

tory, and the physical properties, including viscosity and conductivity, of sols of the type of hydrous ferric oxide are also being investigated.

Summary.

The lack of agreement between the colloid precipitation data of different investigators is shown to be attributable very largely to the varying purities and concentrations of the sols employed.

A number of series of perfectly clear hydrous oxide sols were carefully prepared. In each series the iron concentration was constant while the chlorine content varied. The sols were precipitated by potassium sulfate solution, and the amount of salt required for the complete precipitation of the sol was taken as a measure of its relative stability.

The data show that for a given iron concentration the stability increases with the chlorine content, while for sols of a given purity, *i. e.*, ratio equivalents Fe : equivalents Cl, the stability decreases as the concentration increases, this being most pronounced for very pure sols.

It is shown how the maximum purity of a sol may be found by graphical extrapolation. The maximum purities corresponding to four iron concentrations are obtained. The maximum purity obtainable decreases as the iron concentration increases.

The results of Nicolardot and Duclaux are discussed.

A chemical theory of the constitution of hydrous ferric oxide sols is advanced to explain the relation between stability and composition.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF ILLINOIS, No. 28.]

AN IMPROVED VICTOR MEYER VAPOR-DENSITY APPARATUS.

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The Victor Meyer vapor-density apparatus has remained in nearly its original form since its introduction, in spite of the fact that many thousand molecular-weight determinations are made with it every year in research and instructional laboratories. The few modifications that have been called to the attention of the authors are concerned with the introduction of the substance to be vaporized. Weiser¹ has, however, described a compact form of the apparatus, which has a number of advantages.

The substance whose molecular weight is desired is usually introduced by removing the stopper at the top, and dropping into the apparatus a diminutive glass-stoppered bottle or a bulb with a capillary outlet. Another method consists in breaking the sealed capillary of a bulb hung near the top of the vaporization tube. Either of these methods involves

¹ *J. Phys. Chem.*, **20**, 532 (1916).

chilling the air in the vaporization tube, and unless special precautions are taken, spilling drops of liquid along the tube as the capsule is falling. These difficulties are overcome by means of the simple apparatus shown in Fig. 1, which is a slight modification of an arrangement devised in this laboratory by K. A. Clark. A brass rod, *a*, with a small hook at the lower end, passes through the glass tube *b*, and a gas-tight connection between the two is made by means of the piece of rubber tubing, *c*. The rubber stopper *e* closes the upper part of the vaporization tube. The substance to be vaporized is placed in a small bulb connected with a sealed capillary bent into an inverted U. This is hung on the hook at the bottom of the brass rod, which extends nearly to the bottom of the vaporization tube. In this position the substance in the bulb can attain the temperature of its environment before vaporizing. If the bulb has thick walls and is not completely filled, it does not break even if it is heated 75° above the boiling point of the substance contained in it. By pulling at the top of the brass rod the capillary outlet is broken and vaporization takes place almost instantly. Very little mixing of the vaporized substance with air has time to occur. This scheme has been used with success for several years in laboratory class work. If a gas buret is used to measure the displaced air, the sudden rush of air from the vaporization tube can be taken care of. To make use of the usual arrangement of eudiometer and pneumatic trough, an inverted funnel with its stem drawn to a capillary must be inserted between the outlet and eudiometer tubes. While this breaking apparatus produces a considerable improvement in the results an important source of error still remains. Uniform heating along a tube about 50 cm. long is difficult to obtain if the heating is produced by boiling a liquid in the vapor jacket; ordinarily, then, the air at the bottom of the vaporization tube will be hotter than that at the top. When the substance introduced volatilizes the colder air passes into the measuring apparatus. This colder air will have a larger volume, in the measuring apparatus, than the air immediately displaced by the vaporized substance would have if lowered to the same temperature. This is not of importance if sufficient time elapses after the vaporization to allow the original temperature distribution to be regained. It is, however, difficult to determine when this point is reached. A small volume of air must return from the measuring apparatus to attain this adjustment. This is not possible with all forms of apparatus.

