quite representative of the heat of adsorption in the first layer, and again the $E_1$ value is too high. The entropy curve again falls somewhat above the two-dimensional gas values at low coverages and somewhat below near $v/v_m = 1$.

For krypton adsorption on collagen, Fig. 10, the heat of adsorption curve again rises to form a broad maximum which then decreases as the monolayer is approached. Here the $E_1$ value is far too low while the $\psi_1$ value is much more usual. Very unusual results were obtained for the entropy of the adsorbed krypton. This curve shows a distinct minimum at $v/v_m = 0.4$ and then a maximum where the monolayer is completed. It seems extremely unlikely that this entropy curve represents the actual facts because the minimum entropy is of the order of 2 entropy units which is only about one-fifth of the entropy of solid krypton at the same temperatures. One of the following two possible explanations may be responsible for this situation: The first is that heats of adsorption cannot be considered constant or that a discontinuity in the heat curve with temperature occurs in the range studied. This seems unlikely but other isotherms are being measured at interval temperatures to check this point. In the second place, it may be incorrect to consider that the entropy of the collagen is not changed during the adsorption. This assumption was implicit in the calculations of the entropy of the adsorbed krypton.

In order to establish the certainty of the entropy curve for collagen, the entire series of adsorption measurements and calculations therefrom, were done a second time. These results were similar to those originally obtained. Furthermore, it was estimated from extensive calculations made from the data that the probable error in the entropy curve, allowing the assumptions made, was about ±1 entropy unit at the minimum. Certainly, these unusual results for collagen warrant further investigation.

## Summary

The adsorption of nitrogen and krypton has been measured on a simple hydrocarbon surface, polyethylene, at both liquid nitrogen and liquid oxygen temperatures. For nylon and collagen, krypton adsorption has been measured at the two temperatures and nitrogen adsorption at one temperature. The adsorption isotherms are typical Type II except for a rather gradual break where the monolayer is completed. The adsorption data yielded to BET analysis and gave surface areas of reasonable magnitude which agreed very well for the two gases at different temperatures on the same sample. It is concluded that the BET theory provides a satisfactory method for investigating the surface areas of organic solids with nonpolar gases.

The thermodynamic functions for the adsorptions have been calculated. For krypton, the heat of adsorption curves rise as more gas is added to the surface, and then fall off again after one monolayer is completed. The entropy curves for krypton on polyethylene and nylon fall toward limiting values as one layer is completed. For collagen, on the other hand, an extremely low minimum was obtained at a low coverage and a maximum where one layer was completed. These unusual results for collagen have not been explained.

BETHLEHEM, PENNA. RECEIVED DECEMBER 20, 1949

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[CONTRIBUTION FROM THE UNIVERSITY OF MISSOURI]

# Vapor Pressure Determination by Comparison with a Standard Liquid[1]

BY H. E. BENT AND C. A. KRINBILL, JR.

The purpose in developing a comparison method of determining the vapor pressure of a liquid is to economize on time through the simplification of the method and to take advantage of high precision in the determination of the vapor pressure of a single standard without having to repeat the precautions necessary for such high precision with each succeeding liquid. This paper develops the method and presents the results obtained with bis-(2-chloroethyl) sulfide, so called mustard gas, and diphenyl ether.

From the equation

$$n_2/n_1 = P_2/P_1 = a_2P_2^0/a_1P_1^0 \qquad (1)$$

in which $n$ is the number of moles in the condensate from vapor in equilibrium with solution, $P$ the partial pressure, $a$ the activity in the original solution and $P^0$ the vapor pressure of the pure liquid, it is evident that one can obtain the vapor pressure of one pure component from the vapor pressure of the other component, the ratio of the activities and the composition of the condensate.

