurate measurements of the electrode potential of zinc in solutions of zinc sulfate at various temperatures, but do not seem to have added acid, neither do others who have called attention to precautions needed to obtain exact results.[6]

The zinc employed in our work was a very pure specimen,[7] containing only 0.005% of known impurity, according to careful analysis. Zinc sulfate was prepared from this metal and recrystallized twice after standing in solution for 2 days over excess of zinc. From a carefully prepared molal solution of this salt and a concentrated, standardized solution of sulfuric acid, equivalent normal solutions of zinc sulfate containing various amounts of sulfuric acid were prepared. A small Leeds and Northrup potentiometer measuring to 0.1 mv. was used; it was adjusted with a cadmium cell standardized at the Bureau of Standards.

Since in such measurements solution-junction potentials are inevitable, (unless indeed some other electrode whose potential changes with added acid, such as mercury, mercurous sulfate, zinc sulfate plus sulfuric acid, be linked with the zinc electrode) the effort was made to arrange the apparatus so as to have these definite and reproducible. A separatory funnel attached by a T-tube to each narrow junction-tip made it possible to flush the latter with fresh solution whenever desired. A third separatory funnel made possible the renewal or change of the enclosed bridge solution (which received the two junction-tips) keeping the whole apparatus closed during the operation. Flow from one vessel to the other (with consequent mixture of the liquids) was prevented. By gentle hydrostatic pressure on the contents of the bridge vessel, the liquid junctions could be forced somewhat back into the narrow tubes—a process which favored reproducibility.[8] Each electrode vessel was removed, rinsed and dried in an oven between successive trials. The measurements were all made at 18.0° ± 0.1°.

Nearly all the measurements were made with amalgamated zinc. This was prepared in various ways: by immersing the metal in dilute mercurous nitrate, by rubbing the clean zinc with mercury in the air, and by amalgamating under dilute nitric acid. The methods gave essentially identical results, but the last named method seemed on the whole to give the most constant values. The rods were suspended in such a way that the metal of the connecting wire (usually platinum) was not in contact with the solution. Since zinc forms no solid amalgam, the potential of pure zinc should be identical with that of the saturated liquid amalgam;

[4] Kistiakowsky, Z. Elektrochem., 14, 113 (1908).

[5] Horsch, THIS JOURNAL, 41, 1787 (1919).

[6] Mellencamp, Phys. Rev., 29, 329 (1909). Richards and Forbes, Carnegie Inst. Pub., 56, 1 to 45 (1906). Moore, THIS JOURNAL, 43, 81 (1921).

[7] Kindly provided by the New Jersey Zinc Company.

[8] Doubtless the flowing liquid junction of Lamb and Larson, THIS JOURNAL, 42, 229 (1920), would have given still more satisfactory results, but the arrangement above specified was accurate enough for our purpose.

and under the best conditions this is nearly the case.[9] If the electrode is not amalgamated, however, the result may be vitiated by bubbles of hydrogen as well as by the freshly formed zinc sulfate, when acid is present. Thus in the presence of $2 N$ sulfuric acid we found that the potential of a pure zinc electrode was diminished 6.5 mv. as compared with an amalgamated electrode. When the electrode is too heavily amalgamated, zinc dissolved from the surface of the amalgam may not be instantly replaced by diffusion from the solid zinc rod and the results suffer. Light amalgamation prevents active corrosion of the metal and at the same time leaves a film of mercury so thin that it remains essentially saturated with metallic zinc.

Sometimes the constant final value of the potential attained by such electrodes was several millivolts above the value obtained immediately on immersion. Evidently time was required for the attainment of equilibrium within the film, but the potential finally became constant within ± 0.1 mv. Time should doubtless be allowed that the metal may be transformed superficially into the enantiotropic form most stable at $18°$,[10] if any of the metastable form is present; but this change can hardly be the cause of the effect observed, since it should cause a fall of potential, whereas we usually observed a rise during the first 24 hours.

