

LXIV.—*On certain Views concerning the Condition of the Dissolved Substance in Solutions of Sodium Sulphate.*

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FOR a long time it has been well known that if the decahydrate of sodium sulphate is dissolved in water, the solubility increases with rise of temperature up to about 33—34°, but after that the solubility

decreases. Lowel's (*Ann. Chim.*, [3], **33**, 334, and **49**, 32) results show that, starting with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , the strongest solution obtainable is that which is saturated at about  $34^\circ$ , and contains about 55 parts of  $\text{Na}_2\text{SO}_4$  to 100 of water, the solubility decreasing as the temperature rises until  $120^\circ$  is reached (Tilden and Shenstone, *Phil. Trans.*, 1884).

Other facts which have a bearing on this subject are that when a strong solution is cooled either  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , or  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  may separate, and that supersaturation, with reference to the hydrates, is easily manifested in the case of this salt.

As an explanation of these facts, it has been thought on the one hand that these point to the existence of hydrates in solution—the decahydrate, for instance, decomposing at about  $33^\circ$ , both in solution as well as in the solid state. Others were led to adopt the view that the condition of the dissolved substance is the same in all cases,\* this being the view held by Ostwald (*Lehrbuch*, Bd. I, 1060. 2nd. edit.) and others.

One reason for the adoption of the latter view is, doubtless, to reconcile the explanation of these phenomena with the developed van't Hoff theory of solution, the continuous manner in which all the known properties of a solution of sodium sulphate vary in passing through the temperature  $33^\circ$  being adduced as showing that no fundamental change takes place in the dissolved substance. Such a change might, perhaps, be difficult to detect in the case of dilute solutions, where the mass of the dissolved substance is small in comparison with that of the solvent. Of the various properties which might be examined especially for his purpose, viscosity seemed to be one which might throw further light on the subject; it is, moreover, a property which has not in all cases yielded results easily intelligible according to the van't Hoff theory, but has, on the other hand, in certain cases been thought to show the existence of hydrates and other molecular aggregates in solution, notably the results first observed by Graham of the existence of a solution of sulphuric acid of maximum viscosity corresponding in composition to  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , and like results for other substances.

Again, the change in a solution of a chromium salt, which is produced by raising the temperature of such a solution to about  $80^\circ$ , is one which alters (Sprung, *Ann. Phys. Chem.*, **159**, 34; *Phil. Mag.*, Oct., 1889) the viscosity of the solution, the change in the condition of the dissolved substance being accompanied by an alteration in the viscosity of the solution.

Hence it seemed of interest to determine the viscosity of strong

\* See, for instance, Nicol (*Phil. Mag.*, 1885), and Tilden (*Brit. Assoc. Report*, 1886).

solutions of sodium sulphate when made from the anhydrous salt and from its hydrates—to determine the variation of the viscosity as the temperature is changed—especially for temperatures near  $33^{\circ}$ , and to ascertain whether any change is produced in the viscosity by heating solutions made in the cold, and recooling them. Various observers have determined the viscosities of solutions of this salt, especially of dilute solutions.\*

### *Experimental Method.*

The time of flow through a tube being the basis of the method now universally used in experiments on the viscosity of liquids, an apparatus based on this method was devised to be especially suitable for the solutions to be used, the dimensions being arranged so (1) that the magnitudes of the quantities to be observed should be capable of being determined conveniently to about the same degree of accuracy, (2) that the flow through the tube should be linear and not turbulent, (3) that the correction for the kinetic energy of the liquid issuing from the fine tube should be small and capable of approximate calculation, (4) that the correction for the finite length of the fine tube should also be capable of approximate calculation.

