

# On the Measurements of the Vapour Pressures of Concentrated Aqueous Solutions of Potassium Iodide.

By

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The vapour pressures of the aqueous solutions of various substances were measured at various concentrations by many investigators. But there are only a few examples of measurements for highly concentrated solutions, especially at high temperatures. As for the vapour pressures of the potassium iodide solutions, Tamman,<sup>1</sup> Dieterici<sup>2</sup> and Børsted<sup>3</sup> measured them only in dilute conditions and at temperatures below 100°C, so the writer carried out the measurements of the vapour pressures of the concentrated potassium iodide solutions at high temperatures with the special method<sup>4</sup> which is very convenient for this purpose, and the present paper gives the results of the experiments and some calculations derived from these results.

## **Samples and Method of Experiments.**

The potassium iodide used was that of the Japanese Pharmacopoeia three times purified by recrystallisation. By the action of oxygen and carbon dioxide, potassium iodide easily sets free iodine in its aqueous solution. For this reason, the conductivity water, which was made as free as possible of dissolving air, was used as the solvent. The whole

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<sup>1</sup> Wied. Ann., **24**, 530 (1885); Mem. Acad. Pét., (7), **35** (1891).

<sup>2</sup> Wied. Ann., **42**, 513 (1891).

<sup>3</sup> Zs. physik. Chem., **82**, 633 (1913)

<sup>4</sup> See the method of the determination of the vapour pressure of phosphorus by Smits and Bokhorst: Zs. physik. Chem., **91** 248, (1916).

apparatus used is shown in Fig. 1. S is the pressure indicator made of Pyrex glass, a more detailed construction of which can be seen from Fig. 2. This pressure indicator was connected with a metal tube at *g* in the following way: The glass tubing of the top of the indicator was first coated with platinum, and then on this platinum film copper was electrochemically plated, then this part was closely connected with a metal tube by soldering.

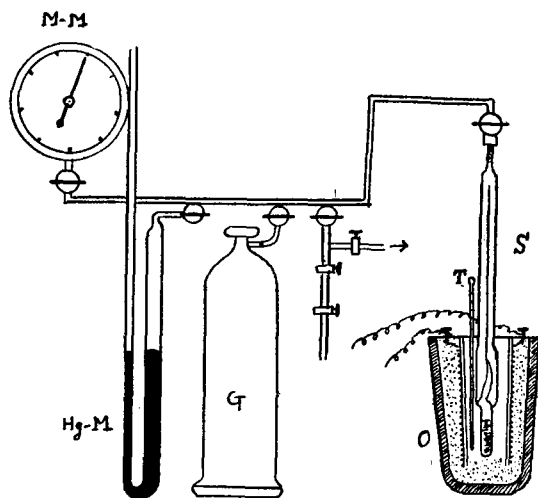


Fig. 1.

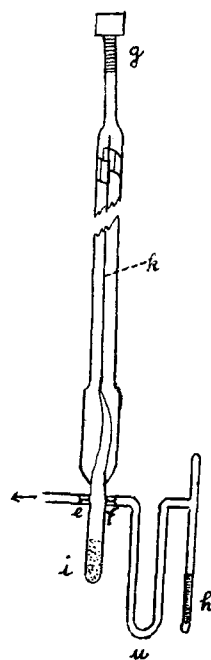


Fig. 2.

A weighed amount of purified potassium iodide was put into *i*, and the measured amount of solvent was poured into *h*. Now *h*, *u* and *i* were evacuated by means of a vacuum pump, while *u* was kept cool with liquid air. In this procedure, the water in *h* was distilled toward *u in vacuo*. After a sufficient vacuum was obtained, the connection between the pressure indicator and the vacuum pump was sealed at *e*. Then water was distilled again from *u* to *i*, and *h* and *u* were sealed off at *f*. Thus a solution of potassium iodide of a known concentration can be obtained in *i*.

The furnace used, which is represented by O in Fig. 1, was made

up of an iron tube, 5 cm. in inner diameter and 33 cm. in length, which was electrically heated by a nichrome wire, and this iron tube was kept in a large crucible filled with asbestos fibre. Through the regulation of current intensity it is able to keep the temperature constant for several minutes. All the connections can easily be seen from Fig. 1. G is the bomb of carbon dioxide which brings high pressure to the system of the apparatus, outside the spring of the indicator. Hg-M is a manometer of mercury for the measurement of pressures up to 3 atmospheres, and M-M is that of metal for higher pressures. The pressure of the solution in the enclosed part *z* at any desired temperature can be read indirectly on the scales of Hg-M and M-M by adjusting the pressure of the system of the measurement to fix always the pointer *k* at zero point.

