

## THE SOLUBILITY OF POTASSIUM PERMANGANATE.

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DETERMINATIONS of the solubility in water of potassium permanganate have been made by Mitscherlich,<sup>1</sup> who found 6.3 parts of salt to 100 parts of water in a saturated solution at 15°, by Guthrie,<sup>2</sup> who found 2.9 parts of salt to 100 parts of water at —0.6°, and by Muthmann and Kuntz,<sup>3</sup> who found 41.81 grams of permanganate dissolved in 1 liter of water at "about 7°." The data obtained in the present investigation cover the above range of temperature and extend as high as 65°.

Potassium permanganate for the determinations was purified by crystallization. The salt was first dissolved in the purest water and the solution was filtered through asbestos in a Gooch crucible without being allowed to come in contact with rubber. The solution was then evaporated in covered flasks to crystallization and the product was twice recrystallized, with centrifugal drainage. In all three crystallizations the hot solution was allowed to stand some time and was carefully decanted from possible sediment before cooling. All the water used in the purification and also in the analyses of the saturated solutions was twice distilled, once from an alkaline solution of permanganate and once from a trace of sulphuric acid. The final product, when dissolved in the purest water, did not appreciably stain clean glass, and showed every outward evidence of purity.

The method of obtaining a saturated solution was the usual one of rotating the substance with water in closed tubes at the desired temperature in a thermostat. By means of electrical regulating apparatus the thermostat was maintained constant at different temperatures to within five hundredths of a degree. The thermometer was carefully corrected by comparison with one standardized by the Physikalisch-technische Reichsanstalt.

Since permanganates are easily reduced by rubber or cork, and since glass stoppers may become loose or may leak, the glass tubes,

<sup>1</sup> Pogg. Ann. 25, 295 (1832).

<sup>2</sup> Phil. Mag. [5] 6, 37 (1878).

<sup>3</sup> Z. Krist. Min. 23, 374 (1894).

2 cm. in diameter, in which the solutions were shaken, were sealed off after the permanganate and water had been introduced.

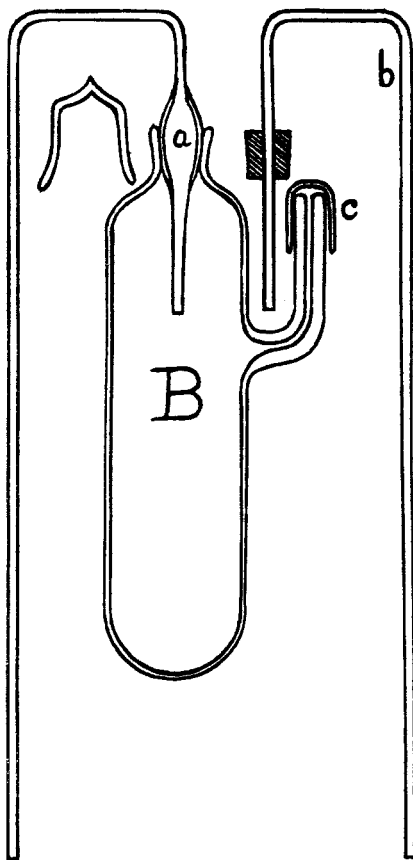
It was found advisable to rotate the tubes for at least four hours although in a few cases the saturation equilibrium was reached in a shorter period. In some experiments the agitation was continued for more than twenty hours but the results in these cases were essentially the same as in those where the solutions were analyzed after four hours' shaking. It was necessary to shake the solutions quite as long at the higher temperatures as at the lower.

After saturation had been attained, the tubes were allowed to stand in a perpendicular position in the thermostat for from two to four hours in order to allow all solid matter to settle. The dark color of the permanganate made it impossible to see whether the solution was absolutely free from small suspended particles of salt, and the nature of the permanganate made it inadvisable to attempt filtration of the solutions. However, since solutions after only two hours' standing showed the same salt content as similar solutions which had settled for four hours, it seems probable that no error was introduced from this source.

