Br^{80} (18 min.) atoms react which are produced as the result of the emission of a conversion electron.

5. In the light of new data, the recoil energies previously thought to account for chemical activation by the isomeric radioactive transition of bromine, are found to be too small to do so.

MADISON, WIS. RECEIVED SEPTEMBER 2, 1939

[CONTRIBUTION FROM THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION, NO. 345]

Partial Vapor Pressures from Nicotine Solutions at 25°*

BY L. B. NORTON, C. R. BIGELOW AND W. B. VINCENT

Little information is available on the loss of nicotine by evaporation and the concentration of nicotine vapor which can be built up when a dilute solution of nicotine is applied to foliage as an insecticide. A knowledge of the partial vapor pressures of both water and nicotine through the complete range of their solutions is therefore of great practical importance from that standpoint, and of theoretical interest in showing the thermodynamic behavior of a highly non-ideal solution.

The published values of the vapor pressure of pure nicotine at ordinary temperatures are in very poor agreement. The values at 25° range from 0.02 mm., determined experimentally by Harlan and Hixon,[1] to 0.17 mm. calculated from the equation found by Gorbachev[2] to be valid from 100 to 250°. A similar equation obtained by Young and Nelson[3] gives 0.12 mm. as the vapor pressure at 25°. No data are available on the evaporation of nicotine from solutions, except some approximate determinations by McDonnell and Young[4] of the final concentration and the loss of nicotine from a dilute solution exposed to the air for a long period at room temperature.

Experimental

Materials.—The nicotine was prepared by purifying the commercial 95% alkaloid, furnished by the Tobacco By-products and Chemical Corporation of Louisville, Ky., according to the method of Ratz,[5] and distilling it *in vacuo*. The product boiled at 125° at 17 mm. pressure, was water-white, and had a specific rotation $[\alpha]^{20}\text{D}$ $-168.90°$. Different samples which were purified at intervals during the investigation varied from this rotation not more than 0.2°. Ordinary distilled water was used as the other component.

Apparatus.—The dynamic gas-saturation method was used for the measurements because of the extremely low vapor pressure of the nicotine. The apparatus was arranged as in Fig. 1. Nitrogen, which was used instead of air to eliminate slow oxidation of the nicotine, was passed from the cylinder A over the mercury trap B, which served as a safety valve and pressure regulator, and into the vaporizers C and D. C was a series of three small bulbs charged with the solution to be measured, which saturated the gas partially, thus preventing appreciable changes in the concentration of the solution in the main vaporizer D by evaporation losses. D was the main vaporizer, consisting of a Friedrichs spiral gas-washing tower containing 200 cc. of the solution under investigation. The upper part of the tower was packed with glass wool saturated with the same solution to stop any spray and to ensure complete saturation of the nitrogen passing out. Both vaporizers were completely immersed in a water-bath maintained at 25 ± 0.02°. The outlet tube E was heated electrically by a winding of resistance wire to prevent condensation of vapor and was connected with a manometer. The nicotine was absorbed in the modified Turner absorption bulb F, which was filled with dilute sulfuric acid. The second absorption bulb G was filled with anhydrous magnesium perchlorate "Anhydrone" to absorb the water vapor coming from the vaporizer and the first absorber. The U-tube H also contained Anhydrone to absorb any water vapor coming back from the aspirator The aspirator bottle I had a capacity of 40 liters and was fitted with a manometer, thermometer, and siphon tube.

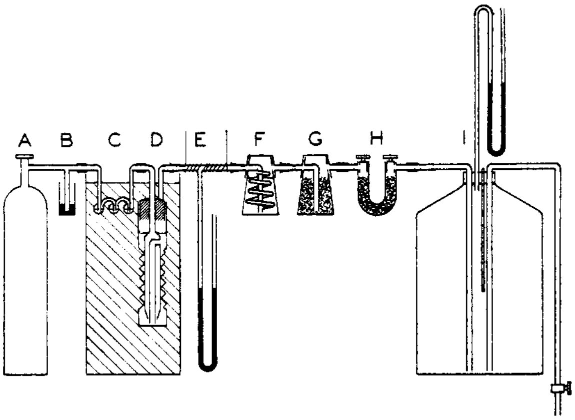

Fig. 1.—Apparatus for vapor pressure measurements.

(*) Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 345, October 30, 1939.

(1) Harlan and Hixon, *Ind. Eng. Chem.*, **20**, 723 (1928).

(2) Gorbachev, *J. Applied Chem.* (*U. S. S. R.*), **7**, 388 (1934).

(3) Young and Nelson, *Ind. Eng. Chem.*, **21**, 321 (1929).

