of all connections when the apparatus might be used for anything not attacking glass.

Summary.

A very satisfactory apparatus for measuring vapor pressures has been devised and tested, of which the saturator has proved extremely efficient, and the aspirator accurate and convenient.

Experiments show that air may be completely saturated with water vapor at the rate of at least 50 liters an hour in the above described saturator.

The efficiency of phosphorus pentoxide as a very rapid absorbing agent is further confirmed.

One determination of the vapor pressure of absolute ethyl alcohol at 25° has been made and a pressure of 58.47 mm. found.

The value of 23.70 mm. for the vapor pressure of water at 24.97° and 23.75 mm. at 25.00° has been obtained by this method.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE POTENTIAL OF THE COPPER ELECTRODE AND THE ACTIVITY OF BIVALENT IONS.

BY GILBERT N. LEWIS AND WILLIAM N. LACEY.

Received March 16, 1914.

The determination of the E. M. F. of cells involving bivalent or multivalent ions presents no greater difficulties than those which are met in the simple case in which only univalent ions are concerned. The interpretation, however, of the measurements of cells of the former type is by no means easy. If ternary salts, such as $CuCl_2$ or K_2SO_4, are employed, we have at present no means of determining the concentration of intermediate ions such as $CuCl^+$ and KSO_4^-, which may be, and probably are, present in considerable amount. Aside from this obstacle, there are at present no adequate data with which to calculate the degree of dissociation or the activity of the ions in salts of higher type than the uni-univalent. For such a calculation it is necessary to determine the free energy of dilution either by measurements of electromotive force, or of freezing point, or of some other property of the solution which is related thermodynamically to these.

The Free Energy of Dilution of Copper Sulfate.—The electromotive forces of the cells Cu, $CuSO_4$, 0.05 M, Hg_2SO_4, Hg, and Cu, $CuSO_4$, 0.005 M, Hg_2SO_4, Hg were first measured. Each cell consisted of two half-cells of the customary form. The copper electrode was prepared by surrounding a copper-plated platinum wire situated at the bottom of the electrode vessel with finely divided copper. This copper was at first obtained by the method of Richards[1] in which a current of concentrated copper sulfate solution passes first through a hot tube containing metallic copper and then through a cold tube where copper is reprecipitated. The metal thus obtained was found, however, to be less satisfactory than that prepared by electrolyzing tenth normal copper sulfate solution at sufficient current density to bring down a spongy nonadherent deposit.[2] The spongy metal was allowed to stand in a solution of copper sulfate, of the concentration to be used in the cell, and was then carefully washed and transferred to the electrode vessel. As in the case of silver, the metal thus prepared seems to be free from the surface strains which characterize electrodes plated with a coherent film. Such electrodes, which have previously been used in the determination of the potential of the copper electrode, are entirely unreliable and will often differ in potential among themselves by a centivolt. When the current density is such as to cause the deposited film to break and to develop as a tree or sponge, the surface strains are, doubtless, to a large extent relieved, and, on standing in contact with the solution, rapid local action, due to the large surface exposed, will remove any portions of the metal which might still have a high potential.

The copper sulfate was prepared from the commercial C. P. product by two recrystallizations. In order that the equilibrium between copper and cupric and cuprous ion might be as nearly as possible established in advance, the solution to be used in the electrode chamber was shaken from ten to twenty hours with finely divided copper in a thermostat at 25°. The half-electrodes were then set up and their electromotive force measured against one another and against the mercurous sulfate electrodes.

The latter electrodes were prepared from pure mercury and from mercurous sulfate obtained by the Hulett method.[3] These substances were washed by shaking them up together with the copper sulfate solution, decanting the solution, and repeating this process as in the preparation of normal calomel electrodes. These electrodes proved to be admirably constant both in tenth and hundredth normal solutions and reproducible to 0.0001 V.