A useful equation for describing deviations from Raoult's law expresses the deviations by means of a single constant for both components,[2] thus

$$\log a_1/N_1 = \beta' N_2^2 \text{ and } \log a_2/N_2 = \beta' N_1^2 \qquad (2)$$

in which $N$ is the mole fraction. These equations are applicable not only to systems which Hildebrand classifies as regular but also to some systems which show negative deviations from Raoult's law.[3a,b]

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[1] Submitted as a thesis in partial fulfillment of the requirements for a Master's Degree at the University of Missouri.

[2] J. H. Hildebrand, "Solubility," Reinhold Publ. Corp., New York, N. Y.

[3] (a) C. W. Porter, *Trans. Faraday Soc.*, **16**, 336 (1921); (b) H. E. Bent and J. H. Hildebrand, THIS JOURNAL, **49**, 3011 (1927).

If we combine the two expressions above we obtain the relation

$$\log a_2/a_1 = \log N_2/N_1 + \beta'(N_1^2 - N_2^2) \qquad (3)$$

from which we see that if the solution is an equimolecular mixture the right-hand side reduces to zero and the ratio of the activities is equal to unity. Thus a single determination of the composition of the vapor above such a solution combined with the vapor pressure of one component will give the vapor pressure of the other.

A refinement of the above treatment is possible in studying liquids which differ appreciably in their molecular volumes. Hildebrand has shown that for such solutions better results may be obtained by using the volume fraction instead of the mole fraction. The deviation from Raoult's law can then be expressed by the equation

$$\log a_1/V_1 = v_1\beta V_2^2 \qquad (4)$$

in which $v_1$ is the molal volume of one component and $V_2$ is the volume fraction of the second component. The equation analogous to equation (3) is now

$$\log a_2/a_1 = \log N_2/N_1 + \beta(v_2V_1^2 - v_1V_2^2) \qquad (5)$$

Knowing the molar volumes of the components we can now choose a concentration which will reduce the value of the expression in parentheses to zero and therefore eliminate the term involving $\beta$. The value for the ratio of the activities will no longer be unity but will be $N_2/N_1$ which can be obtained from the volume fraction of the solution chosen to eliminate $\beta$. A single measurement of the composition of the condensate will give the vapor pressure of the other pure component.

Finally, if in addition to obtaining the vapor pressure of an unknown liquid we wish to evaluate the constant $\beta$ in order to place the compound in an internal pressure series we can do this by making an additional measurement on a solution of some concentration which will make the last term in equation (5) as large as is consistent with precision of measurement.

In undertaking this work we had expected to use the method for the determination of the vapor pressure of mustard and other toxic gases of low vapor pressure. Before the work was finished Francel[4] determined the vapor pressure of mustard and we have therefore used this method to obtain the vapor pressure of diphenyl ether. This value is compared with the value obtained for diphenyl ether using Francel's apparatus.

There are several important advantages in this comparison method as compared with the dynamic method as used by Francel. First, the measurement of the volume of carrier gas is eliminated since it is the composition of the condensate rather than its amount which is important. This is a great saving in time and apparatus and of course, eliminates any errors in the measurement of volume.

Second, the weighing of the product is eliminated, which was the largest single error, and the factor which limited the accuracy in the dynamic method as used by Francel.

Third, several other errors are less important in the comparison method. For example, a change in the temperature of the bath affects the vapor pressure of both liquids and therefore is not so serious as in the study of a single liquid. Similarly, failure to achieve complete saturation or complete condensation will probably be of less importance since it will affect both vapors.

On the other hand, a serious disadvantage of the comparison method is the fact that a method must be devised to analyze the condensate. This means in our determinations the construction of a graph which shows the refractive index as a function of the concentration. It is also necessary that the liquids differ sufficiently in refractive index to give the desired precision in analysis,

A second disadvantage in the comparison method is the fact that it is necessary to make up a solution of a predetermined concentration.

## Experimental

Details have been given[4] for the preparation of the mustard gas and for much of the experimental procedure and therefore will not be repeated here. Additional discussion of precautions and errors can be found in the original theses of Francel and of Krinbill.

