and, therefore, are solid solutions containing a small amount of the sulphate in the hydroxide. In view of the well-known property of hydroxides to carry down other substances with them when precipitated and the utter improbability of any molecule of so large a ratio of base to acid, the latter conclusion seems justifiable.

I am pleased to acknowledge the efficient help of my assistant, Mr. H. B. Pulsifer, who did much of the analytical work and of Mr. M. A. Stewart, who determined the extent of hydrolysis of the normal sulphate in solution and the effect upon the amount of $\overset{+}{H}$ ions present obtained by saturating the same solution with its own carbonate.

The following conclusions seem warranted:

That the only known definite hydrated sulphates of beryllium are $BeSO_4 + 4H_2O$ and $BeSO_4 + 2H_2O$.

That the anhydrous sulphate $BeSO_4$ is difficult to produce entirely free from water or excess of oxide, owing to the difficulty of removing the last traces of water without at the same time driving off sulphuric anhydride.

That the so-called basic sulphates of beryllium do not exist as separate and definite chemical compounds, but are in reality solid solutions of the sulphate in the hydroxide. These are much more basic in composition when equilibrium with the mother-liquors is reached than when first precipitated.

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ON THE MOLECULAR DEPRESSION CONSTANT OF *p*-AZOXYANISOL.

BY H. MONMOUTH SMITH AND W. H. MCCLELLAND.

Received August 1, 1904.

GATTERMANN and Ritschke[1] first prepared *p*-azoxyanisol and found that at 116° it passed into a turbid liquid of fluid crystals, which at 134° became a clear, transparent yellow liquid. Schenck,[2] in studying the compound, showed that both these transition points undergo abnormally large depressions, and from the depression of the "clear-turbid" transition point by seven

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[1] *Ber. d. chem. Ges.*, **23**, 1738.

[2] *Ztschr. phys. Chem.*, **25**, 349.

solutes of various composition he calculated the molecular depression constant as 750.2. Later,[1] from determinations with eighteen solutes, he found values ranging from 503 to 859. Auwers[2] reported the value 545 as the average found by one of us[3] from determinations made with five solutes. In another series of determinations he reported[4] values ranging from 500 to 700.

Such a large depression constant is of special interest because of its size, and because, if it can be determined with accuracy, it will permit molecular weight determinations with the consumption of but a few milligrams of the solute. It seemed of interest then to redetermine this constant in the hope that more concordant results might be obtained.

The apparatus which was used in these experiments was of the usual Beckmann form, with a constant temperature bath of glycerol. The thermometer was divided into tenths of a degree and had been verified by the Reichsanstalt. The azoxyanisol was prepared according to the method of Lachman,[5] for azobenzene, and had transition points of 116° and 134°. The solutes were all of Kahlbaum's manufacture and gave sharp and constant melting-points.

Especial care was taken with reference to the conditions necessary to obtain uniform results and the following points may be mentioned:

(*a*) The glycerol bath must be at the highest possible temperature which will, at the same time, allow the formation of the fluid crystals. With the apparatus used in these experiments this limit was found to be from 2.5° to 3° above the transition temperature of the azoxyanisol. If the bath varied from this limit by a degree, the transition point was found from 0.5° to 1° too high.

(*b*) As a consequence of (*a*) it was found that any deviation whatever in the temperature of the bath during a determination gave discordant results which amounted to 4 per cent. for a temperature change in the bath of 0.5°.

(*c*) It was also noticed that the transition point of the freshly prepared azoxyanisol did not remain constant, but showed a grad-

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[1] *Ztschr phys. Chem.*, **29**, 554.

[2] *Ibid.*, **32**, 60.

[3] H. M. S.

[4] *Ztschr. phys., Chem.*, **42**, 631.

[5] This Journal, **24**, 1178.

ual rise during the first half-hour of heating, after which it became constant and remained so indefinitely.

The results of the determinations are given in Table I.

TABLE I.

