tronic changes taking place during reactions can neither support or refute the theory. On the other hand, if the assumptions of the theory be granted, a useful method of classifying reactions may be derived.

A similar remark applies to the application of the theory to the structure of molecules. The electron theory has been applied by various authors to the structure of such chemical substances as chlorine, hydrogen peroxide, ammonium chloride, etc. If molecules such as these can be satisfactorily explained, it would seem that every conceivable molecule could be explained on the same basis. Apparently some new line of attack, such as that recently undertaken by W. A. Noyes,[1] must be looked to for any decisive argument of a chemical nature for or against the theory.

The classification and relation of compounds and reactions, which has resulted from the application of the electron theory of valence, has been of value. The part played by its fundamental assumption has been largely a means of relating phenomena and the actual movement of the electron is not necessarily involved in the conclusion. That is, it is possible that some other assumption involving the ideas lately proposed by Thomson or those developed by Stark or by Bohr would lead to a similar classification of compounds and reactions.

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AN APPARATUS FOR THE MEASUREMENT OF VAPOR PRESSURES BY THE DYNAMIC METHOD AND DETERMINATIONS OF THE VAPOR PRESSURE OF WATER AT 24.97°.[2]

BY I. H. DERBY, F. DANIELS AND F. C. GUTSCHE.

Received March 19, 1914.

It has been generally conceded that the dynamic, or "air bubbling," methods for determining vapor pressures of liquids offer considerable promise, but, owing to the more or less cumbersome and complicated apparatus required by such processes, these methods have not been utilized save in a few instances. Regnault[3] in 1845 was seemingly the first to use the dynamic method. His procedure consisted in passing a known volume of air over a moist sponge and through moist silk screens, and weighing the water vaporized, thus obtaining values for the vapor pressure of water which agreed very closely with results obtained by static methods. This method of Regnault's was subsequently used with various modifica-

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[1] THIS JOURNAL, 35, 767 (1913).

[2] Presented at the annual meeting of the American Chemical Society, December, 1910.

[3] *Ann. chim. phys.*, 3, 15, 129 (1845).

tions and with varying degrees of success by Tamman,[1] Walker,[2] Will and Bredig,[3] Linebarger,[4] Orndorff and Carrell,[5] Perman,[6] Carveth and Fowler,[7] Kahlenberg,[8] Earl of Berkeley and Hartley,[9] Lincoln and Klein,[10] and Krauskopf.[11]

Linebarger used a saturator of five Liebig bulbs through which a known volume of air was forced. The vapors were chemically analyzed and the partial pressures of a variety of mixtures of miscible liquids thereby determined. Perman used a Liebig bulb with four large compartments and obtained some very satisfactory results. Kahlenberg devised a saturator consisting of a large glass vessel partly filled with the liquid and shaken laterally in a thermostat, air being drawn through by a large aspirator. This device was used successfully by Lincoln and Klein and by Krauskopf. In connection with some work being done in this laboratory it became necessary to determine the vapor composition and partial pressures of alcohol and water mixtures, and with this end in view an apparatus, embodying several new features, was designed; and its description together with evidence of its efficiency as shown by measurements of the vapor pressure of water at 24.97°, is here presented.

The apparatus in its final form is shown in outline in Fig. 1. With the exception of the drying towers and the aspirating bulbs, the whole apparatus was placed in a large electrically heated and regulated water thermostat (100 gallons), in which the temperature could be maintained constant within a few thousandths of a degree. The two large towers for purifying and drying the air were filled (*R*) with soda lime and (*T*) with pieces of pumice stone rolled in phosphorus pentoxide. These were connected with the saturator, Figs. 1 and 2, which is the unique feature of the apparatus.

In the following experiments, and in determinations of vapor pressure and vapor composition which will appear in a later paper, the saturator consisted of two three-inch, thrice tubulated bulbs, filled with glass pearls of about 4 mm. diameter. These bulbs were connected with each other and with the exterior, as shown in Fig. 2, and were held rigidly in position by a wooden frame, (not shown in figure) built in halves, to permit of

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[1] *Wied. Ann.*, **33**, 322 (1888).

[2] *Z. physik. Chem.*, **2**, 602 (1888).

[3] *Ber.*, **22**, 1084 (1889).

[4] THIS JOURNAL, **17**, 615 (1895).

[5] *J. Phys. Chem.*, **1**, 753 (1897).

