

2. The absorption spectra of potassium iodide have been examined under various conditions and it has been found that the satellite band has the same frequency of vibration as the first band of iodine in a potassium iodide solution and can be completely removed with sodium thiosulfate.

3. It has been shown that this satellite band is due to the presence of free iodine dissolved in a solution of potassium iodide and not to the potassium iodide.

4. The use of iodine dissolved in carbon tetrachloride as a light filter to remove visible light and transmit most of the ultraviolet light to a frequency of $1150 f$ (the cut-off point of the solvent) has been suggested.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE VAPOR PRESSURE OF ANHYDROUS OXALIC ACID

BY W. ALBERT NOYES, JR., AND DELBERT E. WOBBE

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In connection with some work on the thermal decomposition of anhydrous oxalic acid¹ it became necessary to know the vapor pressure of anhydrous oxalic acid at temperatures ranging from 120° to 170°. Since anhydrous oxalic acid decomposes quite rapidly in this temperature range it is obvious that direct measurements of the vapor pressure of the anhydrous solid would be very difficult to carry out at these temperatures and that values obtained would be of doubtful accuracy. It seemed advisable to carry out measurements at lower temperatures and to obtain an equation which could be used for purposes of extrapolation.

Some preliminary measurements were made by a static method. Oxalic acid was recrystallized thrice from water and then placed in a flask of about 500cc. capacity sealed to a vacuum line. The flask was surrounded by a salt solution kept at its boiling point (about 105°) and the flask evacuated to as low a pressure as could be obtained with a mercury diffusion pump backed by an efficient oil pump. The evacuation was carried on for 20 to 30 hours. During this time a large portion of the oxalic acid sublimed and condensed along the outlet tube of the flask. The material remaining was usually quite lumpy. The flask was broken off and the outlet covered over with a rubber tip. The lumps were then broken by tapping. The material was kept in a desiccator over phosphorus pentoxide. The preliminary measurements were made by placing some of the anhydrous material in a spiral tube connected with an ordinary manometer. This system was evacuated to as low a pressure as could be obtained with a mercury diffusion pump and was then placed

¹ To be published in the near future.

in an air thermostat capable of regulation to about 0.1° . After sufficient time had been allowed to elapse so that temperature equilibrium was attained, the difference in level was read on the manometer and the vessel removed and plunged into cold water as quickly as possible to stop thermal decomposition. The difference in level was read at room temperature. By making the assumption (later found to be justified) that anhydrous oxalic acid has too low a vapor pressure to be read by ordinary means at room temperature, it is possible to calculate what the pressure exerted by the decomposition products would be at the temperature of the thermostat and to subtract this value from the pressure measured. There are several difficulties in this method. In the first place, according to Berthelot and Gaudechon² oxalic acid decomposes in two ways at least: (1) directly into carbon dioxide, carbon monoxide and water or into carbon dioxide and hydrogen; (2) into formic acid and water, the formic acid subsequently giving carbon dioxide and hydrogen or carbon monoxide and water. Any water formed would, if its pressure were high enough, form $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ at the lower temperature. The vapor pressure of water over hydrated oxalic acid has been carefully determined by Baxter and his co-workers,³ so that if the decomposition proceeded entirely by any one method a calculation of the vapor pressure would still have been possible from this type of data. Unfortunately, this did not seem to be the case and in addition adsorption of the products of decomposition by the glass walls and by the oxalic acid seemed to play a very large role. Consequently this method may be said to give only the order of magnitude. The results we obtained when compared to the results later to be given did indicate that oxalic acid vapor was not greatly associated if at all.

A dynamic method was finally adopted. The volumes of several 5-liter bottles were accurately determined (within about 0.02%) by allowing water from a carefully calibrated volumetric flask to drain into them and filling up the small volume at the end from a calibrated buret. For example, four determinations for one of the bottles gave 4954.0, 4954.8, 4954.3, 4954.3. These bottles were fitted with rubber stoppers and stopcocks and were well dried and then filled with nitrogen dried by passage over calcium chloride. The temperature of the nitrogen was determined at the beginning of the run and the nitrogen was displaced by means of glycerol. The nitrogen subsequently passed through calcium chloride and phosphorus pentoxide drying tubes and through a flowmeter which was used to determine roughly the rate of flow. The gas next passed through about 4.5 meters of tubing inside of the thermostat before passing over the anhydrous oxalic acid. The latter was well distributed in a tube

² Berthelot and Gaudechon, *Compt. rend.*, **158**, 1791 (1914).

