

5. The proportions of  $S_{\mu}$  when acids, such as acetic, phosphoric, sulphuric and hydrochloric interact with sodium thiosulphate have been studied quantitatively.

6. With acetic acid and the thiosulphate no  $S_{\mu}$  is produced, with the other acids the percentages of  $S_{\mu}$  is in each case proportional to the concentrations of the total acid in the mixture at the moment of precipitation.

7. The concentration of ionic hydrogen seems to be a factor in determining the proportions of  $S_{\mu}$ , but it is evident that they determine it jointly with other factors which have not yet been determined.

8. It has been shown that the proportion of amorphous sulphur produced by precipitation is determined in part by the nature of the interacting materials, but that a contact effect of the whole liquid in which the liberated sulphur is suspended exercises a still greater effect. The conclusion is that the freshly liberated sulphur is initially all  $S_{\mu}$ , and that the reversion to  $S_{\lambda}$  is retarded during the hardening by the contact action of the acid or halogen in the liquid, different concentrations of the contact agent permitting differing proportions of  $S_{\mu}$  to overcome the tendency to revert and thus to remain finally as amorphous sulphur. In conclusion, I desire to thank Professor Alexander Smith for all of his kindly assistance during the progress of this investigation.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS].

### SOME NEW FORMS OF APPARATUS.

BY WILLIAM M. DEHN.

Received April 27, 1907

When a drop of pure mercury is placed in a clean tube whose internal diameter is less than 3 mm. the metal assumes and retains a cylindrical form owing to the tension exerted by the mercury surfaces not in contact with the glass. The cylinder of mercury may then act as an air tight piston, possessing very easy mobility<sup>1</sup>. A difference of gas pressure on the two ends of the cylinder results in a movement of the mercury until equilibrium is established, the slight friction of the mercury on the glass and the inertia of the mercury being readily overcome by gentle tapping at the end of the tube or on the glass above the mercury drop. Some of the following experiments have shown that this drop of mercury is sensitive to a difference of pressure less than 0.1 mm.

*Hygrometer.*—The apparatus is constructed as follows:—The bulb C made from a small flask (20-50 cc.) is attached first to the stopcock B and then to the side-tube D. This side-tube is made from a 1 cc. pipette graduated to 0.01 cc. and must have an internal diameter less than 3 mm. The apparatus without A attached is weighed empty and is then filled with

<sup>1</sup> Z. physik. Chem. 11, 587.

water (including the hole of the stopper B) to a readable distance on the graduated scale D. After weighing, the volume of the bulb C to the first mark on the scale of D, plus the volume of the boring of B, may be calculated. After calibrating in this manner, the 2 cc. finely-graduated pipette A and its funnel are attached.

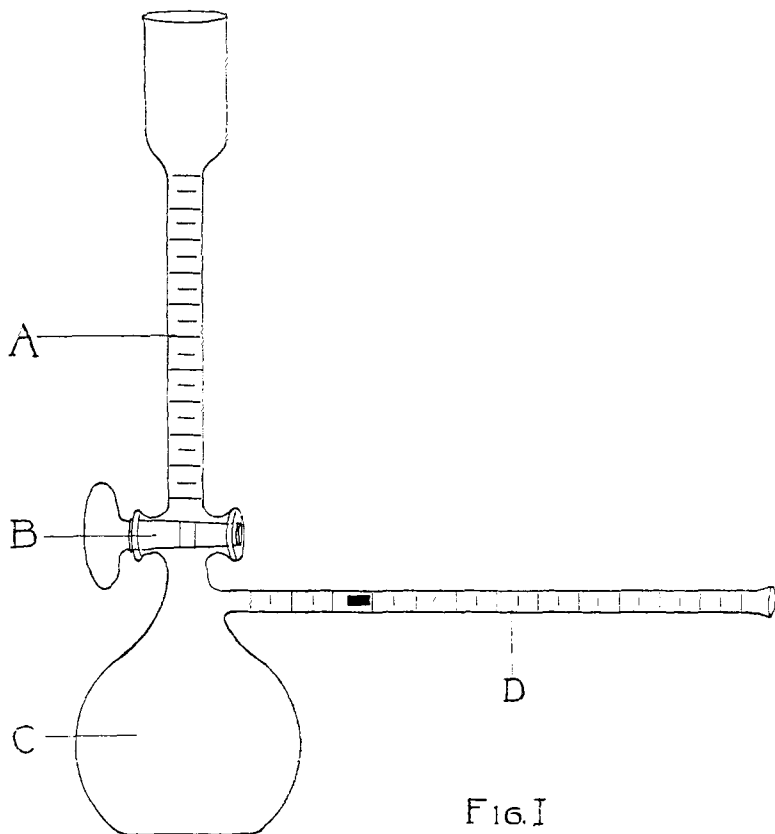


FIG. I

*Methods of Using.*—*Method (a).* The apparatus, after being properly cleaned by washing successively with water, alcohol, and ether, is dried by drawing air through the tube A. It is then filled with air to be tested. This is easily done by aspirating at the top of A while repeatedly and successively stopping the end of D, closing the stopcock B, opening the end of D and opening the stopcock B.