[6] *Proc. Roy. Soc. London*, **72**, 72 (1903).

[7] *J. Phys. Chem.*, **8**, 313 (1904).

[8] *Science*, **22**, 74 (1905).

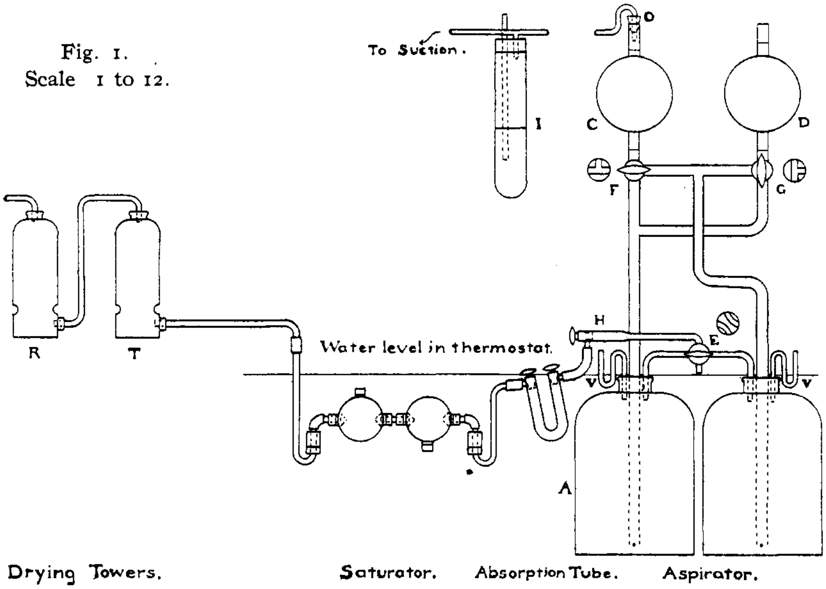
[9] *Proc. Roy. Soc. London*, **77**, 156 (1906).

[10] *J. Phys. Chem.*, **11**, 318 (1907).

[11] *Ibid.*, **14**, 489 (1910).

easy removal and assembling of the parts. A small electric motor, belted to a pulley at one end of the wooden frame, served to rotate it with the contained bulbs. The glass tubes *K*, functioned as axles for the bulbs and rotated in journals of short glass tubing which were supported by clamps. The tubulatures *M*, closed by rubber stoppers, were for the filling and emptying of the bulbs. To retain the pearls in place and prevent the liquid from draining into the connecting tubes, thus cutting off the air passage, their ends were protected by perforated platinum cones *N*; and as the liquid ran down the side of the bulb, it was caught by the cone and drained toward the tip, while any liquid which might get back of the cone was prevented from entering the conducting tubes by flanging the ends and extending them a short distance through the stoppers, not far enough, however, to touch the cones. To form air-tight connections with the rest of the apparatus while still allowing horizontal rotation of the saturator, use was made of mercury seals *S*, and thick-walled soft rubber tubing *L*, bent down through an angle of 90 degrees. This latter connected the tubes *K* with short pieces of glass tubing, *Q*, fitting loosely over the glass tubing from the drying towers and absorption tube and rotating easily on them as axes. These tubes *Q* were fitted with jacketing tubes *P* which formed a tight joint at the upper end but had the annular aperture left open below. The annular space thus formed was coated with paraffine and when connected was half filled with mercury. This device not only doubled the distance which water must pass over to get from the thermostat into the bulbs, but also interposed a trap formed by the air filled

Fig. 1.
Scale 1 to 12.



annular space above the mercury. This arrangement, adopted after the unsatisfactory trial of several other schemes, proved effectual in preventing entrance of water to the saturator by capillary action. It should be further noted that the terminal tubes *Y* of the saturator, where they enter the mercury seals, must extend 2 or 3 cm. above the mercury in the cup, to prevent the suction applied in the aspirators from drawing mercury into the tubes. The saturator, including the mercury seals, was supported by a single ringstand, thus enabling transference independently of the rest of the apparatus.

The absorption tubes employed were five-inch glass stoppered tubes, (Schwarz design), and were filled with granulated pumice stone which had been coated with phosphorus pentoxide. A rubber cap was fitted over the stopcock through which the saturated air entered the absorption tube, so that it might be kept dry because of difficulty in drying the groove around the stopcock. The other stopcock was not submerged. The absorption tube was connected in by means of thick walled flexible rubber tubing, thus allowing easy removal and replacement for the purpose of weighing. Between the absorption tube and the aspirator was placed a small drying tube *H*, also charged with phosphorus pentoxide to prevent back diffusion of water vapor.