For removing the solution from the saturating tubes a pipette of the following form was used. A capillary tube with an enlargement at *a* was ground into the mouth of the bulb *B*. The pipette was filled by cutting off the top of the sealed saturating tube without removing it from the thermostat, inserting the capillary tube *a* into the saturated solution, and applying suction at *c*. *a* was then removed and both the mouth of the bulb *B* and the capillary side-tube were covered with glass caps. The bulb was wiped with a damp cloth, and, after it had been allowed to come to constancy in the balance case, was weighed. Evaporation from one of these pipettes was very slow. A solution at about 20°, on standing in a balance case containing sulphuric acid, lost only 3 mg. in fifteen hours. Since at higher temperatures the danger of evaporation is increased, the solutions were cooled with ice water as soon as they were removed from the saturating tubes.

With solutions saturated at the higher temperatures it was found necessary to warm the capillary tubes before pipetting out the solution, in order to avoid the deposition of crystals in the

enlargement *a*, although no salt deposited in the capillary itself. Capillary tubes of the form *b*, without an enlargement, were also used. These tubes were fitted into the bulb by means of a rubber stopper. The results with these tubes were no different from those obtained by warming the tubes of the form *a*.



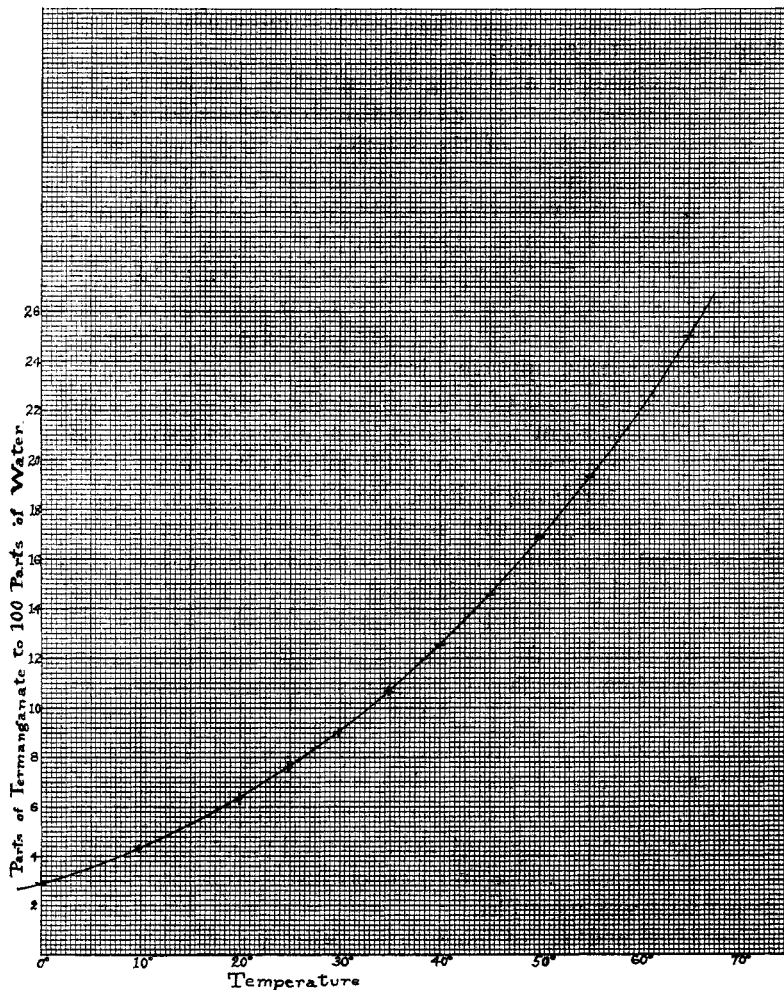
In order to make certain that saturation had been reached from below, the equilibrium was approached also from above. This was done by agitating the solution for an hour or two at a temperature from  $5^{\circ}$  to  $10^{\circ}$  above the temperature in question, and continuing the agitating at the desired temperature for from four to twenty hours. Experiments by this method gave pre-

cisely the same results as those where equilibrium was reached from the other direction.

