THE VAPOR PRESSURE OF BARIUM THIOSULFATE MONOHYDRATE

THESIS FOR THE DEGREE OF M. S.

Elmer Leininger

1930

Barium thiosulphate monohydrate

Chemistry

THE VAPOR PRESSURE
OF
BARIUM THIOSULFATE MONOHYDRATE

A THESIS

Submitted to the Faculty of Michigan State College of Agriculture and Applied Science in Partial Fulfillment of the Requirements for the Degree of Master of Science.

By

ELMER LEININGER

June, 1930.

THE VAPOR PRESSURE OF BARIUM THIOSULPATE MONOHYDRATE.

The original object of the work described in this paper was to measure the vapor pressure of barium thiosulpate monohydrate, $Ba\ S_2\ O_3\ H_2O$, at various temperatures in order to understand better the conditions under which the salt is stable. Such conditions might have an important bearing on the use of the salt as a primary standard for iodine solutions. The work done in obtaining these values, however, incidentally gave some information on the general method involved, so for that reason the method will be fully discussed.

The methods that have been used to determine the vapor pressure of crystalline hydrates may be classified as follows:

I. Static methods in which the hydrate and the next lower hydrate are placed in a tensimeter filled with mercury, (Frowein, Z. Phsik. Chem. 1, 5, also 362 (1887)), or cottonseed oil. (Menzies J. Am. Chem. Soc. 42, 1951 (1920). The apparatus is then evacuated and sealed off. The vapor pressure of the hydrate is then measured by the rise of the confining liquid in an attached manometer tube. Carpenter and Jette (J. Amer. Chem. Soc. 45, 578 (1923))

balanced the pressure of the hydrate against the vapor pressure of water and measured the difference in the manometer tubes.

The difficulties encountered in working with the atatic method are the elimination of adsorbed gases and moisture from the walls of the apparatus, the accurate reading of the small difference in the mercury levels and the time consumed in the case of many salts which are slow in reaching equilibrium.

II. Dynamic or gas-current saturation methods which consist in passing a measured volume of air slowly through a tube containing the hydrate and from the loss in weight of the hydrate calculating the vapor pressure. Baxter and Lansing (J. Am. Chem. Soc. 42, 419 (1920)) modified the procedure by weighing the water removed from the hydrate by the air and obtained very good results. However, as Wilson (J. Am. Chem. Soc. 43, 704 (1921)) points out, no results have been reported on salts which are known to reach equilibrium slowly. Schumb (J. Am. Chem. Soc. 45, 342 (1923)) used the Baxter and Lansing method to determine the vapor pressure of a number of hydrates.

For a long time the results obtained by the gas-current saturation method differed from

those obtained by static methods but Menzies (J. Am. Chem. Soc. 42, 1951 (1920)) pointed out the errors of the older static methods. He obtained check results using both methods.