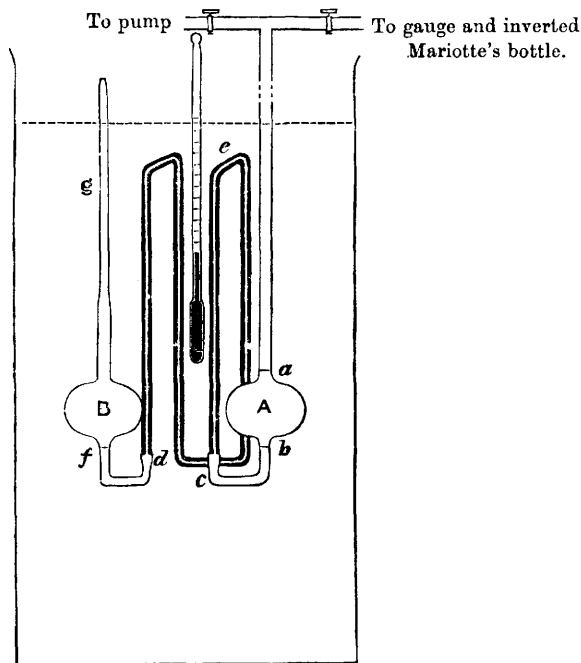
The principal constant of the apparatus was found from experiments with water at  $20^{\circ}$ , the value of the viscosity of this having been accurately determined by various observers. The value used was 0.010051, being the mean of the results of Poiseuille, Sprung, Slotte, and Thorpe and Rodger, and taken from the table given in the work of the last-named observers (*Phil. Trans.*, A, 1893).

In this way it was unnecessary to know the mean radius of the fine tube accurately, or to trouble about small inequalities of cross-section. The figure shows the form adopted, which, it is thought, has some advantages over forms which have been used in some researches on this subject. The bulbs A and B have approximately the same volume (this was secured by determining the volumes of a large number by weighing the water they contained—two experiments gave 4.61 and 4.60 for A, and 4.60 and 4.59 for B—this was before the marks *a* and *b* were etched), the fine tube *ced* is bent six times at right angles, its length is 50.5 cm. approximately, and its radius 0.030. The tube *g*, whose diameter is about 1.5 mm., was fused on to the tube on which B is blown; it was cut off of such a length that when

\* Sprung (*Pogg. Ann.*, 1876) determined the viscosities of solutions of sodium sulphate, and remarked the absence of any irregularity in passing through  $33^{\circ}$ . He did not employ, however, solutions as strong as some of those used in the experiments to be described, and was not primarily concerned with the question under discussion. The point seemed to be one worth investigating in the light of more recent work.

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the apparatus was inverted and the bulb B and its tube filled to *f*, by using the pump, the volume of the liquid so introduced into the apparatus was that required to fill A from *a* to just below *b* when the apparatus was in the upright position as shown in the figure. The



volume between the marks *a* and *b* is 4.70 c.c.; the vertical distance between *a* and *b* is about 2 cm. Hence it is secured that variations in the densities of the liquids used do not affect the effective pressure.

In the experiments described below, this apparatus was immersed in a large beaker containing about  $2\frac{1}{2}$  litres of water, kept constantly stirred. The temperatures were observed by means of a thermometer graduated to  $1/10$ th of a degree. The liquid in A was forced through the fine tube by the pressure produced by a column of water of constant height; this was secured by using a Mariotte's bottle connected with another bottle, which may be called an inverted Mariotte's bottle, as in the experiments of Přibram and Handl (*Wien Sitzungsber.*, 1878 and 1879; Ostwald, *Lehrbuch*, Bd. I, 554).

The pressure was measured by a water manometer, the scale of which could easily be read to  $\frac{1}{5}$  mm. The pressure used was about 40 cm. of water. The numbers tabulated are in each case the

mean of several observations of a very approximately constant pressure, and are corrected for variations of temperature.

Times of transpiration were measured by means of a stop-watch to nominal tenths of a second, which was rated and the necessary corrections applied.

In making an experiment, the water in the beaker was brought to a suitable temperature, the liquid filling the bulb B, then, by connecting with the pump, the liquid was transferred to A through the fine tube; thus very efficient mixing was secured, the top of the liquid being drawn up about 3 cm. above the mark *a*; the connection with the inverted Mariotte's bottle was then made, and the stop-watch started as the meniscus passed the mark *a* and stopped as it passed *b*. During the whole of this process the temperature rarely varied as much as 1/10th of a degree, being kept constant by means of a very small flame. It is considered that the average temperature of an experiment can be relied on to 1/20th of a degree.

With the dimensions chosen, the flow through the tube is linear and not turbulent, for the greatest value of the velocity of efflux should not exceed (Osborne Reynolds, *Phil. Trans.*, 1883 and 1886)  $2000 \eta / 2r\rho = 377$  cm. per sec. Where  $\eta$  denotes the coefficient of viscosity = 0.011335 according to Thorpe and Rodger for water at 15°.

$r$  = radius of tube = 0.030 for tube used.

$\rho$  = density of liquid.