Three methods of analyzing the saturated solutions were employed. The simplest and least satisfactory was that of evaporating weighed portions of the solutions to dryness in platinum crucibles and heating the residues to  $150^{\circ}$  in an air-bath. During the evaporation evidence of slight reduction of the permanganate always appeared. On the other hand it is improbable that all the water was expelled at  $150^{\circ}$ . A temperature much higher than this was found to produce considerable reduction of the salt. However, the two errors mentioned above would affect the results in opposite directions.

The second method of determining the permanganate was to weigh the potassium and manganous sulphates formed by reduction of the permanganate with sulphurous acid. The permanganate, after being weighed, was transferred to a platinum dish and was treated with a slight excess of sulphurous acid. The solution was then evaporated upon the steam-bath, first in the dish, then in a weighed platinum crucible. Finally the greater part of the excess of sulphuric acid was expelled upon a ring-burner and the last traces were eliminated by prolonged heating over a small Bunsen flame. Much care during the final heating was necessary to avoid partial decomposition of the manganous sulphate, with the formation of manganic oxide. It was possible, however, to obtain a product that gave a perfectly clear solution in water, showing that no decomposition had taken place, and which nevertheless was not acid to methyl orange. The sulphurous acid was made from concentrated sulphuric acid and copper, and was redistilled.

The third method of analysis was titration with oxalic acid. This acid was many times recrystallized, first from hydrochloric acid solution, then from water until free from chlorides. In order to bring it to the theoretical composition, it was finely powdered and exposed in a thin layer in a desiccator over sulphuric acid of the specific gravity 1.35. A slight deficiency of oxalic acid was weighed out and dissolved in water. Then, after the addition of a considerable excess of sulphuric acid, the permanganate was slowly introduced into the hot solution of oxalic and sulphuric acids. Finally the slight excess of permanganate was reduced by means of a fifth-normal oxalic acid solution. In a few cases



where the oxalic acid was in excess the end-point was reached by means of a standard solution of permanganate.

Since all three methods gave essentially identical results, it is highly probable that no constant errors affected any one of them to an appreciable extent.

In the following table the starred determinations were made with solutions which had been first supersaturated.

POTASSIUM PERMANGANATE.

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Temperature.	Period of shaking. Hours.	Weight of solution. Grams.	Weight of $\text{KMnO}_4$ . Grams.	Weight of $\text{K}_2\text{SO}_4 \cdot 2\text{MnSO}_4$ . Grams.	Weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Grams.	Per cent. of $\text{KMnO}_4$ .
0°	4.5	12.489*		0.5190		2.759
	4.5	12.438			0.6838	2.758
	4.5	11.791		0.4902		2.760
	4.5	11.798			0.6461	2.747
	4.5	10.684*		0.4443		2.761
	4.5	9.686*			0.5297	2.743
	4.5	12.354*			0.6765	2.747
	Average,					
9.8°	4	10.433*	0.4319			4.140
	4	8.924*			0.735	4.132
	4.5	10.098*	0.4176			4.136
	4.5	9.385*			0.772	4.127
	4	8.944*		0.5577		4.140
	4	9.340*			0.768	4.125
Average,						4.133
19.8°	5	9.609	0.5737			5.970
	5	8.172			0.969	5.948
	18	10.624	0.6342			5.970
	18	10.624		0.9535		5.959
	18	9.012			1.066	5.934
	18	9.870		0.8879		5.973
	16	10.431*		0.9369		5.964
	16	8.870*			1.051	5.944
	16	10.480*			1.244	5.955
	16	9.051*	0.5394			5.960
Average,						5.958
24.8°	4	11.368		1.2081		7.056
	4	11.018*		1.1716		7.060
	4	13.325*		1.4189		7.070
	5	11.301 <sup>1</sup>		1.2000		7.050
	5	14.793 <sup>1</sup>		1.5681		7.038
	5	13.686 <sup>1</sup>		1.4569		7.068
	28	15.758 <sup>1</sup>		1.6728		7.048
	23	12.191 <sup>1</sup>		1.2963		7.060
	5	14.932* <sup>1</sup>		1.5820		7.035
	5	13.939* <sup>1</sup>		1.4826		7.062
	Average,					

