

of air have many times been blown through the liquid, and the cell has been subjected to a series of light shocks, without causing any explosion. That the substance after electrolysis at  $-80^{\circ}$  should be so extremely sensitive to shock, seems to point toward the possible accumulation in the cell of a very explosive compound, perhaps a polymer of nitrogen, during the electrolysis.

#### Summary.

In the present investigation it has been shown that

1. Hydronitric acid, like hydrazine and ammonia, in the pure, anhydrous condition offers a remarkably high resistance to the electric current.
2. The introduction of dry potassium trinitride very greatly increases the conductivity of the anhydrous acid.
3. When a solution of potassium trinitride in hydronitric acid is electrolyzed, the ratio of nitrogen to hydrogen evolved is approximately 3:1, but is somewhat lower under certain conditions. Appreciable amounts of ammonia are obtained during the electrolysis, but no hydrazine is formed.
4. Certain peculiar phenomena are observed in connection with the electrolytic experiments, which may perhaps be explained on the assumption that traces of ozone are formed, but which might possibly be attributed to the formation of small amounts of nitrine, a polymeric modification of nitrogen.

Further work along several different lines suggested by these experiments is now in progress in this laboratory.

The authors take pleasure in expressing their gratitude to Mr. T. W. B. Welsh, of the Department of Chemistry, for considerable assistance in carrying out some of the experimental work described in this article, and to Professor E. M. Chamot and Mr. D. S. Pratt, of the same Department, for microchemical work connected with certain parts of the research.

CORNELL UNIVERSITY.

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(CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.<sup>1</sup>)

### A NEW METHOD OF MEASURING THE PARTIAL VAPOR PRESSURES OF BINARY MIXTURES. (PRELIMINARY COMMUNICATION.)

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No property of a substance is more characteristic of its intimate physical condition than its vapor pressure. The vapor pressure of a single liquid

<sup>1</sup> The study outlined in this communication was begun at New York University in 1906. In the following year one of us (M. A. R.) was called to assume charge of the Department of Chemistry in Clark University. Since then the method here proposed has been employed in the Clark University laboratories in determining iso-

is probably the most pronounced outward manifestation of its molecular state. In mixtures the partial vapor pressures are the immediate expression of the molecular condition and mutual influence of the components. Hence the important rôle played by vapor pressures in physico-chemical science even at present (theory of solutions, heterogeneous equilibria), and the still more important part which that property is destined to play in the development of knowledge in the future: Nernst shows how vapor pressures may be used to evaluate the "chemical constants" of substances; according to Lewis, vapor pressures are closely related to the "escaping tendency" of substances, which describes precisely their entire physico-chemical behavior.

The present paper outlines a new method for measuring the partial vapor pressures of liquid mixtures—a method which permits of determining this property with greater accuracy and reliability than heretofore attained.

§1. *Principle of the New Method.*—If a binary liquid whose components are in the ratio  $x/(1-x)$  is in equilibrium with a vapor containing the same components in the ratio  $p_1/p_2$ , then a saturated vapor of this composition will bubble through the liquid without producing, or itself undergoing, any change. If, on the other hand, a saturated vapor of any other composition, say  $p'_1/p'_2$ , is passed through the same liquid, the composition of the liquid will gradually change until the ratio of its components has become  $x'/(1-x')$  corresponding to the composition  $p'_1/p'_2$  of the vapor. After that the vapor may be passed through the liquid indefinitely without affecting its composition. Further, since condensation or evaporation involves a transfer of heat, and hence a rise or fall in temperature, it follows that if a saturated vapor of definite composition at the temperature  $T$  be passed through a liquid mixture of the same components, the temperature  $T'$  of the liquid will gradually approach  $T$  as equilibrium is attained.