(4) McDonnell and Young, *U. S. Dept. Agr. Bull.*, No. 1312 (1925).

(5) Ratz, *Monatsh.*, **26**, 1241 (1905).

All connections from the vaporizer to the last absorber were made with ground glass joints, since rubber has been shown to take up appreciable quantities of nicotine under these conditions. The joints were lubricated only on their outer parts, and the lubricant was kept away from the inlet hole in the nicotine absorber in order to avoid possible absorption of nicotine by the grease.

Procedure.—The nitrogen was bubbled through the vaporizers for thirty minutes before the absorbers were connected to ensure complete thermal and vapor equilibrium. The rest of the apparatus was then assembled, and the units turned on in order, the absence of leaks being indicated by the lack of bubbles through the vaporizers. all of the nitrogen escaping through the trap B. The outlet from the aspirator was opened last, and the outflow adjusted to 8–10 liters per hour. The tube in the mercury trap B was quickly adjusted to such a height that the saturated gas coming from the vaporizer was at atmospheric pressure, as indicated by the manometer at E. The run was continued, with only occasional slight adjustments necessary, until 15 to 35 liters had passed through.

The barometric pressure was read at the beginning and the end of each run. The manometer and the thermometer in the aspirator were read at the end of the run, and the manometer at E, as mentioned before, was maintained continuously at zero pressure difference. Both of the filled absorbers were weighed before and after the run, any lubricant on the joints being removed with benzene. The water displaced from the aspirator was weighed to 5 g. on a large solution balance. The solution from absorber F and a sample of the solution from the vaporizer D were analyzed for nicotine.

Analysis.—Most of the original solutions were analyzed by polarimetric measurements, which were found to be superior to chemical analyses for the concentrated solutions. The rotation was determined by means of a Schmidt and Haensch triple field polarimeter with a sodium vapor lamp, using a 2-dm. jacketed tube through which water at 20° was circulated. The nicotine content was read from a curve of concentration plotted against angular rotation, based on the data of Jephcott.[6] The solutions containing less than 5% of nicotine and the absorber solutions were analyzed by precipitation of the nicotine with silicotungstic acid.[7]

Calculation.—The method of calculation was similar to that of Young and Nelson[3] with the addition of a correction for the vapor pressure of the water in the aspirator and for the difference in pressure between the aspirator and the atmosphere, and the extension of the formula to two different vapors. The calculation corresponded to the formulas

$$\text{V. P. (nicotine)} = 760nPT/(273P'V + 760T(n + w))$$
$$\text{V. P. (water)} = 760wPT/(273P'V + 760T(n + w))$$

where P is the barometric pressure as read; P' the barometric pressure corrected for water vapor and the manometer reading; T the absolute temperature of the aspirator; V the gross volume of nitrogen passed through, as measured by the weight of water displaced from the aspirator; n the volume at standard conditions of the vaporized nicotine (g. absorbed nicotine × 22,400/162); and w the corresponding volume of water vapor (g. absorbed water × 22,400/18). The weight of the absorbed water is taken as the net gain in weight of the two absorbers less the weight of absorbed nicotine found by analysis.

Errors.—The estimated random errors from the experimental measurements were as follows: pressure, 0.2%; temperature, 1%; weights, 0.1%. The errors from analysis varied from less than 1% to 5% in different parts of the range.

A systematic error of less than 0.1% was incurred in the calculation by the assumption of the validity of the ideal gas laws. The most serious systematic errors probably came from incomplete vaporization or absorption of the vapors, giving consistently low results, or contamination of the heated outlet tube from spray or other sources, giving high results. The apparatus was tested for such errors by determining the vapor pressure of pure water. The average value found by several runs was 23.57 mm., as compared with the accepted value of 23.75 mm., indicating the absence of sources of serious consistent errors. Complete vaporization of nicotine was demonstrated by a series of determinations on a dilute solution of nicotine, in which the same value of the vapor pressure was obtained, within the expected error, when different solutions, including pure nicotine, were used in the bulbs preceding the main vaporizer. A second nicotine absorber following the first yielded no test for nicotine, showing complete absorption in the first. It was concluded therefore that subsequent determinations would include only accidental errors of this type, limited to single runs.

Results and Discussion

Pure Nicotine.—Because of the uncertainty of the previously determined values at low temperatures, the vapor pressure of pure nicotine was measured as accurately as possible. Ten determinations were made, including five different samples of nicotine, yielding a value of 0.0425 ± 0.0003 mm. for the vapor pressure at 25°. This result indicates considerable error in the values of Harlan and Hixon[1] which, however, were only intended to be approximate, as well as those calculated from the equations of Gorbachev[2] and Nelson and Young,[3] which are somewhat uncertain at 25° because of the long distance of the extrapolation from the experimental points considered.