The copper electrodes, on the other hand, showed a greater variability. In the final experiments nine 0.05 M electrodes showed an average deviation from the mean of 0.00023 V. and fifteen 0.005 M electrodes an average deviation of 0.00036 V. Oxidation in the copper electrodes, owing to the presence of air, seemed to play no important role, as shown by the fact that similar results were obtained with electrodes in the complete absence of oxygen. The method of preparation of the copper electrode suggested

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[1] *Z. physik. Chem.*, **32**, 321 (1900).

[2] For the preparation of a similar silver electrode see Lewis, THIS JOURNAL, **28**, 158 (1906).

[3] *Phys. Rev.*, **32**, 257 (1911).

the possibility that occluded hydrogen might be taking part in the electrode process, but if this were the case the potential would vary with the concentration of H^+, whereas experiments showed that the presence of 0.001N sulfuric acid in the copper sulfate solution made no change in the electromotive force.

The mean values for the two cells[1] were

$$\text{Cu, CuSO}_4\ 0.05\ \text{M, Hg}_2\text{SO}_4\text{, Hg; }\mathbf{E} = 0.3928\ \text{V.}$$

$$\text{Cu, CuSO}_4\ 0.005\ \text{M, Hg}_2\text{SO}_4\text{, Hg; }\mathbf{E} = 0.4226\ \text{V.}$$

The difference between these two values, 0.0298 V., is the electromotive force corresponding to the free energy of dilution of copper sulfate from 0.05 M to 0.005 M. Now this difference can also be calculated from the conductance values of $CuSO_4$, assuming Kohlrausch's law and the validity of the laws of perfect solution, by the formula

$$\mathbf{E} = \frac{RT}{2F} \ln \left(\frac{c_1\gamma_1}{c_2\gamma_2}\right)^2$$

where γ is the value of λ/λ_0 at the concentration c. From the conductance tables given by Noyes and Falk,[2] γ (0.05 M) = 0.396, γ (0.005 M) = 0.629, and $\mathbf{E}$ = 0.0472 V., which differs from the measured value by 0.0174 V. It is evident, therefore, that the assumptions upon which the above formulae are based are far less accurate in this case than in the case of the simple uni-univalent salts.

Another method of calculating the free energy of dilution which, like the e. m. f. method, rests upon no questionable assumption, is the one in which the freezing point data are used. Unfortunately, few freezing-point determinations have been sufficiently accurate to justify their use in such a calculation. In the case of copper sulfate, however, the measurements of Hausrath[3] and Bedford[4] between 0.0002 M and 0.03 M seem entirely reliable. Between 0.03 M and 0.1 M no values are available except one obtained by Jones, Getman and Bassett[5] and one by Raoult.[6] We have nevertheless attempted to extrapolate the curve through the points of Hausrath and Bedford up to 0.05 M.[7]

This curve was then employed to determine the free energy of dilution

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[1] All measurements were made in an oil thermostat at 25.00°.

[2] THIS JOURNAL, **34,** 454 (1912).

[3] *Ann. Phys.,* [4] **9,** 544 (1902).

[4] *Proc. Roy. Soc.,* **83A,** 459 (1910).

[5] Landolt-Börnstein-Roth, 4 Aufl., 809.

[6] *Z. physik. Chem.,* **2,** 489 (1888).

[7] The freezing-point curve that we have used passes through the points given in the following table. This table also contains similar data for H_2SO_4 to be used later:

Mol. conc.		0.0005	0.001	0.002	0.005	0.01	0.02	0.03	0.05
Mol. F. P. Lowering	$CuSO_4$	3.23	3.15	3.04	2.87	2.70	2.50	2.41	2.34
	Hg_2SO_4	5.34	5.26	5.15	4.94	4.71	4.46	4.32	4.16

of $CuSO_4$ by means of the formula given by Lewis,[1] $\int d\overline{F}_1 = 292.2 \int (1/c)\, d\theta$, where $\overline{F}_1$ is the partial molal free energy of the solute in calories, and c is the concentration in mols per thousand grams of water, at which the freezing-point lowering is θ. The integration gives for the free energy of dilution between 0.05 M and 0.005 M, 1590 calories, and between 0.005 M and 0.0005 M, 1949 calories.