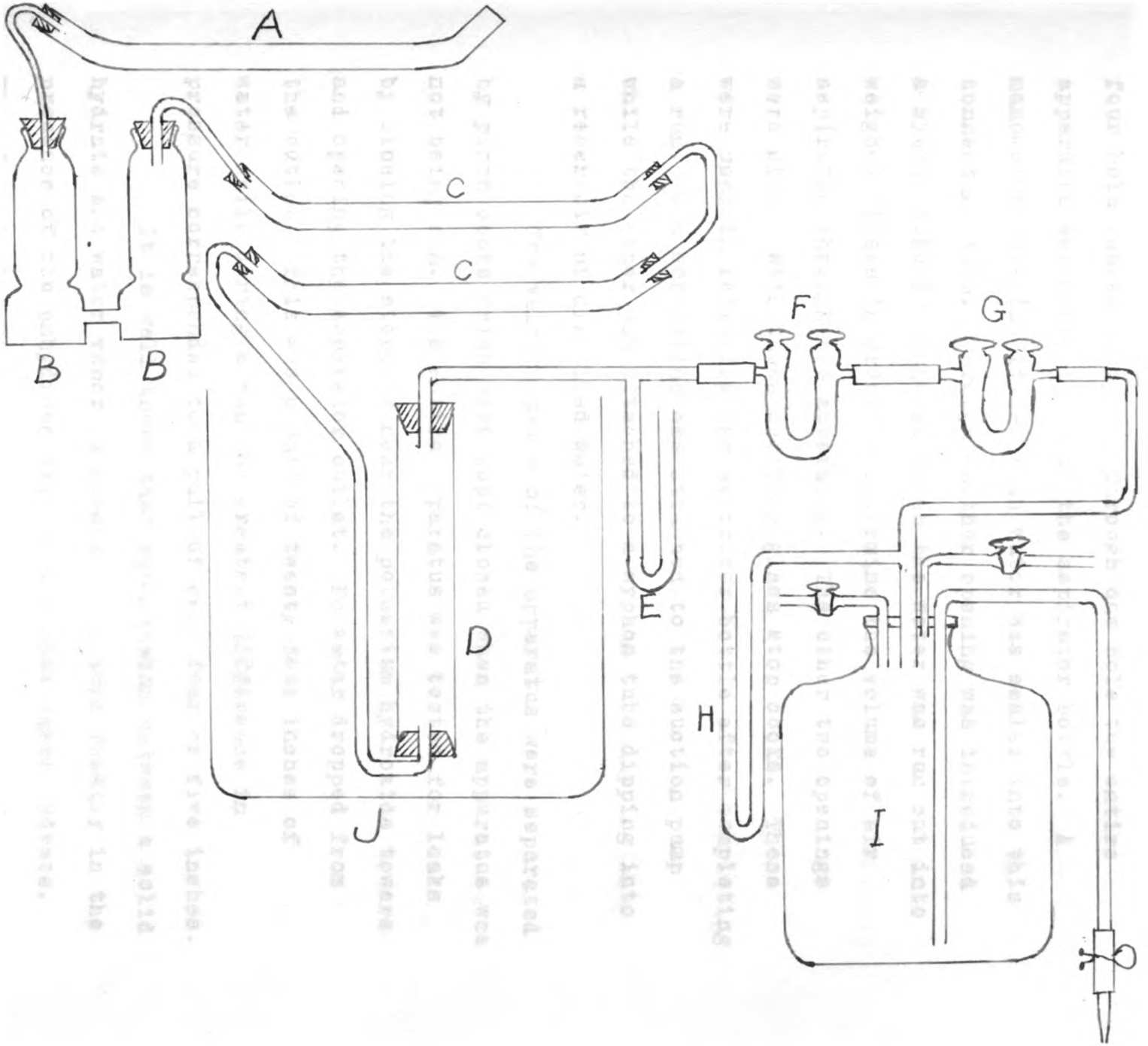
III. Indirect methods in which the hydrate is brought into equilibrium with some liquid whose vapor pressure is known. The well known method of finding the concentration of sulfuric acid over which a pair of hydrates neither gains nor loses weight is an example of such an indirect method.

A somewhat similar method is to equilibrate the hydrate with an organic liquid in which small amounts of the hydrate water dissolve. Then the amount of water taken up by the liquid is measured by following some physical or chemical property of the liquid such as the change in the boiling point, (Linebarger Z Physik. Chem. 13,500 (1894)), density (Foote & Scholes, J. Am. Chem. Soc. 33, 1309 (1911)), or electrical conductivity (A. A. Noyes & L. R. Westbrook, J. Am. Chem. Soc. 43, 726 (1921)). These indirect methods are not satisfactory for salts of low vapor pressure nor for those that are slow in reaching equilibrium.

EXPERIMENTAL.

The method adopted was Baxter and Lansing's modification of the air-current saturation method and the form of apparatus finally used is illustrated in Figure I.

