

The ratio of the working effect of sodic to that of potassic sulphate, as calculated from the numbers given above, is 100·16 : 100, with a probable uncertainty of 1·3 per cent. This is the *mean* value, reckoned by the method of least squares, from the whole of the observations. The rejection of the four experiments marked with an asterisk, which differ somewhat widely from the rest, would give the ratio 99·53 : 100, with a probable uncertainty of 0·73 per cent. ; while the probable error of a single observation would then be reduced from 5·02 to 2·4 per cent. [Owing to the number of determinations made, any error in the result is but very slightly affected by error in the ammonia estimation.]

The conclusions which we think may fairly be drawn from these numbers are :—

- (1.) That sodic and potassic sulphates have a well-marked influence on the reaction to which we have referred ;
- (2.) That as more sulphate is added, the reaction is accelerated ;
- (3.) That equal weights of sodic and potassic sulphates have as nearly as possible the same working effect.

The last conclusion may be otherwise expressed thus :—

If we represent our equivalent of potassic sulphate by a number, then the equivalent of sodic sulphate is represented by the same number.

II. "Researches on Chemical Equivalence." Part II. Hydric Chloride and Sulphate. By EDMUND J. MILLS, D.Sc., F.R.S., and JAMES HOGARTH. Received December 4, 1878.

While carrying out our researches on lactic acid,* it struck us that use might be made of it to compare the dynamical equivalents of acid bodies. We accordingly selected hydric chloride and hydric sulphate for the measurements in question, and prepared solutions of these acids, containing respectively 73 grammes hydric chloride (2HCl), and 196 grammes hydric sulphate ($2\text{H}_2\text{SO}_4$) per litre. An experiment was first tried with 5 grammes lactic acid and 10 cub. centims. of the hydric chloride solution in a total volume of 70 cub. centims. At a temperature of 17°C . there was no change of rotation in twenty-four hours. In a second experiment a similar solution was raised for an hour to 40°C ., and then for an hour to 60°C . ; but without effect on the rotatory power. The temperature of 100°C . was finally adopted, the change at that point taking place at a rate admitting of accurate measurement. The method of experiment was as follows :—A measuring flask was made marked to contain 60 cub. centims. ; in this were placed 50 cub. centims. of a 10 per cent. solution of lactic acid (*i.e.*, 5 grammes), the acid measured in, and the volume made up to

* *Post*, p. 273.

the mark. To prevent evaporation during heating, the neck of the flask was left long, and a narrow bent tube attached by an india-rubber joint. The time was accurately noted when the flask was placed in the bath. After half an hour, the flask was taken out quickly, plunged into cold water, and the contents when cold transferred to the polarimeter tube. The tube used in the researches on lactic acid had to be modified in these experiments, the cement not being able to withstand the action of the acid. In its altered form, the plate glass covers were secured by two screw rods and nuts, a thin washer of gutta-percha tissue being placed between the ends of the tube and the plates. This washer did not materially affect the length of the column, and made the tube perfectly tight. The length of the tube was thus reduced to 216 millims.

The results of these experiments are given in the following table. The quantity of acid is the only varied condition of experiment.

Action of Hydric Chloride and Hydric Sulphate on Lactic Acid.

Total volume in each case 60 cub. centims. Weight of Lactic Acid
= 5 grammes.

Half-hour intervals.	Hydric chloride.				Hydric sulphate.		
	No. 1. 4 cub. centims.	No. 2. 4 cub. centims.	No. 3. 7·5 cub. centims.	No. 4. 8 cub. centims.	No. 5. 4 cub. centims.	No. 6. 4 cub. centims.	No. 7. 7·5 cub. centims.
0	9·565	9·565	9·565	9·565	9·565	9·565	9·565
1	10·327	10·197	10·767	10·717	10·320	10·278	10·843
2	10·812	10·670	11·383	11·340	10·974	10·720	11·423
3	11·218	11·010	11·790	11·633	11·203	11·035	11·643
4	11·400	11·147	11·850	11·742	11·355	11·286	11·850
5	11·490						
6	11·852	11·754	..	11·445	11·850
7							
8	11·770	11·670			11·854	11·607	
9							
10							
11	11·765	11·715					

The equation A is deduced from the average of Nos. 1 and 2 by the method of least squares, the probable error of a single comparison of calculated and experimental numbers being ·0653.

The equation B is similarly deduced from Nos. 5 and 6, its probable error being ·0587.

C is the equation to No. 3 with a probable error ·0818

D " " No. 7 " " " ·1063

E " " No. 4 " " " ·0848

Equations.

A	$y = 9 \cdot 6785 + \cdot 56035x - \cdot 03621x^2$.
B	$y = 9 \cdot 6500 + \cdot 63271x - \cdot 04690x^2$.
C	$y = 9 \cdot 6827 + 1 \cdot 04941x - \cdot 11635x^2$.
D	$y = 9 \cdot 7283 + 1 \cdot 00775x - \cdot 11090x^2$.
E	$y = 9 \cdot 6889 + \cdot 98951x - \cdot 10931x^2$.

In each equation y is the rotation in degrees, x is the time in half-hours. By placing $\frac{dy}{dx} = 0$ in each equation, we find the value of x when y has its highest value. The corresponding value of y is thence calculated by substitution in the equation considered. We thus find data for the comparison of the two acids.

HCl		H_2SO_4	
A	$x = 7 \cdot 74, \quad y = 11^{\circ} \cdot 846$	B	$x = 6 \cdot 74, \quad y = 11^{\circ} \cdot 780$
C	$x = 4 \cdot 51, \quad y = 12 \cdot 048$	D	$x = 4 \cdot 54, \quad y = 12 \cdot 017$
2HCl		H_2SO_4	
E	$x = 4 \cdot 53, \quad y = 11 \cdot 928$	B	$x = 6 \cdot 74, \quad y = 11 \cdot 780$

These results show that though 2HCl may be the "equivalent" of H_2SO_4 in weight for saturation (*i.e.*, in the ordinary sense), it certainly is not the equivalent in the dynamical sense. They also render it highly probable that HCl is equal dynamically to H_2SO_4 . Ostwald,* by a method based on the alteration of the specific volume of solutions, has shown that the ratio $\frac{2HCl}{H_2SO_4} = 1 \cdot 93$, a result which our numbers, though not as perfect as we could wish, nevertheless strongly confirm.†

* "Journ. Prakt. Chem.," N.F. xvi, p. 419.

† If the curve equations be examined, it is found that the highest value of y is practically the same in each. By taking the average value $= 11^{\circ} \cdot 924$, and calculating to specific rotation (assuming that the action involves no change of weight), the number 73.78 is obtained. This falls short of the specific rotation of galactose (83°), and seems to point to the dual nature of lactic acid mentioned in the researches on lactic acid; probably at this point the sugar in solution is Fudakowski's lacto-glucose. ("Deut. Chem. Ges. Ber.," ix, 42-44.)