rather than the view that electrons are transferred from one atom to the other when atoms combine.

I wish to express my appreciation of the valuable assistance of L. C. Johnson, B. R. Honovski, F. O. Anderegg, A. B. Haw, and G. H. Coleman in carrying out the experiments described in this paper.

URBANA, ILL.

VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF NITRIC ACID.

BY WILLIAM C. SPROESSER AND GUY B. TAYLOR.

The partial pressures of water and nitric acid vapors in equilibrium with all concentrations of aqueous nitric acid possess scientific interest and are practically useful to the acid industry. Burdick and Freed[1] have recently supplied data for concentrations ranging from 24% to 70% nitric acid at 25°, 50°, and 75°. The present investigation had as its object the extension of similar data to 100% nitric acid and over a wider temperature range. The dynamic method chosen did not prove suitable for concentrations above 80%, owing to thermal decomposition of nitric acid vapor. The measurements covered the range from 20 to 90% at temperatures from 0° to 80° and, therefore, considerably extend the range, making it possible to draw a series of curves showing the acid composition of minimum vapor pressure within these temperature limits.

Experimental.

The apparatus is shown in Fig. 1. Water from the reservoir A was siphoned into the calibrated bottle B, displacing a known volume[2] of air and forcing it through the dryer C, the carbon dioxide-remover F, the three saturators D, and the absorbers E. The dryer C was a Friedrichs "spiral" gas-wash-bottle containing conc. sulfuric acid. The U-tube F was filled with soda lime. The saturators D were special forms of spiral wash-bottles. In the last bottle a small accurate Anschutz thermometer, 3, was sealed to record the temperature, which was maintained constant to ±0.1°. The three saturators were filled with nitric acid of known composition, fused together, and placed in the Freas constant-temperature oven G. The ground-glass joint, 4, connected the absorbers E to the rest of the system. The whole apparatus was always set up so that nitric acid, liquid and vapor, came in contact with glass only. To avoid condensation in the tube and ground joint protruding from the oven, an electrically heated wire-spiral was placed about the ground joint, 4, to keep the joint warm. The U-tube E, filled with solid sodium hydroxide and followed by two or more such tubes (not shown) containing as well, layers of phosphorus pentoxide on glass wool, was used to absorb the effluent vapors.

[1] Burdick and Freed, THIS JOURNAL, **43**, 518 (1921).

[2] Calculated from the volume of the bottle, temperature and pressure within the bottle, and the barometric pressure.
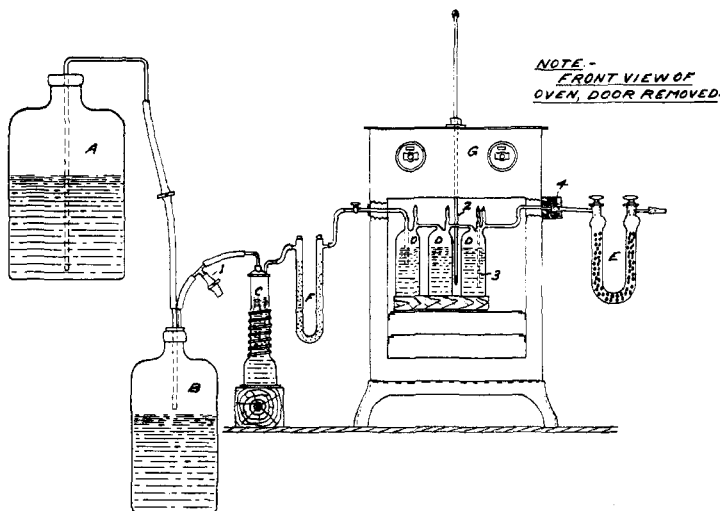
ARRANGEMENT OF APPARATUS USED TO DETERMINE
VAPOR PRESSURES OF NITRIC ACID SOLUTIONS.

After ascertaining the gain in weight of the U-tubes, the nitric acid absorbed by the alkali was determined by the Devarda method and nitrite was estimated by permanganate when found to be present. The results at temperatures from 35° to 82°, were obtained with this apparatus.