The air was purified by allowing it to pass over a solution of silver nitrate (A) and then through two drying towers (B) filled with fused potassium hydroxide. The air next passed over concentrated sulfuric acid contained in the tubes (C) (C). In some of the experiments the sulfuric acid was changed to that of some definite strength so that the air entering the saturator tube had some known vapor pressure. A length of glass tubing immersed in the constant temperature bath (J) carried the air to the saturator tube (D) filled with the salt mixture whose vapor pressure was being determined. The air after reaching equilibrium with respect to the water vapor from the hydrate was passed through a weighed phosphorus pentoxide tube (F) having ground glass joints. A second phosphorus pentoxide tube (G) acted as a guard to keep water vapor from the aspirator bottle from coming in contact with the weighed absorption tube. An oil manometer (E) filled with paraffin oil having a specific gravity of .865 was set in the train between the saturator tube and the weighed phosphorus pentoxide tube.


A
B
B
C
C
D
E
F
G
H
I
J

The air was drawn through the entire apparatus by means of the five gallon aspirator bottle (I) carrying a four hole rubber stopper. Through one hole the entire apparatus was connected with the aspirator bottle. A manometer tube (H) filled with water was sealed into this connecting tube. Through another opening was introduced a syphon tube by means of which the water was run out into weighed flasks in order to determine the volume of air aspirated through the apparatus. The other two openings were closed with tubes carrying glass stop cocks. These were used in refilling the aspirator bottle after completing a run. One connection was attached to the suction pump while the other was attached to a syphon tube dipping into a reservoir of distilled water.

The various parts of the apparatus were separated by pinch cocks which were kept closed when the apparatus was not being run. The entire apparatus was tested for leaks by closing the stopcock near the potassium hydroxide towers and opening the aspirator outlet. No water dropped from the outlet. This was a pull of twenty-four inches of water while during a run the greatest difference in pressure corresponded to a pull of only four or five inches.

It is well known that equilibrium between a solid hydrate and water vapor is reached much more readily in the presence of the anhydrous salt or the next lower hydrate. Therefore in the work on oxalic acid, a quantity of Bakers

C.P. $H_2 C_2 O_4 \ 2H_2O$ was ground to a fine powder in an agate mortar and part of it dehydrated by heating in an electric oven at 100°. Then ten percent of the anhydrous acid was mixed with the hydrated acid and the two mixed by grinding together in an agate mortar. A quantity of glass beads were digested in dichromate-sulfuric acid cleaning solution, rinsed thoroughly and then dried in the electric oven. The saturator tube was filled with alternate layers of the beads and the oxalic acid mixture.

In the work on barium thiosulphate monohydrate the material used was Bakers C.P. Special for Standardizing, and was used without any further purification. The crystals were very fine so that grinding was not necessary. Some of the monohydrate was dehydrated by keeping it in a desiccator over phosphorus pentoxide for some time. This was mixed with the hydrate in such proportions as to give a mixture containing about ten percent of the anhydrous salt. The tubes used in getting equilibrium between the hydrate and air containing more than the proper amount of moisture, were made up with about twenty percent anhydrous salt. The saturator tubes were of several shapes and sizes and these will be described later.

The thermostat in which the saturator tube was immersed was of the DeKhotinsky type controlled by a mercury thermoregulator. The temperature was constant to plus or minus several hundredths of a degree and was set

with a Beckman thermometer which had been calibrated against a Bureau of Standards thermometer.

A very definite and uniform method of weighing the phosphorus pentoxide tube was strictly adhered to, since the amount of water taken up was small. After a run was completed, the absorption tube was closed, disconnected and allowed to stand for about ten minutes so that it might come to room temperature. The reaction between the phosphorus pentoxide and the water liberated heat and also the tube absorbed heat from the constant temperature bath which was very close to it. A counterpoise consisting of a similar tube containing about the same amount of glass beads and phosphorus pentoxide was always counterbalanced against the absorption tube. A stopcock on each tube was opened momentarily to equalize the pressure and then both tubes were dried by gentle wiping with a clean linen towel. The tubes were hung on the balance pans and allowed to stand for ten minutes to dissipate any electric charge. The difference in weight was then obtained with weights calibrated against class M weights. Upon wiping the tubes again and reweighing, they came back to the same weight within .1 milligram. If they were allowed to stand on the pans longer than ten minutes they still gave the same values.

