

XI.—ON THE VARIATION OF DENSITY WITH CONCENTRATION IN
WEAK AQUEOUS SOLUTIONS OF COBALT AND NICKEL
SULPHATES.—BY A. M. MORRISON, B. A.

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In a paper which I had the honor of reading before the Institute last session,* I gave the results of a short series of observations of the density of weak aqueous solutions of Cobalt Sulphate. The solutions used were prepared by mixing weighed quantities of water and of crystals of the salt, which, on what seemed to be satisfactory information, were taken to be heptahydrated crystals. The amounts of anhydrous salt present in the solutions used were calculated on this assumption.

On comparing the differences between the specific volumes of these solutions and the volumes, in the free state, of their constituent water, with similar differences in the case of solutions of other sulphates, as determined by Prof. MacGregor,† it was evident that either the dilute solutions of this salt exhibited the phenomenon of contraction in a very remarkable manner, or that the information on which I relied as to the constitution of the crystals used was incorrect. I therefore made several careful chemical analyses of the crystals and found that they contained not seven but six molecules of water.

This being so, the constitutions of the solutions whose densities are given in the paper referred to, are consequently inaccurately specified. I have therefore re-calculated them, and the results are given in the first two columns of the following table:

* Trans. N. S. Inst. Nat. Sci., Vol. VII (1890) p. 480.

† Trans. Roy. Soc. Can., Vol. VIII (1890) Sec. iii, p. 19.

Percentage of anhydrous Co SO_4 in solution.	Density at 20° C. (Grms. per cu. cm.)		Difference.
	Observed.	Calculated.	
0.6952	1.00552	1.00554	+ 0.00002
1.6373	1.01533	1.01540	+ 0.00007
1.8558	1.01766	1.01768	+ 0.00002
2.5926	1.02541	1.02539	- 0.00002
2.9654	1.02954	1.02929	- 0.00025
5.3693	1.05498		
8.5699	1.09047		

These corrected results agree much more closely with Nicol's* observation, which gave 1.04123 as the density at 20° C. of a solution, containing 4.1434 per cent. of the anhydrous salt, than the erroneous results formerly published. Graphical treatment of the above results gives 1.0418 as the density of Nicol's solution. They agree much less closely with Wagner's† result, which gave 1.0860 as the specific gravity of a solution containing 7.239 per cent. of salt. This observation was made at the temperature of the laboratory, which is not given in his paper. The temperature of the water to which his specific gravities are referred is also not given. If we assume that the temperature of the laboratory was 15° C., and that the specific gravity given by him is referred to water at the same temperature, and if we further assume that the thermal expansion of the solution under consideration is practically the same as that of water, we find for the density (in grammes per cubic centimetre) of this solution at 20° C., the value 1.0841. My observations treated graphically give 1.0755 as the density of this solution. Probably, therefore, the above assumptions made in calculating Wagner's density are not correct.

* Phil. Mag., Ser. 5, Vol. XVI (1833) p. 122.

† Wied. Ann., Bd. XVIII (1833) p. 269.

Prof. MacGregor* having shown that in the case of a great many salts, the curves exhibiting the relation of the density of dilute solutions to their percentage composition, are practically (to the fourth decimal place of the density when it is expressed in grms. per cu. cm.), straight lines, I have thought it well to determine to what degree of concentration the same is true for solutions of this salt. I find that the first four of the above observations may, to the fourth place of decimals, be represented by the formula—

$$D_{20} = 0.99827 + 0.01046 p.$$

where D_{20} is the density of solutions at 20° C., and p the percentage of anhydrous salt in solution, 0.99827 being the density of water at 20° C. according to Volkmann.† The third column of the above table gives the densities of the first five solutions calculated by means of this formula, and the fourth column, the amounts by which the calculated values exceed the observed values. It will be seen that for solutions containing 2.6 or 2.7 per cent. of anhydrous salt, or less, the curve referred to is, to the fourth place of decimals, a straight line.

Nickel Sulphate.

No observations of the density of very dilute solutions of Nickel Sulphate having, so far as I know, been made hitherto, I have made the few which were necessary to extend our knowledge of the density of solutions of this salt to extreme degrees of dilution. The solutions were prepared and their composition and density determined in the way described in my former paper, referred to above. The results obtained are given in the first two columns of the following table:—

* Trans. Roy. Soc. Can., Vol. VII, (1889), Sec. iii, p. 23.

† Wied. Ann., Bd. XIV. (1881), p. 260.

Percentage of anhydrous Ni SO ₄ in solution.	Density at 20° C. (Grms. per cu. cm.)		Difference.
	Observed.	Calculated.	
1.2512	1.01155	1.01158	+ 0.00003
2.0799	1.02046	1.02040	- 0.00006
3.9633	1.04064	1.04044	- 0.00020

The only results by which we can check the above are Nicol's single observation* and Favre and Valson's series of observations.† Nicol found that a solution consisting of half a molecule of crystallised salt to 100 of water has, at 20° C., a specific gravity, relatively to water at 20° C., of 1.04296, or, as a simple calculation will show, that a solution containing 3.9711 per cent. of anhydrous salt has a density, in grms. per cu. cm., of 1.04116. Graphical treatment of my observations gives 1.0408 as the density of this solution. The weakest solution examined by Favre and Valson consisted of 14.05 parts of crystallised salt and 100 parts of water, and therefore contained 6.772 per cent. of anhydrous salt. The next weakest contained about twice this percentage. The densities of solutions so strong as these cannot be found by the aid of my observations above. But if a curve of densities *versus* percentage compositions be plotted by means of my observations and theirs combined, it shows no discontinuity between the two portions.

The following formula represents to the fourth decimal place the densities of solutions of this salt up to a concentration of about 2.5 per cent. :—

$$D_{20} = 0.99827 + 0.0164 p.$$

The densities calculated by means of this formula are given in the third column of the above table, and the amounts by which

* Phil. Mag., Ser. 5, Vol. XVI, (1883), p. 122.

† Comp. Rend., T. LXXIX, p. 968.

the calculated values exceed the observed values are given in the fourth column. They will be seen to bear out this statement.

It may be well to note that the values of the constant multipliers of p in the two formulæ given above, that is, the values of the mean rate of change of density with concentration, throughout concentration ranges of from zero to about 2.5 per cent., in the case of these salts, are approximately the same. They are also approximately the same* as the same rates of change in the case of zinc and magnesium sulphates, and not very different from those of iron, cadmium, copper, aluminium and other sulphates.

* Trans. Roy. Soc. Can., Vol. VII, (1889), Sec. iii, p. 31.