Part II.—The Vapour Pressures of Concentrated Solutions.

By G. R. Paranjpé, M, Sc., Springer Research Scholar of the University of Bombay.

Accurate values of the vapour pressures of concentrated solutions of potassium hydroxide are sometimes required in gas-analysis, where these solutions are largely used as absorbents. There are no data available for concentrated potassium hydroxide solutions containing 50 gm of anhydrous substance and more in 100 gm of water for temperatures above 20°C.

The most extensive series of measurements was made by Wuellner (Pogg. Ann. 1860, *110*, 566) for different concentrations of solutions of sodium and potassium hydroxides over a temperature range of 10° to 99°C.

Gerlach (Zeitschr. Analyt. Chem. 1887, *26*, 413) has given the boiling points at 760 mm pressure of sodium and potassium hydroxide solutions of various strengths.

Tammann's (Mém. de l'Acad. Petersb. 1887, *7*, 35) results supply the vapour pressures of solutions of sodium hydroxide, potassium hydroxide, calcium chloride and other salts for different concentrations at 100°C. The highest concentrations are, however, about 75 gm of salt in 100 gm of water.

Emden (Wied. Ann. 1887, *31*, 170) made measurements between 19° and 40°C of solutions of calcium chloride but the range of concentration was very small, lying between 12 to 20 gm. of anhydrous salt in 100 gm. of water.

Perman and Price (Trans. Faraday Soc. 1912, *8*, 68) carried out some accurate measurements on the vapour pressures of calcium chloride solutions for different concentrations and at temperatures of 70° and 90°C, by using the dynamical method.

Dieterici (Wied. Ann. 1891, *42*, 513; 1893, *50*, 47; 1897, *62*, 616) has given figures for sodium hydroxide, potassium hydroxide and calcium chloride solutions of different strengths at 0°C. Reference will be made to these later on.

Potassium hydroxide solutions were investigated by Smits (Zeitschr. Physik. Chem. 1902, *39*, 385; 1905, *51*, 33) at 0° but the highest concentration used by him was only 14·6 gm. of salt in 100 gm. of water.

For satisfactory and complete absorption work, solutions of considerably greater concentration than 50 gm. in 100 gm. of water are used and the room temperature in this country is nearly always above 20°C. This made the work of direct measurements of vapour pressures over a greater range of concentrations and temperatures desirable. An extrapolation with the help of already existing results is unsatisfactory, firstly because the laws governing the vapour pressures of concentrated solutions are not known, and secondly because the change of vapour pressure with temperature is very rapid and approximate estimations on the basis of some assumed law may introduce a considerable error.

Various theories have been put forward dealing with the vapour pressures of concentrated solutions of salts in water, but the measurements necessary to verify them are few in number. In order to supply more data for this purpose the present measurements have been extended to solutions of caustic soda and calcium chloride.

Experimental.

The general method of carrying out this series of experiments was, with a few modifications, identical with that adopted for the determination of the vapour pressure of acetone (*cf.* pp. 47, 48, 56.)

Instead of admitting the solution under examination directly into a glass container, a small thin silver tube of 22 mm. diameter and 60 mm. height was used. This precaution was necessary in order to prevent the concentrated alkaline solutions from acting on glass, particularly as the solution occasionally remained in the vessel for a week or more. The silver vessel was contained in a tight fitting glass tube which was directly fused on to the manometer.

In the rubber cork, which closed this glass tube, containing the solution, there was a funnel to carry water; the latter consisted of a series of five bulbs of various sizes blown on a very fine capillary and calibrated carefully between marks on successive portions of the capillary with air-free distilled water. These were joined through a tap on to a wider capillary which was long enough to reach about half the length of the silver tube. By this means known quantities of water could be added to the solution. The wider bore of the lower part of the funnel, *i. e.* below the tap, was necessary to allow the water to drain out of it freely.

The weight of water delivered out of each of these bulbs is given below and was found to be a consistent figure. The topmost bulb is numbered 1 and so on.

Bulb No.	Wt. of distilled water (delivered)
1	0·7356 grams.
2	0·7596 ,,
3	1·0520 ,,
4	1·5632 ,,
5	2·4382 ,,

The bore of the capillary tube was determined, so that, in the event of the water not reaching exactly to a mark, a correction would be applied. One millimeter length of this capillary had a volume of 0·15 cubic millimeters, so that the magnitude of the correction is exceedingly small.