The water from the aspirator bottle was allowed to drop into weighed two-liter flasks and the

water was weighed to the closest gram on an accurate balance. The tip of the syphon tube dipped well into the neck of the flask. To further minimize vaporization of water from the flask, it was covered with paper.

In order to ascertain whether an appreciable amount of water was vaporized from the flask under these conditions, a separate aspirator bottle filled with water, syphon and receiver were set up. The aspirator was weighed and also the receiver, then the water was allowed to drop from the aspirator to the receiver at about the same rate as was used in the determinations. Then the aspirator and receiver were again weighed. The loss in weight of the aspirator was within .1 gram of the increase in weight of the receiver which was about a thousand grams. The amount of water lost in this way is therefore negligible.

The barometric pressure was taken every two hours from a U. S. Weather Bureau type of a barometer. As each run usually occupied two days and a night, all the readings could not be taken from the barometer adjacent to the apparatus. However, the barograph records of the East Lansing station of the U. S. Weather Bureau were available and were used to fill in at the times when it was impossible to get the readings from the barometer in the Kedzie laboratory. The readings of the two barometers agreed very well.

The oil manometer was put into the apparatus in order to find out just where the greatest pressure drop occurred. It was found that the pressure at the oil manometer was almost identical with that at the water manometer in the aspirator. Evidently the greater share of the resistance to the passage of the air was in the saturator while very little resistance was met in the phosphorus pentoxide tubes. Since the two pressures agreed so well the water manometer reading was taken as the drop in pressure through the saturator tube.

In order to make clear the method of calculating the vapor pressures from the data collected an illustration will be given:

Weight of water withdrawn from aspirator = 7954.9 grams.

Temperature of water in aspirator = 23.8°C.

7954.9 grams of water at 23.8°C = $\frac{7954.9}{.99627}$ = 7984 ccs. of water.

Water manometer at the end of experiment =

44 mm = $\frac{44}{13.6}$ = 3.2 mm. Hg.

Barometer reading at end of experiment = 744.4 at 23.5°C.

Correction of barometer to 0° = 2.8

Correction for aqueous tension at 23.8 = 21.9

Corrected pressure in aspirator = 744.4 - 3.2 - 2.8 - 21.9 = 716.5

$7984 \times \frac{716.5}{760} \times \frac{273}{296.8}$ = 6923 ccs. air at standard conditions.

Gain in weight of phosphorus pentoxide tube = .0198 grams.

Volume of water vapor = $.0198 \times \frac{22410}{18.016}$ = 24.63 ccs.

Average barometer during run = 746.2

Corrected average pressure in saturator =

746.2 - 2.8 = 743.4

Partial pressure of water vapor = $\frac{24.63}{6923 + 24.63}$ = .003545

Vapor pressure = .003545 x 743.4 = 2.64

The method as given by Baxter and Lansing was first tried out using oxalic acid dehydrate, $H_2 C_2 O_4 \cdot 2 H_2O$. The saturator tube was in the shape of a large U tube having an inside diameter of 1.8 cm. and containing a column of the acid mixture 71 cm. in length.

The results are given in Table I. The average vapor pressure for $H_2 C_2 O_4 \cdot 2 H_2O$ obtained at 25.0°C was 2.62 mm. For the same compound Baxter and Lansing obtained the value 2.65. These results would indicate that the apparatus was in working order and that saturation had been reached. If the rate of passing the air current through the tube was increased beyond one liter per hour the results were much lower indicating that saturation had not been reached. Schumb (6) has criticized the type of saturation used by Baxter and Lansing saying that saturation could not be reached with narrow tubes. Baxter and Lansing used tubes 1.5 x 30 or 40 cm. while Schumb used tubes 4.5 to 5 x 30 to 50 cm. However, comparing the results obtained by both on $Sr Cl_2$ 6 - 2 H_2O and $Na_2 SO_4$ 10-0 H_2O we find them in agreement.