The first of these values when multiplied by the mechanical equivalent of heat and divided by twice the Faraday equivalent gives 0.0344 V., which should be identical[2] with the difference between the E. M. F. of the above cell with 0.05 M and 0.005 M $CuSO_4$, namely, 0.0298 V. The difference of 0.0046 V. is probably due to our choice of too high values of the freezing-point lowering at concentrations above 0.03 M, where it was necessary to extrapolate from the experiments of Hausrath and Bedford.

The second value, 1949 cal., corresponding to 0.0422 V., enables us to calculate from the E. M. F. at 0.005 M the E. M. F. at 0.0005 M, namely,

$$Cu, CuSO_4\ 0.0005\ M, Hg_2SO_4, Hg;\ \mathbf{E} = 0.4648\ V.$$

Now we will assume that at this high dilution the degree of dissociation is measured accurately by the conductivity, and the activities of the ions are proportional to the concentrations so measured. We may then write the equation,[3]

$$\mathbf{E} = \mathbf{E}^\circ - (RT/2F) \ln (Cu^{++})(SO_4^{--}).$$

Now from $\mathbf{E} = 0.4648$ V., taking the degree of dissociation in 0.0005 M as 0.862, we find $\mathbf{E}^\circ = 0.2658$ V. This is the electromotive force which would be exhibited by such a cell with Cu^{++} and SO_4^{--} each at (hypothetical) molal concentration. $\mathbf{E}^\circ$ is the difference between the two *normal* electrode potentials Cu, Cu^{++} and Hg, Hg_2SO_4, SO_4^{--}.

The Free Energy of Dilution of Sulfuric Acid.—Cells of the form H_2, H_2SO_4, Hg_2SO_4, Hg were also investigated. The Hg_2SO_4 electrodes were made up as before. The hydrogen electrode was of the form employed in other investigations in this laboratory and will be described in another place. Both electrodes showed excellent constancy and reproducibility and the following results, representing in each case the mean of several determinations, may be considered correct to 0.0001 V.:

$$H_2, H_2SO_4\ 0.05\ M, Hg_2SO_4, Hg;\ \mathbf{E} = 0.7545\ V.$$

$$H_2, H_2SO_4\ 0.005\ M, Hg_2SO_4, Hg;\ \mathbf{E} = 0.8160\ V.$$

In the case of a ternary electrolyte, which certainly dissociates in part into intermediate ions, conductivity data alone are insufficient for the

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[1] THIS JOURNAL, 34, 1635 (1912).

[2] The freezing-point data give the free energy values at about 0° and not at 25°, but the difference is smaller than the probable experimental error.

[3] For a discussion of these equations and the notation employed, see Lewis, THIS JOURNAL, 35, 23 (1913).

calculation of the concentration of the various constituents, even when the principle of Kohlrausch is assumed. Noyes and Stewart[1] have attempted to determine the composition of solutions of sulfuric acid by combining the conductivity data, (*a*) with transference data, (*b*) with "isohydric" data. The results of their calculations of the molal concentrations of H^+, HSO_4^- and SO_4^{--} at concentrations 0.05 M and 0.005 M are given in the following table:

		H^+.	HSO_4^-.	SO_4^{--}.
0.05 M....................	(*a*)	0.0625	0.0315	0.0155
	(*b*)	0.0585	0.0355	0.0115
0.005 M....................	(*a*)	0.0081	0.0017	0.0032
	(*b*)	0.00825	0.00155	0.00335