In brief, then, if a mixed vapor of constant composition is passed through a liquid mixture of the same components, the composition and temperature of the liquid will steadily change until complete equilibrium, as regards both temperature and pressure, has been established. A stationary temperature will demonstrate the attainment of equilibrium. The vapor bubbling through the liquid may then be condensed in *any desired quantity* and analyzed. Identity of composition of two or more piecemeal the partial pressures of binary mixtures of a number of liquids. On the other hand, isothermal measurements have been carried on at New York University. The present paper was withheld from publication while experimental proof was thus being produced of the practical usability of the method under various circumstances and in case of various pairs of liquids. At present we are able to recommend the new method without hesitation. The results obtained by means of it will appear in the form of separate publications very soon.

consecutive samples of the condensed vapor will be *additional* proof that perfect equilibrium had been established between liquid and vapor. On the other hand, the liquid can be drawn off and its composition determined by analysis.

Assuming that the ratio of the partial pressures in the vapor equals the molar ratio of the components (an assumption admissible in most ordinary cases, as shown by the investigations of Herwig,<sup>1</sup> of Wüllner and Grotrian,<sup>2</sup> and of Schoop,<sup>3</sup> and knowing the total pressure from direct observation, the partial pressures  $p_1$  and  $p_2$  can be obtained by a simple calculation. In those cases in which the assumption here made is not admissible, it is possible to determine the exact relation between molar ratios and partial pressures by separate experiments.

§2. *The Older Methods.*—In order to appreciate the merits of the method proposed in this paper, it is necessary to pass in cursory review the methods used before.

The oldest method used consisted in compressing a gaseous mixture of known composition at constant temperature, preferably with agitation, until condensation has barely commenced. This is only a modification of the so-called "dynamic method" which has been most frequently used to measure the partial pressures of liquid mixtures. The dynamic method<sup>4</sup> consists in distilling off a small amount from a large quantity of a given binary mixture and determining the composition of the distillate. During the distillation either the total pressure is measured under which the given liquid mixture boils at a fixed temperature, or conversely, the temperature is observed at which boiling takes place under a given constant pressure. This method attained its final development in the hands of Zawidzki<sup>5</sup> working in Ostwald's laboratory. Zawidzki measured the partial pressures of some thirteen binary liquid mixtures, the results demonstrating the correctness of the well-known differential equation of Duhem and Margules,<sup>6</sup> which connects the variation of partial vapor pressures with variations in the composition of liquid mixtures.

Zawidzki himself points out a number of defects in his method. In the first place, the quantities of liquid used (100–120 cc.) were in some cases too small and consequently the composition and boiling point did not remain sufficiently constant during distillation. To reduce the resulting error as much as possible, Zawidzki reduced the distillate to the

<sup>1</sup> *Pogg. Ann.*, 137, 19 and 593 (1869). *Ibid.*, 141, 83 (1870).

<sup>2</sup> *Wied. Ann.*, 11, 545 (1880).

<sup>3</sup> *Ibid.*, 12, 550 (1880).

<sup>4</sup> See Winkelmann, *Wied. Ann.*, 39, 99 (1890). Lehfeldt, *Phil. Mag.* (5), 40, 397 (1895). *Ibid.* (5), 46, 42 (1898).

<sup>5</sup> *Z. physik. Chem.*, 35, 129 (1901).

<sup>6</sup> Duhem, *Ann. de l'École normale sup.* (3), 4, 9 (1887). Margules, *Sitzungsbericht der Wiener Akademie*, 104, II, 1243 (1895).

smallest possible amount. The duration of a distillation was consequently very short and Zawidzki rightly raises the question, whether in so short an interval of time vapor and liquid could actually come into equilibrium. One's doubt regarding this point is strengthened by the fact that the temperature of boiling liquids is known to be often appreciably different from that of their vapors. Kuenen writes concerning this method: "*Die Dampftemperatur zeigt sich sehr variabel, und es besteht ein bisweilen bedeutender Unterschied zwischen den Temperaturen von Dampf und Flüssigkeit; diese Erscheinungen werden wieder teilweise durch Ueberhitzung der Flüssigkeit verursacht, und teilweise wie bei Lösungen durch die Abkühlung des Dampfes; dieselbe ruft eine teilweise Kondensation hervor und begleitende Änderungen der Zusammensetzung und der beobachteten Temperatur. Es kommt Kohnstamm bei einer ausführlichen Untersuchung der dynamischen Methode zu dem Schluss, dass ihre Genauigkeit bei Gemischen viel kleiner ist als gewöhnlich angenommen wird.*"<sup>1</sup> We have been independently led to similar views by a somewhat extensive series of observations.