Whereas the value for water at 20° was 4.2 cm. per sec., and for the solution numbers of the same order of magnitude for the solutions used; therefore, the motion was linear.

The correction for kinetic energy is very small in every case, seldom being as much as 0.2 per cent. It was calculated from Couette's formula.

$$\frac{\rho V}{8\pi(l + L)t}$$

$\rho$  = the density of the liquid;  $V$  = the volume going through the fine tube in a time,  $t$ ;  $l$  = the length of the tube;  $L$  = the correction for finite length taken as  $2.8 \times 0.06$ ;  $V = 4.7$  c.c.;  $l = 50.5$  cm.

Only a very rough value of this was required for the experiments here described. The value of  $\eta$  for the various solutions was found as follows, the complete expression for giving  $\eta$ , the coefficient of viscosity in absolute units being

$$\eta = \frac{\pi R^4 h \rho' g t}{8V(l + L)} - \frac{\rho V}{8\pi(l + L)t}$$

$R$  = radius of fine tube;  $h$  = height of manometer;  $\rho'$  = density

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of liquid in manometer;  $t$  = time of flow;  $V$  = volume of liquid going through fine tube;  $L$  = correction for finite length as above;  $\rho$  = density of liquid experimented on.

Which for a given apparatus may be written as

$$\eta = ah\rho't - \frac{\rho b}{t},$$

$a$  and  $b$  being constants, neglecting the expansion of the glass which is certainly admissible in the experiments described, the value of  $a$  was found from experiments on water as mentioned previously by putting

$$b = \frac{4.7 \times 7}{8 \times 22 \times 212.4 \times (50.5 + 2)} = 0.00369 \text{ approx.}$$

$$0.010051 = a \times 38.91 \times 212.4 - \frac{1 \times 0.00369}{212.4}$$

the average time of flow of water at  $20^\circ$  through the fine tube when the pressure was 38.91 cm. of water at  $16^\circ$ , being 212.4 seconds. Hence  $a = 0.000001218$ .

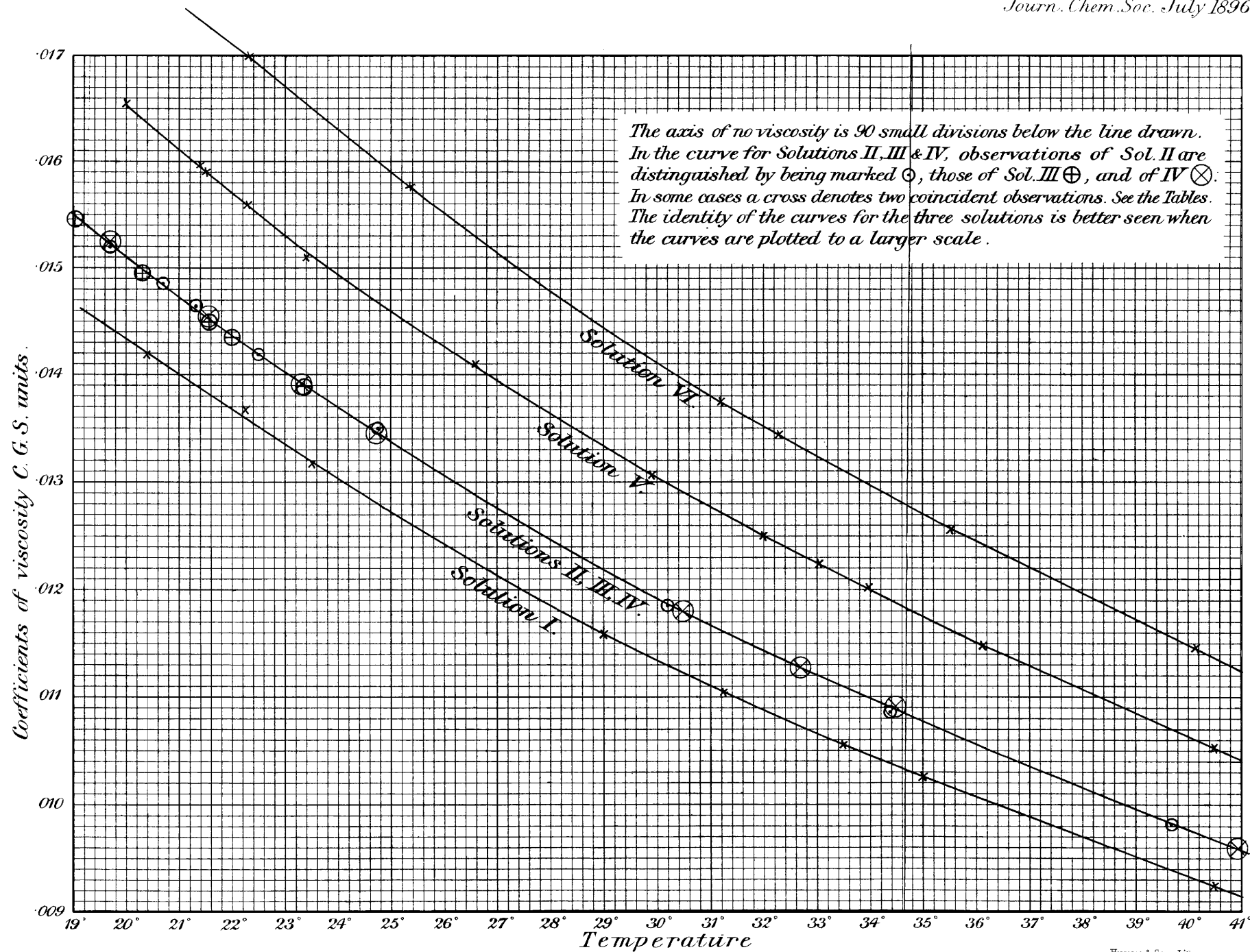
Six solutions were used; the second and third were made by dissolving the pure decahydrate (calculated to  $\text{Na}_2\text{SO}_4$ ), the others from the anhydrous salt (see Tables, pp. 999–1001).