**Results of the Experiments.**

The vapour pressures of the potassium iodide solutions of various concentrations were measured by the above-mentioned method at every interval of five degrees between 30°--200°C. Only the results obtained above 100° are shown in the following tables (from II to XI).

Table I

t° C.	p <sub>0</sub> (atms)	Thp <sub>0</sub>	CT	L/R
100	1	0.	4867.7	4868
105	1.19	65.8	4932.9	4867
110	1.41	131.6	4998.1	4866
115	1.67	199.0	5063.4	4865
120	1.96	264.5	5128.6	4864
125	2.29	329.8	5198.9	4864
130	2.67	396.8	5259.2	4862
135	3.09	460.4	5324.4	4864
140	3.57	525.7	5389.6	4864
145	4.10	589.9	5455.0	4865
150	4.69	653.8	5520.1	4866
155	5.36	718.7	5585.4	4867
160	6.10	783.1	5650.6	4868
165	6.92	847.4	5715.9	4869
170	7.82	911.3	5781.1	4870
175	8.81	975.0	5846.4	4871
180	9.89	1038.2	5911.7	4854
185	11.09	1102.2	5977.0	4875
190	12.39	1165.5	6042.1	4877
195	13.80	1228.6	6107.4	4879
200	15.34	1292.0	6172.6	4881

Table II

H<sub>2</sub>O 86.86 g.       $\frac{N_1^*}{N_2} = 61.5$       C=12.87  
 KI 13.14 g.

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
100	0.926	-28.7	4800.5	4829	0.926
105	1.17	59.4	4864.9	4806	0.983
110	1.37	120.6	4929.2	4809	0.972
115	1.60	182.4	4993.6	4811	0.958
120	1.87	246.0	5057.9	4812	0.954
125	2.22	317.5	5122.2	4805	0.969
130	2.55	378.2	5186.6	4808	0.955
135	2.95	441.5	5250.9	4810	0.955
140	3.45	511.5	5315.3	4804	0.966
145	3.92	571.1	5379.7	4809	0.956
150	4.49	635.4	5444.0	4809	0.957
155	5.14	700.8	5508.4	4801	0.959
160	5.85	764.3	5572.7	4809	0.959
165	6.62	828.0	5637.1	4809	0.957
170	7.40	886.8	5701.5	4815	0.946
175	8.34	950.4	5765.8	4815	0.947
180	9.45	1017.6	5830.1	4813	0.956
185	10.50	1077.1	5894.5	4817	0.947
190	11.65	1137.0	5958.9	4822	0.940
195	12.85	1195.3	6023.2	4828	0.931
200	14.44	1263.4	6087.5	4824	0.942

\* N<sub>1</sub>, N<sub>2</sub> are the molar fractions of water and of potassium iodide respectively.

Table III

H<sub>2</sub>O 77.48 g.       $\frac{N_1}{N_2} = 31.26$ ,      C=12.80  
 KI 22.52 g.

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
100	0.90	-39.5	4774.4	4814	0.900
105	1.10	36.9	4838.4	4802	0.924
110	1.31	103.4	4902.4	4799	0.929
115	1.53	165.0	4966.4	4801	0.916
120	1.78	226.7	5030.4	4804	0.908

t°C	p (atms)	T <sub>mp</sub>	CT	L/R	p/p <sub>0</sub>
125	2.10	295.3	5094.4	4799	0.917
130	2.44	350.5	5158.4	4798	0.914
135	2.83	424.5	5222.4	4798	0.917
140	3.28	490.7	5286.4	4796	0.919
145	3.78	555.9	5350.4	4795	0.921
150	4.32	619.1	5414.4	4795	0.921
155	4.92	682.1	5478.4	4796	0.918
160	5.58	744.6	5542.4	4796	0.915
165	6.38	811.8	5606.4	4795	0.921
170	7.20	874.7	5670.4	4796	0.923
175	8.02	932.9	5734.4	4802	0.910
180	8.98	994.5	5798.4	4804	0.908
185	10.05	1057.1	5862.4	4805	0.906
190	11.09	1114.2	5926.4	4812	0.895
195	12.30	1174.7	5990.4	4816	0.891
200	13.61	1234.8	6054.4	4820	0.887