The complete series of partial vapor pressure measurements are presented in Table I, and the vapor pressures are plotted against the mole fractions in Fig. 2. It will be noted that the vapor pressures of the two components are plotted on different scales in Fig. 2 since they are of a quite different order of magnitude.

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[6] Jephcott, *J. Chem. Soc.*, **115**, 104 (1919).

[7] "Assoc. Official Agr. Chem., Official Methods," 61 (1935).

TABLE I

VAPOR PRESSURES OF NICOTINE AND WATER FROM SOLUTIONS AT 25°

Nicotine, %	V. P. nicotine, mm.	V. P. water, mm.	Nicotine, %	V. P. nicotine, mm.	V. P. water, mm.
0.000	0.00000	23.57	80.50	0.0196	19.55
.108	.00035	...	82.10	.0217	19.50
.186	.00045	...	82.40	.0221	19.33
.281	.00049	...	84.30	.0207	18.27
.648	.00100	...	85.55	.0247	18.36
1.318	.00227	...	87.80	.0245	17.80
2.00	.00341	...	89.16	.0267	17.16
4.00	.00442	...	91.95	.0309	15.30
5.00	.0057	23.61	92.19	.0317	15.39
9.80	.0081	23.32	92.70	.0282	14.41
12.60	.0088	23.10	94.80	.0314	12.72
26.65	.0097	22.86	95.60	.0330	13.04
33.28	.0093	23.12	96.20	.0311	11.73
40.30	.0105	23.02	96.90	.0330	11.42
47.95	.0112	22.88	97.50	.0336	10.27
55.90	.0125	22.63	98.07	.0382	8.38
61.55	.0138	22.25	98.82	.0375	5.71
65.23	.0154	22.00	99.22	.0405	4.39
68.89	.0163	21.69	99.60	.0402	3.09
79.45	.0214	20.30	100.00	.0425	0.00

Raoult's Law.—The dotted lines in Fig. 2 represent the ideal curves to be expected if both components followed Raoult's law. The close approach of the upper ends of both experimental curves to these ideal curves shows that either nicotine or water follows Raoult's law reasonably well over a limited range of dilute solutions of the other. Throughout the rest of the range both components show abnormally high vapor pressures. At the lower ends of the curves the very dilute components approximately follow Henry's law over an appreciable range, although the deviations from Raoult's law are very large. Of particular interest is the very abrupt rise in the vapor pressure of nicotine in dilute solutions. Zawidzki[8] obtained a pair of curves from water and pyridine almost identical in form with these.

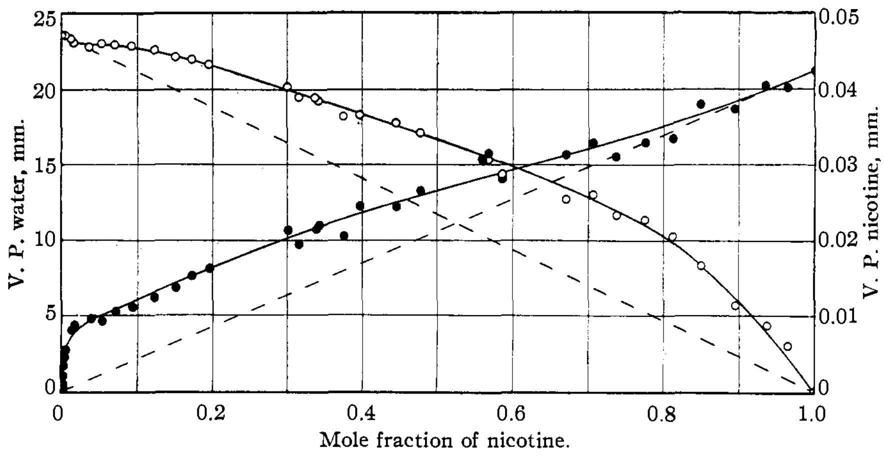

Fig. 2.—Partial vapor pressures from nicotine solutions at 25°.

The Duhem Equation.—The Duhem equation, $d \ln P_1/d \ln x = d \ln P_2/d \ln (1 - x)$, permits the calculation of the partial vapor pressures of the nicotine from those of the water. Following Zawidzki's procedure,[8] we derived the following empirical equation for the partial vapor pressures of the water, neglecting the points at the extreme ends of the curve

$$\text{Log } P_1 = 1.3714 + 1.50 \log x + 0.643(1 - x) - 0.709 (1 - x)^2 + 1.23(1 - x)^3$$

where x represents the mole fraction of the water.