Solutions II, III, and IV were made of very nearly the same strength, I was more dilute, V and VI were stronger, as shown in the following table.

Solution	I contained	11.65 grams $\text{Na}_2\text{SO}_4$ to 100 grams water.
"	II	13.30
"	III	13.27
"	IV	13.28
"	V	15.97
"	VI	18.50
A solution saturated at $20^\circ$ as regards $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ contains		19.4
		100

In making these, the solid taken was dissolved in the requisite quantity of water—added by means of a calibrated burette—the temperature not being raised above  $20^\circ$  (except in the case of VI). The solutions were filtered, and appeared to be free from any particles in suspension. The variations in the viscosities of these solutions for temperatures near  $33^\circ$  were determined.

The results are given in the tables and plotted in the curves. Nothing points to any abrupt change taking place in the solution at any temperature near  $33^\circ$ , the results obtained verifying Sprung's earlier observations.



The viscosities of solutions II, III, and V were determined both before and after heating to  $90^{\circ}$ , for if hydrates existed in these solutions, it is perhaps conceivable that the viscosity of a solution might depend on its previous thermal history, as is the case in a chrome alum solution, especially if supersaturation was in any way dependent on the formation or non-formation of hydrates. No such effect was, however, noticeable.

The results obtained are, therefore, in complete accordance with the view indicated by other properties, and seem to show that there is no abrupt change in the condition of the dissolved substance in passing through the temperature  $33^{\circ}$ , and that a solution made from the anhydrous salt is identical with one made from the decahydrate in spite of the differences of solubility of these substances.

Experiments were also made with solutions of the heptahydrate, and, as far as they went, seemed to confirm the results obtained with the decahydrate; as, however, there was a difficulty in getting satisfactory specimens of this hydrate, the results are not considered sufficiently trustworthy to be given.

The experiments described give the dependence of viscosity on concentration for these strong solutions; the viscosity of the stronger solutions is seen to diminish with increasing temperature more rapidly than is the case with the more dilute solutions.

I have much pleasure in thanking my friend, Dr. Ruhemann, for giving me the requisite facilities for doing this work in his laboratory.