Table IV

H<sub>2</sub>O 63.37 g.       $\frac{N_1}{N_2} = 15.95,$       C=12.68  
 KI 36.63 g.

t°C	p (atms)	T <sub>mp</sub>	CT	L/R	p/p <sub>0</sub>
100	0.83	-69.5	4729.6	4799	0.830
105	1.01	3.8	4793.0	4789	0.841
110	1.18	63.4	4856.4	4793	0.837
115	1.38	125.0	4919.8	4795	0.826
120	1.67	201.6	4983.2	4782	0.852
125	1.92	259.7	5046.6	4787	0.838
130	2.23	324.1	5110.0	4786	0.835
135	2.55	382.0	5173.4	4791	0.825
140	2.96	448.3	5236.8	4789	0.829
145	3.42	514.1	5300.2	4786	0.834
150	3.94	580.1	5363.6	4784	0.840
155	4.49	642.9	5427.0	4784	0.838
160	5.12	707.3	5490.4	4783	0.839
165	5.76	767.0	5553.8	4787	0.832
170	6.46	826.6	5617.2	4791	0.826
175	7.30	890.7	5680.6	4790	0.829

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
180	8.19	952.8	5744.0	4791	0.828
185	9.15	1014.1	5807.4	4793	0.825
190	10.18	1074.6	5870.8	4796	0.822
195	11.20	1130.8	5934.2	4803	0.812
200	12.48	1194.1	5997.6	4804	0.814

Table V

$$\begin{array}{l} \text{H}_2\text{O} \quad 50.08 \text{ g.} \\ \text{KI} \quad 49.92 \text{ g.} \end{array} \quad \frac{N_1}{N_2} = 9.20, \quad C = 12.53$$

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
100	0.765	-99.9	4673.7	4774	0.765
105	0.921	31.1	4736.3	4768	0.774
110	1.12	44.4	4799.0	4755	0.794
115	1.30	101.8	4861.6	4760	0.778
120	1.50	159.4	4924.3	4765	0.765
125	1.74	220.5	4986.9	4767	0.760
130	2.05	290.1	5049.6	4760	0.768
135	2.40	357.3	5112.2	4755	0.777
140	2.78	422.3	5174.9	4753	0.779
145	3.15	479.7	5237.5	4758	0.768
150	3.72	544.3	5300.2	4756	0.772
155	4.15	609.2	5362.9	4754	0.774
160	4.71	671.1	5425.5	4754	0.772
165	5.38	737.1	5488.1	4751	0.777
170	6.05	797.6	5550.8	4753	0.774
175	6.80	858.9	5613.4	4755	0.772
180	7.58	917.7	5676.1	4758	0.766
185	8.45	977.4	5738.7	4761	0.762
190	9.36	1035.6	5801.4	4766	0.756
195	10.38	1095.3	5864.0	4769	0.752
200	11.39	1150.8	5926.7	4776	0.743

Table VI

H<sub>2</sub>O 45.50 g.       $\frac{N_1}{N_2} = 7.70,$       C=12.48  
 KI 54.50 g.

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
100	0.722	-121.5	4655.0	4777	0.722
105	0.861	-56.6	4717.4	4764	0.724
110	1.07	25.9	4779.8	4754	0.759
115	1.25	86.6	4842.2	4756	0.749
120	1.47	151.4	4904.6	4753	0.750
125	1.70	211.2	4967.0	4756	0.742
130	1.94	267.8	5029.4	4762	0.727
135	2.29	338.1	5091.8	4754	0.741
140	2.65	402.6	5154.2	4752	0.742
145	3.04	464.8	5216.6	4752	0.742
150	3.45	523.9	5279.0	4755	0.736
155	3.93	585.9	5341.4	4756	0.733
160	4.50	651.4	5403.8	4753	0.738
165	5.14	717.2	5466.2	4749	0.743
170	5.81	779.6	5528.6	4749	0.743
175	6.54	841.5	5591.0	4750	0.742
180	7.35	903.8	5653.4	4750	0.743
185	9.19	963.3	5715.8	4753	0.739
190	8.09	1022.1	5778.2	4756	0.734
195	10.10	1077.8	5840.6	4763	0.725
200	10.94	1131.8	5903.0	4771	0.713

Table VII

H<sub>2</sub>O 40.00 g.       $\frac{N_1}{N_2} = 6.14,$       C=12.45  
 KI 60.00 g.