	Baxter & Lansing	Schumb
$Na_2 SO_4$ 10-0 H_2O at 25°	19.20	19.16
$Sr Cl_2$ 6-2 H_2O at 25°	8.37	8.52

TABLE I.

VAPOR PRESSURE OF $H_2 C_2 O_4 2H_2O$ AT 25.0°C.

Weight of Water Grams	Temp. of Water °C	Water Manometer mm.	Final Barometer mm.	Final Corrected Pressure in Aspirator	Volume Air at Standard Conditions	Weight of Water Absorbed	Average Barometer	Rate Liters per Hour	Corrected Average Pressure in Saturator	Vapor Pressure
5531.1	23.0	79.	730.5	702.6	4733.	.0137	732.2	1.0	729.5	2.62
7954.9	23.8	44.	744.4	716.5	6923.	.0198	746.2	.7	743.3	2.64
7844.6	24.4	55.9	752.5	744.5	6876.	.0193	751.3	.7	748.6	2.61
7212.2	23.3	30.5	740.9	715.2	6295.	.0169	735.8	.7	733.1	(2.44)
6097.3	23.8	30.5	731.7	705.0	5220.	.0153	727.3	.7	724.6	2.63

Average = 2.62

A saturator tube similar to the one used for the oxalic acid was then made up with the barium thiosulfate mixture. A series of runs were made at 25.0°C using a very slow air current. The average rate was about 200 cc. per hour. Each value obtained was less than the preceding one. The values decreased steadily from about 4 mm. to about 1 mm. Then sulfuric acid having a vapor pressure of about 1.5 was put into the drying tubes in place of the concentrated sulfuric acid. Two runs gave 1.43 and 1.78. The sulfuric acid was changed again to that having a vapor pressure of 1.7 with which the values 1.80, 1.65 and 1.54 were obtained for barium thiosulfate. With this same strength acid in the train three runs at 35°C gave 3.08, 2.50 and 2.23.

The conclusion drawn from these results was that the amount of barium thiosulfate used did not offer sufficient surface to obtain equilibrium. As more runs were made the surface of hydrated barium thiosulfate became less thus causing a further falling off in the values obtained. By slowing up the air current it should be possible to at least come closer to establishing equilibrium but the air rate was already as slow as could be maintained practically.

In order to remedy this fault in the apparatus, a large tube having an internal diameter of 3.8 mm. was filled with a column of the beads and barium thiosulfate mixture 48 cm. in length. The results at once became more

constant.

Series of consecutive runs were then made at 25, 35, and 45°C using these larger tubes. Equilibrium was approached from both sides. That is, some runs were made in which moisture was actually removed from the hydrate by the air while others were made in which moisture was taken up from the air by the anhydrous barium thiosulfate. This was accomplished by using sulfuric acid of the desired strength in the train. A trial run was always made to get the actual vapor pressure of the air after it had passed over the sulfuric acid and in each case, the experimental value agreed well with the theoretical value. Not all of these values were obtained on the same tube, but three different tubes were used, each containing over two hundred grams of the hydrate mixture.

The results are tabulated in Tables II, III, and IV. The average results are graphed.

TABLE II.

VAPOR PRESSURE OF BARIUM THIOSULFATE MONOHYDRATE AT 25.0°C.

