

by sodium hydroxide or hydrochloric acid, respectively. For this reason a method for obtaining the half-way end-point for these acids, or salts of these acids, by titrations with sodium hydroxide or hydrochloric acid is highly desirable. In this paper results have been presented which show that the conductance method can be used in obtaining the acid oxalate end-point of oxalic acid by titration with a standardized sodium hydroxide solution. Doubtless the reverse is also possible, that is, the titration of neutral sodium oxalate with hydrochloric acid by the conductance method.

PHILADELPHIA, PENN.

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

MAGNETIC SUSCEPTIBILITY OF MIXTURES OF LIQUIDS.

By ALPHEUS W. SMITH AND ALVA W. SMITH.

Received June 14, 1918.

A study of the physical properties of mixtures of liquids affords an interesting field of investigation, for by it those properties which follow the additive law can be discovered. Such properties must be uninfluenced by intramolecular actions and are, therefore, determined solely by conditions which exist within the atom or molecule. With the increasing care and accuracy of investigation the number of such truly additive properties has been found to be small. Recently Morgan and Griggs¹ and Morgan and Scarlett² studied the surface tension of several series of liquid mixtures and found marked departures from the additive law in most cases. The viscosities of certain mixtures of liquids have been examined by Kendall and Monroe,³ who show that in this case the cube root of the viscosity seems to be an additive function. Many other properties of mixtures of liquids have been studied as a means of testing the validity of the additive law but a fairly careful examination of the literature on the subject seems to indicate that the magnetic susceptibility of mixtures of liquids has not been studied, although the additive law has often been used in calculating the magnetic susceptibility of a salt from the susceptibility of the solution and of the solvent. It seemed worth while, therefore, to study the magnetic susceptibilities of a few series of mixtures of liquids in order to see how nearly the observed susceptibility agrees with that calculated from the concentration of its components by an application of the additive law.

The method of taking the observations was that devised by Quincke as modified by Oliver and recently used by Piccard⁴ in his study of the magnetic susceptibility of water. The arrangement of the apparatus

¹ Morgan and Griggs, *THIS JOURNAL*, **39**, 2261 (1917).

² Morgan and Scarlett, *Ibid.*, **39**, 2275 (1917).

³ Kendall and Monroe, *Ibid.*, **39**, 1787 and 1802 (1917).

⁴ Piccard, *Arch. Phys. Nat. Sci.*, **35**, 340 (1913).

is shown in Fig. 1. It consists essentially of a capillary tube, bent in the form indicated, with one end dipping into the beaker D containing the liquid to be studied, the meniscus B within the tube being between the poles C of the electromagnet. The meniscus B is as nearly as possible at the center of the magnetic field and is viewed with a fixed microscope, A. The beaker D rests on a base which can be raised or lowered by means of a micrometer screw, F, which was made by the Geneva Society and was so calibrated that displacements could be measured to 0.001 mm. When the magnetic field is established the meniscus B either rises or falls in the capillary tube; in order to obtain the susceptibility of the liquid it is necessary

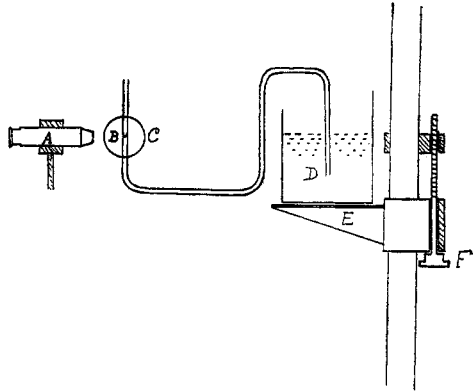


Fig. 1.

to measure, besides the density of the liquid and the magnetic field, the elevation or depression of the meniscus B, caused by the magnetic field. Instead of measuring the elevation or depression of the meniscus B it is more accurate to measure the amount by which the beaker D must be displaced in order to bring the meniscus B back to its original position, tangent to the cross hair in the eye-piece of the microscope A. This condition of tangency is always approached by lowering the meniscus in the capillary tube in order that the form of the meniscus may be as nearly as possible the same for each observation. The magnetic field is first established and the beaker displaced until tangency is realized. The electric current in the magnet is then interrupted so that the magnetic field disappears and the displacement of the beaker necessary to bring the meniscus B back to its original position is measured as before. The mean of these two displacements is taken as the observed displacement caused by the magnetic action, thus nearly eliminating the error due to drift in the temperature. This series of observations was repeated 10 times for each substance. From the mean of these 10 observations the magnetic susceptibility of the substance was calculated in the following way:

The susceptibility k per unit volume is defined as $k = I/H$, where I is the intensity of magnetization and H the magnetic field in dynes. To get the susceptibility per unit mass which will be called α , the susceptibility per unit volume is divided by the density d of the substance. Hence $\alpha = k/d$. If h is the difference in level between the surface of the liquid in the beaker and that in the capillary tube caused by the magnetic

action, then the force per unit area acting on the liquid tending to displace it is

$$(k - k_0) \frac{H^2 - H_0^2}{2},$$

where $k_0 = 0.27 \times 10^{-6}$ approx. is the susceptibility of the air per unit volume in contact with the meniscus, and H_0 the magnetic field at the surface of the liquid in the beaker. This pressure is balanced by the hydrostatic pressure arising from the column of liquid of height h and density d . Hence,

$$hgd = (k - k_0) \frac{(H^2 - H_0^2)}{2},$$

and

$$k - k_0 = \frac{2ghd}{H^2 - H_0^2}.$$

Since H_0^2 is very small in comparison with H^2 , the formula becomes

$$x = \frac{2gh}{H^2} + \frac{k_0}{d}. \quad (1)$$

In order to obtain the true displacement h of the meniscus B from the observed displacement it is necessary to take account of the displacement of the surface of the liquid in the beaker because of the fact that in one position a greater amount of the capillary tube is immersed in the liquid than in the other. This correction amounted to about 0.5%. A second small correction is necessary because the barometric pressure on the surface of the liquid in the beaker differs slightly between the two positions of the beaker. This correction amounted to only about 0.1% and was neglected. For a complete discussion of these sources of error reference is made to the paper by Piccard.¹

If the magnetic susceptibility is an additive property, the susceptibility of a binary mixture can be calculated from the equation

$$x = \frac{d-p}{d} x_1 + \frac{p}{d} x_2,$$

where x is the susceptibility of the mixture, x_1 the susceptibility of the first component of the mixture, x_2 the susceptibility of the second component, d the weight of 1 cc. of the mixture and p the number of grams of the second component in 1 cc. of the mixture. By means of this equation the susceptibility has been calculated for each of the mixtures in the four series of the binary mixtures studied in this paper and these calculated values have been compared with the values found by observation.

¹ *Loc. cit.*

TABLE I.—MAGNETIC SUSCEPTIBILITIES OF MIXTURES.

Acetone and Water.			
% water.	$\kappa \times 10^6$ obs.	$\kappa \times 10^6$ cal.	% deviation.
0	0.572
9.6	0.590	0.586	+0.68
25.2	0.614	0.608	+0.98
40.2	0.628	0.629	-0.17
54.3	0.650	0.649	+0.17
70.4	0.670	0.671	-0.17
89.8	0.697	0.700	-0.43
100	0.714
Acetic Acid and Water.			
% water.			
0	0.520
19.7	0.560	0.559	+0.2
39.3	0.596	0.596	0.0
60.0	0.641	0.637	+0.7
79.5	0.680	0.674	+0.88
100	0.714
Acetic Acid and Benzene.			
% benzene.			
0	0.520
20.3	0.554	0.554	0.0
38.7	0.588	0.587	-0.17
59.1	0.626	0.621	+0.79
82.3	0.660	0.661	-0.17
100	0.691
Acetone and Ethyl Alcohol.			
% alcohol.			
0	0.619
14.8	0.630	0.635	-0.79
30.9	0.648	0.651	-0.45
53.3	0.676	0.670	+0.90
74.5	0.692	0.694	-0.29
100	0.72

The accompanying table, together with the curves, show the results of these observations, made at a temperature of about 20° in a magnetic field of 19,740 gauss. The second column gives the susceptibility which was directly observed, the third column that calculated from the application of the additive law, and the last the percentage deviation. It will be observed that these percentages are always small and nearly always well within the error of observation, so that there does not seem to be any systematic departure from the additive law in any of these 4 systems. These same facts are brought out more clearly in the curves in which the observed and the calculated susceptibilities have been plotted against the concentrations of one of the components in the mixtures. It is obvious that the susceptibility is a linear function of the concentration of one of the components.