The method used for measurements at 0° was somewhat different from that described above. Air was purified from carbon dioxide and dried by passing in succession through a caustic solution and conc. sulfuric acid. The purified air was then bubbled through the saturators, which were entirely immersed in ice-water. Leaving the saturators, the air was passed in succession through (1) a Vanier bulb containing a known amount of standard caustic solution, (2) a large U-tube containing stick sodium hydroxide, at the exit end of which were several layers of phosphorus pentoxide on glass wool, and finally (3) a gas meter accurate to 0.001 cu. ft. The experiments were conducted in a constant-temperature room in order to determine accurately the volume of air passed through the saturators. At the exit end of the saturators there was a pressure of about 10 mm. mercury (above atmospheric) and in the vapor-pressure calculations a correction was made for this added pressure.

Equilibrium was assured at all temperatures by the usual expedient of varying the rate of air flow. Much faster rates than those used in any of the final experiments gave the same results.

TABLE I.

SUMMARY OF EXPERIMENTAL RESULTS.

| Nitric acid. % .	Temp.,°C.	Composition of vapor, %HNO₃.	%H₂O.	%NO₂.	Calculated vapor pressures (mm. Hg). Total.	HNO₃.	Partial. H₂O.	NO₂.
21.25	0.0	0.00	100.00	....	3.8	...	3.8	...
20.65	35.0	0.21	99.79	....	36.8	...	36.8	...
20.65	50.0	0.13	99.87	....	79.9	...	79.9	...
20.65	65.0	0.19	99.81	....	155.6	0.1	155.5	...
20.65	80.0	0.42	99.58	....	293.9	0.4	293.9	...
40.82	0.0	2.02	97.98	....	2.5	...	2.5	...
40.03	35.1	4.38	95.62	....	26.1	0.3	25.8	...
40.03	50.0	3.81	96.19	....	55.6	0.6	55.0	...
40.03	65.0	5.11	94.89	....	117.6	1.8	115.8	...
40.03	80.0	6.40	93.60	....	224.2	4.2	220.0	...
56.26	0.0	22.49	77.51	....	1.4	0.1	1.3	...
56.16	35.0	33.12	66.88	....	17.0	2.1	14.9	...
56.16	50.0	33.87	66.13	....	39.4	5.0	34.4	...
56.16	64.9	33.69	66.31	....	84.6	10.6	74.0	...
56.16	82.0	34.39	65.61	....	182.5	23.5	159.0	...
68.64	0.0	81.03	18.97	....	1.1	0.6	0.5	...
68.42	35.3	69.15	30.85	....	15.9	6.2	9.7	...
68.42	50.1	69.06	30.94	....	35.7	13.7	22.0	...
68.42	74.0	68.76	31.24	....	118.3	45.6	72.6	...
68.42	80.1	68.32	31.68	....	152.8	58.2	94.6	...
79.07	0.0	94.87	5.13	....	2.7	2.4	0.3	...
80.23	35.0	88.56	11.44	....	22.1	15.2	6.9	...
80.23	52.0	89.03	10.92	0.05	50.3	35.2	15.1	....
80.23	65.0	88.49	11.43	0.08	90.0	61.9	28.0	0.1
80.23	82.1	87.13	12.38	0.49	195.2	129.3	65.0	0.9
88.24	0.0	97.75	1.06	1.19	7.8	7.3	0.3	0.2
90.63	35.8	98.27	1.62	0.11	69.7	65.9	3.7	0.1
90.63	50.0	96.55	2.40	1.05	136.2	123.6	10.7	1.9

Discussion of Results.

Table I summarizes the experimental results, giving averages of duplicate runs. The vapor pressures were calculated from the data in the usual manner, *i. e.*, the volume of air and weights of water and nitric acid were calculated to volumes under standard conditions, from which mol fractions were derived. Mol fraction multiplied by the measured pressure prevailing over the solution in the last saturator bottle gave the respective partial pressures. This method of calculation assumes that both water and nitric acid vapors follow the laws of perfect gases.