The drop of mercury (3 mm. or more in length) is placed in the end of D and is caused to move along the scale toward the zero point near<sup>1</sup> the

<sup>1</sup> Clean, dry mercury should be used. It is conveniently kept in a small flask whose neck is drawn out to a moderately small capillary tube. From this a regulated quantity of mercury can easily be poured out.

bulb C. The stopcock B is closed and the correct position of the mercury drop is regulated and read. Concentrated sulphuric acid is then placed in the pipette A to a readable height, and, after draining down, the position of its meniscus is read. The acid is then carefully admitted so as to cause the mercury to move toward, and lodge near the center of the tube D; the moisture contained in the confined air is quickly absorbed, the air-volume of C being correspondingly decreased. After 1-2 minutes the final positions of the mercury drop and of the meniscus of the acid are read.

*Calculation.*—Let C equal the volume of the bulb C plus the stopper boring;  $c$  the volume of air in D when the mercury does not start at the zero point; and  $s$  the volume of sulphuric acid admitted. Now if the air were perfectly dry, the volume occupied by the contained air and sulphuric acid would be  $C+c+S$ . But moisture ( $w$ ) contained in the air is absorbed by the sulphuric acid and decreases the volume to  $C+c+S-w$  the quantity  $w$  being most easily calculated by subtracting the difference of the mercury readings from the difference of the sulphuric acid readings. Therefore, the per cent. of moisture of the air is  $100w/C+c$ ; and the aqueous pressure ( $a$ ) is

$$a = \frac{wp}{C+c} \quad (I)$$

wherein  $p$  is the corrected atmospheric pressure at the time of the experiment.

*Method (b).* Here water instead of sulphuric acid is admitted to the bulb C; the vapor of the water quickly saturates the contained air and proportionally increases the volume  $C+c$ . This increase in volume ( $i$ ), calculated by subtracting the difference of the water readings from the mercury readings, and a table of aqueous vapor pressure give the data necessary for calculating the volume of the moisture, or the aqueous vapor pressure of the air tested. Let  $W$  equal the known aqueous vapor pressure at the temperature of the experiment, then the *increase* of aqueous vapor pressure when water is admitted is:

$$a' = \frac{ip}{C+c+i}$$

and the *initial* aqueous vapor pressure is:

$$a = W - \frac{ip}{C+c+i} \quad (II)$$

Now the sum of  $a$  determined by the sulphuric acid method and  $a'$  de-

<sup>1</sup> Owing to imperfections of construction, air-bubbles may lodge at the bottom or along the sides of the pipette A; they are easily dislodged by a long, closed capillary tube or by a wire of suitable metal.

terminated by the water method must be equal to the known aqueous vapor pressure,  $W$ , at the given temperature, else the two methods described are at fault. The following experiments illustrate not only the accuracy of these two methods but also the sensitiveness of the mercury piston:

Temp.	$a$	$a'$	$a + a'$	$W$
17.5	4.61	10.24	14.85	14.91
19.2	4.70	11.95	16.65	16.57
24.6	11.22	11.48	22.75	22.99
28.3	12.25	16.40	28.65	28.60
4.6	4.50	1.75	6.25	6.35

When the *relative humidity*  $h$ , of the atmosphere is sought, the formula:

$$h = a/w \quad (\text{III})$$

admits of its easy calculation.

During foggy or misty days apparently greater aqueous vapor pressures than the known vapor pressures at the given temperatures were obtained:

Conditions	Temp.	$a$	$W$	$p$
1. Sleet.....	$-1.2^{\circ}$	8.45	4.20	744.7
2. " .....	$-1.0$	8.70	4.26	"
3. Mist .....	$-0.2$	6.63	4.51	735.3

Evidently these excesses represent either *supersaturation* or the quantity of finely divided water held in *suspension*; if the latter, the weight in grams in a liter of air ( $m$ ) can be calculated by means of the formula:

$$m = \frac{a - W(1000)}{p}$$

which gives for the above experiments the following:

1. Mist.....	5.707 g.
2. " .....	5.962 g.
3. Fog .....	2.882 g.

quantities which certainly seem excessive, and suggest rather a preponderance of the condition of *supersaturation*.