Yet the weakest point of this method is in the small quantity of distillate available. More or less accidental conditions (form and extent of surface of the boiling apparatus and condenser) are liable to produce a relatively large disturbing effect. Moreover, it may be said with certainty that it is almost impossible to transfer for analysis one cubic centimeter of a mixture of volatile organic liquids from a large distillation apparatus into a receiving vessel without considerable volatilization taking place, accompanied by change in the composition of the liquid, and the introduction of an error probably greater than all the other errors of the method combined.

An interesting modification of the dynamic method, devised by Carveth, may be found described in the original memoir<sup>2</sup> and in Young's *Fractional Distillation* (p. 81). Young compares some results obtained by Carveth with those obtained in the same case (carbon disulphide and benzene) by Brown, and finds himself unable to explain the very large discrepancies in the figures, or to decide which of the two methods involved is the more reliable. Few facts point so clearly to the need of a demonstrably reliable method for measuring partial pressures as do these two disagreeing sets of results reproduced by Young.

Still another method, which was used a few years ago by Cunaeus,<sup>3</sup> consists in introducing the given liquid mixture into an evacuated vessel kept in a thermostat, and allowing sufficient time for equilibrium to be established, then analyzing liquid and vapor directly. The method is far

<sup>1</sup> Kuenen, Verdampfung und Verflüssigung von Gemischen (Leipzig, 1906), pp. 9-10.

<sup>2</sup> *J. Phys. Chem.*, 3, 193 (1899).

<sup>3</sup> *Z. physik. Chem.*, 36, 232 (1901).

from being accurate, owing to the large error necessarily involved in the analysis of the vapor. Thus, in spite of using an apparently delicate physical method of analysis, Cunaeus was unable to obtain satisfactory results.

Mention must finally be made of the determination of partial pressures by saturating an indifferent gas with a vapor of a binary mixture by slowly bubbling the gas through the liquid.<sup>1</sup> In those cases in which the partial pressures are very small the method yields comparatively good results. If the substances involved are volatile, the results become unreliable. Moreover, as Zawidzki observes,<sup>2</sup> the method is complicated and tedious.

§3. *The New Method and the Apparatus.*—Our method, as outlined above, consists in passing a saturated mixed vapor of constant composition through a liquid mixture of the same substances.<sup>3</sup> The inner tube, marked *A* in Fig. 1, is where this takes place. This tube, which forms the most essential part of the apparatus, resembles the inner tube of the familiar Landsberger-Beckmann boiling point apparatus, and will be referred to as the equilibrium chamber. It is surrounded by a second vessel, *B*, in which the required vapor of constant composition is produced by boiling a liquid mixture whose composition is kept constant by the introduction of the more rapidly evaporating component in such quantities as to keep the sensitive thermometer *C*, whose bulb is immersed in the boiling liquid in *B*, stationary.

The vapors produced in this way have a perfectly constant composition. This was demonstrated by condensing several consecutive fractions and analyzing them. Thus a mixture of carbon tetrachloride and toluene containing 64.48 per cent. of the former was distilled with gradual addition of carbon tetrachloride, the boiling point being thus easily kept within five one-hundredths of a degree. The four consecutive samples, each of about 25 grams, were found to contain respectively the following percentages of carbon tetrachloride: 86.38, 86.43, 86.39, and 86.41. Similarly, a mixture of the same substances containing 48.01 per cent. of carbon tetrachloride and kept boiling at  $95.04^\circ \pm 0.02^\circ$  under a pressure of 761.07 mm., yielded seven consecutive samples of distillate containing respectively the following percentages of carbon tetrachloride: 77.75, 77.70, 77.71, 77.74, 77.78, 77.82, and 77.86. Equally excellent results have been obtained in every other case tried.