**Solutions.**—The mustard and diphenyl ether were fractionally distilled under reduced pressure. Five fractions of mustard gave the same refractive index but only the three middle fractions were used. Table I gives the refractive index, using sodium light, as a function of the concentration.

TABLE I

REFRACTIVE INDEX–COMPOSITION DATA FOR DIPHENYL ETHER AND BIS-(2-CHLOROETHYL) SULFIDE AT 30°

| Mole fraction of "mustard" | Refractive index |
|---|---|
| 1.0000 | 1.52264 |
| 0.9236 | 1.52695 |
| .8377 | 1.53187 |
| .7505 | 1.53688 |
| .6496 | 1.54237 |
| .5654 | 1.54698 |
| .4483 | 1.55341 |
| .3662 | 1.55778 |
| .2223 | 1.56530 |
| .1097 | 1.57114 |
| .0000 | 1.57690 |

The refractometer could be read to the sixth significant figure, but readings are assumed to be accurate to only the fifth, that is the next to the last digit given. The error thus introduced in the determination of the mole fraction is 0.002. Interpolation for values not given in Table I was conveniently accomplished by taking advantage of the fact that the refractive index is very nearly a linear function of the mole fraction. The deviations from linearity were therefore plotted on a large scale and the smoothed curve used in the actual determination of all compositions. This smooth curve served further to verify our estimate of the accuracy of the data since no point de-

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[4] H. E. Bent and R. J. Francel, THIS JOURNAL, **70**, 634 (1948).

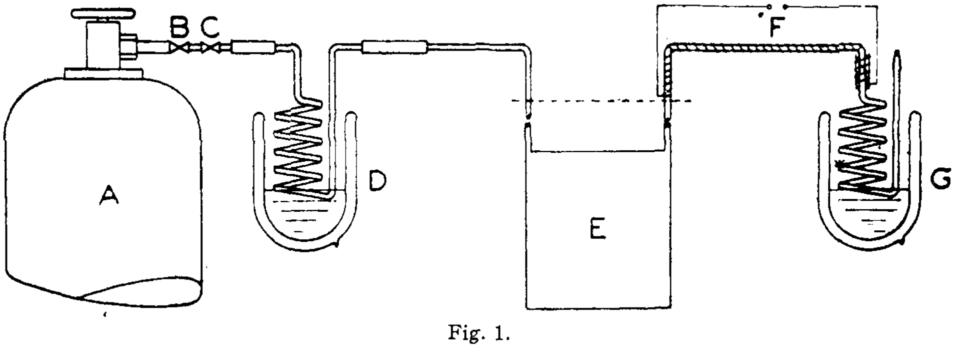

Fig. 1.

viated from the curve by as much as 0.0001 in the refractive index.

The first solution was intended to have a mole fraction of mustard of 0.5297 since at this composition the term involving $\beta$ becomes zero. In calculating this concentration we used the data in the literature for the molecular volumes[5,6] of mustard and diphenyl ether, respectively, 128.0 cc. for the former and 162.3 cc. for the latter at 50°. The composition of the solution we used was 0.5264 which necessitated a slight correction in the final calculations for the fact that we did not obtain precisely the concentration desired. A second solution was prepared for the purpose of evaluating $\beta$. The data on both solutions are given in Table II.

**Apparatus.**—The apparatus shown in Figs. 1, 2 and 3 is simpler than that used by Francel, the supply of nitrogen being simply a cylinder of compressed gas. (Figure 2 will be found in the paper by Francel but is not reproduced here in order to conserve space.) The spiral condenser over liquid air, which has been found very efficient in as much as it avoids too rapid cooling and therefore eliminates the formation of a fog, is used at D to dry the nitrogen and at G to condense the vapors. Two alternative forms of the saturator at E in Fig. 1 are shown in detail in Fig. 2 and in Fig. 3. The saturator shown in Fig. 3 was used for the most dilute solution of mustard which has a low vapor pressure. The air lift at P circulates the solution over the column O packed with three-eighths inch glass helices. This column will handle a much greater flow of nitrogen than the spiral type saturator. In addition to the advantages for the spiral type of saturator mentioned in connection with the dynamic method we should emphasize its value in continually stirring the solution and exposing a fresh surface of liquid over the nine-foot length of glass tubing. At the beginning and end of a series of runs the liquid in the saturator was analyzed to correct for change in composition. Particular attention must be given to mixing the condensate before making an analysis since there is a fractionating effect in the condensation of the vapors. As a consequence of the small amount of material condensing, small droplets adhere to the wall of the tube and a drop removed for analysis may not have the composition of the total condensate. Without mixing, different samples gave values for the refractive index which differed by as much as one in the fourth significant figure. After carefully mixing, a series of four runs differed by less than two in the sixth significant figure.