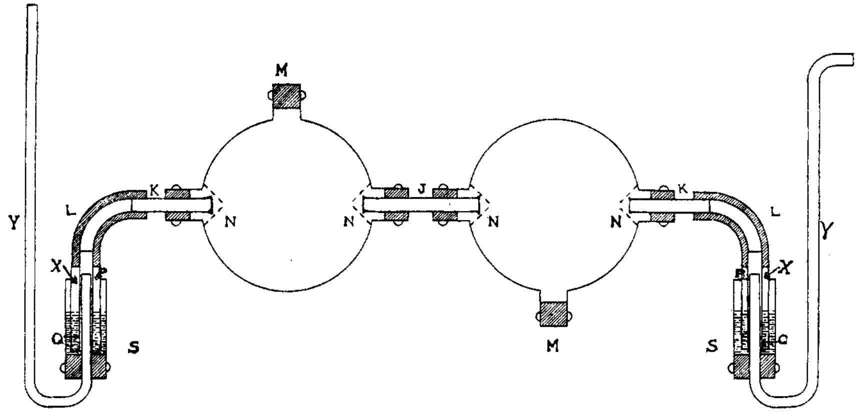


Fig. 2.
Scale 2 to 7.

The aspirator consisted of two calibrated bulbs, *C* and *D*, connecting interchangeably, through the three-way cocks *F* and *G*, with the two eight-liter bottles *A* and *B*. By this arrangement one bottle served as aspirator while the other received the drain from the bulbs. In this way the aspiration became practically a continuous process independent of the size of the aspirating bottles *A*, *B*, since one bulb drained while the other was filling. These two bulbs were calibrated to take up 1135 cc. each between the etched lines *cc dd*, at a temperature of 25°, when allowed to drain for ninety seconds. Each bottle was fitted with a manometer *V*, and a four-way stopcock *E* placed between the bottles made it possible to connect either one of them with the air and the other with the saturating and absorbing train. A rubber stopper *O*, fitted with a glass tube, was connected with the water air pump through a mercury pressure regulator *I*, designed to preserve any desired constant exhaustion, thus regulating the speed of aspiration. The connection *O* could be shifted from one aspirating bulb to the other.

This disposition of the apparatus keeps the aspirator water at the temperature of the thermostat, within narrow limits, thus making the temperature of the aspirated air and the vapor pressure of water, over which it collects, definitely fixed values.

In conducting an experiment the saturation bulbs, filled with glass pearls, were charged with the liquid to be investigated to a level a few millimeters (2 or 3) below the lower edges of the cones. If too much liquid be added any slight tilt of the apparatus throws it into the connecting tubes. The saturator was then placed in the thermostat and connections made with the purifying towers at one end and the aspirator, through the carefully weighed absorption tube, at the other, as shown diagramatically in Fig. 1. The absorption tubes charged with the phosphorus pentoxide were counterpoised in pairs and the members of a pair were then used alternately. This arrangement was adopted to eliminate, as far as possible, errors due to changes in barometric pressure, temperature and humidity. Weights were taken to the nearest 0.1 mg. although the scale was sensitive to 0.03 mg. It was found necessary to allow the tube used for the absorption to stand nearly an hour before a constant weight was obtained. Trouble was at first experienced due to condensation of vapor in the side arm when the absorption tube was first connected. This difficulty was avoided by slightly warming the tube before making connections. After assembling and connecting the apparatus, 40 to 50 minutes were allowed, in order that the saturator and the aspirator might come to the temperature of the thermostat, previous to the first determination. For subsequent determinations no waiting was necessary, provided the saturator remained continuously immersed. When temperature equilibrium had been attained the saturator was first set rotating at a rate of thirty or forty turns per minute. The aspiration was then started. When sufficient air had been aspirated, in the experiments on water of 25°, usually 8 to 10 liters, a few seconds were allowed to elapse before closing the stopcocks, in order to permit establishment of barometric pressure throughout the apparatus. The water manometers *V*, Fig. 1, showed conclusively when this condition obtained. The absorption tube could then be closed, disconnected and prepared for weighing and one of another pair substituted for a new run. With three pairs of tubes a number of determinations may be carried out in a single day. At the conclusion of an experiment only three observations are necessary; first, the total volume of saturated air aspirated and measured by the water passed through the calibrated bulbs *CD*; second, the barometric pressure; third, the gain in weight of the absorption tube. In our experiments the time actually taken for the aspiration was also recorded, mainly for the purpose of comparison.