The thermostat consisted of a large Dewar's cylindrical vacuum vessel, filled with water at the desired temperature. The accuracy with which it was proposed to measure the temperatures of the solutions was 0.1°C and it was found possible by means of a stirrer and an electric heater, to keep the temperature of the thermostat steady within a smaller range than this for at least an hour. The heater was made of nichrome wire, 532 mm. long and 3 ohms resistance, enclosed in a glass sheath. A rough calibration was done to obtain an idea of the current that must be sent through this heater to produce enough heat to balance the loss due to radiation, etc. at various temperatures.

It was not found convenient to place a thermometer directly in the solution under observation, so the temperature measurements were made in the bath as close as possible to the silver tube containing the solution. A mercury thermometer graduated in 1/5° and carefully calibrated with a standard instrument was used. Readings were only taken when the pressure in the manometer was quite steady and with this condition there seems no reason for suspecting that equilibrium between the solution and the thermostat liquid was incomplete.

Every time an experiment was started, a weighed quantity of the substance under investigation was introduced into the silver tube, the stirrer adjusted, and the cork, carrying the bulbs filled with air-free distilled water, mounted and cemented with a mixture of beeswax and resin. All possible air in the apparatus was removed by means of the pump after the solution tube was cooled below—60°C in alcohol cooled in liquid air. The water from the first bulb was then let into the silver tube under constant agitation of the electro-magnetic stirrer. The solution was afterwards repeatedly frozen and the gases above it pumped out rapidly a number of times to get all possible air out of the solution. The temperature was then kept as constant as possible and measurements of the vapour pressure were made at intervals by reading the pressure difference in the manometer. Under suitable conditions the equilibrium was maintained for half an hour at least, to minimize the errors due to changes in temperature. Afterwards similar series of readings were taken at different temperatures of the thermostat. The contents of the second bulb of water were then emptied into the solution and the same process gone through as before. When the measurements had been completed, the quantity of the anhydrous substance was estimated either by titration or gravimetrically. Thus, knowing the weight of the anhydrous substance, the original weight taken of the moist substance, and the weight of water in each of the bulbs, the concentrations of the various solutions could be calculated. All concentrations in these experiments are expressed as g grams of the anhydrous substance dissolved in 100 grams of water. This is the method followed by Tammann, Dieterici and others.

It is to be remembered that the vapour pressure of ice below—60°C is lower than 0·002 mm. (Weber, Science Abstract; 1917, *20*, 411,) and hence the vapour pressure of the solution at that temperature is lower still; so that, if the evacuation is effected rapidly enough, while the solution is frozen at a temperature below —60°, no measurable quantity of water is removed from the solution and there is no appreciable change in the concentration.

A possible error when dealing with concentrated solutions might arise from the amount of water present in the apparatus as vapour although assumed to be in the solution.

The total volume of the dead space above the solution and in the manometer was 100 cc., so that the weight of water vapour it would hold at 10 mm pressure is 0·0095 gm. The smallest weight of water ever in the silver tube was 0·8 gm and the greatest pressure with this quantity about 10 mm so that the water in the dead space would weigh the above amount and the difference in concentration produced is probably beyond the limit of experimental error.

Another error may arise from impurities in the substances used. It is very difficult to work with sodium and potassium hydroxides quite free from carbonate, and analysis showed that the samples used both contained on an average 2·0% of carbonate. As however the potassium hydroxide contained about 16% of water while the sodium hydroxide was practically anhydrous, the ratio of carbonate to hydroxide was greater in the former case.

Now 2 g of sodium carbonate is equivalent to 1·5 g of hydroxide and the vapour pressure of 98 g of hydroxide mixed with 2 g of carbonate in a solution may be assumed very nearly equal to that of 99·5 g of pure hydroxide. Consequently if the mixture is estimated volumetrically with methyl orange as indicator and the concentration calculated as that of pure hydroxide, for the purpose of vapour pressure measurements, the error would be negligible. It will be observed, however, that if this is done, the weight of water obtained by difference will be 0·5 g too large. As in the largest concentrations used about 76 g of water were taken to 100 g of hydroxide, this small extra quantity would not affect the results. The same holds good for potassium hydroxide.

Results.

The results of direct observations are given in Tables I, II and III. The logarithms of the vapour pressures for each solution were first plotted against the corresponding temperatures and smooth curves drawn through the points as shown in diagram No. 2.

This method of plotting is adopted because the pressure-temperature diagram is given approximately by an exponential curve so that the *log p* and *t* curve is nearly a straight line.

From these curves a second set was drawn showing the variation of vapour pressure with change in concentration for a constant temperature. These are shown in diagram No. 3 and the results are tabulated below in Tables IV, V and VI.

