A slight error is present in the gage as described and constructed, due to lack of parallelism of the two arms of the tube containing mercury; it is probably less than the errors of calibration and construction. For the most accurate work this could be eliminated by making the gage in the somewhat more inconvenient form of a U-tube with parallel limbs.

It is obvious that the longer the radius of the scale is, and the shorter AB, the greater will be the reading accuracy, and the less will be the range of the scale of the instrument. The maximum range of the gage is from $h = 0$ to $h = d$, and of the scale S, 90°.

When designed with a volume ratio $V{:}v$ suitable for vacua too high to permit the use of rubber tubing, an oil-sealed metal union or a mercury-sealed, ground-glass joint can be used as the pivot.

Thanks are due Professor R. S. Tour for suggestions as to the graphical calibration of the scale.

Summary

The construction and calibration of a new type of vacuum gage has been described. The gage is designed for laboratory use and is simple to construct and operate. In accuracy and range it stands between the simple U-tube manometer and the McLeod gage.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE VAPOR-PRESSURE LOWERING OF AQUEOUS SULFURIC ACID SOLUTIONS AT 25°

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Introduction

The object of this investigation was to determine very accurately the vapor pressures of aqueous sulfuric acid solutions in order to have means of calculating the various functions derivable from such data. Sulfuric acid entering into so many chemical reactions merits considerable attention because of the practical use to which quantitative studies of its properties and behavior may be applied. A study of the vapor pressure of its aqueous solutions is especially desirable inasmuch as the only measurements of this kind heretofore recorded deal with concentrated solutions and lack the accuracy prerequisite for a study of more dilute solutions. Moreover, such studies furnish an excellent confirmation of relationships correlating vapor-pressure measurements with those of freezing points and electromotive force as will be seen in the latter part of this paper. This substance would also serve admirably for isotenoscopic determinations of vapor pressures, being easily analyzed and serving as a rapid dehydration agent.

Experimental Method

The method employed in this investigation was that originally described by Frazer and Lovelace,[1] and successfully applied and modified in a series of later investigations.[2]

Only incidental modifications allowing more rapid and convenient readings were introduced in this work. Instead of allowing air to enter the apparatus while changing solutions, the former was excluded and hydrogen used instead, thus expediting somewhat the process of obtaining "air-free" solutions. A new arrangement of the illumination of the Rayleigh manometer points prevented optical strain due to repeated readings.

Preparation of Materials

The sulfuric acid was prepared by heating the fuming acid (from the contact process) and absorbing the evolved sulfur trioxide in distilled water. The solution thus obtained is free from the metallic constituents found in the ordinary acid and may be freed from sulfurous acid and other volatile impurities by boiling it, while passing a stream of nitrogen through the solution. The resulting product when it shows no reducing action on dil. permanganate solution is diluted to the required concentration and then, after addition of sufficient water, is boiled to drive off all dissolved air. In order to obviate the possibility of any action on the mercury, this was done in a bulb whose stem after the solution had cooled was broken under mercury and the contents introduced into the apparatus as described in previous papers.

The measurements were made at 25° (±0.01) over a range of concentrations (up to 3 M).

Accuracy of the Method

In view of the frequent application of data obtained by this method to cases where such use is unwarranted, due to the experimental errors involved, it is necessary to point out here the limits of its accuracy.

The readings of the Rayleigh manometer used in these measurements are made on a metallic millimeter scale and since the absolute accuracy of the eye in such readings is 0.2 mm., it is obvious that readings may be in error in the third decimal place and hence are not recorded beyond that point in this paper.

In most calculations, the molal lowering is used instead of the direct reading, and care must be taken in using such values to remember that their degree of accuracy varies inversely as the concentration. Solutions above molal remain accurate in the third decimal place but the error in the molal lowering for a 0.1 M solution being multiplied ten-fold becomes manifest in the second decimal place, which makes the agreement in the case of lower concentrations much worse than in higher ones. In the case of very dilute solutions (less than 0.1 M) the error of reading is 10% or

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[1] Frazer and Lovelace, This Journal, **36**, 2439 (1914).

[2] Lovelace, Frazer and Miller, *ibid.*, **38**, 515 (1916). Frazer, Lovelace and Rogers, *ibid.*, **42**, 1793 (1920). Lovelace, Frazer and Sease, *ibid.*, **43**, 102 (1921). Lovelace, Bahlke and Frazer, *ibid.*, **45**, 2930 (1923).

more of the total reading, and the use of such data must necessarily lead to the absurdities which have been obtained from them.

Experimental Results

In Table I are given the experimental results which are plotted in Fig. 1.