In order to call attention to the way in which some of the other physical properties of these solutions depart from the additive law, there has also been plotted in Fig. 2 the surface tension of mixtures of acetone and water

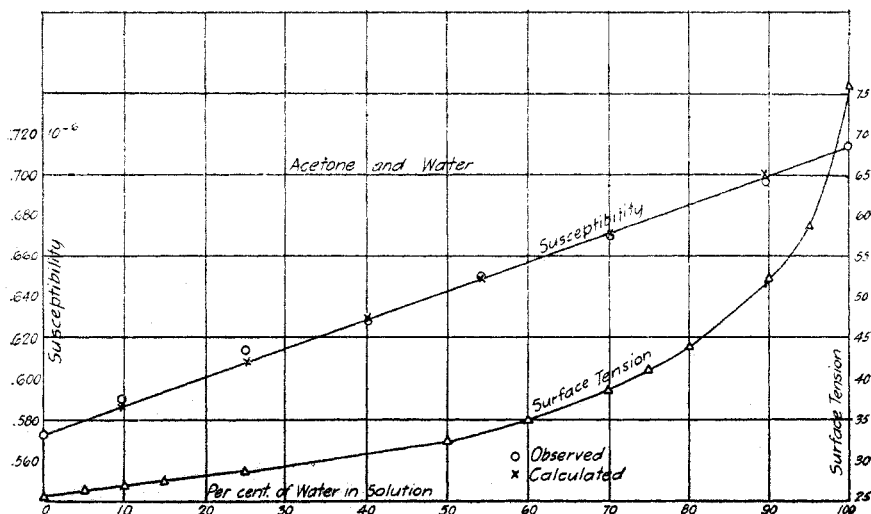


Fig. 2.

against the concentration of the water in the solution. Similarly, in Fig. 4, the surface tension of mixtures of acetic acid and benzene has been

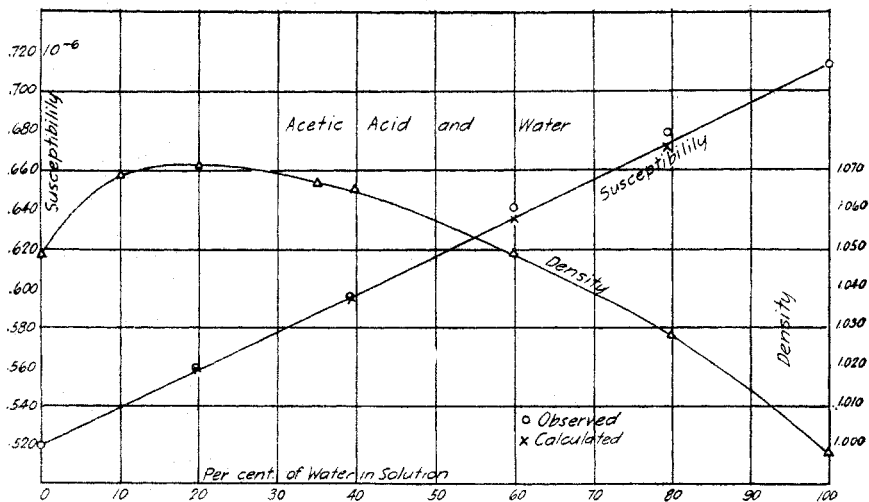


Fig. 3.

plotted against the percentage of benzene in the solution. The data for these curves were taken from the paper by Morgan and Scarlett.¹ In

¹ *Loc. cit.*

Fig. 3 is included a curve showing how the density of mixtures of acetic acid and water depends upon the concentration of the water in the solu-

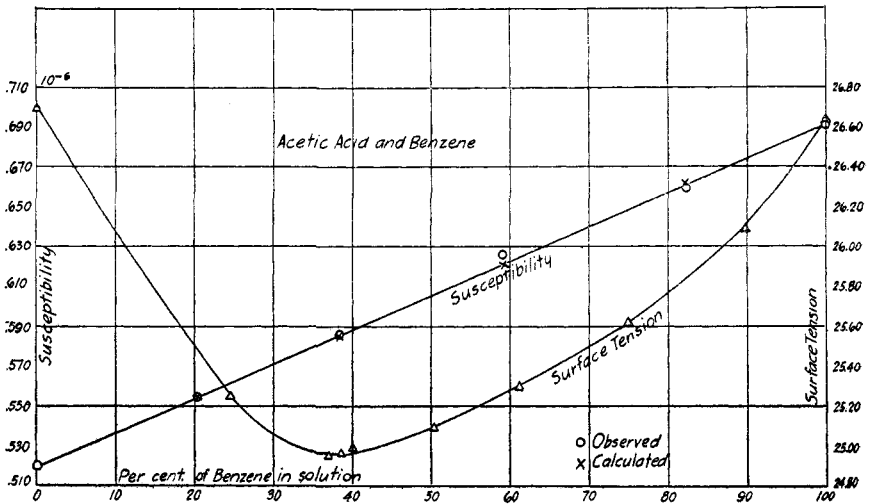


Fig. 4.

tion. In contrast to the behavior of the susceptibility these physical properties show marked departures from the additive law.