## Experimental Results

The experimental results given in Table II are in each case averages of four or more runs. The vapor pressure is calculated for diphenyl ether using the value for mustard obtained by Francel of 0.6824. The value obtained for diphenyl ether is 0.1593. A small correction, which is less than the experimental error, is

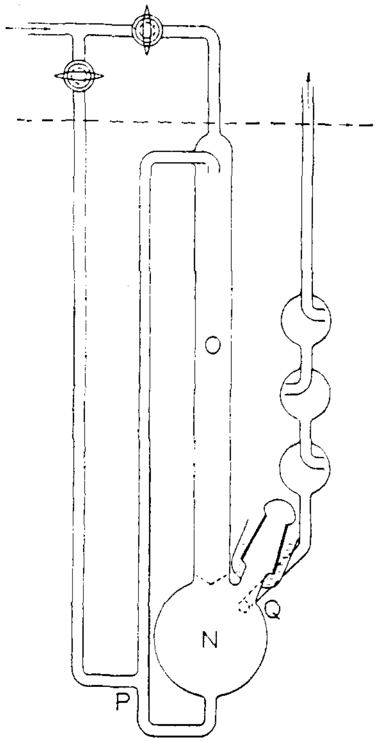

Fig. 3.

applied after evaluating $\beta$. This correction is a result of the fact that we did not measure a solution of precisely the desired concentration. The corrected value for the vapor pressure of diphenyl ether is then 0.1597. The difference between the value reported in this paper and the

TABLE II

DATA ON SOLUTIONS OF "MUSTARD" IN DIPHENYL ETHER AT 50° COMPARED WITH PUBLISHED DATA BY FRANCEL BY THE DYNAMIC METHOD

| | | | |
|---|---|---|---|
| Mustard mole fraction in liquid | | 0.5264 | 0.1119 |
| Mustard mole fraction in vapor | | .8264 | .4123 |
| Vapor pressure of diphenyl ether, mm. | Comparison method | .1597 | ..... |
| | Dynamic method | .1648 | ..... |
| $\beta$ | Comparison method | .... | .00110 |
| | Dynamic method | | .00124 |

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(5) Wilkinson and Wernlund, THIS JOURNAL, **42**, 1382 (1920).

(6) Zhuravlev, *J. Phys. Chem., U. S. S. R.*, **9**, 875 (1937).

value by the dynamic method is probably entirely experimental error. The error in the ratio of the mole fractions is twice the error in the mole fraction for one component, since the mole fractions of the two components must add up to unity.

The values obtained for $\beta$ in the last two columns of Table II probably differ no more than can be expected from the experimental errors. When one considers that $\beta$ expresses only the deviation from Raoult's law it is evident that a 10% error in this constant is of relatively little significance in a partial pressure determination in which the total deviation, for example at a mole fraction of 0.5, will be but 6%.

## Summary

A comparison method is described, applicable to mixtures which obey the laws of regular solutions, whereby it is possible to determine the vapor pressure of an unknown liquid providing one knows the vapor pressure of a known liquid and the composition of the vapor. It is not necessary to know the deviations from Raoult's law exhibited by the solution.

This method is applied to solutions of bis-(2-chloroethyl) sulfide in diphenyl ether and the results compared with the dynamic method.