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS

Molality, M	0.073	0.241	0.315	0.549	0.636	0.892
Lowering obs., dp	.060	.201	.264	.469	.547	.791
Mol. lowering, dp/M	.822	.834	.838	.854	.860	.887
Molality, M	1.097	1.282	1.671	1.772	2.009	2.468	2.871
Lowering obs., dp	0.995	1.193	1.664	1.786	2.086	2.698	3.337
Mol. lowering, dp/M	.907	0.931	0.996	1.008	1.038	1.093	1.162

Row 1 gives the molality (M) of the solutions expressed in moles of sulfuric acid per thousand grams of water; Row 2 gives the lowering (dp)

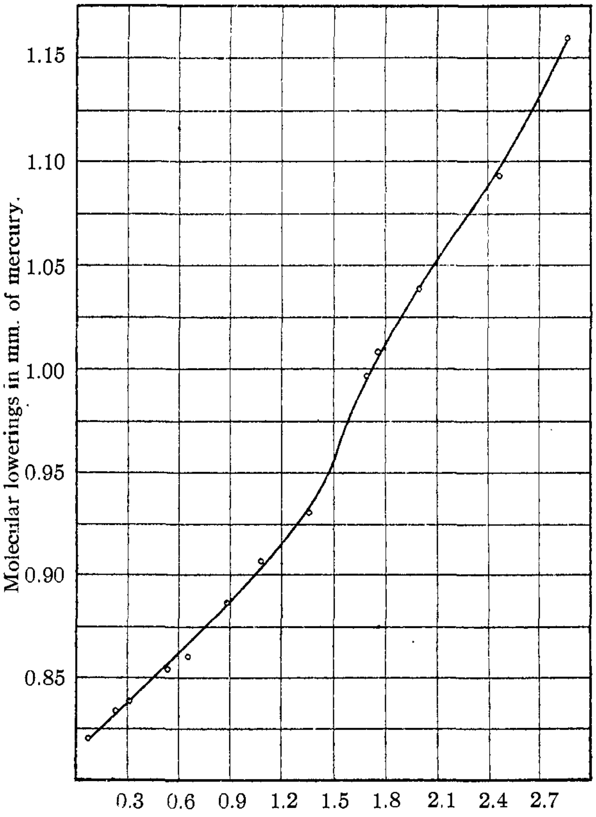

Fig. 1.

expressed in millimeters of mercury corrected to 0°; and Row 3 gives the molecular lowering (dp/M).

As has been shown by Thomas and Ramsay,[3] the partial pressure of sulfuric acid over its aqueous solutions is negligible in the range and at the temperature of this investigation; hence no corrections for this factor are necessary.

Thermodynamic Considerations

Dil. aqueous sulfuric acid solutions have been accurately studied both from the standpoint of their freezing points[4] and from the electromotive force of the cell,[5] H_2, H_2SO_4, Hg_2SO_4, Hg. Lewis and Randall[5] have made use of these data to calculate the activity coefficients of sulfuric acid at 25°.

In order to test the data of this investigation as well as to substantiate activity coefficients as derived by other methods, they have been calculated as shown in Table II. The method used for their calculation is that described by Lewis and Randall.[7]

TABLE II

ACTIVITY COEFFICIENTS FROM VAPOR PRESSURE MEASUREMENTS

I M	II $10 + \log (p/p_0)$	III N_1/N_2	IV $k\gamma$	V γ
0.073	9.99890	760	31.9	0.319
.241	9.99632	230	21.2	.212
.315	9.99441	176	21.8	.218
.549	9.99135	101	17.3	.173
.636	9.98989	87.3	16.6	.166
.892	9.98530	62.2	15.3	.153
1.097	9.98142	50.6	14.6	.146
1.282	9.97763	43.3	14.4	.144
1.671	9.96848	33.2	14.3	.143
1.772	9.96607	31.3	14.3	.143
2.009	9.96010	27.6	14.4	.144
2.468	9.94766	22.5	14.9	.149
2.871	9.93429	19.3	15.8	.158

Col. II gives the values of $10 + \log(p/p_0)$ where p is the vapor pressure of the solution and p_0 that of the pure solvent. The value of the latter has been taken as 23.763 mm. which is the value given by Scheel and Heuse[8] corrected to 0°.

Col. III gives N_1/N_2, the mole ratio of the solvent to solute, that is, 55.51 divided by the values of M, given in Col. I.

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[3] Thomas and Ramsay, *J. Chem. Soc.*, **123**, 3256 (1923).

[4] Drucker, *Z. Elektrochem.*, **17**, 400 (1911). Roth and Knothe, Landolt-Börnstein "Tabellen." Pickering, *Z. physik. Chem.*, **7**, 392 (1891). Barnes, *Trans. Roy. Soc. Canada*, II, [3] **6**, 37 (1900).

[5] Randall and Cushman, THIS JOURNAL, **40**, 393 (1918).