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
100	0.712	-126.7	4643.9	4771	0.712
105	0.859	-57.5	4706.1	4784	0.722
110	0.991	-3.5	4768.4	4772	0.703
115	1.12	42.6	4830.6	4788	0.686
120	1.36	120.3	4892.9	4773	0.694
125	1.57	179.8	4955.1	4775	0.686
130	1.83	244.6	5017.4	4773	0.685

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
135	2.16	314.6	5079.6	4765	0.699
140	2.48	375.4	5141.9	4767	0.695
145	2.82	433.4	5204.1	4771	0.688
150	3.26	499.3	5266.4	4768	0.694
155	3.72	562.4	5328.6	4766	0.694
160	4.26	627.7	5390.9	4763	0.698
165	4.85	691.6	5453.1	4762	0.701
170	5.47	752.9	5515.4	4763	0.700
175	6.11	811.0	5577.6	4763	0.694
180	6.87	873.2	5639.9	4763	0.695
185	7.74	937.4	5702.1	4765	0.698
190	8.60	996.4	5764.4	4768	0.694
195	9.57	1057.9	5826.6	4769	0.694
200	10.41	1107.8	5888.9	4781	0.679

Table VIII

H<sub>2</sub>O 32.50 g.       $\frac{N_1}{N_2} = 4.43,$       C=12.43  
 KI 67.50 g.

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
100	0.605	-165.5	4636.4	4802	0.605
105	0.720	-124.2	4668.5	4823	0.605
110	0.902	-39.5	4760.7	4800	0.640
115	1.01	3.9	4822.8	4819	0.605
120	1.22	78.2	4885.0	4807	0.622
125	1.41	136.8	4947.1	4810	0.616
130	1.62	194.9	5009.3	4814	0.607
135	1.90	261.9	5071.4	4810	0.615
140	2.20	326.7	5133.6	4807	0.616
145	2.52	386.4	5195.7	4809	0.615
150	2.95	457.7	5257.9	4800	0.620
155	3.40	523.9	5320.0	4796	0.634
160	3.90	589.4	5382.2	4793	0.639
165	4.44	653.0	5444.3	4791	0.642
170	5.00	713.1	5506.5	4793	0.639
175	5.60	771.9	5568.6	4797	0.636
180	6.25	830.3	5630.8	4801	0.632
185	6.97	889.4	5692.9	4804	0.626
190	7.75	948.2	5755.1	4807	0.626
195	8.55	1004.5	5817.2	4813	0.620
200	9.40	1060.1	5879.4	4819	0.613



Table IX

H<sub>2</sub>O 27.05 g.       $\frac{N_1}{N_2} = 3.42,$       C=12.19  
 KI 72.95 g.

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
120	*1.12				
125	*1.30				
130	*1.51				
135	*1.76				
140	*2.04				
145	2.32	351.8	4995.4	4644	0.566
150	2.70	420.2	5056.4	4636	0.576
155	3.15	492.3	5117.3	4625	0.588
160	3.60	554.7	5178.3	4624	0.590
165	4.10	618.1	5239.2	4621	0.593
170	4.62	678.1	5300.2	4622	0.591
175	5.17	736.1	5361.1	4625	0.587
180	5.76	793.4	5422.1	4629	0.582
185	6.45	853.9	5483.0	4929	0.582
190	7.20	914.2	5544.0	4630	0.581
195	7.85	964.5	5604.9	4640	0.569
200	8.72	1024.5	5665.9	4641	0.568

The values which are marked \* coincide with the vapour pressures of the saturated solution.