In the case of the lower concentrations and higher temperatures, direct measurements of the vapour pressure could not be made, as water distilled from the solution and condensed in the manometer as soon as the vapour pressure of the solution rose above about 23 mm. The figures given in brackets were obtained by extrapolation along curves running parallel to the water vapour pressure curve, and any error introduced should be slight, since all the curves were approximately parallel except at the higher concentrations. The vapour pressures for water are taken from the measurements by Scheel and Heuse (Ann. d. Physik. 1910, *31*, 715).

The experiments were carried out regardless of the solubility of the substance under examination, and consequently, in several cases there was a solid present in the solution. When this condition occurs the vapour pressure should remain constant with increasing quantities of solid and be equal to that of the saturated solution. In practice, it was found that the vapour pressure continued to diminish after passing the saturation point, but more slowly than before, and sometimes an approximate constancy was found. The decrease is probably due to supersaturation and was most marked in the case of calcium chloride. As the solutions were in a silver tube it was not possible to observe the point at which solid separated, but in many cases the mass became viscous and difficult to stir, and the readings were irregular, showing that equilibrium was not properly established.

A mark is made on the curves at the saturation point as determined by Pickering (Journ. Chem. Soc. 1893, *63*, 908) and concentrations apparently greater than this are underlined in the tables. The change in direction of the curves begins very approximately with these points.

The final results do not agree very closely with those of other observers as may be seen from table VII. The greatest discrepancies are found in the case of Dieterici's values for potassium hydroxide (a) although his figures for sodium hydroxide and calcium chloride (b) are almost identical with the present measurements. The author does not state the method he used for determining the concentrations of his solutions and he gives the vapour pressure at 0° for a solution containing 173 g of potassium hydroxide to 100 g of water while the solubility according to Pickering (Journ. Chem. Soc. 1893, *63*, 908) is only 97 gms.

If Dieterici's values are recalculated, assuming that his potassium hydroxide contained 76% of salt, the figures in column four—table VII (a)—are obtained, agreeing almost exactly with the present measurements. It appears therefore that there is some error in the calculation of these figures.

It is interesting to notice that the isothermal curves have the same shape as Tammann's curves for potassium and sodium hydroxide and calcium chloride at 100°C and those of Perman and Price for calcium chloride at 70° and 90°C.

A comparison of Wuellner's results with those obtained here in the case of potassium and sodium hydroxide indicates that the former are invariably higher. Table VII (c, d).

Summary.

It is shown that under proper conditions the statical method can be conveniently used for measuring the vapour pressures of solutions of various concentrations.

Measurements are made between temperatures 0° and 40°C of vapour pressures for solutions of:—

1. Potassium hydroxide for concentrations between 18·81 and 138·2 gms. of anhydrous salt in 100 gms. of water.
2. Sodium hydroxide for concentrations between 14·62 and 113·1.
3. Calcium chloride for concentrations between 14·81 and 119·5.

In the case of potassium hydroxide, it is pointed out that the accuracy of Dieterici's determinations of vapour pressures at 0° is doubtful.

I have great pleasure in expressing my sincere gratitude to Dr. H. E. Watson for his valuable advice and constant interest in the course of these experiments. My best thanks are also due to Dr. J. J. Sudborough for allowing me to work in these laboratories.

DEPARTMENT OF GENERAL AND ORGANIC CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

TABLE 1.

Potassium Hydroxide.

g grams of anhydrous salt in 100 grams of water.

g=18·8		g=22·4		g=28·5		g=29·3		g=33·1	
t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm
0·0	3·93					0·0	3·42	0·0	3·18
9·3	7·48	23·0	17·37	27.7	21.22	10·5	6·99	9·9	6·04
19·1	14·31	28·4	24·27	32·4	27·67	19·7	12·78	21·4	12·64
25·3	20·78	30·0	26·69	36·4	32·68	21·5	14.24	27·2	18·99
						28·3	21·61		

g=34·8		g=37·4		g=41·2		g=44·0		g=45·7	
t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm
								0·0	2·52
20·0	12·49	21·1	12·18	5·0	4·18	25·7	14·55	10·5	5·17
27·8	19·48			19·9	10·64	27·5	16·54	19·3	9·21
30·1	22·07			30·3	19·93	31·6	20·81	29·1	16·95
33·2	26·36					36·3	26·97		

g=53·8		g=54·8		g=57·3		g=62·3		g=73·3	
t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm
		0·0	2·00					0·0	1·28
21·9	9·21	9·6	4·13	15·2	5·35	17·6	5·65	9·6	2·51
29·0	14·02	19·1	7·67	18·3	6·63	23·4	8·15	19·5	4·79
32·0	16·97	30·1	14·87	24·5	9·90	30·2	12·39	30·0	9·33
40·1	26·71			30·1	14·06	35·2	16·60	40·0	16·68
				34·8	18·37	39·1	20·99		

g=84·9		g=87·1		g=92·7		g=94·4		g=101·2	
t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm
						0·0	0·68		
20·4	3·73	18·8	3·19	21·5	3·19	9·0	1·36		
26·1	5·43	19·2	3·29	22·5	3·39	21.7	3·33	24·5	3·09
28·0	6·13	24·2	4·65	22·8	3·50			30·0	4.46
36·0	9·95	30·7	6·91	30·4	5·68	30·3	5·63		
40·6	12·98	41·0	12·57	40·2	10·18	39·9	9·68	40·0	7·69

TABLE 2.