The formula used for calculating the vapor pressure is essentially the same as that employed by Tamman,[1] except that it was found unnecessary to introduce any corrections for change of volume of the aspirating bulbs, since they were calibrated and used at the one temperature, namely, 25° C. The symbols employed and their significance together with the numerical constants used in developing the formula are as follows:

P. Corrected barometer pressure.

V. Volume of saturated air measured by aspirator.

$P_0 = 760.0$. Standard barometer pressure.

$t = 24.97°$. Temperature of aspirator.

$p_3 = 23.7$ mm. Vapor pressure of water in aspirator at temperature t.

$a = 0.003571$. Coefficient of expansion of air.

$d = 0.0012728$. The density of dry air at 0°, 760 mm.

$V_0 = 22400$ cc. The gram molecular volume of air at 0°, 760.

M. Hypothetical molecular weight of air from the gram molecular volume of air, as determined from the gram molecular volumes of its constituents.

$M_1 = 18.015$. Molecular weight of water vapor calculated from the atomic weights.

p. Partial pressure of air in mm. in saturation bulbs when equilibrium is established.

p_1. Partial pressure of water vapor in mm. in saturation bulbs when equilibrium is established.

V_1. Volume of air and saturated water vapor in cc. formed in saturation bulbs during an experiment.

w. Weight in g. of air aspirated.

w_1. Weight in g. of water vapor determined by weighing.

Using the symbols as listed and assuming the gas laws to hold, three fundamental equations are readily formulated:

$$(1). \qquad P = p + p_1.$$

$$(2). \qquad PV_1 = \frac{w}{M} RT.$$

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[1] *Loc. cit.*

$$(3).\qquad p_1V_1 = \frac{w_1}{M_1} RT.$$

Solving (2) and (3) for V_1, equating and substituting for p its equivalent value from (1), then solving for p_1 gives

$$(4).\qquad p_1 = \frac{P}{1 + \dfrac{M_1w}{Mw_1}}.$$

We may place

$$(5).\qquad M = dV_0.$$

The weight of w is readily obtained from the general gas law relation involving that term

$$(6).\qquad (P - p_3)V = \frac{w}{dP_0} P_0V_0(1 + at)$$

Which solved for w gives

$$(7).\qquad w = \frac{(P - p_3)Vd}{P_0(1 + at)}.$$

Substituting in (4) the equivalent of M from (5) and w from (7) gives the general formula

$$(8).\qquad p_1 = \frac{P}{1 + \dfrac{(P - p_3)\ VM_1}{w_1(1 + at)P_0V_0}}.$$

Substituting numerical constants gives

$$(9).\qquad p_1 = \frac{P}{1 + \dfrac{(P - p_3)\ V\ 18.015}{w_1(1 + 0.003671t)\ 760 \times 0.22400}}$$

The value of 18.015/760 × 0.22400 for all experiments with water or water solutions is constant and may be reduced to one term.

$$\frac{18.015}{760 \times 0.22400} = 0.0000010582.$$

(log. 0.0000010582 = 4.02457 — 10) which substituted in (9) gives

$$(10).\qquad p_1 = \frac{P}{1 + \dfrac{(P - p_3)V\ 0.0000010582}{w_1(1 + 0.003671t)}}.$$

the formula used for calculating the results of Gutsche's experiments.

If, as was the case in all subsequent experiments, t is a constant (in this case 24.97) then $(1 + 0.003671t)$ becomes a constant and

$$\frac{18.015}{(1 + 0.003671 \times 24.97)\ 760 \times 0.22400} = 0.0000009694.$$

(log. 0.0000009694 = 3.98649 — 10) which may be used in all experiments, giving for the formula

$$p_1 = \frac{P}{1 + \frac{(P - p_3)V\ 0.0000009696}{w_1}} \qquad (11).$$

Further, V may be kept constant in any series of determinations, thus still further simplifying the calculations. This was done in the two series of determinations listed in Tables II and III.