*Tensimeters.*—*Form (1).* The hygrometer used above may conveniently serve the purpose of a *tensimeter*; in fact in the above experiments its use was that of a tensimeter. Accurate determinations of the vapor pressures of liquids at ordinary temperatures are easily made in the manner indicated; when vapor pressures at temperatures higher or lower than room-temperatures are desired, or when accurate hygrometric determinations are to be made, a rubber tube extension on D will permit of the tensimeter being immersed to the necessary depth in a water-bath whose temperature may be controlled by a thermostat and a stirrer. With this *open* tensimeter, the following determinations were made:

Substance	Temperature	Vapor pressures	
		Found	Known
Benzene	26.4°	99.80	100 <sup>1</sup>
Brombenzene	26.3°	3.90	4 <sup>1</sup>
Acetic Acid	30.0°	20.20	20.0-20.6 <sup>2</sup>
Ethyl Acetate	30.0°	117.80	118.7 <sup>3</sup>
Benzyl Chloride	41.1°	1.82	
" "	50.2°	2.66	
" "	60.1°	10.26	
" "	70.0°	16.36	
" "	80.0°	23.76	
Benzal Chloride	60.0°	4.03	
" "	70.0°	6.57	
" "	90.0°	11.00	
Benzotrichloride	60.0°	1.88	
" "	70.0°	9.65	
" "	80.0°	10.90	
" "	90.0°	18.38	

*Form (2).* When the vapor pressures of solids or small quantities of liquids are to be determined, the following form of apparatus are found to be more convenient. The essential difference is a shortened, funnel-like portion A and a stopcock B possessing a wide boring through the stopper. The substance to be tested is introduced directly or better is weighed in a capillary tube, narrow enough to pass through the boring to the proper depth and long enough to be held from without while the lower portion containing the substances is quickly clipped off by a sharp

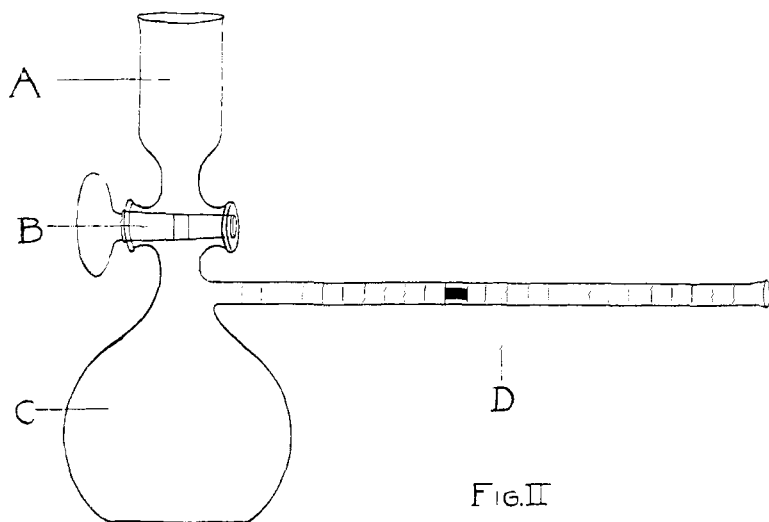


FIG. II

<sup>1</sup> Kahlbaum, Z. physik. Chem., 26, 603.

<sup>2</sup> Ibid. 7, 433; 13, 34; J. Chem. Soc., 49, 790.

<sup>3</sup> J. Chem. Soc., 63, 1191

turn of the stopcock (See Fig. III). The volumes occupied by the glass and by the substance introduced must, of course, be subtracted from  $C+c$ , when very accurate results are desired.