Two series of experiments were made. In Series I the zinc (about half immersed in solutions containing N zinc sulfate, with varied amounts of added acid) was measured against a calomel electrode through a bridge of saturated solution of sodium sulfate (which was chosen because of its considerable specific gravity, helpful in diminishing diffusion at the liquid junction). In Series II the bridge-vessel was filled with N zinc sulfate solution, and the acidified zinc electrode was thus measured directly against another zinc electrode immersed in equivalent normal zinc sulfate without any acid, in order to simplify (as much as possible) the liquid-junction potentials. Here the only liquid-junction potential was due to the presence of acid on one side and not on the other. Zinc sulfate was used (rather than the chloride) because it forms only 2 ions on dissociation, and because it is less hydrolyzed than the chloride. No especial precaution was taken against the oxygen of the air, since results of very high precision were not sought.

The last two columns show the increase of potential due to adding acid to the solution around the amalgamated zinc electrode as measured with, and also without, a sodium sulfate bridge. Evidently, the presence of this bridge in connection with the calomel electrode tends, in every case,

[9] Richards and Lewis, *Proc. Am. Acad.*, **34,** 98 (1898).

[10] Cohen, *Proceedings Kon. Akad. Wetenschappen Amsterdam*, **16,** 565 (1913).

TABLE I

CHANGE OF POTENTIAL OF ZINC CAUSED BY ACIDIFYING ENVIRONMENT

N ZnSO$_4$; N H$_2$SO$_4$

N	Total Potential[11] With bridge and calomel electrode	Change of potential	
		I. With Na$_2$SO$_4$ bridge	II. Without Na$_2$SO$_4$ bridge
		Mv.	Mv.
0.0	1.0777	0.0	0.0
0.1	1.0828	5.1	6.0
0.5	1.0971	19.4	21.6
1.0	1.1066	28.9	32.6
2.0	1.1173	39.6	45.3
4.0	1.1277	50.0	57.2
0.0 again	1.0771	(−0.6)	0.0

to reduce by about 12% the difference of potential observed, within the limit of error of the measurements.

The fact stands out that, with or without a salt-bridge, the addition of acid very decidedly *raises* the single electrode potential of zinc. This result is in the direction indicated by the hypothesis of electrolytic dissociation. Adding sulfuric acid to zinc sulfate should diminish the dissociation of the latter, and therefore should tend to diminish the concentration of active zinc in the solution and hence increase the potential of the electrode. The change is, however, much larger than one would expect from this cause. Hence part of the effect must be ascribed to the solution-junction potential, and most of this must be ascribed to the effect of the high mobility of the hydrogen ion. Lack of knowledge as to the concentration of the bivalent sulfate ion in sulfuric acid prevents the application to this junction potential of the equations of Planck or of Lewis and Sargent or of Henderson, but on any assumption evidently the presence of the hydrogen ion would increase the potential of the electrode containing it, since its rapid migration would tend to establish a potential difference in the same direction as that produced by the formation of the ionized zinc at the electrode. Although no accurate theory for this junction potential exists, the effect may be estimated approximately by the substitution in the present case of less rapidly migrating ions for hydrogen, making the assumption that the associating effect produced by alkali sulfates would be not very different from that produced by sulfuric acid. Accordingly, cells were set up with sodium or potassium sulfate added to the zinc sulfate solution on one side, the latter salt being always of equiva-

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[11] The single electrode potential of zinc thus determined is 0.518, assuming the calomel electrode potential = 0.560 volt, if the electrolyte is normal as to zinc sulfate and making no allowance for the two liquid-junction potentials. The cell Zn, ZnSO$_4$, KCl, HgCl, Hg has an e.m.f. of about 1.083 at 18°. Saturated Na$_2$SO$_4$ as a bridge diminishes the e.m.f. by about 0.005. See also Horsch, Ref. 5.

lent normal concentration. Limited solubility prevented, of course, the use of very concentrated solutions of the alkali salts. The following table gives the rise of potential observed with increasing amounts of these substances, as measured against a pure zinc electrode (equivalent normal as to zinc sulfate and without any addition of foreign sulfate).

