[CONTRIBUTION FROM CAMP DETRICK]

The Use of Diffusion Coefficients in the Measurement of Vapor Pressure

BY WALTER L. CRIDER

RECEIVED SEPTEMBER 15, 1955

From the measured rates of evaporation of water vapor from the surface of pure water into pure nitrogen, hydrogen and carbon dioxide, the mutual coefficients of diffusion have been determined at temperatures of 34, 56 and 76°. By using these values as here determined for the N_2–H_2O system and the measured rates of evaporation of water vapor from solutions of sucrose and from sodium chloride solutions into nitrogen, a new method was used to measure vapor pressures of these solutions by making use of the diffusion theory and a transposed form of the diffusion equation. The sucrose solutions ranged in concentration from 1 to 60% sucrose and the sodium chloride solution studies were from 1 to 25% sodium chloride. Vapor pressures were determined for each concentration of solution at 56 and 76°.

I. Introduction

The theory and experimental procedures of diffusion coefficient measurements were studied in order to find a more accurate and convenient method of measuring vapor pressures of solutions at elevated temperatures. Much previous work[1] has been carried out to determine mutual coefficients of diffusion of water vapor and several common gases from the evaporation rates of water into the gas, and the methods and results of these workers have been carefully considered in the planning of the present experiments. The work of Schwertz and Brow[2] especially was of much value in designing the present apparatus and procedure.

II. Theory of the Method

The rate of evaporation of water into the atmosphere was first used by Stefan[3] to determine the mutual coefficient of diffusion of water vapor and air. More recent studies of the theory of diffusion of water vapor into gases were made by Hippenmeyer,[4] Partington[5] and Jost.[6]

In order to have experimental conditions meet the requirements of the theory, it is necessary to have the liquid container in an isothermal atmosphere of a gas flowing at a sufficient rate to maintain a negligible concentration of vapor at the open end of the tube.

The liquid container was made in such a manner that there was a liquid reservoir of large diameter (5 cm.) from which a diffusion tube of smaller diameter (0.6 cm.) extended. By this construction the liquid level remained essentially constant during a detectable loss in weight of liquid from the container; and further, such loss in weight produced a negligible change in the concentration of the relatively large volume of solution that was placed therein.

The general diffusion equation developed previously for these conditions is expressed as

$$D = WhP_s/APd_s \ln[P/(P - P_s)] \qquad (1)$$

where

D = diffusion coefficient, cm.^{2}/sec.
W = wt. of water lost from container per unit time, g./sec.
h = distance from water level to vapor exit, cm.
P_s = satn. vapor pressure at expt. temp., mm.
A = cross-sectional area of diffusion tube, cm.^{2}
P = total pressure in the diffusion chamber, mm.
d_s = density of vapor at saturation pressure, g./cm.^{3}

For vapor pressure measurements, a transposed form of the above equation was used.

III. Diffusion Apparatus and Experimental Procedure

This experiment utilized an all-glass apparatus similar to that of Schwertz[2] and differing therefrom mainly by the use of a large reservoir of evaporating liquid, as described above. A cathetometer was used to measure the length of the diffusing vapor column while the mass diffused was determined by weighing the remaining liquid periodically in its container.

Before reliable data could be collected, it was necessary to be certain that the theoretical conditions as set forth in the preceding section were being maintained. In order to ensure that a negligible concentration of water vapor was being maintained at the open end of the diffusion tube, the mutual coefficient of diffusion of water vapor and nitrogen was determined at 56° for a series of gas flow rates ranging from 330 to 765 cm.^{3}/min. The results are given in Table I.

TABLE I

MUTUAL COEFFICIENTS OF DIFFUSION[a] OF WATER VAPOR AND NITROGEN AT VARIOUS GAS FLOW RATES

Gas flow rate (cm.^{3}/min.)	D (N_2–H_2O) (cm.^{2}/sec.)
330	0.314
475	.317
605	.315
740	.306
765	.312

[a] At 55.8° and 760 mm. pressure.

Similar experiments were conducted using hydrogen and carbon dioxide.

In order to determine if the diffusion was taking place in an isothermal region, the temperature in the diffusion tube and in the space surrounding the liquid container was measured with a copper–constantan thermocouple having a sensitivity of 0.06°. No temperature differences were detected.

The effect of gas solubility in the liquid on evaporation rates was measured in the CO_2–H_2O system by determining the diffusion coefficients of air saturated water and of carbon dioxide saturated water. The results of these experiments are given in Table II.

In order to eliminate the meniscus of water in the diffusion tube, and thus facilitate the measurement of the level of water below the top of the tube, a very thin coating of "Dry Film"[7] was applied to the inner surface of the tube.

Bottled commercial gases were used in all the experiments. The suppliers' analyses indicated that the purity of each was 98.5+%. The sucrose and sodium chloride were Baker Analyzed Reagents.[8]

---

[1] A bibliography was included in the work of E. R. Gilliland, *Ind. Eng. Chem.*, **26**, 681 (1934).

[2] F. A. Schwertz and J. R. Brow, *J. Chem. Phys.*, **19**, 640 (1951).