Sodium Hydroxide.

g grams of anhydrous salt in 100 grams of water.

g = 14·6		g = 15·3		g = 17·5		g = 21·2		g = 27·1		g = 33·6	
t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm
		0·2	3·94	0·4	3·88						
23·1	18·38	7·2	6·33					1·4	3·42		
23·6	19·18	15·2	10·80	15·2	9·76			8·9	5·79	20·4	10·50
		22·8	17·71	20·9	15·23	24·1	17·45	15·4	8·86	24·8	13·71
				28·0	23·59			21·7	13·22	30·3	19·30
								23·2	14·44		
								28·8	20·53		
								30·1	22·11		

g = 43·1		g = 53·6		g = 60·2		g = 63·5		g = 89·5		g = 113·1	
t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm
				0·0	1·03						
9·8	3·74	18·2	4·76	10·4	2·10	9·7	2·03			9·2	0·51
11·7	4·29	19·9	5·35	19·3	4·02			20·3	1·85	20·1	1·24
20·0	7·58	23·2	6·70			25·1	5·42			23·2	1·48
22·4	8·95	30·1	10·41	30·3	8·31	30·5	7·63	30·4	3·88	30·3	2·55
29·8	14·02	35·4	14·13	40·6	15·58			35·1	5·22		
		40·1	18·81			40·4	13·90	40·2	7·28	40·3	4·57

TABLE 3.

Calcium Chloride.

g grams of anhydrous salt in 100 grams of water.

g = 14·81		g = 21·05		g = 27·74		g = 33·17		g = 37·32		g = 43·57	
t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm
0·0	4·24	0·0	3·81			0·0	3·33	0·0	3·26	0·0	2·95
8·8	7·69	9·7	7·43	4·3	5·78	9·6	6·82	9·1	6·05		
21·6	17·59	14·9	11·07			22·0	14·99	22·2	14·31	14·4	7·66
22·7	18·85	23·4	18·25	22·2	16·48	28·6	22·01	29·8	22·02	23·5	13·44

g = 52·58		g = 62·12		g = 68·68		g = 83·66		g = 119·5	
t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm	t°C	p mm
0·0	2·48	0·0	1·95			0·0	1·09	0·0	0·97
8·1	4·39	7·4	3·28	15·5	4·61	9·8	2·73		
18·0	8·32	12·2	4·50	20·0	6·17	15·4	4·69	18·7	3·69
23·3	11·68	19·4	7·28	24·4	8·25	21·5	6·13	22·2	6·26
26·2	13·93	21·2	8·19	30·2	11·90	25·2	6·77	29·7	6·88
33·5	21·07	29·8	14·07	35·3	16·18	29·9	9·04	39·6	10·95
		34·1	18·04	40·2	21·30	53·2	12·58	40·5	11·20

TABLE 4.

Potassium Hydroxide.

g grams of anhydrous salt in 100 grams of water.

g.	0°C p mm	10°C p mm	20°C p mm	25°C p mm	30°C p mm	40°C p mm
20	3·88	7·78	14·87	20·24	(27·14)	(47·48)
25	3·66	7·23	13·85	18·85	(25·26)	(44·37)
30	3·42	6·60	12·76	17·35	23·55	(41·18)
35	3·15	6·03	11·63	15·90	21·70	(37·70)
40	2·87	5·52	10·56	14·53	19·87	(34·43)
45	2·57	5·03	9·56	13·21	18·09	(31·20)
50	2·25	4·53	8·61	11·90	16·35	(28·16)
55	1·98	4·05	7·70	10·66	14·71	(25·34)
60	1·75	3·61	6·85	9·49	13·13	22·71
65	1·52	3·19	6·09	8·40	11·58	20·27
70	1·33	2·82	5·39	7·38	10·24	18·02
75	1·15	2·47	4·83	6·45	9·00	15·94
80	1·01	2·17	4·22	5·55	7·87	14·06
85	0·87	1·88	3·64	4·87	6·95	12·35
90	0·75	1·67	3·10	4·24	6·05	10·81
95	0·64	1·50	2·60	3·74	5·26	9·44
100	0·56	1·30	2·31	3·22	4·54	8·25
105			1·99	2·79	3·95	7·28
110			1·74	2·46	3·46	6·45
115			1·56	2·22	3·07	5·73
120			1·48	2·06	2·81	5·09
125			1·46	1·94	2·60	4·59
130			1·44	1·88	2·45	4·15
135			1·42	1·82	2·33	3·63

TABLE 5.