TABLE II
EFFECT OF DISSOLVED HYDROGEN, SODIUM AND POTASSIUM SULFATES ON THE ZINC ELECTRODE (N ZnSO$_4$)

Added sulfate N	H$_2$SO$_4$ Mv.	Na$_2$SO$_4$ Mv.	K$_2$SO$_4$ Mv.
0.0	0.0	0.0	0.0
0.1	6.0	1.7	3.2
0.5	21.6	7.2	12.1
1.0	32.6	11.8[12]	..
2.0	45.3	17.1	..

These results are plotted (Curves A, C, and D) together with the values obtained with the sodium sulfate salt bridge and calomel electrode (Curve B) in the accompanying diagram. As was anticipated, the ordinates
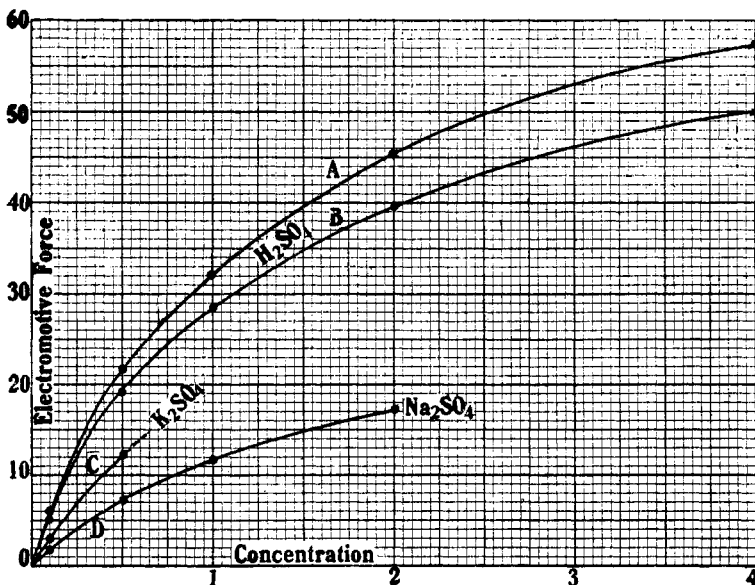

Fig. 1.—Rise of potential caused by addition of sulfuric acid and two sulfates to the normal zinc electrode. The normality of the added sulfate in the solution is plotted in the direction of abscissa; e.m.f. in millivolts, as ordinates. The concentration of zinc sulfate was normal: the same in all cases. Curve B was obtained through a salt bridge; Curves A, C, and D by direct connection with a zinc electrode surrounded by pure N zinc sulfate solution.

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[12] Abegg and Labendzinski report 9 mv. for this datum, Z. Elektrochem., 10, 77 (1904).

of the $(H_2,K_2,Na_2)SO_4$ curves lie in the order of the transport numbers of the respective cations in the sulfate solutions. This is seen in the table below. From recent data,[13] the probable values of these transport numbers in halieds are as follows.

	Transport numbers	Relative ordinates of curves
H	0.83	1.00
K	0.49	0.56
Na	0.39	0.33

In concentrated solutions, the mobility of the sulfate ion is much less than that of the potassium ion, but possibly somewhat more than that of the sodium ion.[14] Assuming the absence of junction potential with sodium sulfate, one would infer that the difference between this salt (Curve D) and the acid (Curve A), that is, about $2/3$ of the effect of the added acid, may be due to the excess of mobility of the hydrogen. The effect of sodium sulfate, 0.007 volt, when both salts are normal, is about the change of potential at the metallic surface which one would expect from the associating effect of sulfuric acid on zinc sulfate. It would appear, therefore, that well-known tendencies are of magnitudes entirely adequate to account for the total effect. Moreover, the order of magnitude of the deviation generally to be expected in other similar cases is indicated. The more exact elucidation of the question involves a better knowledge of the solution-junction effect as well as of the mode of dissociation of sulfuric acid than is now at hand. We have obtained a variety of additional data bearing upon junction potentials, but these have not yet been correlated.