The experimental results given in Table I were plotted on a large scale to give the usual pressure-temperature curves. Curves were drawn for each acid composition and for the total and partial pressures. These curves were then carefully smoothed out so as to be consistent. From these smoothed curves the plot, Fig. 2, was constructed. On the original large scale plot, 1 mm. = $^1/_{20}$ inch. The smoothed values

read graphically from this large scale plot are assembled in Table II, where the results are recorded to the nearest half millimeter,—no further significant figures being warranted by the precision of the experimental data and methods of calculation. The values in Table II and Fig. 2 are satisfactory for all technical calculations involved in acid manufacture.

Other measurements of the vapor pressures of nitric acid solutions have been made by Saposhnikoff,[3] Burdick and Freed,[4] and Creighton and Githens.[5] Saposhnikoff made his measurements at 15° on concen-
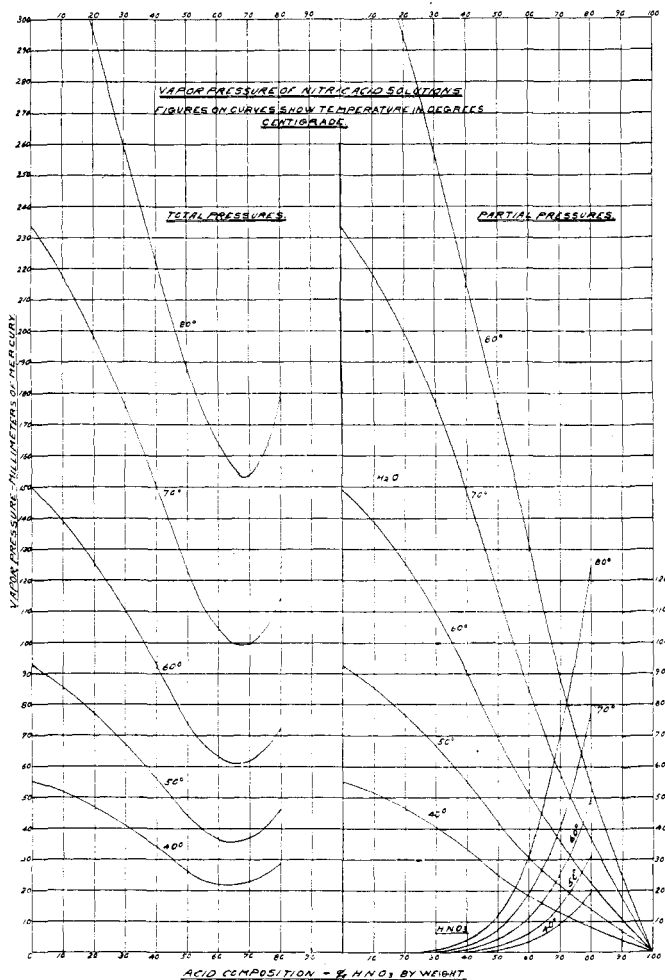
[3] Saposhnikoff, *Z. physik. Chem.*, **53**, 225 (1905).
[4] Burdick and Freed, THIS JOURNAL, **43**, 518 (1921).
[5] Creighton and Githens, *J. Franklin Inst.*, **179**, 161 (1915).

trations of nitric acid ranging from 65 to 100%. Decomposition of nitric acid vapor into nitrogen oxides was encountered at the higher concentrations. Saposhnikoff used a dynamic experimental method and fails to give the method of computation of his results.

TABLE II.

VAPOR PRESSURES OF NITRIC ACID SOLUTIONS.

Pressure in Millimeters of Mercury.

