occur, (a) surface adsorption of the physical type, (b) surface adsorption of the activated type, and (c) solubility. Under certain conditions one process may predominate, while under other conditions two or more of these phenomena may occur simultaneously, so that the total observed sorption is the sum of the amounts taken up in the several ways.

3. Within the range investigated, nitrogen shows only physical adsorption, characterized by a rapid rate and a small heat of adsorption.

4. Hydrogen exhibits all three processes. At the lowest temperatures only physical adsorption occurs, at $-78.5°$ activated adsorption is the predominating process, while at 0° both activated adsorption and solution occur. The amounts of hydrogen taken up in each of the three ways have been determined.

5. In the case of carbon monoxide three different processes also are found. Two of these are shown to be physical and activated adsorption, while the third is either solubility or a second kind of activated adsorption.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

AN APPARATUS FOR MEASURING PARTIAL VAPOR PRESSURES OF BINARY LIQUID SYSTEMS

BY O. A. NELSON

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One of the commonest methods used in the determination of partial vapor pressure of binary mixtures is the so-called dynamic method. This method consists essentially in distilling off a small portion from a large volume of mixture, and then analyzing the distillate obtained. That this method is open to rather serious objections is admitted by many investigators. Zawidski[1] has pointed out that the volume of the mixture used is often too small, and as a result the composition and boiling point vary too much during the distillation. Kuenen[2] stated that the temperature of the vapor varied considerably, and that there was often an appreciable difference in temperature between the liquid mixture and the vapor, due probably to superheating of the liquid or cooling of the vapors. Another drawback to this method according to Rosanoff and co-workers[3] is the fact that only relatively small quantities of the distillate are available for analysis. Other methods might be discussed, but the reader is referred to the article by Rosanoff[3] for more complete criticisms of methods available.

[1] Zawidski, *Z. physik. Chem.*, **35**, 129 (1901).

[2] Kuenen, "Verdampfung und Verflüssigung von Gemischen," Leipzig, 1906.

[3] Rosanoff and co-workers, THIS JOURNAL, **31**, 451 (1909).

Discussion of Method.—Rosanoff and co-workers[3] added gradually to the distilling mixture during distillation such quantities of the lower boiling component as would keep the distillation temperature constant. Also to make certain that equilibrium between liquid and vapor was established they passed the vapors through an equilibrium chamber containing a liquid mixture of the same components as the distilling mixture. They state in this connection, "True equilibrium can only be attained and its attainment demonstrated by passing the vapor of a composition obtained by one or another method through a liquid mixture of the same components." Rosanoff's method, while a decided improvement over the older methods, suffers from the weakness that it is very difficult to add the lower boiling component at such a rate as to maintain a mixture of constant composition in the boiling chamber. This method was tried by Young and Nelson[4] in their work on the binary mixture carbon tetrachloride–ethylene dichloride, but it was found to be almost impossible to prevent changes in composition in the boiling mixture. Very satisfactory results were obtained by a combination of the methods of Rosanoff and of Carveth[5] the latter of whom, instead of adding one pure component, added a mixture of approximately the same composition as the distillate and obtained good results. The method was carried out in two steps. In the first the pure components were added alternately and in small increments to maintain an approximately constant boiling temperature, and in the second the distillate obtained during the first step was added to the boiling mixture at as nearly as possible the same rate as distillation proceeded. The boiling point of the mixture during this step could be kept within ±0.01° indicating very constant composition.

In the apparatus shown in Fig. 1[6] the two-step method has been done away with, although the principles involved have not been changed. In this apparatus, designed toward the end of the work referred to,[4] the process is made automatic by adding to the apparatus a tube through which liquid flows back from the receiver to the boiler exactly as fast as other liquid distils into the receiver. The distillation is continued until the temperature of the distilling liquid becomes constant over a long period of time. The equilibrium chamber suggested by Rosanoff is retained as a further assurance that equilibrium is reached. The apparatus is made of Pyrex glass and in one piece, all points being sealed to prevent leaks of vapors or liquids. The dimensions of the different parts are as follows. The boiler was made from a 250-cc. round-bottomed flask and the receiver from a 200-cc. flask. The chamber containing the thermometer well is about 12.7 cm. long and 2.5 cm. in diameter, and the thermometer well itself is just large enough to accommodate the end of a Beckmann thermometer. Some mercury is poured into the thermometer well in order to make better contact between the hot liquid mixture and the thermometer. The equilibrium chamber is

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[4] Young and Nelson, *Ind. Eng. Chem., Anal. Ed.*, **4**, 67 (1932).

[5] Rosanoff and Carveth, *J. Phys. Chem.*, **3**, 193 (1899).

[6] The author is indebted to Mr. R. M. Baker of the Division of Chemical Engineering for preparing the drawing of this apparatus.

also about 12.7 by 2.5 cm. and is surrounded by a jacket 14 cm. long by 5 cm. in diameter. The condenser is 23 cm. long, and the return tube from the receiving flask is placed in such a position that about 150 cc. of the distillate is made available for analysis. The return tube obviously must slope downward from the receiver to the filling tube to facilitate the return of distillate. The reflux condensers are ordinary 20–25 cm. stock condensers.