³ Baxter and Lansing, *THIS JOURNAL*, **42**, 419 (1920). Baxter and Cooper, *ibid.*, **46**, 923 (1924).

about 12 mm. in diameter and 75 cm. long. The oxalic acid was placed at least 10 or 12 cm. below the level of the liquid in the thermostat. The gas emerging from the thermostat passed through a tube more than a meter long. Most of the oxalic acid condensed just above the level of the liquid in the thermostat, and it was assumed at the beginning that no error had been introduced by assuming complete condensation in the tube. This assumption was found not to be justified. Accordingly, a U-tube was sealed to the end of the outlet tube and was immersed in an ice-water mixture. After the conclusion of the passage of the gas, the liquid was withdrawn from the thermostat to a point about 12 cm. below its former level, the tube was carefully washed off and then sealed with an oxygen flame at a point sufficiently removed from the condensed oxalic acid to preclude the possibility of any decomposition. The tip of the tube was broken off inside an Erlenmeyer flask and the tube washed out with dil. sulfuric acid. The resulting solution was titrated with approximately 0.01 *N* potassium permanganate solution. This solution was made by dilution from a solution of approximately 0.1 *N* potassium permanganate that had been standardized both by iron wire and by hydrated oxalic acid which had been shown to be about 99.98% pure by titration with sodium hydroxide. A set of weights calibrated by the method described by Richards⁴ and using a 2g. weight standardized by the Bureau of Standards as the absolute standard, was used. The values obtained by means of the oxalic acid are as follows: 0.09202, 0.09212, 0.09207, 0.09209, 0.09209, 0.09213; av., 0.09209. The values obtained by the iron wire method are 0.09202, 0.09222, 0.09190; av., 0.09205. The value used was 0.09207, from which the largest deviation was 0.18%.

In titrating, the solution was warmed and a blank was always run, using the same volume of the dil. sulfuric acid. The color intensities were matched in Nessler tubes, and the amount required for the blank was subtracted from the amount used in the titration of the unknown. It was found that the titration was not accurate unless the colors matched were very faint, preferably with not more than one drop of the 0.01*N* permanganate in excess.

There are several important sources of error in the method as used. (1) If the oxalic acid is associated in the vapor state, our values would all be in error. The fact that the logarithm of the pressure when plotted against the reciprocal of the absolute temperature gives a fairly straight line would indicate that the degree of association at least remained constant in the temperature interval studied. We have already mentioned the evidence obtained in the preliminary work. (2) Any decomposition of the oxalic acid in the bath would cause a larger volume of gas to pass out than we had thought and would probably make our results too high. By

⁴ Richards, *THIS JOURNAL*, **22**, 144 (1900).

extrapolation of our results on thermal decomposition this error was shown to be much less than 0.1% even at the highest temperature used. (3) The volume of gas at the temperature of the thermostat was calculated by means of the formula $v = a(t - t_0)v_0 + v_0$, where v is the volume at the temperature of the thermostat, t is the temperature of the thermostat, t_0 is the temperature of the gas at the beginning of the run, v_0 is the volume of the bottle and $a = 0.003672$.⁵ This assumes that the temperature of the drying columns remained constant and that the gas was as dry when its volume was determined as after it had passed through the drying columns. Neither of these assumptions is strictly justified, although any error introduced would be probably less than 0.1%. In order to reduce the second objection as far as possible, two volumetric flasks were calibrated and the air in them was dried by standing over sulfuric acid. The air was displaced subsequently by sulfuric acid. This caused no appreciable change in results. (4) We have already mentioned the difficulties in titration. All of the buret readings were checked by at least two observers. The error in titration is undoubtedly great at the lower temperatures studied. (5) Any lack of saturation of the gas with the vapor would make our results too low. The rate of flow was varied by a factor of nearly four, and only with the most rapid rate of flow used did there seem to be any indication that the gas was not saturated. (6) The temperature of the thermostat was read by means of a thermometer calibrated by the Bureau of Standards. The thermometer was calibrated only at the 10° intervals, so that temperatures other than those in the immediate neighborhood of the 10° marks would be less accurately known. The temperature of the thermostat remained constant to about 0.1°, except at the highest temperature used (105°) for which considerably less variation was noted. Since the temperature coefficient of the vapor pressure is rather high, lack of constancy would introduce an appreciable error. (7) The vapor pressures are calculated by means of the perfect gas law, $pV = nRT$. The assumption of the perfect gas law at such low pressures would seem to be justified. The increase in volume of the gas due to the presence of the vapor was determined from the approximate value of the vapor pressure and this corrected volume used in the calculations. The correction amounted to less than 0.1% even at the highest temperature used. The results should be accurate to about 2%, except at the lowest temperature studied (60°). All of the points obtained after the procedure described was adopted are given in Table I, with the exception of one point which was about 50% too low due to the fact that some of the acid had been decomposed in sealing off the tube at the end of the run.