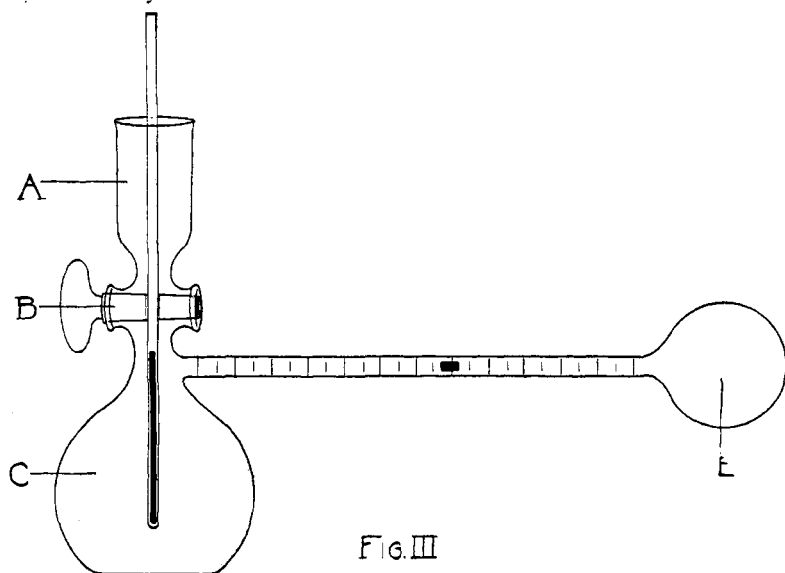


FIG. III

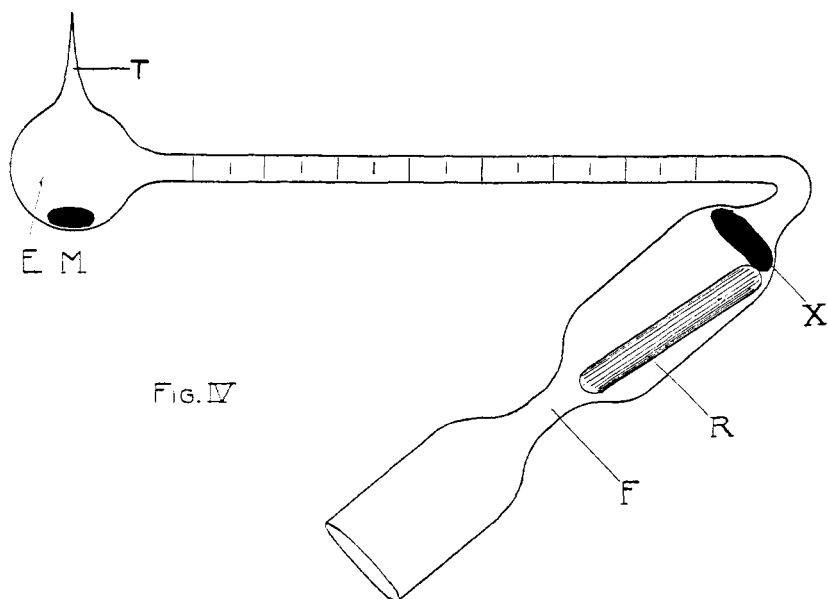


FIG. IV

Since by means of these instruments vapor pressure determinations at ordinary temperatures are easily made, it would seem that these physical constants may often and conveniently serve the purpose of identifying or

testing the purity of a number of organic compounds. For instance ethyl alcohol and its denaturated product, containing wood alcohol, can now be distinguished more quickly by vapor pressure determinations than by the process of distillation. Of course, convenient tables of vapor pressures at all ordinary temperatures must be prepared; a task which it is intended to undertake in this laboratory.

*Forms 3-5.* When vapor pressures at high temperatures are desired or when a series of vapor pressures whose determination may extend over periods of time involving changes of atmospheric pressure, are to be made, the following *closed* forms of tensimeter are more convenient; in fact for most purposes the forms depicted in figures IV and V are the most convenient.

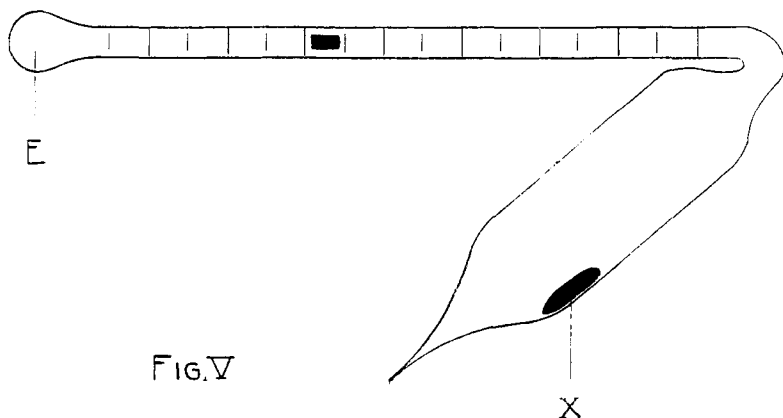


FIG. V

*Methods of Using.*—After the instruments have been thoroughly dried,<sup>1</sup> the mercury drop is introduced.<sup>2</sup> The substance X, whose specific grav-