Table X

H<sub>2</sub>O 24.44 g.       $\frac{N_1}{N_2} = 2.98,$       C=11.62  
 KI 75.56 g.

t°C	p (atms)	Tlnp	CT	L/R	p/p <sub>0</sub>
140	*2.04				
145	*2.29				
150	*2.61				
155	*2.97				
160	*3.29				
165	*3.76				
170	4.24	640.0	5147.7	4508	0.542
175	4.75	698.2	5205.8	4508	0.539
180	5.31	756.5	5263.9	4507	0.537
185	5.92	814.6	5322.0	4507	0.534
190	6.60	873.9	5380.1	4506	0.533
195	7.30	930.5	5438.2	4508	0.529
200	8.10	989.6	5496.3	4507	0.528

Table XI  
 $\left. \begin{array}{l} \text{H}_2\text{O} \\ \text{KI} \end{array} \right\}$  the saturated solution at each temperature

t°C	p (atms)	p/p <sub>0</sub>	Solubility. gr. in 100g. Solution	N <sub>1</sub> /N <sub>2</sub>
100	0.606	0.606		4.43
105	0.723	0.606	68.3	4.29
110	0.861	0.611	69.0	4.13
115	0.998	0.596	69.5	4.05
120	1.12	0.571	70.0	3.95
125	1.30	0.568	70.5	3.85
130	1.52	0.570	71.0	3.76
135	1.77	0.573	71.5	3.69
140	2.04	0.571	72.0	3.59
145	2.30	0.561	72.25	3.55
150	2.62	0.559	72.7	3.46
155	2.97	0.554	73.5	3.33
160	3.30	0.541	74.0	3.24
165	3.76	0.543	74.5	3.17
170	4.24	0.542	75.0	3.07
175	4.68	0.531	75.5	2.98
180	5.11	0.517	76.0	2.91
185	5.71	0.515	76.75	2.80
190	6.32	0.510	77.5	2.68
195	6.92	0.502	78.0	2.64
200	7.58	0.494	78.5	2.53

Fig. 3

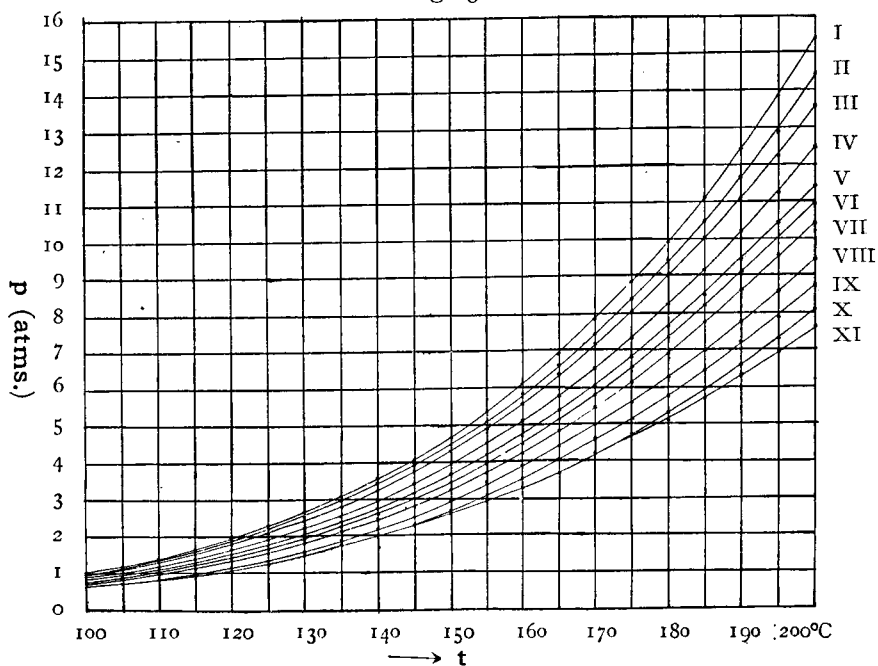
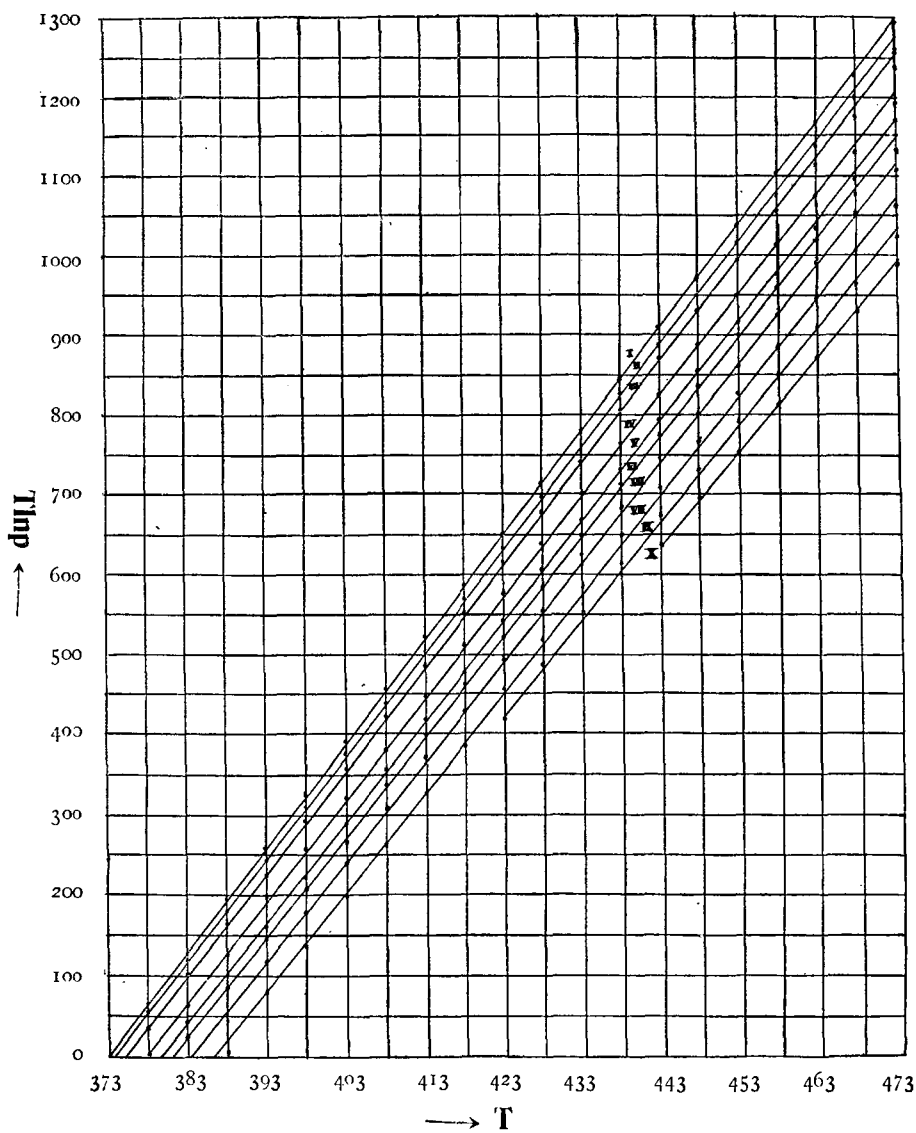