<sup>1</sup> Walker, *Z. physik. Chem.*, 2, 602 (1888). Winkelmann, *Loc. cit.* Linebarger, *THIS JOURNAL*, 17, 615 (1895). Gahl, *Z. physik. Chem.*, 33, 195 (1900).

<sup>2</sup> Zawidzki, *Loc. cit.*, p. 132. See also Young, *Fractional Distillation*, pp. 36 ff.

<sup>3</sup> The idea of passing a vapor "from another solution" (and hence *not* a vapor of strictly constant composition) into a two-component mixture "roughly" in equilibrium with it, occurred to Carveth some years ago (*J. Phys. Chem.*, 6, 256, 1902), but according to his own statement the idea was abandoned after unsuccessful trial. Carveth's idea was unknown to us until our experiments had been completed.

Before we had devised the above method for obtaining a vapor of constant composition, we tried a method which was used by F. D. Brown as early as 1881. Brown's method consists in passing the vapor from a

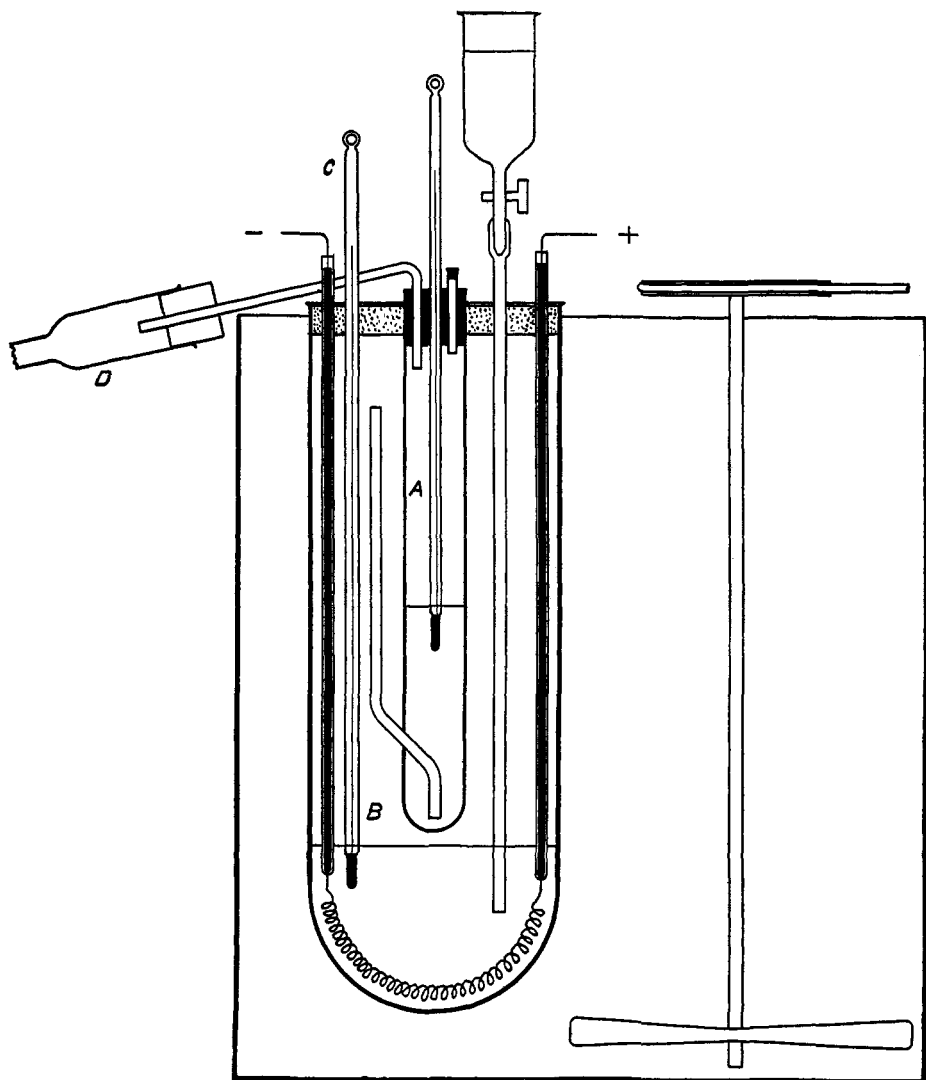


Fig. 1.