<sup>1</sup> The chief difficulty to be guarded against in the use of these closed tensimeters is moisture persistently clinging to the inner surfaces. When the instruments are washed successively with water, alcohol, and ether and are then exhausted by means of the water pump—even while heating in the smoky flame—traces of moisture may remain in the closed end and will exert a most disturbing influence. Backward movement of the mercury when the instrument is first heated indicates the presence of this moisture. Successive washings with water, alcohol, and benzene have given better results than when water, alcohol, and ether have been used. The only safe way, however, is to open the bulb end (E), (See Fig. IV), to heat in the smoky flame and to draw dry air through the apparatus while cooling. The bulb is best opened by heating in one spot, attaching a small hot glass rod and drawing out a capillary tube. This capillary tube, when broken off, will permit of air being drawn through the instrument; and, after drying, can easily be fused off to the rounded surface of the bulb.

<sup>2</sup> When the form shown in Fig. V is employed the end E may be calibrated by first bringing the mercury into this end, and reading the scale; then bringing the mercury into the middle of the scale and reading its volume. When larger bulbs E are used they may be calibrated by filling with mercury to a mark on the scale and then all of the mercury is poured out and weighed. A calibration of the side containing the substance, in figures IV-VI, is easily made after the apparatus has been used. The fused end is cut off sharply and the instrument is emptied and cleaned; then some water from a finely-calibrated burette is first run in and by aspirating gently is caused to rise on the graduated scale to a readable distance. Finally enough water from the burette is dropped in to fill flatly the substance-side and the portion of it cut off.

ity must be known, is weighed and introduced through the funnel-like portion F shown in Fig. IV. The constriction of this funnel is then carefully narrowed in the flame to a mere capillary tube. While cooling, the atmospheric temperature ( $t$ ) and the corrected atmospheric pressure ( $p$ ) are read. The position of the mercury drop is carefully regulated by tapping, and, while holding the instrument so as not to heat it above the room temperature, the capillary tube is quickly sealed off in a narrow flame. The position of the mercury drop and its volume are read, then the instrument is heated to the successively higher temperatures ( $t'$ ) and the resulting positions of the mercury are read and recorded.

*Calculation.*—In Fig. VI let  $a$  equal the air volume of the air-cushion side, let  $c$  equal the air of the side containing the substance X and let  $b$  equal the increase of volume of  $c$  (and the decrease of volume of  $a$ ) when the mercury is moved by the additional vapor pressure of X. Now when the tube is heated and X contributes no increase of vapor pressure, the position of the mercury remains unchanged. Though remaining equal the pressure ( $p'$ ) on both sides of the mercury are increased in value as

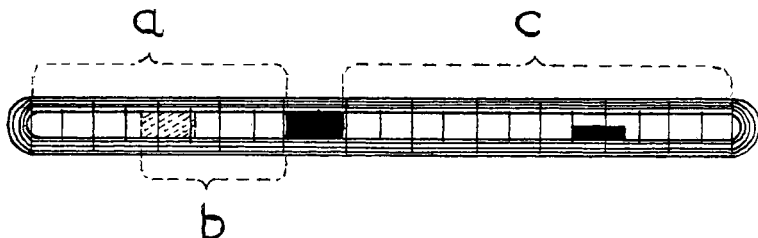


FIG. VI

shown in the equation,  $p' = t'p/t$ . When X contributes pressure, the mercury moves along to the new position and  $a$  decreases in volume to  $a-b$ ; the pressure ( $p''$ ) now in this side is indicated by the equation:

$$p'' = \frac{a}{a-b} \times \frac{t'p}{t}, \text{ or } \frac{apt'}{(a-b)t} \quad (\text{IV})$$

The increase of tension in  $c$ , as shown by the movement of the mercury, has resulted from the increase of volume ( $v$ ) of the vapor in  $c$ ; the volume occupied by this vapor can be calculated by means of the equation:

$$v = \frac{(a+c)b}{a} \quad (\text{V})$$

Now since the volume occupied by this vapor, plus the original air, is equal to  $c + b$ , the pressure ( $p'''$ ) exerted by the vapor is equal to  $\frac{v}{c+b}$  times the pressure ( $p''$ ), in the other, or the air-cushion side. This is expressed:



$$p''' = p'' \frac{c'}{c+b}$$

By substituting in this equation the values of  $p''$  and  $c'$  derived from the two preceding equations:

$$p''' = \frac{a}{a-c} \times \frac{t'p}{t} \times \frac{(a+c)b}{a} \times \frac{1}{c+b}$$

or

$$p''' = \frac{(a+c) b p t'}{(a-b)(c+b)t} \quad (\text{VI})$$

an equation is thus obtained which admits of easy calculation of vapor pressures of liquids and solids, exerted in these closed forms of apparatus.