Weight of Water Grams	Temp. of Water °C	Water Manometer mm.	Final Barometer mm.	Final Corrected Pressure in Aspirator	Volume Air at Standard Conditions	Weight of Water Absorbed	Average Barometer	Corrected Average Pressure in Saturator	Rate: cc per hour	Vapor Pressure of H_2SO_4 in Drying Train	Vapor Pressure
7016	20.7	10.	735.3	714.2	6148	.0160	738.7	735.7	250	1.7	2.38
7685	20.9	10.	733.8	712.3	6711	.0163	729.3	726.2	240	1.7	2.19
6400	23.4	14.	735.5	710.4	5527	.0141	737.6	733.9	190	1.7	2.39
7597	21.2	8.	733.0	708.3	6591	.0156	736.7	733.7	240	2.1	2.16
5782	20.5	10.	747.4	726.2	5155	.0125	742.2	739.1	220	2.1	2.22
80952	22.2	8.	735.0	712.0	7036	.0192	737.2	732.9	270	2.1	2.47
7458	21.0	28.	722.8	699.9	6378	.0176	733.1	728.7	250	3.3	2.48
8236	22.0	31.	732.0	708.0	7113	.0213	726.5	722.1	240	3.3	(2.68)
8267	22.0	38.	729.4	704.7	7117	.0199	730.5	725.4	220	3.3	2.51

Average = 2.35

TABLE III.

VAPOR PRESSURE OF BARIUM THIOSULFATE MONOHYDRATE AT 35.0°C.

Weight of Water Grams	Temp. of Water °C	Water Manometer mm.	Final Barometer mm.	Final Corrected Pressure in Aspirator	Volume Air at Standard Conditions	Weight of Water Absorbed	Average Barometer	Corrected Average Pressure in Saturator	Rate ccs. per hour	Vapor Pressure of H_2SO_4 in Drying Train	Vapor Pressure
5811	24.5	43.	741.4	713.	5022	.0228	737.4	731.8	190	3.3	4.11
5765	24.0	25.	739.8	713.5	4993	.0224	731.0	726.8	170	3.3	4.01
5274	240	11.5	740.3	714.8	4576	.0220	736.2	732.8	190	3.3	4.35
6502	22.6	8.9	7382	714.7	5675	.0241	737.4	734.3	160	3.3	3.86
4789	23.0	8.9	732.4	708.3	4131	.0175	733.9	730.7	130	4.5	3.83
4652	21.5	11.5	736.1	712.5	4665	.0198	738.6	735.4	100	4.5	3.86
4873	23.0	7.6	744.4	720.3	4274	.0174	745.2	742.0	140	4.5	3.74