Temperature.	Period of shaking, Hours.	Weight of solution, Grams.	Weight of $\text{KMnO}_4$ , Grams.	Weight of $\text{K}_2\text{SO}_4 \cdot 2\text{MnSO}_4$ , Grams.	Weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , Grams.	Per cent. of $\text{KMnO}_4$ .
29.8°	4	9.141		1.1391		8.274
	4	9.804		1.2237		8.287
	4	9.021			1.491	8.292
	3	9.015*	0.7474			8.291
	3	9.015*		1.1239		8.278
	3	9.972*		1.2440		8.283
	20	8.803		1.0963		8.269
	20	9.857			1.628	8.286
						Average, 8.283
34.8°	4	8.170*			1.5700	9.640
	4	8.691*		1.2652		9.666
	4.5	8.986			1.723	9.619
	4.5	11.202	1.0815			9.655
	4.5	9.874			1.892	9.613
	4	13.749			2.638	9.625
	4	9.694		1.4066		9.634
	4	8.542*			1.644	9.655
	4	6.675*		0.9715		9.664
4	8.916*			1.717	9.661	
						Average, 9.643
40°	18	10.934			2.4286	11.143
	18	9.498			2.1134	11.163
	18	9.374		1.5740		11.149
	18	11.123		1.8617		11.113
	18	10.704			2.3809	11.159
	18	11.245			2.4996	11.151
	18	11.774*	1.3174			11.189
	18	10.063*			2.2414	11.174
						Average, 11.155
45°	4	10.562*			2.682	12.739
	4	11.403*			2.895	12.736
	4	9.812			2.486	12.710
						Average, 12.728
50°	20	11.499			3.3095	14.438
	20	10.965			3.1571	14.443
	20	10.455		2.2764		14.457
	20	9.794			2.817	14.429
	36	12.182*			3.508	14.446
	30	11.896*		2.5920		18.465
						Average, 14.446

Temperature.	Period of shaking. Hours.	Weight of solution. Grams.	Weight of $\text{KMnO}_4$ . Grams.	Weight of $\text{K}_2\text{SO}_4 \cdot 2\text{MnSO}_4$ . Grams.	Weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Grams.	Per cent. of $\text{KMnO}_4$ .
55°	25	9.960			3.216	16.198
	25	9.995		2.4404		16.212
	25	8.675			2.802	16.203
	17	12.090*			3.904	16.199
	17	8.481*		2.0685		16.193
	17	8.675*			2.802	16.203
	Average,					
65°	4	7.801		2.3531		20.028
	4	6.987			2.744	19.988
	4	9.049			3.607	19.994
	4	7.810*		2.3597		20.060
	4	6.763*		2.0382		20.010
	4	6.809*		2.0555		20.043
Average,						20.021

Temperature. Degrees.	Per cent. of $\text{KMnO}_4$ .	Parts of $\text{KMnO}_4$ to 100 parts of water.
0	2.75	2.83
9.8	4.13	4.31
19.8	5.96	6.34
24.8	7.06	7.59
29.8	8.28	9.03
34.8	9.64	10.67
40.0	11.16	12.56
45.0	12.73	14.58
50.0	14.45	16.89
55.0	16.20	19.33
65.0	20.02	25.03

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## THE NITRIDES OF ZINC, ALUMINIUM AND IRON.

BY ALFRED H. WHITE AND L. KIRSCHBRAUN.

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THE action of ammonia at high temperatures upon metals has already been investigated by Beilby and Henderson<sup>2</sup> who showed that almost all metals are profoundly modified in their physical properties upon exposure to ammonia gas at a red heat. In their experiments nitrides of approximately definite composition were formed from some metals, but in more cases the percentage of

<sup>1</sup> These determinations were prepared by Mr. Hubbard, the remainder by Mr. Boylston.

<sup>2</sup> J. Chem. Soc. 79, 1245.