Since  $a$ ,  $c$ ,  $p$ , and  $t$  are constant in a series of determinations with the same instrument, the factor  $\frac{(a+c)p}{t}$  can be calculated and its value  $k$  may be substituted in the above equation:

$$p''' = \frac{k b t'}{(a-b)(c+b)} \quad (\text{VII})$$

In experiments involving water or substances effected by water, *the aqueous vapor pressure of the air* contained in the substance-side must be taken into consideration, if accurate results are desired. The aqueous vapor in the air-cushion side may be ignored, because, at ascending temperatures, this vapor will behave like air itself. In respect to the aqueous vapor pressure on the substance-side, four possible cases arise; the substance may (1) absorb water; (2) evolve water at room temperature; (3) evolve water only at elevated temperatures; or (4) remain unaffected by water. In the last case, for instance with benzene, chloroform, etc., the aqueous vapor pressure on the substance-side may be ignored because here as on the air-cushion side the water vapor will behave like an equivalent volume of air.

When the substance absorbs or evolves water, a number of methods of manipulation may be employed.

*Method (a).* *The tensimeter may be filled with dry air.* This is the absolute method and is conveniently employed as follows: A capillary tube is drawn out from the bulb E (See Fig. IV); the mercury drop M is first introduced, then the glass rod R and finally the substance X. The substance should fill, as completely as possible, a small, *thin-walled*, capillary tube which is to be sealed before being introduced. The two ends of the tensimeter are attached to sulphuric acid wash bottles and air is drawn through the entire apparatus until the contained air is dry. The capillary T is then fused off and the constriction F is drawn down to a small capillary. After cooling, the capillary is quickly fused off, the mercury drop is adjusted along the scale and its position is read; the tube containing the substance is then carefully broken by means of the enclosed rod without disturbing the position of the mercury. When

the tube containing the substance is *thin-walled*, no difficulty at any stage is encountered in this method.

*Method (b).* The tensimeter may be filled with ordinary air and the substance may be introduced as in the preceding method. When the tensimeter is filled at low temperatures ( $0^{\circ}$ - $11^{\circ}$ ), errors of vapor pressures equal to 4-8 mm. may be introduced. In many experiments these errors are negligible; however, if they are to be avoided, a determination of the aqueous vapor pressure ( $z$ ) of the air must be made, and its value must be interpolated in the calculation. This may be interpolated fairly accurately by adding  $z$  to the vapor pressures calculated by means of the formula VI, or with entire accuracy by means of the formula:

$$p^{10} = \frac{(a'+c')(ap+cp-zc)b't}{(a+c)(a'-b')(c'+b')} \quad (\text{VIII})$$

which is derived as follows: When  $z$  in the substance-side is eliminated by absorption, the volume of air in the entire apparatus is reduced by the factor  $\frac{zc}{p}$  and becomes equal to  $a+c-\frac{zc}{p}$ . The pressure ( $p^z$ ) then becomes:

$$p^z = \frac{a+c-\frac{zc}{p}}{a+c} p \text{ or } \frac{ap+cp-zc}{a+c} \quad (\text{IX})$$

which being substituted for  $p$  in formula III, now involving  $a'$ ,  $b'$ , and  $c'$ , the new readings of the position of the mercury drop, yields equation VIII.

*Method (c).* The tensimeter may be filled with ordinary air and the substance may be introduced in the exposed condition. Here the substance is introduced directly into the apparatus (See Fig. V.) and the stopcock or the capillary is closed. After standing for some time the tube is quickly opened and closed; this process is repeated until equilibrium is established between the contained air and the substance. Before the final closing, the mercury drop is regulated and its position is read; of course,  $p$  and  $t$  are determined at this time.

This is a very convenient method of procedure and gives accurate vapor pressures for all substances that evolve water or absorb water (*e. g.*, partially dehydrated salts). It must be remembered, however, that the vapor pressures of substances at the temperatures of sealing are not indicated by this method; only the *relative* vapor pressures above the initial temperature. But as relative pressures are usually desired, and since the pressures at the temperatures of sealing are usually so small that they are negligible, this method is found to be very practicable.