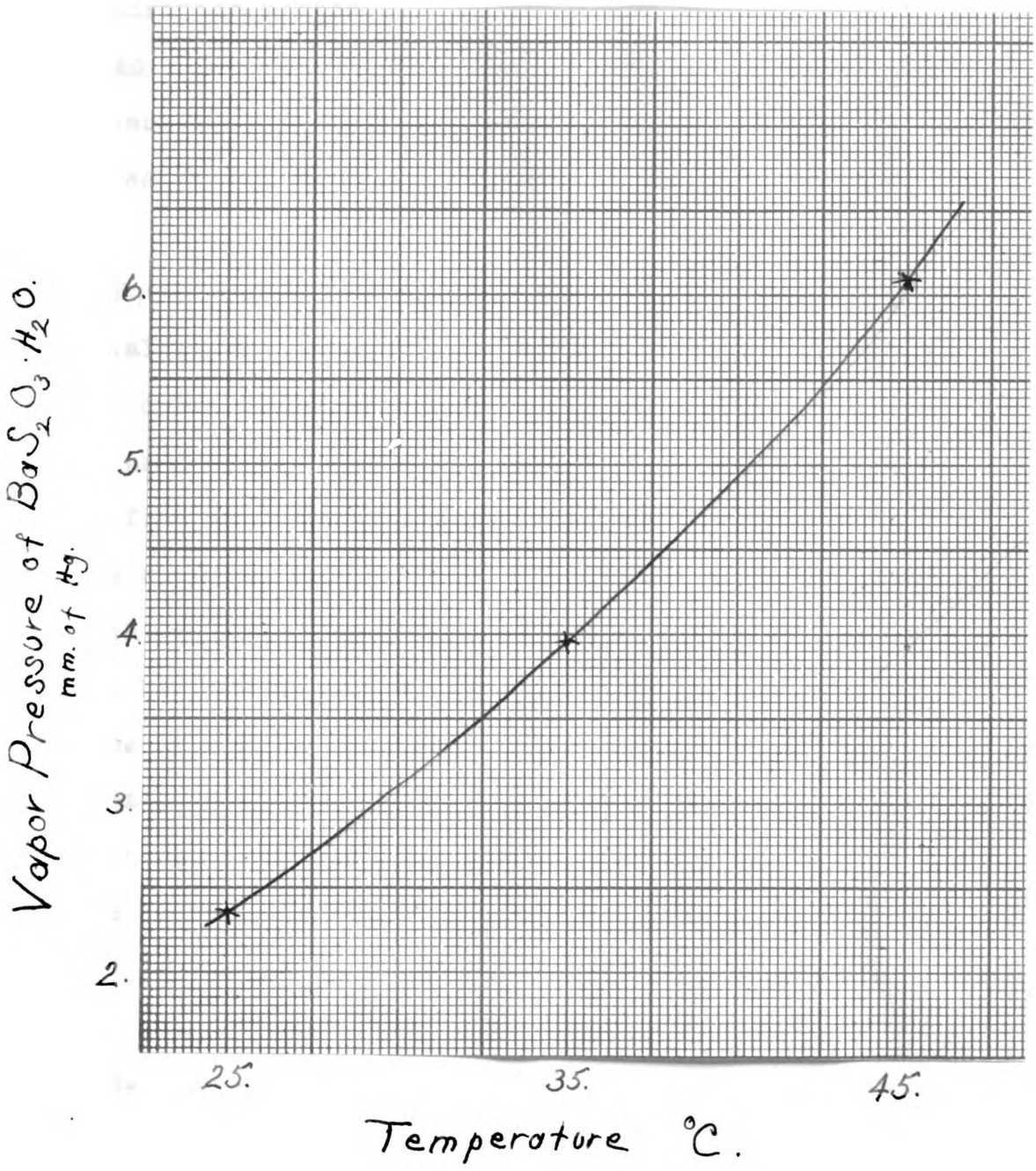
Average = 3.96

TABLE IV

VAPOR PRESSURE OF BARIUM THIOSULFATE MONOHYDRATE AT 45.0 C

Weight of Water Grams	Temp. of Water C	Water Manometer mm	Final Barometer mm.	Final Corrected Pressure in Aspirator	Volume Air at Standard Conditions	Weight of Water Absorbed	Average Barometer	Corrected Average Pressure in Saturator	Rate ccs. per hour	Vapor Pressure of H_2SO_4 in Drying Train	Vapor Pressure
4396	21.0	23.	736.5	713.9	3845	.0245	730.7	724.6	120	4.5	(5.70)
5373	22.0	18.	735.8	712.3	4676	.0315	729.8	725.9	150	4.5	6.03
6129	22.4	42.	749.3	723.3	5407	.0361	747.6	741.7	180	6.0	6.11
5977	21.0	24.	741.8	719.1	5268	.0358	737.7	733.5	180	6.0	6.15
6420	21.6	6.	745.1	723.1	5678	.0373	744.1	741.3	200	6.0	6.01

Average = 6.08


Vapor Pressure of $BaS_2O_3 \cdot H_2O$.
mm. of Hg.
6.
5.
4.
3.
2.
25.
35.
45.
Temperature °C.

This is the first data on a hydrate that is slow in reaching equilibrium that has been done by the air-current saturation method.

An idea of the difference in speed with which barium thiosulfate monohydrate and oxalic acid dihydrate lose their water may be obtained from the following experiment:

Equal weights of the two compounds were put in small crystallizing dishes of the same size which in turn were put in desiccators of the same size and shape containing phosphorus pentoxide. Each sample weighed twelve grams. In five days the barium thiosulfate sample lost .39% of its original weight while the oxalic acid lost 3.23% of its weight. After standing eighteen days the barium thiosulfate had lost 1.22% of its weight while the oxalic acid had lost 11.85%. This amounts to a loss of 18.1% of the total water for the barium thiosulfate compared to 41.4% for the oxalic acid. In six months the barium thiosulfate had lost 1.72% of its original weight and the oxalic acid 28.5%. This amounts to a loss of 25% of the total water for the barium thiosulfate and 99.6% for the oxalic acid.