Fig. 4



For comparison, the vapour pressures of pure water quoted from the Landolt Tables are given in Table I.<sup>1</sup>

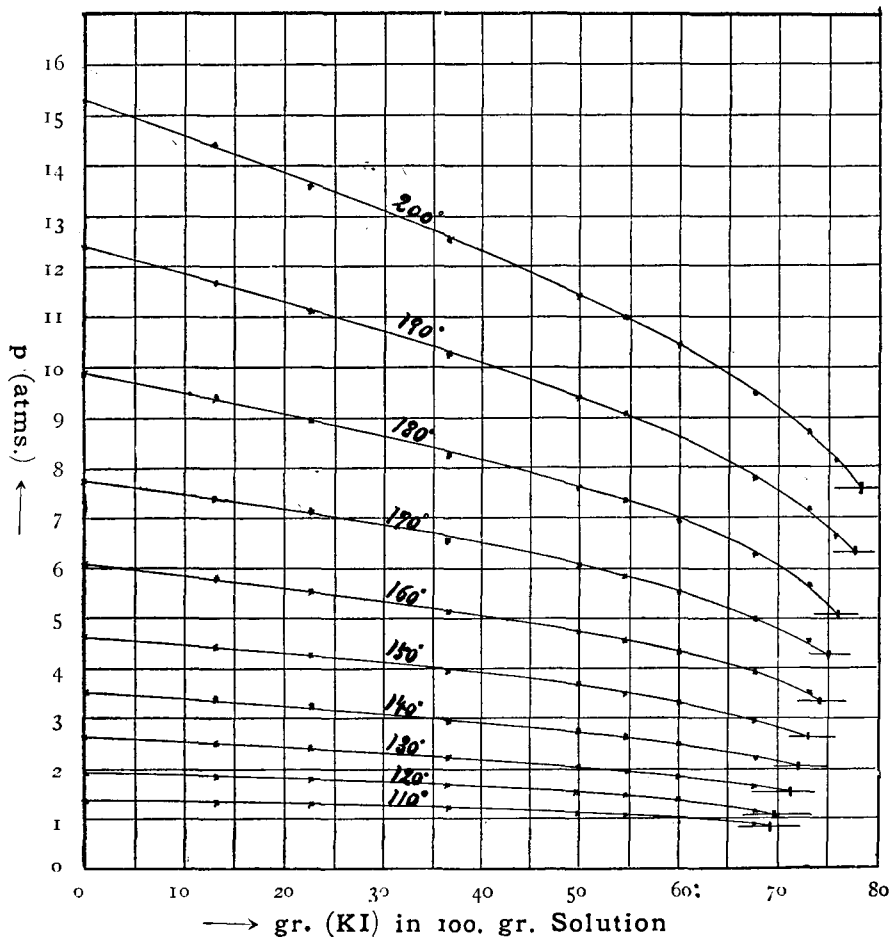
The results obtained are plotted on the pressure-temperature diagram