From this empirical equation and the equation of Duhem, the corresponding equation for the partial vapor pressures of nicotine is

$$\text{Log } P_2 = -1.3716 + 0.02 \log(1 - x) - 0.643x + 1.14x^2 - 1.23x^3$$

A comparison of the calculated with the observed values is given in Table II.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED VAPOR PRESSURES

Mole fraction nicotine	V. P. water Obsd.	V. P. water Calcd.	V. P. nicotine Obsd.	V. P. nicotine Calcd.
0.98	1.3	0.9	0.0415	0.0413
.95	3.2	2.8	.0403	.0397
.90	6.0	5.9	.0384	.0374
.80	10.3	10.3	.0350	.0342
.70	12.8	12.9	.0321	.0318
.60	14.9	14.8	.0292	.0296
.50	16.7	16.5	.0267	.0271
.40	18.3	18.3	.0238	.0240
.30	20.0	20.0	.0203	.0202
.20	21.6	21.7	.0164	.0158
.10	22.7	23.0	.0123	.0114
.05	23.0	23.4	.0100	.0093
.02	23.2	23.5	.0082	.0078

The agreement of the calculated with the observed values for water shows the faithfulness of the empirical equation. The simultaneous agreement of the corresponding values for nicotine shows that the Duhem equation is valid for this system. The equations are, however, not suitable

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(8) Zawidzki, *Z. physik. Chem.*, **35**, 129 (1900).

for calculations at very low or very high concentrations.

Activity.—In view of the extreme abnormality of the lower end of the nicotine vapor pressure curve, it is of interest to calculate the corresponding change in the activity of the nicotine with concentration in this region. The ratio of vapor pressure to mole fraction appears to approach a value of approximately 1.6 in very dilute solutions. The region where $P = 1.6x$ was therefore chosen as the standard state, and the relative activity coefficients calculated as the ratios $P/1.6x$ for solutions up to 0.1 mole fraction, using a large-scale plot of this section of the curve for interpolation of the vapor pressure values. The resulting activity coefficients are shown in Table III.

Table III

Activity Coefficients of Nicotine in Dilute Solutions

Mole fraction nicotine	γ nicotine
0.001	0.90
.005	.63
.010	.45
.020	.26
.030	.19
.040	.15
.050	.13
.100	.08

The activity coefficients decrease extremely rapidly at first with increasing concentration, then show a slow decrease in more concentrated solutions. These values are in satisfactory agreement with the activity coefficients calculated from freezing point data to be published later. It will be noted that the standard state for the nicotine in dilute solution yields an extrapolated value of 1.6 mm. for the ideal vapor pressure of pure nicotine widely different from the actual value of 0.0425 mm.

Rate of Evaporation.—From a practical standpoint the most desirable information is the relative speed of evaporation of the components as a function of the percentage composition. It can be assumed that the rate of evaporation in the open air at low humidity will be roughly proportional to the vapor pressure. The large difference in molecular weight between the components introduces two factors altering the curves in Fig. 2. First, with equal vapor pressures of the two, the evaporation of the nicotine by weight will be nearly ten times as great; second, the lower part of the curves will be greatly lengthened and the higher greatly compressed in changing from mole fractions to percentage composition. Accordingly, after the first rapid rise in the vapor pressure of nicotine at low concentrations, neither the water nor the nicotine changes greatly from 10 to 70%. Even at 90% nicotine, both vapor pressures are about half those of the pure components. The relative losses by evaporation through most of the range will be of the order of 200 of water to 1 of nicotine by weight.

Under actual conditions the ratio will be somewhat less, because of the presence of water vapor already in the air, which will have the effect of subtracting a definite pressure from the effective vapor pressure of the water. The final concentration of any nicotine solution exposed to the air can be determined from the curves as that concentration at which the vapor pressure of the water is equal to the partial pressure of water vapor in the air.

Summary

The partial vapor pressures of nicotine and water in all their binary solutions at 25° have been determined by the dynamic method.

The deviations from Raoult's law are found to be very large and in the direction of higher vapor pressures for both components.

The results are shown to agree with the Duhem equation.

The activity coefficients of nicotine in dilute solutions are found to decrease very rapidly with increasing concentration.

With increasing percentages of nicotine the loss of nicotine relative to that of the water first increases rapidly, then remains nearly constant over a long range, and finally increases very rapidly during free evaporation.

Geneva, New York Received November 1, 1939