It seemed desirable, therefore, to design a vaporization tube from which inequalities of temperature could be eliminated. A number of forms of this tube were constructed, all more compact than the Victor Meyer type. The most successful forms of the tube are shown in Fig. 2*a* and 2*b*. The arrangement shown in Fig. 2*a* should be particularly useful as it can be constructed out of material to be found in any laboratory. The vaporiza-

tion vessel *V* which is 25 cm. long and 5 cm. wide carries a rubber stopper, *B*, through which passes a capillary delivery tube, *C*, and another tube, *E*, of 15 mm. bore and about 28 cm. long. Into this latter tube a breaking apparatus as described above is placed. The whole arrangement is enclosed in the boiling tube *H*, which is closed by the split stopper *S*. A sheet of asbestos supported by a rubber band at *m* deflects the steam away from the top of the breaking apparatus and increases the comfort of the operator.

In order to get the advantage of the central tube it is important that the small capsule containing the substance to be vaporized should re-

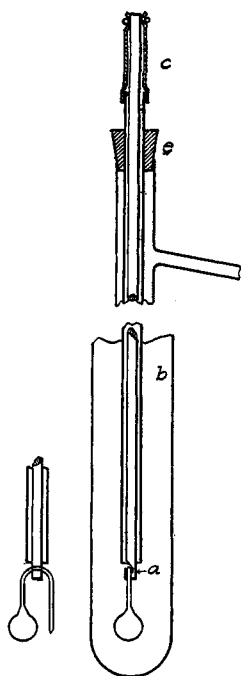


Fig. 1.

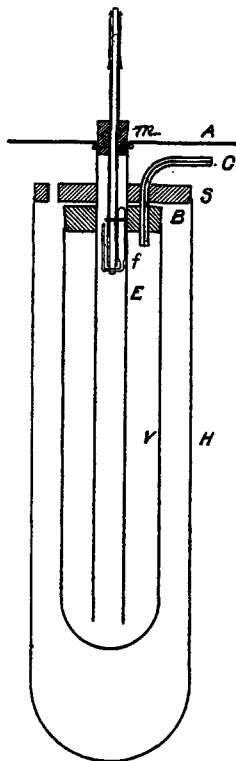
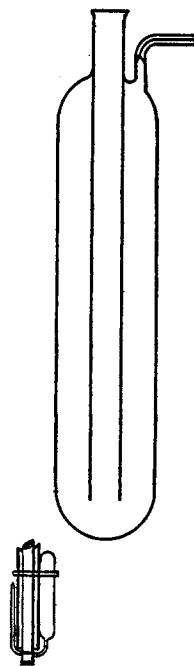


Fig. 2a.



2c. 2b.

main at the position *f* shown in the diagram. This can be accomplished by making the capsule from a short piece of narrow tubing, and fastening it, as shown in Fig. 2c, to the breaking apparatus with a rubber band.

Bromine is useful for the purpose of determining the distribution of a substance after the capsule containing it has been broken and the substance vaporized. The greater portion of the bromine can be located by its color, and the presence or absence of traces of the vapor can be es-

established by the use of potassium iodide-starch paper. With the apparatus shown in Fig. 2a, for instance, the red vapor filled the inner tube and extended about half way up the tube V when a capsule containing 0.17 g. was broken. A piece of the test paper in the outlet tube did not change color, showing that no bromine vapor passed into the gas buret.

In using these new forms of apparatus the usual eudiometer tube and pneumatic trough for collecting the displaced air did not work as the air could not escape quickly enough. A gas buret was satisfactory. The results were, however, improved if the leveling tube of the buret was lowered, producing a partial vacuum in the apparatus. It was also found necessary to have the temperature of the vapor jacket at least 50° above the boiling point of the substance under investigation.

In Table I is given a series of determinations of the vapor densities of bromine, ethyl alcohol, and ether. The first two were measured in Apparatus 2a and the last in Apparatus 2b. The weights (Line 1) are corrected for air displacement. The volumes of air displaced (Line 2) were measured in a carefully calibrated gas buret. The barometric pressure (Line 5) was determined with an accurate barometer and corrected to 0°. Pres-

TABLE I.
BROMINE.