Assuming the activity of these ions to be proportional to their concentration we would have the equations,

$$\mathbf{E} = \mathbf{E}^\circ - (RT/2F) \ln (H^+)^2(SO_4^{--})$$

$$\mathbf{E}' = \mathbf{E}^{\circ\prime} - (RT/2F) \ln (H^+)(HSO_4^-)$$

From our measurements $\mathbf{E} = \mathbf{E}' = 0.7545$ V. at 0.05 M, and $\mathbf{E} = \mathbf{E}' = 0.8160$ V. at 0.005 M. Substituting these values and the concentrations from the table in the formulae we find at 0.05 M, $\mathbf{E}^\circ = 0.6299$ V. (*a*) and 0.6243 V. (*b*); at 0.005 M, $\mathbf{E}^\circ = 0.6186$ V. (*a*) and 0.6197 V. (*b*). The discrepancy between the values found at the two concentrations, amounting to 11 millivolts (*a*) and 5 millivolts (*b*), shows in this case also, either that very serious errors have been made in determining the concentration of the ions, or that the activities are far from proportional to the concentrations. The corresponding calculation of $\mathbf{E}^{\circ\prime}$, involving only univalent ions, gives, as might be expected, more concordant results; thus at 0.05 M, $\mathbf{E}^{\circ\prime} = 0.6745$ V. (*a*) and 0.6752 V. (*b*); while at 0.005 M, $\mathbf{E}^{\circ\prime} = 0.6724$ V. (*a*) and 0.6714 V. (*b*).

The freezing-point data for sulfuric acid are far more numerous, but also less concordant, than those for copper sulfate. We have attempted, after plotting all the data, to construct the most probable curve between 0.05 M and 0.0005 M. Sample points of the curve have been given in one of the previous footnotes. From this curve we calculate for the electromotive force corresponding to the dilution from 0.05 M to 0.005 M, $\mathbf{E} = 0.0613$ V., which agrees surprisingly well with the difference between the two E. M. F.'s measured above, namely, 0.0615 V. The similar calculation from 0.005 M to 0.0005 M gives 0.0731 V., so that we may calculate,

$$H_2,\ H_2SO_4\ 0.0005\ M,\ Hg_2SO_4,\ Hg;\ \mathbf{E} = 0.8891\ V.$$

By a sort of extrapolation from the values given by Noyes and Stewart at higher concentrations we estimate that in 0.0005 M H_2SO_4 the concentrations of H^+ and SO_4^{--} are, respectively, 0.00097 M and 0.00047 M.

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[1] THIS JOURNAL, **32**, 1148 (1910).

Assuming now that at this high dilution the activities of the ions are proportional to the concentrations thus determined, we may as before write

$$\mathbf{E} = \mathbf{E}^\circ - (\mathrm{RT}/2\mathbf{F}) \ln (\mathrm{H}^+)^2(\mathrm{SO}_4^{--}),$$

and substituting the numerical data we find $\mathbf{E}^\circ = 0.6127$ V. This is therefore the difference between the *normal* electrode potentials H_2, H^+ and Hg, Hg_2SO_4, SO_4^{--}.

The Potential of the Copper Electrode.—In the two preceding sections we have calculated for two cells the normal E. M. F., that is, the E. M. F. when the ion concentrations are (hypothetical) molal, namely,

$$\mathrm{Cu}, \mathrm{Cu}^{++} \parallel \mathrm{SO}_4^{--}, \mathrm{Hg_2SO_4}, \mathrm{Hg};\ \mathbf{E}^\circ = 0.2658\ \mathrm{V}.$$

$$\mathrm{H}_2, \mathrm{H}^+ \parallel \mathrm{SO}_4^{--}, \mathrm{Hg_2SO_4}, \mathrm{Hg};\ \mathbf{E}^\circ = 0.6127\ \mathrm{V}.$$

By subtracting we therefore find,

$$\mathrm{Cu}, \mathrm{Cu}^{++} \parallel \mathrm{H}^+, \mathrm{H}_2;\ \mathbf{E}^\circ = -0.3469\ \mathrm{V.},$$

and taking the normal hydrogen potential as zero[1] the normal potential of the copper electrode is —0.3469 V.