1. Landolt-Börnstein, Tabellen, 5. Aufl.

in Fig. 3. As may be seen from the diagram, an increase in the concentration causes a fairly remarkable lowering of the vapour pressure. These values stand under  $p/p_0$  in the Tables. Curves IX and X coincide with the vapour pressure curve of the saturated solution, which was represented by curves XI, until  $140^\circ$  and  $175^\circ$  respectively, and above these temperatures they move upward from the latter. These are the points which denote the solubilities of potassium iodide at these temperatures.

For the application of the well known Clapeyron-Clausius formula  $T \ln p = -\frac{L}{R} + CT$ ,  $T$ - $T \ln p$  curves were plotted from the above experimental results, then we have, as shown in Fig. 4, straight

Fig. 5



lines, running nearly parallel to each other for the solutions of different concentrations and we can easily calculate the value  $L$  and  $C$ . But, exactly speaking, a slight difference of inclination exists between these straight lines and in fact the constant  $C$  varies with the concentrations of the solutions, as 13.05, 12.87, 12.80, etc. The term  $C$  has a close relation with the internal pressure of the solution, and its change with the concentration would be of interest from the theoretical standpoint of concentrated solutions, and the writer leaves it for later study.

The heats of vaporization  $L$ , calculated from the Clapeyron-Clausius formula, are also shown in the Tables.

### Calculation of the Solubility

The determination of the solubilities of the substance in water at higher temperatures is very difficult, and so it is very remarkable that from the results now obtained the calculation of solubility appears to be possible. Theoretically the points where the isothermals reach the height of the vapour pressures of the saturated solutions at the respective temperatures on the concentration-vapour pressure diagram show the solubilities at those temperatures. These relations can easily be gathered by Fig. 5, and Table XI gives the solubilities thus obtained. They agree fairly well with the above information as to the curves IX and X. The solubility curve now obtained also continues smoothly with the solubility curve below 100°C measured by Mulden,<sup>1</sup> and as a whole, the increase of solubility is linear with respect to temperature.

### Activity.

From the results obtained above the activities of the solvent can easily be calculated. The expression of the activity for the solvent is

$$a_1 = \frac{p}{p_0} ; \text{ already given in Tables I—XI.}$$

As to the activity of the solute, the expression is

$$\ln a_2 = - \int_0^{N_2} \frac{N_1}{N_2} d \ln \left( \frac{p}{p_0} / N_1 \right),$$

where  $N_1$  and  $N_2$  are molar fractions of solvent and solute,  $p$  the vapour pressure of the solution and  $p_0$  that of the solvent. The integration of this equation cannot be wholly carried out because of the lack of

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<sup>1</sup> Landolt-Börnstein, Tabellen, 5 Aufl., 1, 661.

the measurements at dilute concentrations.

#### **Summary.**

1) The vapour pressures of the concentrated aqueous solutions of potassium iodide were measured at various concentrations. The heats of vaporization of these solutions were calculated and it was noted that the values of  $C$  in the Clapeyron-Clausius equation vary with the concentration.

2) The solubilities of potassium iodide at high temperatures were calculated from the data of the vapour pressures.

3) The activities of the solvent were calculated.

The writer wishes to express his hearty thanks to professor S. Horiba for his kind and helpful directions.

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