[3] J. Stefan, *Ann. Physik*, **41**, 725 (1890).

[4] B. Hippenmeyer, *Z. angew. Physik*, **1**, 549 (1949).

[5] J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Co., New York, N. Y., 1949, pp. 910–912.

[6] W. Jost, "Diffusion in Solids, Liquids, Gases," Academic Press, Inc., New York, N. Y., 1952, pp. 8–10.

[7] Trade name of a General Electric Corp. product.

[8] J. T. Baker Chemical Co., Phillipsburg, N. J.

TABLE II

EFFECT OF GAS SOLUBILITY ON DIFFUSION COEFFICIENT DETERMINATION

System	Av. temp. (°C.)	Diffusion coefficients (cm.²/sec.)	Av. value (cm.²/sec.)
CO_2–H_2O satd. with CO_2	55.6	0.191 .202 .201	0.198
CO_2–H_2O satd. with air	55.5	.185 .189	.187

IV. Experimental Results

Table III compares the results of the present diffusion work with determinations of previous investigators. When hydrogen and carbon dioxide were used, the present results were somewhat lower than those previously reported. The reason for these differences is thought to be in the differences in solubility of the gases in water.

TABLE III

COMPARATIVE VALUES OF DIFFUSION COEFFICIENTS

	H_2–H_2O		CO_2–H_2O		N_2–H_2O	
	34.0°	55.5°	55.5°	34.1°	55.8°	76.0°
Present work	0.915	0.961	0.198	0.257	0.313	0.354
Schwertz	1.02	1.12	.211	.256	.303	.359
Winkelman	0.91	0.99	.192			
Arnold (calcd.)	.792	.895	.183			
Gilliland (calcd.)	.827	.911	.208			
Elastic spheres[a]	1.02	1.13	.232			

[a] As calculated by F. A. Schwertz and J. R. Brow, ref. 2.

The results of the vapor pressure experiments using sucrose solutions as the evaporating medium are listed in Table IV. In order that the vapor pressures of solutions of various concentrations might be calculated for a wider range of temperatures, these experiments were conducted at two temperatures, *viz.*, 56 and 76°.

TABLE IV

VAPOR PRESSURES OF SUCROSE SOLUTIONS AS DETERMINED IN A N_2–H_2O DIFFUSION SYSTEM

Concn. of sucrose, %	Av. temp., °C.	Av. vapor pressure, mm.	No. of experiments
1	76.0	301.7 ± 3[a]	2
3	76.1	304.0 ± 4	4
	56.0	121.3 ± 1	3
5	76.0	302.3 ± 6	4
	56.0	118.6 ± 3	3
13	76.1	299.8 ± 3	3
	56.0	118.0 ± 2	3
20	76.2	299.2 ± 4	3
	56.0	117.5 ± 1	3
30	76.1	294.6 ± 1	3
	55.9	114.7 ± 1	3
40	76.3	288.5 ± 3	4
	56.0	112.5 ± 2	4
50	76.3	285.4 ± 7	4
	56.1	109.0 ± 1	4
60	76.2	261.7 ± 2	3
	56.0	104.7 ± 2	3

[a] Average value ± extreme experimental deviation.

The results of the vapor pressure experiments using sodium chloride solutions as the evaporating medium are listed in Table V.

TABLE V

VAPOR PRESSURES OF SODIUM CHLORIDE SOLUTIONS AS DETERMINED IN AN N_2–H_2O DIFFUSION SYSTEM

Concn. NaCl, %	Av. temp., °C.	Av. vapor pressure, mm.	No. of experiments
1	76.2	307.2 ± 2[a]	3
	55.9	119.3 ± 1	3
3	76.5	302.9 ± 2	3
	56.3	118.0 ± 1	3
5	76.5	303.6 ± 6	3
	56.1	118.7 ± 2	3
10	76.1	287.3 ± 3	3
	55.9	112.7 ± 3	3
20	76.6	260.3 ± 3	3
	56.0	103.4 ± 1	3
25	76.4	238.2 ± 5	3
	56.1	95.6 ± 2	3

[a] Average value ± extreme experimental deviation.

V. Conclusions

From the values as shown in Table IV and V the reproducibility of measurements for this new method of vapor pressure determination is good. The average deviation for each group of measurements ranged from less than ±1% to less than ±3%.

By extrapolating values given in the "International Critical Tables" for the vapor pressures of various concentrations of sodium chloride solutions to the temperatures used in these experiments, it was found that the two sets of data are in good agreement.

Some advantages other than good reproducibility and accuracy of vapor pressure measurements by this new method are found to be: (1) there are no vacuum problems, (2) the problem of maintaining a constant temperature is greatly reduced, (3) the apparatus, once set up, is simple to operate, and (4) it is adaptable for measurements over a wide range of temperatures.

Acknowledgment.—The author is indebted to Mr. Harold Forstat, Pfc. Gordon C. Hunt and Pfc. Richard H. Milburn, Camp Detrick, and to Dr. F. A. Schwertz, Mellon Institute, for advice and encouragement.

FREDERICK, MARYLAND