If, instead of using the data for 0.0005 M solutions, we make a similar calculation using the data at 0.005 M, taking the average values of Noyes and Stewart, and making the same assumptions as to proportionality of activity and concentration, we find $\mathbf{E}^\circ = -0.3445$ V. The difference between this value and that obtained from 0.0005 M solutions, amounting to 0.0024 V., might possibly be due to errors in the freezing-point data which we have employed, but probably indicates that even at a dilution of 0.005 M the simple laws of dilute solutions do not hold accurately when bivalent ions are involved. We shall therefore accept as the best obtainable value for the *normal electrode potential of copper against cupric ion at 25°*, $\mathbf{E}^\circ$ = *—0.3469 V.*, which is probably correct to about one millivolt.

A more obvious method of determining the normal electrode potential of copper is at present less accurate, but we have attempted to use this method also. Cells were constructed of the type: Cu, $CuSO_4$ 0.005 M, $CuSO_4$ 0.05 M, $MgSO_4$ 0.05 M, KCl 0.1 M, KCl 1.0 M, HgCl, Hg, giving $\mathbf{E} = +0.0232$ V. The first liquid potential $CuSO_4$ 0.005 M, $CuSO_4$ 0.05 M was calculated from the formula

$$\mathbf{E} = \frac{u - v}{u + v}\,\frac{\mathrm{RT}}{2\mathbf{F}} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2}.$$

Taking u as 78.8 and v as 54.2, $\mathbf{E} = +0.0044$ V. This value must, however, be considered uncertain, as it is doubtful how valid the formula is in a case of this kind. The potential $CuSO_4$ 0.05 M, $MgSO_4$ 0.05 M may be

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[1] Lewis, This Journal, 35, 24 (1913). It should be emphasized that the potential so stated is not the same, either in magnitude or sign, as the value ϵ_h stated according to the recommendations of the committee of the Bunsen Gesellschaft.

neglected, since the mobilities of Mg^{++} and Cu^{++} are almost identical; in fact, the omission of $MgSO_4$ from the chain altered the total E. M. F. by only 0.0001 V. The potential $MgSO_4$ 0.05 M, KCl 0.1 M has been measured directly by Faragher[1] and found to be +0.0016 V. The potential KCl 0.01 M, KCl 1.0 M is calculated to be +0.0004 V. We have therefore exclusive of liquid potentials Cu, $CuSO_4$ 0.005 M || N. E.; **E** = 0.0168 V. Assuming that the concentration of Cu^{++} is 0.00315 M in $CuSO_4$ 0.005 M, and that the activity is proportional to the concentration, we calculate for the normal potential of copper against the normal electrode

$$\text{Cu, Cu}^{++} \parallel \text{N. E.; } \mathbf{E}^\circ = -0.0571 \text{ V.}$$

Now we have

$$\text{H}_2\text{, H}^{+} \parallel \text{N. E.; } \mathbf{E}^\circ = +0.2776 \text{ V.}^2$$

and subtracting gives

$$\text{Cu, Cu}^{++} \parallel \text{H}^{+}\text{, H}_2\text{; } \mathbf{E}^\circ = -0.3347 \text{ V.}$$

which is the value obtained in this way for the normal potential of copper. This differs from the more accurate value obtained above by more than one centivolt. The large discrepancy is doubtless partly due to the assumption that the concentration and activity of Cu^{++} in $CuSO_4$ 0.005 M can be calculated directly from the conductivity, but is probably chiefly to be ascribed to the uncertainty in the liquid potentials, especially that between $CuSO_4$ 0.005 M and 0.05 M.

BERKELEY, CAL.

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THE TRANSFERENCE NUMBER, CONDUCTANCE, AND IONIZATION OF HYDRIODIC ACID AT 25°.

BY E. K. STRACHAN AND VEE GIH CHU.

Received March 23, 1914.

CONTENTS.

1. Purpose of the Investigation.

When the degree of dissociation of an electrolyte is calculated from the conductivity ratio in the usual manner, the assumption is made that the relative mobilities of the ions and hence also the transference numbers for the electrolyte are independent of the concentration. This assumption is approximately true for most dilute salt solutions, but in some in-

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[1] This work is about to be published.

[2] Based upon measurements of Sebastian about to be published.