We are indebted to the Carnegie Institution of Washington and to a generous anonymous fund for some of the apparatus employed.

Summary

1. Measurements of the potential of zinc in acid solutions of zinc sulfate, measured against the calomel electrode (through a sodium sulfate bridge) and also directly against a zinc electrode containing pure N zinc sulfate solution, showed marked rise in potential as the acid concentration was increased.

2. The magnitude of this rise in potential indicated that it must be due partly to liquid-junction potential, owing to the presence of the hydrogen ion.

3. Equal concentrations of the sulfate ion in the form of alkali sulfates added to the zinc sulfate solution gave smaller elevations in the potential,

[13] A. A. Noyes and Falk, THIS JOURNAL, 33, 1456 (1911).

[14] See, for example, Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Teubner, 1898, p. 200.

which elevations were in the order of the transport numbers of the cations concerned. If it is assumed that the change in junction potential produced by sodium sulfate is small, one may infer that about $^2/_3$ of the change produced by sulfuric acid is due to solution-junction potential and the other third to a real increase in the single electrode potential of zinc, due presumably to the depression of the electrolytic dissociation of zinc sulfate.

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THE HEATS OF NEUTRALIZATION OF POTASSIUM, SODIUM AND LITHIUM HYDROXIDES WITH HYDROCHLORIC, HYDROBROMIC, HYDRIODIC AND NITRIC ACIDS, AT VARIOUS DILUTIONS

BY THEODORE W. RICHARDS AND ALLAN W. ROWE

The quantity of heat developed by the neutralization of acids with bases has been the subject of numerous investigations. Hess,[1] Graham,[2] Andrews,[3] Favre and Silbermann,[4] Favre,[5] Thomsen,[6] Berthelot,[7] v. Steinwehr,[8] Wörmann,[9] Rümelin,[10] Mathews and Germann[11] and Muller[12] (among others) have made measurements of this kind, using many different methods and varying the conditions widely. The fact observed by the earlier experimenters that with strong acids and bases the heat liberated is almost (but not quite) independent of the base or acid used, found explanation when the theory of electrolytic dissociation was developed by Arrhenius.[13] As every chemist knows, the action is now considered as being essentially that between hydrogen and hydroxyl ions alone, the other ions remaining almost if not quite undisturbed in the process. The experimental results coincided approximately with this theory, but the data available at the time when this investigation was begun were

[1] Hess, *Pogg. Ann.*, **50,** 385 (1840); **53,** 499 (1841); **57,** 569 (1842).
[2] Graham, *Ann. chim. phys.*, [3] **13,** 188 (1845).
[3] Andrews, *Pogg. Ann.*, **54,** 208 (1841); **143,** 101 (1871).
[4] Favre and Silbermann, *Ann. chim. phys.*, [3] **37,** 494 (1853).
[5] Favre, *Compt. rend.*, **73,** 772 (1871).
[6] Thomsen, "Thermochemische Untersuchungen," Barth, vol. I, **1882.**
[7] Berthelot, "Thermochimie," Ganthier, vols. I and II, **1897.**
[8] v. Steinwehr, *Inaug. Diss.*, Göttingen, **1900.**
[9] Wörmann, *Ann. Physik*, [4] **18,** 775 (1905).
[10] Rümelin, *Inaug. Diss.*, Göttingen, **1905.**
[11] Mathews and Germann, *J. Phys. Chem.*, **15,** 73 (1911).
[12] Muller, *Bull. soc. chim.*, [4] **23,** 8 (1918).
[13] S. Arrhenius, *Z. physik. Chem.*, **1,** 631 (1887).