1. Weight of substance, g.....	0.1970	0.2015	0.1475	0.2059	0.1861	0.1699	0.1809
2. Volume air displaced.....	30.33	30.15	22.71	31.05	29.00	26.42	28.31
3. Temperature.....	24°	25°	23°	25°	24.5°	24.5°	24.5°
4. Relative humidity.....	0.49	0.47	0.49	0.47	0.48	0.48	0.48
5. Atmospheric pressure.....	74.645	74.645	74.645	76.645	73.965	73.965	73.965
6. Mol. wt. (Gas Law).....	163.7	164.4	163.0	166.9	163.8	164.0	163.0
7. Mol. wt. (Berthelot Eq.)....	159.9	160.6	159.3	(163.0)	160.0	160.3	159.3
8. Mol. wt. (accepted).....	159.8

ETHYL ALCOHOL.

1. Weight of substance, g.....	0.0494	0.0612	0.0561	0.0587	0.0599	0.0486	0.0527
2. Volume air displaced.....	27.23	33.68	30.54	32.04	33.51	26.53	28.58
3. Temperature.....	23.5°	23.5°	23.5°	23.5°	25°	25°	25°
4. Relative humidity.....	0.47	0.47	0.47	0.47	0.51	0.51	0.51
5. Atmospheric pressure.....	73.617	73.617	73.617	73.617	74.612	74.612	74.612
6. Mol. wt. (Gas Law).....	46.3	46.8	46.9	46.7	46.6	46.4	46.7
7. Mol. wt. (Berthelot Eq.)....	45.9	46.4	46.4	46.3	46.1	45.9	46.2
8. Mol. wt. (accepted).....	46.05

ETHYL ETHER.

1. Weight of substance, g.....	0.1023	0.1159	0.0971	0.1040
2. Volume air displaced.....	35.33	40.40	33.68	35.90
3. Temperature.....	32.5°	33.2°	32.0°	29.0°
4. Relative humidity.....	0.58	0.58	0.66	0.59
5. Atmospheric pressure.....	743.95	743.95	744.0	738.0
6. Mol. wt. (Gas Law).....	75.72	75.26	74.9	75.7
7. Mol. wt. (Berthelot Eq.)....	74.2	73.8	(73.5)	74.2
8. Mol. wt. (accepted).....	74.08

tures are corrected for aqueous tension and the relative humidity (Line 4) as directed by Evans.¹

Since the substances under investigation do not follow the perfect gas law in the vapor state, the use of this law can not lead to correct molecular weights from vapor-density measurements. Usually, however, the deviations are of no practical significance. In the present case it is interesting to find out whether these deviations are those to be expected from the substances used or are due to experimental error. For this purpose an equation of state more accurate than the perfect gas law is necessary. Berthelot's equation is useful for this purpose as it expresses the behavior of most substances closely and the data to substitute into it are readily available. Rearranged to give the molecular weight, it may be stated as follows:

$$M = \frac{mRT'}{PV'} \left[1 - \frac{9 PT_c}{128 P_c T} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right]$$

In this equation M is the true molecular weight, m the mass of the substance; R is the gas constant; P and P_c are the (corr.) barometric pressure and the critical pressure, respectively. T , T' and T_c are, in turn, the temperature at which the substance is vaporized, the temperature at which the volume of air is measured, and the critical temperature. V' is the volume of the displaced air. V' and T' can be substituted for T and V of the original equation if the volume of the displaced air is proportional to the absolute temperature. This is almost exactly true in the range involved, as can be seen by substituting the appropriate constants for oxygen and nitrogen into Berthelot's equation. Referring to the table it will be seen that the molecular weight calculated by using the perfect gas law (Line 6) is one or two units higher than the accepted molecular weight (Line 8) while the molecular weight from Berthelot's equation (Line 7) varies by only a few tenths of a unit.

URBANA, ILL.

A NEW OXYCHLORIDE OF TIN.

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While engaged upon the chemical examination of certain objects brought from the Indian mounds of Florida by Mr. Clarence B. Moore, of this city, the writer's curiosity was aroused by minute brilliant crystals which he observed in a cavity inside of a metallic mass found in an aboriginal cemetery on Hogtown Bayou, Santa Rosa County, Florida.

This mass was of lenticular form, as if the metal had been melted in a shallow vessel, rather more than 5 cm. in diameter, and about 4 mm. in

¹ THIS JOURNAL, 35, 958 (1913).