By the use of these closed forms of apparatus, the vapor pressures of a number of hydrated salts have been determined; the data will be given in a future contribution in connection with another subject. The

experience of a large number of determinations has shown that these instruments possess advantages not completely shared by the Bremer-Frowein<sup>1</sup> and other forms.

(1). They are easily prepared, (2). They are compact, (3). They measure a large range of pressures, (4). They are easily heated, (5). They establish equilibrium rapidly, (6). They are rapid and accurate.

That the instruments are cheaply and easily constructed is sufficiently indicated in the descriptions given above.

In respect to *compactness* and *range* it is easily seen that with instruments only 10-15 cm. in length, pressures exceeding 15 atmospheres may be measured; in fact, the pressure that can be measured is limited only by the tensile strength of the glass used.<sup>2</sup> On the other hand, by making bulb E large in proportion to the volume of D, one can secure any desired degree of fineness of reading; for instance if D is readable to 0.001 cc., the fineness of reading ( $f$ ) can be calculated by means of the equation:

$$f = \frac{pD}{1000 E} \quad (X)$$

It is readily seen that the bulb E must be made small (Fig. V) when high pressures are measured; and large, when finely-read, small pressures are measured.

The compactness of these instruments admits of their being heated easily; and quickly brings about a condition of equilibrium between the substance and its vapor. For many purposes the instruments may be heated (slowly of course) in porcelain dishes containing water; for more accurate results, they are placed on the horizontal shelves of water-baths controlled by thermostats and stirrers. For the determination of vapor pressures at higher temperatures, the instruments may be placed on bricks or iron blocks in air baths supplied with mica-plate windows. For accurate determinations at high temperatures, oil-baths, etc., may be employed.

The chief objection to long tensimeters of the Bremer-Frowein type is the sluggishness of establishment of equilibrium. This is owing (1) to the large internal volume, and (2) a tendency to condense water on the mercury—the substance being heated up more rapidly than the mercury. The strong surface-tension of the water condensed on the mercury then retards the establishment of equilibrium, even after a uniformity of temperature has been established in the system. While long heating will, of course, bring about a condition of true equilibrium, short tensi-

<sup>1</sup> Z. physik. Chem., 1, 5; 17, 52.

<sup>2</sup> With the Bremer-Frowein form the height of the instrument must, of course, be greater than the column of mercury sustained by the pressure.

meters of the mercury-piston type avoid these difficulties and admit of almost immediate establishment of equilibria.

*Factors of Error.* In the mercury-piston type of tensimeter no corrections for the expansion of mercury need be made; the small expansion incurred is practically compensated (1) by the *compression* of the mercury at the increased pressure and (2) by the *loss* of mercury incurred by the vapor pressure of mercury. However, if these factors of error are to be taken into consideration, a reading of the volume of the mercury-piston may be made at any stage of the experiment.

At high temperatures it might be supposed that the vapor pressure of the mercury itself will exert an appreciable effect; however, as the vapor pressure of mercury on both sides of the mercury-piston is equal in quantity, it can be shown, both theoretically and practically, that it does not enter as a factor of error.

Air enclosed in salt crystals exerts practically no effect, the instrument itself being filled with air; in instruments exhausted to absolute *vacua*, the air expelled from the lamina of crystals exerts a most disconcerting effect.

Since a loss in volume of the solid or liquid is incurred by its partial or complete vaporization, a factor of correction must be introduced, if absolute precision is desired. The volume of the vapor may be reduced by calculation to an equivalent volume of the solid or liquid and this, really an insignificant factor, may be added to the volume of the vapor. (See equation V).

*Molecular Weight Determination.* When small quantities of liquids and easily volatilized solids, weighed in capillary tubes, are enclosed in the apparatus depicted in figures IV and V, and the heating is increased and continued until all of the substance is vaporized, the mercury-piston will finally come to a state of rest. When the volume  $b$  is read at this point, a calculation of the molecular weight of the substance is possible and may thus practically be determined. The *volume* of the vapor at this ( $t'$ ) and higher temperatures is given in equation V:

$$v = \frac{(a+c)b}{a}$$

the *pressure* under which this vapor is held is given in equation IV:

$$p'' = \frac{apt'}{(a-b)t}$$

therefore, its volume under standard conditions is:

$$V = \frac{b(a+c)}{a} \times \frac{apt'}{(a-b)t} \times \frac{273}{760t'} \text{ or } \frac{bp(a+c)273}{t(a-b)760} \quad (\text{X})$$

and the molecular weight is:

$$\text{Mol. wt.} = 22.393 W \times \frac{bp(a+c)273}{t(a-b)760}, \text{ or } \frac{t(a-b)W62.37}{bp(a+c)} \quad (\text{XI})$$

in which  $W$  is the weight of the substance used. It will be observed that this equation is *independent of the final temperature*, consequently the apparatus only needs to be placed in an ordinary air-bath and to be heated above the temperature of complete vaporization. Since upon discontinuing the heating and opening the air-bath, considerable time usually elapses and a marked fall of temperature is incurred, before the mercury-piston begins to move back toward its original position, no difficulty in reading the volume  $b$  is met with.