Composition of solution. % HNO₃ by weight.	Tota pressures.								
	0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.	80°.
0	4.5	9.0	17.5	31.5	55	92	149.5	234	..
10	4.0	8.0	16.5	30.5	52	86	139	219	..
20	3.5	7.5	15.5	29.0	47	77	126	199	295
30	3.0	7.0	14.0	25.5	41	67	110	176	259
40	2.5	6.5	12.5	21.0	34	55.5	92	151	222
50	2.0	5.5	10.5	16.5	25.5	44	73.5	124	188
60	1.5	4.0	8.0	13.0	22	36.5	63	104	164
70	1.0	3.5	8.0	12.5	22.5	37	61.5	99.5	153.5
80	3.0	6.0	10.5	17.0	28.5	46	72	114	179
	Partial pressures of water vapor.								
0	4.5	9.0	17.5	31.5	55	92	149.5	234	
10	4.0	8.0	16.5	30.5	52	86	139	219	
20	3.5	7.5	15.5	29.0	47	77	126	199	295
30	3.0	7.0	14.0	25.5	41	67	110	176	258
40	2.5	6.5	12.5	21.0	33.5	55	91	149	217
50	2.0	5.5	10.5	16.5	25	42	69	117	176
60	1.5	4.0	8.0	11.5	18.5	31	51	85	132
70	0.5	2.0	4.5	6.5	13	21.5	36	58	89.5
80	0.5	1.5	2.5	4.5	8.5	14	23	37	54
	Partial pressures of nitric acid vapor.								
0	...	...	...	....	....	....	....	....	.....
10	...	...	...	....	....	....	....	....	.....
20	...	...	...	....	....	....	....	....	.....
30	...	...	...	....	....	....	....	....	1.0
40	...	...	...	....	....	0.5	1.0	2.0	5.0
50	...	...	...	....	0.5	2.0	4.5	7.0	12.0
60	...	...	...	1.5	3.5	5.5	12.0	19.0	32.0
70	0.5	1.5	3.5	6.0	9.5	15.5	25.5	41.5	64.0
80·	2.5	4.·5	8.0	12.5	20.0	32.0	49.0	77.0	125.0

Burdick and Freed's measurements were also made by the dynamic method, and cover the range 24 to 70% acid at three temperatures, 25°, 50°, and 75°. Their results agree very well with those disclosed in this article. Below are compared the data of the two investigations for acid concentrations employed by both and at 50°.

% HNO₃		Partial Pressure H₂O		Partial Pressure HNO₃		Total Pressure	
(S.-T.)	(B.-F.)	(S.-T.)	(B.-F.)	(S.-T.)	(B.-F.)	(S.-T.)	(B.-F.)
40.03	40.2	55.0	53.6	0.6	0.75	55.6	54.3
68.42	69.9	22.0	17.7	13.7	16.6	35.7	34.3

Creighton and Githens measured total vapor pressures by a static method. They determined the boiling temperatures under reduced pressures down to 75°. Their results are considerably higher than ours at corresponding temperatures and concentrations.

Kaltenbach[6] gives graphically the boiling points of nitric acid solutions at atmospheric pressure and the composition of the vapors in equilibrium with the boiling solutions. His results for the partial pressures of nitric acid vapor appear to be lower for concentrations below the acid of maximum boiling point and higher for those above than extrapolation of our results would indicate.

Summary.

1. The total and partial vapor pressures of nitric acid solutions of concentrations approximately 20, 40, 56, 68, and 80% by weight at temperatures of 0°, 35°, 50°, 65°, and 80° have been measured.

2. From these data vapor pressures for each 10% increase in concentration and 10° rise in temperature have been calculated by graphic methods.

3. Attempts to measure the vapor pressure of 90% nitric acid were unsuccessful owing to decomposition of the acid at all the experimental temperatures except at 0°.

The authors wish to acknowledge the helpful advice of Mr. Roger Williams during the course of the investigation and the assistance of Mr. F. C. Blake in constructing the curves.

HENRY CLAY, DELAWARE.

A HIGH PRESSURE DUE TO ADSORPTION, AND THE DENSITY AND VOLUME RELATIONS OF CHARCOAL.[1]

(Papers on Surface Energy and Surface Forces.)

BY WILLIAM D. HARKINS AND D. T. EWING.

1. The Compression of Liquids by Charcoal.

While working on Problem 108 of the National Research Council in the year 1918 the writers discovered an interesting relationship, which is that the volume of different liquids adsorbed by the same charcoal

---

[6] Kaltenbach, *Chimie Ind.*, 2, 143 (1919).

[1] Presented at the Philadelphia meeting of the American Chemical Society, September 1919. This problem was suggested to the National Research Council by the senior author. The data for one charcoal with 11 liquids were published in February 1920 (Harkins and Ewing, *Proc. Nat. Acad. Sciences*, 6, 49–56 (1920)). The present paper is an abstract of a thesis presented to the University of Chicago in August 1919 by D. T. Ewing, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.