TABLE I.—*Solution I, containing 11.65 Grams of  $\text{Na}_2\text{SO}_4$  to 100 Grams of Water.*

Mean temperature.	Pressure cm. of water at $16^{\circ}$ .	Time seconds.	<i>aht.</i>	Kinetic energy correction.	$\eta$ .
23.49°	38.92	277.7	0.013165	0.000016	0.01315
20.39	"	299.2	0.01419	15	0.014175
22.22	"	286.0	0.01356	16	0.01354
29.00	"	244.6	0.011605	18	0.01159
31.32	"	233.1	0.01105	19	0.01103
33.50	"	222.9	0.010565	20	0.010545
35.00	"	216.4	0.01026	20	0.01024
40.53	"	195.0	0.009242	23	0.009219



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TABLE II.—*Solution II, containing 13.30 Grams of Na<sub>2</sub>SO<sub>4</sub> to 100 Grams of Water.*

Mean temperature.	Pressure cm. of water at 16°.	Time seconds.	<i>aht.</i>	Kinetic energy correction.	$\eta$ .
19.73°	38.92	320.8	0.01521	0.000014	0.01520
21.27	"	309.2	0.01465	14	0.01464
23.31	"	294.5	0.01396	15	0.01394
24.78	"	285.0	0.01351	16	0.01349
24.76*	"	284.8	0.01350	16	0.01348
22.51	"	299.8	0.01421	15	0.01419
20.74	"	313.8	0.01487	14	0.01486
21.31	"	309.5	0.01467	14	0.01466
30.2	38.57	252.9	0.01188	18	0.01186
34.38	"	231.6	0.01088	19	0.01086
39.70	"	209.3	0.009832	21	0.00981

TABLE III.—*Solution III, containing 13.27 Grams of Na<sub>2</sub>SO<sub>4</sub> to 100 Grams of Water.*

Mean temperature.	Pressure cm. of water at 16°.	Time seconds.	<i>aht.</i>	Kinetic energy correction.	$\eta$ .
19.02°	38.88	326.2	0.01545	0.000014	0.01544
20.24	"	315.8	0.01495	14	0.01494
22.00	"	303.6	0.01438	15	0.01436
23.37	"	293.6	0.01391	15	0.01389
23.39*	38.84	293.8	0.01390	15	0.01388
21.57	"	306.3	0.01449	14	0.01448
20.38	"	316.0	0.01495	14	0.01494

TABLE IV.—*Solution IV, containing 13.28 Grams of Na<sub>2</sub>SO<sub>4</sub> to 100 Grams of Water.*

Mean temperature.	Pressure cm. of water at 16°.	Time seconds.	<i>aht.</i>	Kinetic energy correction.	$\eta$ .
23.29°	38.92	293.9	0.01393	0.000016	0.01391
24.77	"	284.4	0.01348	16	0.01346
19.75	"	321.4	0.01524	14	0.01523
21.58	"	307.4	0.01457	14	0.01456
34.48	"	230.8	0.01094	19	0.01092
40.96	"	203.0	0.009622	22	0.009600
32.75	"	238.3	0.01130	19	0.01128
30.49	"	219.6	0.01183	18	0.01181

\* Solution heated to 90° and re-cooled.

TABLE V.—*Solution V, containing 15·97 Grams of Na<sub>2</sub>SO<sub>4</sub> to 100 Grams of Water.*

Mean temperature.	Pressure cm. of water at 16°.	Time seconds.	<i>aht.</i>	Kinetic energy correction.	$\eta$ .
20·0°	38·93	349·1	0·01655	0·000013	0·01654
21·39	"	337·0	0·01598	13	0·01597
23·38	"	319·1	0·01513	14	0·01511
26·6	"	297·4	0·01411	15	0·01409
23·69*	"	318·0	0·01509	14	0·01508
22·30	"	329·4	0·01562	14	0·01561
21·47	"	335·8	0·01592	13	0·01591
29·90	38·92	275·6	0·013065	16	0·01305
32·00	"	264·2	0·01252	17	0·01250
33·05	"	258·4	0·01225	18	0·01223
33·97	"	253·8	0·01203	18	0·01201
36·13	"	242·4	0·01149	19	0·01147
40·52	"	222·4	0·01054	21	0·01052

TABLE VI.—*Solution VI, containing 18·50 Grams of Na<sub>2</sub>SO<sub>4</sub> to 100 Grams of Water.*

Mean temperature.	Pressure cm. of water at 16°.	Time seconds.	<i>aht.</i>	Kinetic energy correction.	$\eta$ .
22·27°	38·92	358·8	0·01701	0·000012	0·01700
25·35	"	333·0	0·015783	14	0·01577
31·20	"	290·6	0·013773	16	0·013757
32·33	"	284·2	0·01347	16	0·01345
35·54	"	265·4	0·01258	18	0·01256
40·16	"	242·3	0·011485	19	0·011466

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\* Solution heated to 90° and cooled again.