boiling liquid mixture through a reflux condenser maintained at a constant temperature. The success of the method was found to depend greatly on the *form* of the condenser or still-head employed. After numerous trials we adopted a form which ought to be capable of a variety of uses

and may therefore be described here *en passant*. Our still-head consists of a double-walled metallic cylinder open at both ends and immersed in a liquid kept at a constant temperature and, of course, vigorously stirred. The annular space *a a* (see Fig. 2) between the two walls of the cylinder

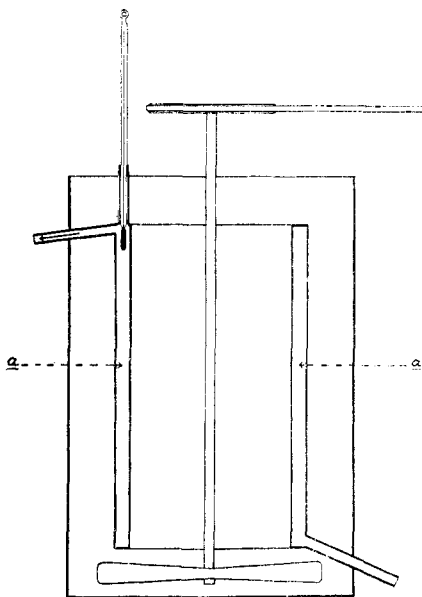


Fig. 2.

is bounded by a very large condensing surface; it is connected at the bottom with a flask containing the boiling mixture, and ends in a delivery tube at the top. This condensing apparatus is 10 inches in height; its outer cylinder is 6 inches in diameter and its inner cylinder 5 inches in diameter, the two walls being thus about half an inch apart. The remarkable efficiency of this still-head may be seen from some figures following. A mixture of carbon tetrachloride and toluene, containing 72.57 per cent. of the former, was boiled in a flask and the vapors collected after passing through our still-head kept at a temperature varying between 78.9 and 79.0°. Four large consecutive samples of the vapor

were found to contain respectively the following percentages of carbon tetrachloride: 93.03, 92.97, 93.08, and 93.19. During this distillation the percentage of carbon tetrachloride in the boiling liquid in the flask fell from 72.57 to 56.21. In a similar experiment the temperature of the still-head was kept constant at 80.4 to 80.5°. While the percentage of carbon tetrachloride in the distilling liquid was falling from 70.62 to 61.67, the three large samples of distillate collected were found to contain, respectively, 92.27, 92.31, and 92.31 per cent. of carbon tetrachloride.

The still-head was finally abandoned in connection with our main problem, obviously not because of imperfect working, but because less handy than the apparatus adopted.

Carveth has succeeded in producing a vapor of constant composition by introducing into a given boiling mixture, not (as we did) the more rapidly evaporating component, but a liquid "which had approximately the same composition as that which was being removed and in the same amounts." It might be assumed that the vapor given off under the conditions maintained both by Carveth and ourselves is in true equilibrium with the boiling liquid with respect to pressure and temperature. If it were, this in itself would constitute a simple method of measuring partial

pressures. But it is obvious that while such a method would permit of obtaining any desired quantity of distillate, and would thus constitute an improvement on the ordinary form of the dynamic method, the attainment of equilibrium would by no means be less uncertain than in the simple distillation method used by Zawidzki and others. So far as we can see, *true equilibrium can only be attained, and its attainment demonstrated, by passing the vapor of constant composition, obtained by one or another method, through a liquid mixture of the same components.*

To return to our apparatus: the vapor of constant composition produced in *B* enters the equilibrium chamber near its bottom, bubbles through the liquid contained in it, then passes through the condenser *D*, and finally enters a receiving vessel. Here provision is made for withdrawing consecutive samples of the distillate without interrupting the distillation or disturbing the total pressure within the apparatus. A delicate thermometer, with the bulb immersed in the liquid within the equilibrium chamber, yields the first indication that true equilibrium has been attained, and this is subsequently further demonstrated by the identity in composition of the consecutive samples of distillate.