Sodium Hydroxide.

g grams of anhydrous salt in 100 grams of water

g	0°C p mm	10°C p mm	20°C p mm	25°C p mm	30°C p mm	40°C p mm
15	3·97	7·77	15·18	20·52	(27·73)	(48·37)
20	3·69	7·08	13·90	18·84	(25·54)	(44·90)
25	3·34	6·30	12·50	17·04	23·23	(40 82)
30	2·92	5·56	11·11	15·13	20·56	(36·41)
35	2·51	4·83	9·75	13·22	17·91	(32·10)
40	2·16	4·12	8·40	11·33	15·35	(27·67)
45	1·82	3·51	7·17	9·72	13·21	23·62
50	1·50	2·98	6·08	8·25	11·27	20·26
55	1·20	2·52	5·13	7·01	9·59	17·44
60	0·92	2·13	4·31	5·97	8·23	15·10
65		1·83	3·61	5·06	7·05	12·99
70			3·07	4·36	6·12	11·30
75			2·62	3·66	5·29	9·86
80			2·26	3·23	4·61	8·74
85			1·95	2·74	4·07	7·77
90			1·74	2·49	3·56	6·93
113·1			1·18	1·66	2·35	4·57
134·2			1·06	1·56	2·30	3·91
173·1					2·29	3·76

TABLE 6.

Calcium Chloride.

g grams of anhydrous salt in 100 grams of water.

g	0°C p mm	10°C p mm	20°C p mm	25°C p mm	30°C p mm	40°C p mm
15	4·26	8·39	15·73	21·22	(28·63)	(50·37)
20	4·02	8·04	15·34	20·42	(27·24)	(48·18)
25	3·78	7·62	14·48	19·26	(25·78)	(45·25)
30	3·52	7·17	13·58	18·09	(24·29)	(42·52)
35	3·29	6·70	12·63	16·89	22·66	(39·64)
40	3·06	6·21	11·62	15·65	21·04	(36·74)
45	2·92	5·69	10·54	14·32	19·48	(33·88)
50	2·61	5·12	9·59	13·11	17·93	(31·12)
55	2·29	4·60	8·64	11·90	16·38	(28·46)
60	2·01	4·13	7·72	10·72	14·85	(25·95)
65	1·74	3·68	6·81	9·59	13·40	23·59
70	1·51	3·32	5·98	8·50	12·09	21·45
75	1·30	3·03	5·46	7·72	10·91	19·49
80	1·12	2·78	5·13	7·10	9·85	17·73
85	1·01	2·68	4·95	6·62	8·84	16·17
119·5	0·97					10·90

TABLE 7.

(a)

*In this column Dieterici's re-calculated values are given (cf. p. 64.)

KOH g	Dieterici 0° p mm	Paranjpé 0° p mm	Dieterici* 0° p mm
27·14	3·898	3·56	3·52
40·40	3·470	2.84	2·79
66·86	2·593	1·45	1·40
107·2	1·547	0·38	

(b)

NaOH g	Dieterici 0° p mm	Paranjpé 0° p mm	$CaCl_2$ g.	Dieterici 0° p mm	Paranjpé 0° p mm
20·50	3·598	3·65	18·16	4·137	4·12
27·24	3·112	3·15	35·83	3·296	3·27
35·18	2·516	2·49	54·34	2·277	2·26
47·44	1·624	1·63			

(c)

KOH g	10° p mm		20° p mm		30° p mm		40° p mm	
	Wuellner	Paranjpé	W	P	W	P	W	P
20	8·13	7·78	15·42	14·87	27·61	27·14	47·8	47·48
30	7·16	6·60	13·80	12·76	25·41	23·55	43·5	41·18
40	6·50	5·52	12·40	10·56	22.91	19·87	38·46	34·43
49	5·62	4·63	10·75	8·80	20.89	16·70	34·51	28·77

(d)

NaOH g	20° p mm		30° p mm		40° p mm	
	Wuellner	Paranjpé	W	P	W	P
20	14·0	13·90	26·0	25·54	45·7	44·90
30	11·9	11·11	22·4	20·56	40·5	36·41