Grams solvent.	Grams solute.	Observed depression.	Grams solute in 100 grams solvent.	Molecular depression constant, K.
	Naphthalene, molecular weight 128.			
8	0.0562	3.09	0.7025	561
8	0.1164	6.49	1.4550	570
8	0.1705	9.46	2.1310	566
			Average,	566
	α-Nitronaphthalene, molecular weight 173.			
8	0.0616	2.61	0.7700	586
8	0.1188	5.17	1.4840	601
8	0.1659	7.17	2.0737	598
			Average,	595
	Anthracene,[1] molecular weight 178.			
8	0.0586	2.20	0.7325	536
8	0.1311	4.61	1.6390	503
8	0.2021	7.14	2.5260	503
			Average,	514
	o-Acetotoluide, molecular weight 149.			
8	0.0627	3.51	0.7821	624
8	0.1207	6.69	1.5081	617
8	0.1626	9.26	2.0330	633
			Average,	625
	Acetamide,[1] molecular weight 59.			
8	0.0589	6.83	0.7362	546
8	0.0582	6.10	0.7275	495
			Average,	521
	p-Acetotoluide, molecular weight 149.			
8	0.0548	2.49	0.6844	542
8	0.1042	4.84	1.3020	554
8	0.1411	6.44	1.7640	544
			Average.	547
	Phenetol, molecular weight 122.			
8	0.0321	1.85	0.4006	564
8	0.0981	5.65	1.2250	567
8	0.2095	12.25	2.6130	572
			Average,	567
	Cinnamic acid, molecular weight 148.			
8	0.0515	2.59	0.6437	595
8	0.1147	5.47	1.4330	564
8	0.1606	7.31	2.0070	539
			Average,	566

Grand average, 562.

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[1] Slightly volatile.

This average of 562 agrees better with that of 545, found by Auwers than with that found by Schenck.

Among the solutes used by Auwers[1] was benzil, which gave a value of 860 for the depression constant. This was so abnormal that it was not included by him in the average which he gave. On repeating this determination we obtained likewise an abnormal value which led us to try the action of three other bodies of ketone structure, the results of which are given in Table II.

TABLE II.

Grams solvent.	Grams solute.	Observed depression.	Grams solute in 100 grams solvent.	Molecular depression constant, K.
		Benzil, molecular weight 210.		
8	0.0571	2.80	0.7137	824
8	0.1310	6.20	1.6370	795
8	0.2014	9.81	2.5170	818
			Average,	812
		Benzoin, molecular weight 212.		
8	0.0619	3.52	0.7738	963
8	0.1176	6.83	1.4700	984
8	0.1714	9.64	2.1420	964
			Average,	967
		Benzophenone, molecular weight 182.		
8	0.0511	2.81	0.6387	802
8	0.1032	5 60	1.2890	790
8	0.1512	8.24	1.8900	793
			Average,	795
		Michler's ketone, molecular weight 168.		
8	0.0367	1.24	0.4587	723
8	0.0817	2.84	1.0200	745
8	0.1200	3.94	1.5000	705
			Average,	724
		Grand average, 825.		

The average of these four ketones gives a depression constant of 825, or 32 per cent. higher than that found by the eight substances in Table I.

The differences between the values heretofore found for the molecular depression constant have been attributed by Hulett[2] to the possible solubility of the solutes in the fluid crystals. Since

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[1] *Ztschr. phys. Chem.*, **32**, 60.

[2] *Ibid.*, **28**, 642.

our determinations have been made, de Kock[1] has shown, in an exhaustive study of the subject, that such is the case, and that a small difference in the solubility coëfficients of the solutes in the two modifications of the solvent may produce variations in the depression constant. It appears then from the fairly uniform values in Table I that these substances have solubility coëfficients which do not differ widely, and for such substances azoxyanisol might be used in cryoscopic work, but it also appears from the results of the experiments with ketones, as given in Table II, that there are compounds which have large variations in the solubility coëfficients, and that it is these variations which are responsible for the differences in the molecular depression constant, and hence render cryoscopic work with azoxyanisol unreliable.

SYRACUSE UNIVERSITY,
June, 1904.

A CRITICISM OF CLARKE'S NEW LAW IN THERMOCHEMISTRY.[2]

BY H. E. PATTEN AND W. R. MOTT.

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A DISCUSSION of F. W. Clarke's paper, "A New Law in Thermochemistry," by W. v. Löben, appeared some time ago in the *Zeitschrift für anorganischen Chemie* (34, 175 (1903)), and in a later article Julius Thomsen stated his opinion that Clarke's results have no significance.

v. Löben maintains, and rightly, that Clarke has reasoned in a circle and that his constant is not a constant, since in the equation

$$\frac{4K}{12a + 6b - c - 8n} = \text{const.},$$

the different heats of combustion of isomers will change the value of K, while the denominator of that term takes no account of isomerism.

The authors of this paper look upon the work of Clarke as a painstaking and commendable attempt to reduce the data of ther-

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[1] *Ztschr. phys. Chem.*, 48, 151.

[2] A. A. Noyes, in his abstract of Clarke's paper (This Journal, 25, R 256), suggests that possibly the choice of even integral numbers of henotherms to represent the various elementary heat effects may have brought about the agreement between the calculated and the observed heat effects as given by Clarke.