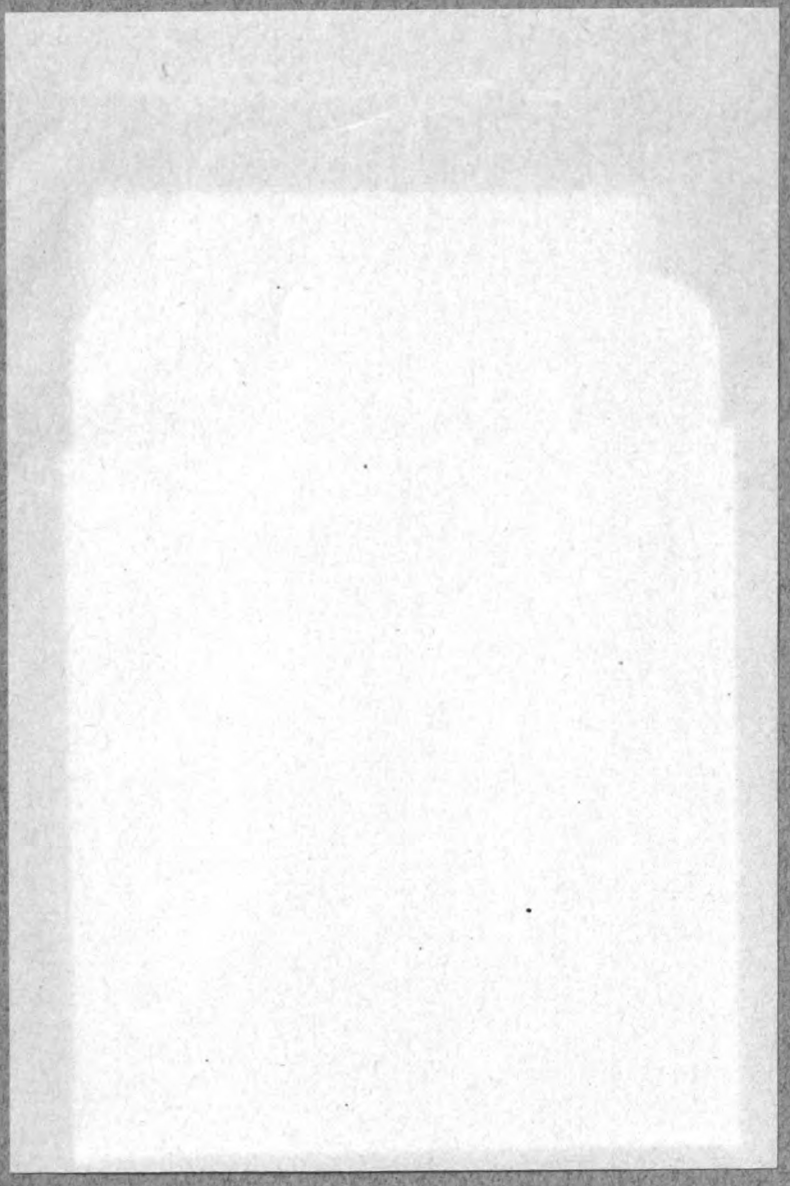
With a hydrate coming to equilibrium so slowly it is improbable that accurate values could be obtained by the air-current saturation method unless the air entering the saturator tube was already close to equilibrium.

This work was carried out in the physical chemistry laboratories under the direction of Dr. D. T. Ewing, whose kind assistance and timely advice is gratefully acknowledged.

CONCLUSIONS.

The vapor pressure of barium thiosulfate monohydrate has been measured at 25.0°, 35.0° and 45.0° by approaching equilibrium from both sides.

The air-current saturation method has been applied to a hydrate which loses its water very slowly.



T546 L531 102366

Leininger