The advantages of this comparison method over the dynamic method are enumerated.

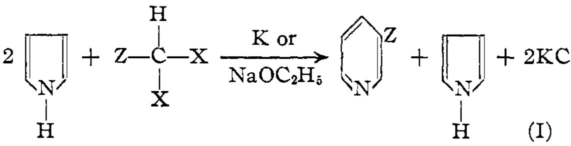
COLUMBIA, MO. RECEIVED OCTOBER 27, 1949

# NOTES

## The Formation of 3-Substituted Pyridines from Pyrrole[1]

BY ELLIOT R. ALEXANDER, AARON B. HERRICK AND THOMAS M. RODER

One of the most interesting reactions of pyrrole chemistry is the formation of 3-substituted pyridines from pyrrole, a dihalomethane and a strong base. Substituted pyrroles[5] and indoles[6] also give the same ring enlargement.



(I)

(Z = halogen,[2] hydrogen,[3] or phenyl[4])

The yields obtained from this reaction, however, are often very poor. Ciamician,[2] for example, obtained 3-bromopyridine from bromoform and pyrryl potassium in about 10% yield, while Dennstedt[3] obtained only an analytical sample of pyridine chloroplatinate from methylene iodide and one-half mole of pyrrole.

In an attempt to study the mechanism of this unusual transformation, we have reexamined the reaction conditions for the process and investigated other organometallic combinations in the hope of making the reaction a useful one synthetically. In Table I, however, are summarized some of our experiments. It is immediately evident that in our hands, too, the yields were very low regardless of the organometallic combination or the technique which was employed.

TABLE I

REACTIONS OF PYRROLE WITH SUBSTITUTED DIHALOMETHANES

| | | Yield, % | | | |
|---|---|---|---|---|---|
| Reactant | Product | Pyrryl-Li in ether | Pyrryl-Na[3] in ethanol (sealed tube) | Pyrryl-Na[7] in boiling ethanol | Pyrryl K[2] in ether |
| $CHCl_3$ | 3-Chloropyridine | 12.8 | 1.6 | 3.8 | 7.2 |
| $CHBr_3$ | 3-Bromopyridine | 8.6 | <0.5 | 2.5 | ... |
| $C_6H_5CHCl_2$ | 3-Phenylpyridine | 1.3 | 0.7 | 0.5 | ... |
| $CH_2I_2$ | Pyridine | 0.0 | <0.5 | 0.0 | ... |

The use of pyrryllithium, which does not appear to have been investigated before, gave the best yields with chloroform, benzal chloride, and bromoform, but failed with methylene iodide. Pyrryl potassium is better than pyrrylsodium in the one case which was investigated but the technique is more complicated. Pyrrylmagnesium bromide did not effect the transformation with chloroform. Prolonged heating in a sealed tube is necessary only in the case of methylene iodide. Thus, with the exception of the reaction in which methylene iodide was employed, the use of

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[1] Taken in part from a thesis by Thomas M. Roder submitted to the faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Bachelor of Science.

[2] Ciamician and Dennstedt, *Ber.*, **14**, 1153 (1881); **15**, 1172 (1882).

[3] Dennstedt and Zimmerman, *ibid.*, **18**, 3316 (1885).

[4] Ciamician and Silber, *ibid.*, **20**, 191 (1887).

[5] (a) Bocchi, *Gazz. chim. ital.*, **30**, I, 89 (1900); (b) Plancher and Ponti, *Atti. Accad. naz. Lincei*, [5] **18**, II, 473 (1909); (c) Bocchi, *Gazz. chim. ital.*, **30**, I, 94 (1900).

[6] (a) Plancher and Carrasco, *Atti. Accad. naz. Lincei*, [5] **13**, I, 575 (1904); (b) Magnanini, *Gazz. chim. ital.*, **17**, 249 (1887).

[7] Carried out in accordance with the general procedure of Dennstedt and Zimmerman[3] except that the reaction mixture was refluxed in excess ethanol.