To test the efficiency of the saturating and absorbing parts of the apparatus, a number of determinations were made on the vapor pressure of water at 24.97°. Table I shows the first results obtained by Gutsche on water, and a single determination with absolute ethyl alcohol, prepared by drying over lime and distillation from sodium. In these experiments the aspirating bottles were, as is customary, outside of the thermostat. They were calibrated for total volume and operated by a syphon. The significance of each column is indicated by the symbol above it the meaning of which has been given in the course of developing the formula.

TABLE I.

No. of expt.	t.	V.	P.	w_1.	p_1.	Time of aspiration in minutes.
1	21.55	8043	736.7	0.1958	23.55	10
2	20.30	8120	739.0	0.1974	23.60	14
3	20.80	8400	738.9	0.2015	23.30	35
4	19.90	8121	737.7	0.1969	23.50	11
		Alcohol.				
				w_2.[1]	p_2.[1]	
5	19.40	8456	738.8	1.3692	58.47	21

TABLE II.

No. of expt.	V.	P.	w_1.	p_1.	Time of aspiration in minutes.
1	8000	745.8	0.1841	23.73	11
2	8000	734.4	0.1819	23.45	29
3	8000	737.1	0.1829	23.58	47
4	8000	743.4	0.1844	23.76	11
5	8000	734.3	0.1834	23.65	21
6	8000	736.4	0.1824	23.52	13
7	8000	736.4	0.1840	23.72	12
8	8000	738.7	0.1833	23.63	12
9	8000	735.0	0.1844	23.77	11
10	8000	735.0	0.1833	23.63	43
11	7992	730.6	0.1829	23.60	25
12	8000	738.8	0.1842	23.75	13
13	8000	738.8	0.1845	23.73	13
14	8000	731.7	0.1846	23.80	37
			Average,	23.67	

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[1] w_2 and p_2 stand for the weight of alcohol evaporated and the calculated vapor pressure, respectively. Phosphorus pentoxide was used for absorbing the alcohol vapor. The absorption was complete and nearly as vigorous and rapid as with water,

The next experiments, Table II, were performed by Daniels and were made with the aspirating bottles submerged in the thermostat; but the water was drawn off by a syphon into standard liter flasks and a measure of the volume of air aspirated thus obtained.

In addition to the errors of volume introduced, because of the clumsy method of aspiration, a slow leak was later detected in one of the rubber connections which may account for the lower values, especially of the longer time intervals.

In Table III are the more accurate results, also obtained by Daniels with the final form of apparatus as detailed above. All rubber connections were made of heavy walled tubing and wired, and the apparatus was tested before each determination by closing the first stopcock of the absorption tube and withdrawing some water from the aspirator. The manometer rose and was observed for several minutes, and if the level in the manometer did not change, the apparatus must be air-tight.

TABLE III.—VAPOR PRESSURE OF WATER AT 24.97°.

No. of expt.	V.	P.	w_1.	p_1.	Time in minutes for expt.
1	10,215	734.9	0.2344	23.67	20
2	10,215	749.0	0.2348	23.71	15
3	10,215	745.1	0.2349	23.72	15
4	10,215	746.2	0.2350	23.73	20
5	10,215	736.8	0.2345	23.68	14
6	10,215	742.5	0.2345	23.68	20
7	10,215	740.7	0.2349	23.72	12
8	10,215	741.5	0.2348	23.71	23
			Average,	23.70	
9[1]	10,215	741.5	0.2352	23.75	40

The temperature of the thermostat for all the experiments (Tables I, II and III) was maintained at 25.00 ± 0.01 as indicated on a standard thermometer divided into 0.1° and easily read to within 0.01°. This thermometer had been calibrated by the Reichsanstalt in 1903 and was at that time without correction at 25.00°.

In the summer of 1911, following the above work which was carried out in 1910 to 1911, the thermometer was recalibrated by the U. S. Bureau of Standards and found to have a correction of —0.035°. The true temperature of the experiments then was 24.97° instead of 25.00°. After receiving the new calibration the thermostat was brought to exactly 25.00° and one more determination was made with the result recorded. By interpolation from the variations of pressure per degree from 24–26°, 0.035° C. corresponds to a change in the vapor pressure of water of 0.05

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[1] Temperature, 25.00°.

mm., which added to the vapor pressure values listed in Tables I, II and III, gives the values for 25.00°. It is significant, but can be taken only as a coincidence, that 0.05 mm. added to the average of the determinations 1 to 8 in Table III give the values found in the single determinations at 25.00°. Table IV shows a comparison of the results obtained in this work with values given by several other observers at the same temperatures.