From these observations one concludes that the susceptibilities of mixtures of liquids obey closely the additive relation. In view of this

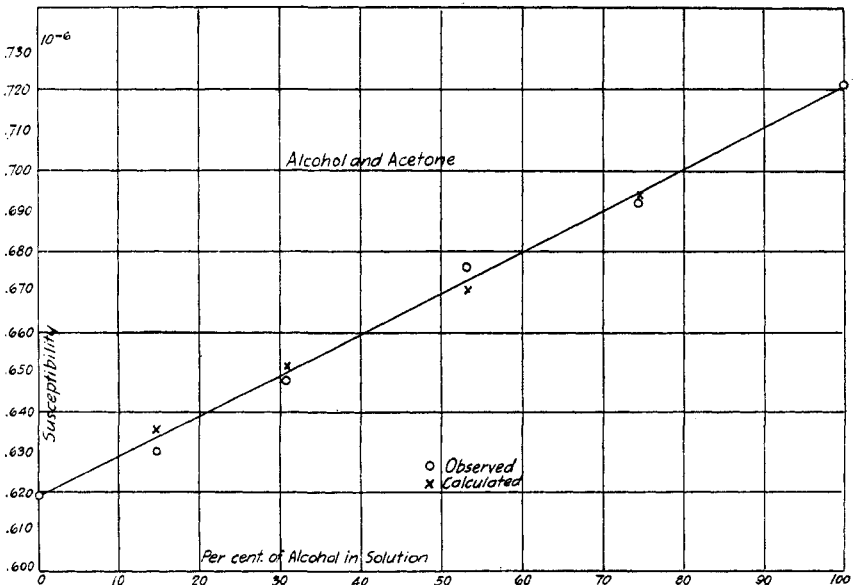


Fig. 5.

fact it is possible, from a knowledge of the susceptibility of a binary mixture in which the components are known, to determine the concentration of each of the components. To accomplish this, it is only necessary to know the susceptibility of each of the components in the pure state and the susceptibility of the mixture. When the susceptibility of one of the components differs very considerably from that of the other the accuracy of the method is sufficient for many purposes.

COLUMBUS, OHIO.

NOTE.

A New Hydrogen Sulfide Generator.—Many types of apparatus have been designed and are sold for use as hydrogen sulfide generators. Of these, some are self-contained and portable, while others consist of various arrangements of bottles, stoppers, tubes, etc., and, like the water still and steam bath, are regarded as laboratory fixtures. In spite of the many designs of generators, the big problem of the instructor in qualitative analysis is still the hydrogen sulfide supply. The average small generator requires the instructor's constant attention, and is then generally failing to supply gas or is wasting it.

As a contribution toward the solution of this problem for chemical laboratories, the writer has designed the generator shown in the accompanying illustration, which is a quarter section, side elevation of a generator embodying the design.

The apparatus consists of an outside container, 5, which is closed at its upper end by a cover, 11, securely clamped at its edges by suitable clamps, 4. A gasket, 3, is interposed between the cover and the upper edge of container 5, to make a gas-tight connection.

Within container 5 is an intermediate container, 6, open at its upper end and communicating with the interior of container 5 at this point. The base of container 6 is provided with an annular flange, which serves to keep it in a central position within the outer container, and thereby form between the lateral walls of the containers an annular chamber for the reception of the iron sulfide.

Coöperating with containers 5 and 6 is the container 1, having an enlarged spherical upper end, and a reduced downwardly tapering lower end which passes centrally through a ground-glass joint in cover 11 and communicates with container 6 at its bottom.

The cover 11 is formed with a gas outlet, 15, into which is fitted a capillary tube of such size that gas from the generator is delivered through it in a slow, steady stream. Within a depression formed in the cover and surrounding the capillary tube is a quantity of water through which the gas must bubble as it passes from the apparatus. A glass stopper, 12,