Only those values obtained after the final procedure was adopted are given in the table. Some of the earlier values (for which the U-tube

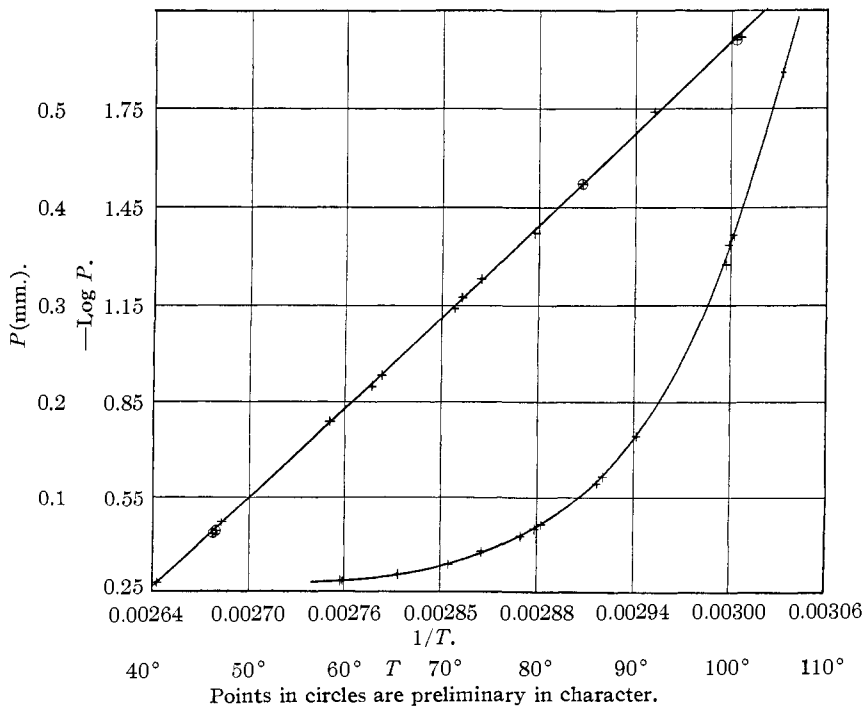
⁵ Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 114.

TABLE I
RESULTS

Temp., °C. ±0.1°	Approx. rate of flow, L. per hour	Vol. of dry air at temp. of thermo- stat, Liters	0.009194 N KMnO ₄ , cc.	P, mm.	P (calcd.)
59.55	0.78	20.27	1.15 ^b	0.0108	0.0103
65.65	1.72	22.69	4.28	.0183	.0186
74.40	1.76	17.59	7.51	.0426	.0417
78.40	2.7	5.966	3.48	.0588	.0596
79.82	0.93	12.07	8.02	.0672	.0676
80.50	0.73	9.747	6.94	.0722	.0716
86.17	2.44	6.105	3.44 ^b	.1161	.1164
86.90	2.19	12.07	7.18 ^b	.1236	.1234
90.31	1.22	10.06	15.88	.1645	.1643
99.49	0.74	3.042	9.72	.3412	.3437
105.28 ^a	1.42	5.219	25.88	.5374	.5374

^a ±0.03°.^b 0.01838 N KMnO₄ used.

immersed in ice was not used) agree well with those given, particularly if the rate of flow is small, or the temperature high. Thus a preliminary



value at 59.80° gave 0.0109, calcd. 0.0106. The values in the column marked "calcd." are obtained from the equation $\log p = -(4726.9499/T) + 12.22292$. This equation was obtained by making a large scale plot of

the logarithm of the pressure against the reciprocal of the absolute temperature and drawing the best straight line through the points, giving somewhat more weight to the points obtained at higher temperatures. The agreement is within 2% except at the lowest temperature used. Since this equation fits the data as well as any other type of equation we tried, the heat of vaporization must be very nearly constant at 21,650 calories per mole. It is very difficult to estimate with accuracy what the specific heat of the vapor should be. It would undoubtedly be higher than that of ethane, which also has eight atoms in the molecule. The specific heat of solid anhydrous oxalic acid has been determined by Nernst, Koref and Lindemann,⁶ who find 25.07 calories per mole for the interval 3° to 47°. The specific heat of solid acetic acid is much higher (about 37).⁷ By use of the equation given by Henglein⁸ for the vapor pressure of glacial acetic acid it is found that ΔC_p is about 4.5 calories between 0° and 50°. If 29 is taken as an average specific heat per mole for liquid acetic acid over this range, the specific heat of the vapor would be about 24.5 calories per mole. This result would make it appear that it might not be unreasonable to expect a small value of ΔC_p for the vaporization of solid oxalic acid. Since the heat of sublimation is very high, one might expect, therefore, an equation of the type used to fit the data fairly well.

Extrapolation of this equation gives a value differing but slightly at 150° from the values obtained by means of more complicated equations.

Summary

1. The vapor pressure of solid anhydrous oxalic acid has been determined between 60° and 105°.
2. The values are found to be satisfactorily represented by the equation $\log p = -(4726.9499/T) + 12.22292$.
3. It may not be unreasonable to expect the specific heat of the vapor to be only slightly different from that of the solid. The heat of sublimation as given by the equation would be 21,650 calories per mole.

CHICAGO, ILLINOIS

⁶ Ref. 5, p. 1271.

⁷ Ref. 5, p. 1269.

⁸ Henglein, *Z. physik. Chem.*, **98**, 1 (1921).