THE VAPOUR PRESSURES OF HYDROGEN CYANIDE(1)

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Received March 12, 1926. Published April 28, 1926.

The vapour pressures of hydrogen cyanide were measured at various temperatures between 0°—46° by two of the present authors(2), and, between −15°—183°, by Bredig and Teichmann(3). In the present experiments, the vapour pressures at the low temperatures below zero degree centigrade were measured and the experimental equations for the vapour pressures of solid and liquid hydrogen cyanide were obtained.

The pure hydrogen cyanide obtained in the same way as in the previous experiment(4) was twice fractionally distilled with the aid of solid carbon dioxide and liquid air in the closed system, which had been previously evacuated perfectly; and the final distillate was again distilled into the measuring bulb. The bulb was placed in the thermostat whose temperature was automatically regulated constant within 1/100 degree(5). A closed type manometer was connected to the bulb and the difference of the mercury levels was measured with a cathetometer made by the Société Genevoise.

The results were tabulated in the tables 1 and 2, of which the former was relating to the liquid and the latter to the solid. In both of them, the second columns give the absolute temperatures measured by a platinum thermometer, and the third columns, the observed vapour pressures, each of which is the mean of the several independent observations at the same temperature. These values of the pressures are given in the height of the mercury at 0°, reduced to the sea level at 45° latitude.

(1) This paper is an abstract from the original one, which was read before the monthly meeting of the Chemical Society of Japan in Tokyo on March 6th., 1926, and which is to be published in the Journal of the Chemical Society of Japan (in Japanese) and the Technology Reports of the Tohoku Imperial University (in English).

(2) Hara and Sinozaki, *J. Soc. Chem. Indust. Japan*, 26 (1923), 884. *Technology Reports, Tohoku Imperial University*, IV, (1924), 145.

(3) Bredig and Teichmann, *Z. Electrochem.* 31 (1925), 449.

(4) Hara and Sinozaki, loc. cit.

(5) Sinozaki and Hara, *J. Soc. Chem. Indust. Japan*, 29 (1926).

TABLE 1.

Exp. No.	$T°$ abs.	P obs. mm.	P calc. (1) mm.	P calc.(1) -P obs. mm.	P calc. (2) mm.	P calc.(2) -P obs. mm.	P calc. (3) mm.	P calc.(3) -P obs. mm.
29′	256.74	120.05	120.92	+0.87	118.40	− 1.65	119.84	−0.21
5′	259.92	140.78	141.90	+1.12	140.00	− 0.78	141.16	+0.38
28′	260.07	142.32	142.92	+0.60	141.08	− 1.24	142.23	−0.09
26′	261.12	149.80	150.57	+0.77	148.81	− 1.76	149.85	+0.05
27′	262.12	157.58	158.16	+0.48	156.41	− 1.75	157.36	−0.22
4′	262.85	163.16	163.95	+0.79	162.24	− 0.92	163.10	−0.06
3′	265.63	186.54	187.36	+0.82	185.98	− 0.56	186.50	−0.04
2′	268.96	219.81	219.08	−0.73	218.14	− 1.67	218.21	−1.6
1′	272.40	256.31	256.47	+0.16	256.02	− 0.29	255.54	−0.77
16	273.18	265.2	265.7	+0.5	265.33	+ 0.1	264.73	−0.5
1	277.19	316.8	317.3	+0.5	314.86	− 1.9	316.34	−0.5
2	280.07	358.6	359.3	+0.7	360.15	+ 1.6	358.34	−0.3
3	283.09	407.8	408.2	+0.4	409.59	+ 1.8	407.28	−0.5
4	286.27	465.4	465.5	+0.1	437.44	+ 2.0	464.66	−0.7
5	288.98	519.4	519.4	—	521.79	+ 2.4	518.67	−0.7
6	291.97	584.7	584.6	−0.1	588.72	+ 4.0	584.17	−0.5
7	294.90	654.4	655.0	+0.6	658.17	+ 3.8	654.82	−0.4
8	297.75	730.6	730.1	−0.5	733.27	+ 2.7	730.10	−0.5
9	300.78	816.2	817.7	+1.5	820.37	+ 4.2	817.75	+1.6
10	303.75	911.1	911.2	+0.1	913.48	+ 2.4	911.84	+0.7
11	307.08	1028.4	1026.6	−1.8	1027.5	− 0.9	1027.6	−0.8
12	309.78	1128.2	1128.2	—	1127.9	− 0.3	1130.0	+1.8
13	313.25	1272.2	1271.1	−1.1	1268.0	− 4.2	1273.5	+1.3
14	316.02	1393.2	1395.5	+2.3	1389.2	− 4.0	1398.4	+5.2
15	319.39	1564.1	1559.2	−4.9	1548.3	−15.8	1563.4	−0.7

TABLE 2.