The operation of the apparatus is almost self-evident. Briefly, however, it is as follows. The boiler and receiver of the apparatus are filled either with the same liquid mixture, or the receiver may be filled with a mixture somewhat richer in the lower boiling components. The boiler is heated electrically. During operation the mixture in the boiler spurts against the thermometer well, and also against the equilibrium chamber. The slightest change in composition of the mixture is readily detected by the temperature change, as shown by means of a Beckmann thermometer. Vapors from the liquid thrown against the thermometer well pass into the equilibrium chamber, where a portion condenses to form a liquid for the vapors to bubble through. The top part of the equilibrium chamber is then gently heated by means of an electric heater, to prevent refluxing of the escaping vapors. When the proper amount of heat is supplied, the level of the liquid in the equilibrium chamber remains constant. With high boiling mixtures the equilibrium chamber should be insulated with a layer of asbestos or other suitable insulating material. As the boiling is continued the vapors are condensed and caught in the receiver for the distillate. This receiver, of about 200 cc. capacity, is fitted with a return tube, which carries the distillate back to the boiler. If now the returning distillate does not have the same composition as the mixture in the boiler, the composition will gradually change, as will be observed from the change in boiling point. The process must obviously be continued until no change in temperature can be detected. The composition of both liquids may then be determined either chemically or by physical means depending on the components.

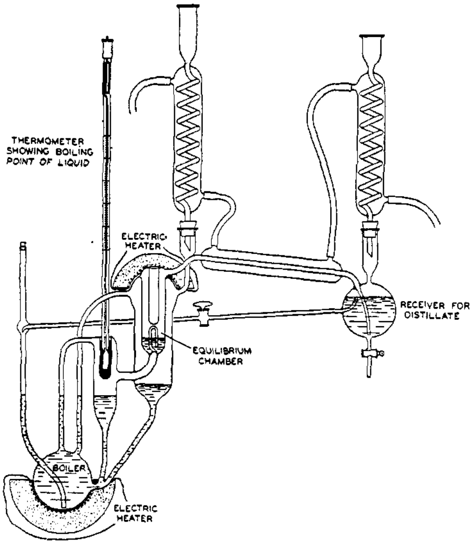

Fig. 1.—Apparatus for measuring partial vapor pressures of binary mixtures.

The total pressure being known, in most cases the partial pressures of the components are readily calculated from the ratio of the components, expressed in moles.

It is evident that for very accurate work the changes in atmospheric pressures must be allowed for. If such variations of pressure become appreciable, a monostat should be constructed and attached. This device may be connected to the upper end of the reflux condensers.

This apparatus was used toward the end of the work on ethylene dichloride–carbon tetrachloride mixtures, and all points previously obtained were checked. The values obtained by this apparatus agreed perfectly with those obtained by the method described previously. It is felt that the use of this apparatus offers a rapid as well as a very accurate means for determining partial vapor pressures of binary mixtures.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTRON AFFINITY OF FREE RADICALS. III. FURTHER STUDIES OF FREE RADICALS CONTAINING BIPHENYL AND NAPHTHYL GROUPS

BY HENRY E. BENT AND MAURICE DORFMAN

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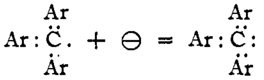
The addition of an alkali metal to an unsaturated compound is a type of reaction which is peculiarly adapted for study in connection with the problem of finding the effect on the strength of a given bond of various substitutions in a molecule. Heats of combustion and dissociation constants of acids give similar data but have their own peculiar limitations. Heats of combustion are commonly so large as to mask very largely changes in a single bond. Ionization data for acids are difficult to obtain in solvents which have a stronger affinity for the proton than the base from which the acid is derived. The addition of alkali metals to unsaturated compounds supplies a very wide range of reactions to be studied and reactions which are at least in some cases reversible.

Not only will sodium add to such unsaturated single bond compounds as organic free radicals but it will also add to some double bond compounds such as ketones and olefinic compounds and to apparently saturated molecules such as triphenyl boron and triphenyl aluminum. The variety of reactions which may be studied is, therefore, all that can be desired providing equilibrium measurements are possible. It has been shown[1] that the sodium may be removed from the free radical addition compounds with the aid of mercury and that by knowing the concentration of the amalgam which is in equilibrium with the free radical and the addition compound, the free energy for the addition of sodium to the free radical may be calculated (Equation 2). A comparison of various free radicals, since in every case sodium ion is formed, is, therefore, a comparison of the reaction



$$\mathrm{Ar}:\overset{\mathrm{Ar}}{\underset{\overset{\cdot\cdot}{\mathrm{Ar}}}{\ddot{\mathrm{C}}}}\,. + \ominus = \mathrm{Ar}:\overset{\mathrm{Ar}}{\underset{\overset{\cdot\cdot}{\mathrm{Ar}}}{\ddot{\mathrm{C}}}}: \qquad (1)$$

of formation of the negative ion from the free radical (Equation 1). The equilibrium studied experimentally is

$$\mathrm{Na} + \mathrm{R} = \mathrm{Na}^+ + \mathrm{R}^- \qquad (2)$$

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[1] H. E. Bent, THIS JOURNAL, **52,** 1498 (1930).