The distilling apparatus, consisting of the equilibrium chamber and its surrounding jacket, is placed in a thermostat kept at a temperature slightly higher than that prevailing within the distilling apparatus. The employment of a thermostat might, on superficial theoretical consideration, appear unnecessary. Experience has shown it to be indispensable.

The introduction of the more rapidly evaporating component into the vessel *B* may be regulated by means of a ground glass stop-cock. Other means of regulation will be described in later papers.

The following results have been obtained by the method here described, the first at New York University, the last three by Dr. C. W. Easley, working under the direction of one of us (M. A. R.) at Clark University:

1. A mixture of carbon tetrachloride and toluene was subjected to distillation in our apparatus. When equilibrium had been attained, the temperature in the equilibrium chamber *A* was without difficulty maintained constant within  $0.02^{\circ}$ . Three large consecutive samples of the vapor were found to contain, respectively, 79.28, 79.26, and 79.28 per cent. of carbon tetrachloride. The mixture in the equilibrium chamber contained 55.26 per cent. of carbon tetrachloride.

2. A mixture of carbon disulphide and carbon tetrachloride boiling in the equilibrium chamber of our apparatus gradually attained a temperature which could be kept constant within one one-hundredth of a degree. While a Beckmann thermometer gave the temperature readings 1.72, 1.72, 1.72, 1.71, 1.71, two large samples of the vapor were collected and were found to have respectively the indices of refraction,  $39^{\circ} 40'$  and  $39^{\circ} 41'$ .



3. After the two samples just mentioned had been collected, the regulation was interrupted. The equilibrium was soon destroyed and the temperature gradually rose. Then the original temperature was re-established by regulating the addition of carbon disulphide to the boiling mixture in *B*, and two new samples were collected. They had respectively the refractive indices  $39^{\circ} 41'$  and  $39^{\circ} 41'$ .

4. Once more the equilibrium was disturbed, and once more the original temperature re-established in *A*. While the temperature remained practically constant, again two samples of vapor were collected. They were found to have the refractive indices  $39^{\circ} 40'$  and  $39^{\circ} 40'$ .

These few results, taken from among a considerable number of preliminary observations, are mentioned as a first proof of the reliability of the method. The conclusion that may be drawn from them is thoroughly corroborated by an extensive experience accumulated since these preliminary results were obtained.

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### THE MUNROE CRUCIBLE.

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The use of platinum felt as the filtering medium in a crucible of the Gooch pattern was first suggested by Charles E. Munroe, in an article entitled "Filtration with Filters of Metallic Felt," published in the *Journal of Analytical Chemistry*, Vol. 2, July, 1888.<sup>1</sup>

Crucibles prepared by the method suggested by Munroe have many advantages not possessed by any other type of apparatus used for filtration, and since the use of such crucibles is by no means as general as their merit would warrant, it seems desirable to again briefly describe the preparation and uses of crucibles of this type.

*Preparation of the Munroe Crucible.*—A concentrated solution of chlorplatinic acid is precipitated by ammonium chloride, the latter reagent being added in slight excess. The resulting precipitate of ammonium platonic chloride is washed several times with water, and is finally washed with alcohol, the excess of alcohol being poured off as soon as the ammonium chlorplatinic acid has settled. A perforated platinum crucible (one preferably in which the perforations are numerous and small) is then placed upon several layers of filter paper, and held firmly in this position while the alcohol-moist mass of ammonium chlorplatinic acid is poured into it, usually until it is filled to a height of from 0.25 to 0.5 cm. The alcohol will be rapidly absorbed by the filter paper upon which the

<sup>1</sup> And reprinted, *Chem. News.*, 58, p. 101, 1888.