Observer.	Method.	Pressure.
Regnault[1]	Dynamic	23.55
Lincoln and Klein[1]	Dynamic	23.76
Holborn and Henning[2]	Static	23.69
Eckholm[3]	Interpolation formula	23.79
Scheel and Heuse[4]	Static	23.76
Krauskopf[1]	Dynamic	23.71
Derby and Daniels	Dynamic	23.75

The limits of error of observation allowable are fairly large, considering the weight of water evaporated in each experiment. A variation of 0.01 mm. pressure in the above results corresponds to a weighing error of 0.1 mg.; a volume error in measuring the aspirated air of 5 cc.; a temperature fluctuation of 0.007°, or an error of 1 mm. in the barometer reading. The extreme variation in the final, most reliable, series of determinations is seen to be 0.06 mm. which is a smaller variation than is found in the results of most other users of the dynamic method. This agreement is considered especially satisfactory, since most observers have used much larger volumes of air, and evaporated larger quantities of water. As may be noted, the volume of water evaporated is equivalent to not more than five or six drops from an ordinary buret.

The speed at which air becomes saturated with vapor has been considered by previous investigators and while several believed this to be a slow process and consumed days for a single determination, Lincoln and Klein[1] proved that a rate of at least 16 liters per hour was not too fast, and Regnault[1] stated that 25 liters per hour gave satisfactory results. The above experiments go further and prove that air becomes completely saturated with water vapor in the saturator if run through as rapidly as 50 liters per hour (Determination No. 7, Table III) and this is probably far from the maximum speed with the above described saturator. This establishes the efficiency of the saturator as well as that of the absorption tube. It is evident, then, that a determination may be made in a very short time, the most time being consumed in waiting for the absorption tubes

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[1] *Loc. cit.*

[2] *Ann. d. Phys.*, **26**, 865 (1908); calculated from results above 50°.

[3] *Arkiv. Math. Astr. Phys.*, **4**, 29 (1908).

[4] *Ann. d. Phys.*, [4] **31**, 715 (1910).

to come to constant weight, and this delay is avoided, as indicated, by having two or three sets of tubes.

An important feature of the apparatus lies in the fact that barometric pressure is maintained throughout, except that a slight reduction of pressure is caused by the resistance of the whole train to the passage of the air during aspiration. This effect is negligible in the saturators where equilibrium is established. This is a distinct advantage over most previous apparatus, in which air has been bubbled through the liquid for saturation or through sulfuric acid in the absorption tube; for any error or correction due to the hydrostatic pressure of the liquid is avoided.

In working with mixtures or solutions, the vapor pressure is not affected by change in concentration or cooling from evaporation, because the volume of the solution is large relative to the amount evaporated, and any slight lowering of the vapor pressure due to the above causes in the first bulb is corrected for by the passage through the fresh liquid in the second bulb in which little evaporation takes place and, hence, a negligible cooling and change of concentration occur. The rotation, too, prevents the formation of layers of different concentrations, insures a thorough mixing of the liquid and exposes a large, continuously fresh surface from which evaporation takes place. In addition to the above mentioned advantages, the apparatus, with the exception of the large thermostat, may be cheaply and simply made from materials available in any laboratory.

The chief disadvantage of the apparatus lies in the fact that for a determination of each new liquid the saturator must be taken apart and the pearls removed, washed and dried, but with two saturators this delay is reduced to a minimum. A little practice is necessary, also, to operate the stopcocks accurately and rapidly. The method, too, is hardly suitable for use with liquids of extremely high vapor pressures unless the absorbent is changed frequently.

The apparatus as described is suitable for the measurement of vapor pressures not only of simple liquids but also of solutions and liquid mixtures, and has been applied, as previously stated, for the determination of the vapor composition and partial pressures of water ethyl alcohol mixtures. These results are soon to appear. The apparatus should be further admirably adapted to the accurate determination of vapor pressure of saturated solutions and solubility, for in place of the glass pearls the saturator might be filled with the crystallized salt, the liquid added being a nearly saturated solution.

With the rubber connections the applications of the apparatus are limited to substances which do not affect rubber. The recent discovery,[1] however, of a method by which any substance may be metallic-plated by nearly any metal might allow of the gold or silver plating of the interior

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[1] Schoop.

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