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**.

[7] Ref. 6, p. 331.

[8] Scheel and Heuse, *Ann. Physik*, **31**, 715 (1910).

From the relationship $\int d \log a_2 = -\int \frac{N_1}{N_2} d \log a_1$, in which a_1 and a_2 are the activities of solvent and solute, respectively, it is obvious that if we plot the values of N_1/N_2 against those of $\log(p/p_0)$ (which we may assume equal to $\log a_1$) and determine the area under the curve so obtained, we have a quantity proportional to $\log a_2$. Extracting the cube root of these values and dividing by the molality gives a series of quantities proportional to the activity coefficients. Such values,[9] $k\gamma$, are given in Col. IV.

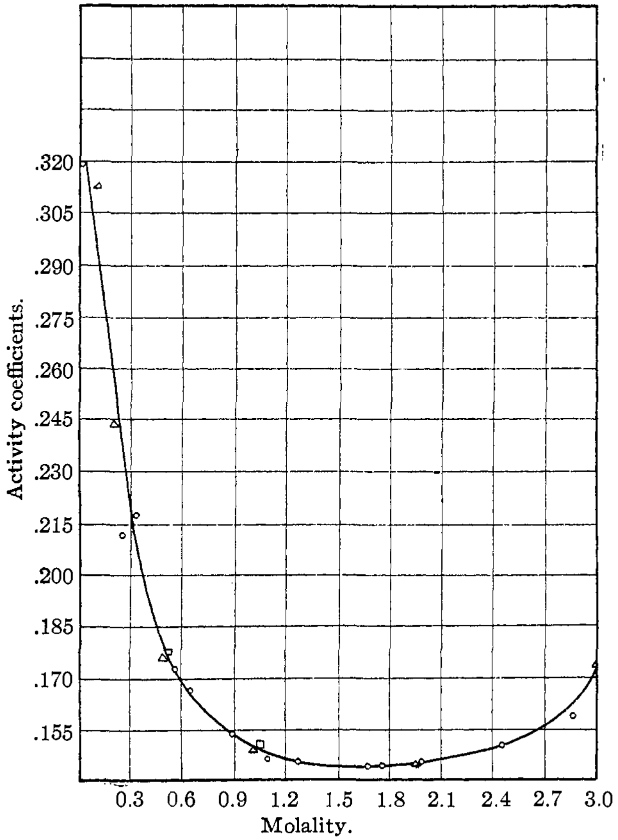

Fig. 2.—The circles represent vapor pressure, the triangles freezing points and the squares electromotive force.

Comparison with Activity Coefficients as Derived by Other Methods

The activity coefficients as calculated by Lewis and Randall[10] from freezing points and e.m.f. measurements are plotted in Fig. 2. The former

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[9] Compare Ref. 6, p. 332.

[10] Ref. 6, p. 354.

are calculated directly while the latter are obtained from relative values as in the case of vapor-pressure measurements. On interpolating the values so obtained to the concentrations covered in this investigation, the values so obtained were seen to be in almost every case exactly one-hundredth of those given in Col. IV. Hence, if we assume $k = 100$, we obtain values for the activity coefficients, γ, which are plotted, together with those obtained from freezing points and e.m.f. measurements, in Fig. 2. Such values are given in Col. V of Table II. The agreement between the two sets of data is quite remarkable. The wide deviation of the first two values is due undoubtedly to the error of extrapolation involved in their evaluation.

Comparison with Other Vapor-Pressure Data

The only other vapor-pressure measurements for sulfuric acid solutions whose accuracy merits attention are those of Brönsted[11] whose measurements at 20° and 30° have been interpolated by Lewis and Randall[12] to give values at 25° from which to calculate activities at this temperature. The marked deviation of these values from those obtained by Brönsted in the range covered by this investigation would indicate the accuracy of Brönsted's measurements to extend to the first decimal place only instead of the third as quoted and used.

In Table III, the values of Brönsted as quoted by Lewis and Randall[13] are compared with the values interpolated from the results of this investigation.

TABLE III

COMPARISON OF RESULTS WITH THOSE OF BRÖNSTED

M	dp (Brönsted)	dp (observed)	Deviation
1.236	0.964	1.144	−0.180
2.467	2.869	2.697	+ .172

If this be true, the use of Brönsted's data beyond the first decimal point is both unjustifiable and erroneous.

Summary

1. The vapor pressures of aqueous sulfuric acid solutions at 25° have been measured to a concentration of about 3 M.

2. From the values so obtained are calculated the activity coefficients which are in complete agreement with values from other sources.

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[11] Brönsted, *Z. physik. Chem.*, **38**, 693 (1910).

[12] Ref. 6, p. 331.

[13] Ref. 6, p. 331.