By the use of these instruments the following molecular weight determinations were made:

Substance	B. P.	$t'$ (Heated)	Mol. wt.	
			Found	Theory
Carbon Tetrachloride .....	76.7	110	152.8	153.6
Ethyl Acetate .....	77.1	92	86.5	88.0
Ethyl Bromide .....	131.6	190	191.0	188.0
<i>n</i> -Propyl Iodide .....	101.7	145	161.6	160.0
Xylene .....	137.5-142.6	173	108.1	106.0

The above experiments show not only the accuracy of the equation but also the accuracy of the method. When it is remembered that the instrument may not only be constructed (starting with a 1 cc. finely-graduated pipette) but the entire determination may be made within an hour, it may be anticipated that this method will take precedence over some of the more laborious methods. Furthermore, for reasons of (1) compactness of apparatus, (2) ease of construction, preparation and heating, (3) use of small quantities of substance, and (4) the possible simultaneous determination of vapor pressure, of dissociation and of boiling points (see below) this method promises to vie with Victor Meyer's method in practical application.

*Dissociation of Vapors.* Since some vapors dissociate at temperatures above their boiling points, a *secondary* movement of the mercury-piston is a manifestation of this dissociation and may be made a measure of the same. Calculations of the molecular weights at each of the higher positions of the mercury indicate, of course, the degrees of dissociation. When, on cooling, the mercury fails to return to its original position, a *non-reversible dissociation* is revealed. It must be remembered, however, that if special precautions are not observed on cooling, vapors will condense on the walls of tube D; these may then be passed by the mercury and will partially vitiate the reading of non-reversible dissociation.

#### Resume.

Instruments involving the moving mercury-drop may, therefore, be used to determine:

(1). Humidity. (2). Vapor pressure. (3). Molecular Weight. (4). Dissociation. (5). Boiling point.

When the pressure is equal to 760 mm. the boiling point is indicated. Other applications of the moving drop of mercury are being planned.

I am greatly indebted to Mr. Edward O. Heuse for assistance rendered in connection with this investigation.

URBANA, ILLINOIS

April 25, 1907.

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## THE USE OF TIN AS A CATHODE FOR THE RAPID QUANTITATIVE ELECTROLYTIC DEPOSITION OF ZINC, COPPER, SILVER, CADMIUM AND NICKEL.

BY LAURENCE T. SHERWOOD AND GELLERT ALLEMAN.

Received May 21, 1907.

The high price of platinum, together with other minor considerations, led to an investigation in this laboratory in order to determine if metallic cathodes, other than platinum, could be used for the quantitative electrolytic deposition of various metals, and, if so, to determine the exact conditions productive of the best results. While it is intended to continue this investigation using other metallic cathodes, especially tungsten, this article has to deal entirely with the tin cathode, and the deposition on it of the five elements named in the title.

Attention is directed to the fact that all the results obtained are published in the tables—none having been rejected.

While not so generally applicable as platinum, it was found that for the estimation of the metals enumerated, tin could be substituted for the more expensive material. The attempt has not yet been made to use this cathode in determining any other of the metals but judging from the work thus far it seems quite possible that it may be used for all of those which are deposited in the metallic state.

Platinum has been regarded as about the only suitable cathode material because of its insolubility and immunity from corrosion, and, of course, these were anticipated as the chief defects of tin. The solvent action of electrolytes was especially feared, but with certain precautions which will be mentioned under the special considerations there was no loss of tin during the determination even with such powerful solvents as sulphuric acid and potassium cyanide. Corrosion of other natures gave no trouble whatever.

The following general facts regarding the care of the dishes may be worth mentioning:

Solutions which have not a solvent action may during the progress of an analysis be heated in them upon a sheet of asbestos (thickness exceeding a quarter inch) or upon an electric stove without fear of oxidizing the tin.

On account of the low melting point of tin the dish cannot, of course,