Exp. No.	$T°$ abs.	P obs. mm.	P calc. (5) mm.	P calc. (5)−P obs. mm.	P calc. (6) mm.	P calc. (6)−P obs. mm.
21′	187.09	0.132	0.143	+ 0.011	0.161	+ 0.029
20′	194.52	0.376	0.382	+ 0.006	0.411	+ 0.035
19′	199.76	0.745	0.729	− 0.016	0.733	− 0.012
18′	206.44	1.562	1.564	+ 0.002	1.602	+ 0.04
17′	207.11	1.673	1.685	+ 0.012	1.720	+ 0.047
16′	212.41	2.97	2.95	− 0.02	2.98	+ 0.01
15′	217.52	4.97	4.93	− 0.04	4.93	− 0.04
14′	221.84	7.48	7.43	− 0.05	7.39	− 0.09
13′	227.00	11.78	11.85	+ 0.07	11.75	− 0.03
12′	229.02	13.92	14.13	+ 0.21	14.00	+ 0.08
11′	233.13	19.72	19.99	+ 0.27	19.79	+ 0.07
10′	238.87	31.24	31.69	+ 0.45	31.42	+ 0.18
9′	243.96	46.26	46.71	+ 0.45	46.43	+ 0.17
8′	248.78	66.03	66.34	− 0.31	66.13	+ 0.10
7′	254.02	96.26	95.33	− 0.93	95.53	− 0.73
30′	254.46	97.97	96.27	− 1.70	98.45	+ 0.48
22′	258.83	131.29	130.99	− 0.36	131.97	+ 0.68
6′	258.87	131.93	131.26	− 0.67	132.35	+ 0.42
23′	259.18	134.29	133.98	− 0.31	135.03	+ 0.74
24′	259.56	137.45	137.30	− 0.15	138.53	+ 1.08

From the values of the above tables, the following experimental equations were obtained, in which (1) to (4) were those for liquid, and (5) and (6) were those for solid.

$$\log P_{\text{mm.}} = \frac{-1836.63}{T^{1.05}} + 7.5030 \quad \dots\dots\dots(1)$$

$$\log P_{\text{mm.}} = \frac{-1556.14}{T} + 1.75 \log T - 0.0038273\,T + 4.90192 \quad \dots\dots(2)$$

$$\log P_{\text{mm.}} = \frac{-1460.04}{T} + 0.47647 \log T - 0.0007344\,T + 6.82130 \quad \dots\dots\dots(3)$$

$$\log P_{\text{mm.}} = \frac{-1732.58}{T} + 1.75 \log T - 0.010760\,T + 8.3163 \times 10^{-6}\,T^2 + 6.82130 \quad \dots\dots\dots(4)$$

$$\log P_{\text{mm.}} = \frac{-9745.56}{T^{1.35}} + 7.5030 \quad \dots\dots\dots(5)$$

$$\log P_{\text{mm.}} = \frac{-2014.39}{T} + 1.75 \log T - 0.004077\,T + 6.82130 \quad \dots\dots(6)$$

The equations (1) and (5) are those of Henglein type[(1)], and the values calculated by those equations and the differences from the observed values are given in the fourth and the fifth columns of both tables.

The equations (2) and (6) are those of Nernst type. The values calculated with the equation (6) are given in the sixth column in the table 2, which coincide with those observed as indicated in the seventh column of the same table. But the values calculated with the equation (2) for the vapour pressure of the liquid do not coincide with those observed. The present authors, therefore, modified the equation (2) as (3) and (4), of which the equation (3) was obtained by the least square method from the observed values, the last term being taken as the same as that in the equation (6), and the equation (4) was obtained also by the least square method, whose second and the last terms being taken as constant. Of these two equations, the former gives the best calculated values for the liquid as indicated in the 8th and 9th columns of the table 1, and the latter gives only a little better values than those from the equation (2).

The full details of the experiments and some thermodynamical calculations are to be found in the original paper.

February 28, 1926.

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