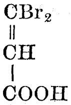
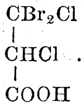
PAPERS READ BEFORE SECTION C.

On γ-dichlordibrompropionic and γ-dichlorbromacrylic acids.

BY C. F. MABERY AND H. H. NICHOLSON.

When dry chlorine is passed through β-dibromacrylic acid, the reaction is easily accomplished, and the product may be purified without difficulty by crystallization from carbonic disulphide. This acid is very sparingly soluble in water, more soluble in hot than in cold carbonic disulphide and chloroform. It melts at 100°. Its salts were carefully studied, but the silver salt was found so unstable that it could not be prepared in a state of purity. Since β-dibromacrylic acid has, without doubt, the form  $\begin{matrix}CBr_2\\ \|\\ CH\\ |\\ COOH\end{matrix}$, the chlorine addition product would have the form  $\begin{matrix}CBr_2Cl\\ |\\ CHCl\\ |\\ COOH\end{matrix}$. This acid is entirely decomposed when heated with an excess of any alkaline hydrate. If, however, the reaction is allowed to progress in the cold, keeping the hydrate in slight excess, the elements of hydrobromic acid are easily removed, with the formation of the corresponding dichlordibromacrylic acid. In order to distinguish this from two other products which have already been obtained, it will be called the γ-acid. It is prepared by the action of baric hydrate upon γ-dichlordibrompropionic acid, and the reaction proceeds so rapidly that it is difficult to keep the solution alkaline. Upon acidifying the baric hydrate solution with hydrochloric acid, γ-dichlorbromacrylic acid is precipitated partly as a crystalline solid, and is easily purified by crystallization from hot water. It is sparingly soluble in cold, readily in hot water, and in alcohol, ether, carbonic disulphide, and chloroform. It crystallizes in pearly-white scales, which melt at 78° to 80°. For further identification, the acid was analyzed, and its salts submitted to careful study.

The sub-aqueous dissociation of certain salts.

BY JOHN W. LANGLEY AND CHARLES K. McGEE OF ANN ARBOR, MICH.

The question as to whether salts are dissociated into their components when simply dissolved in water has been attacked by different chemists in various ways. The method described in this paper seems to have furnished some remarkable results, which may help in pointing the way to the final answer of this important problem.

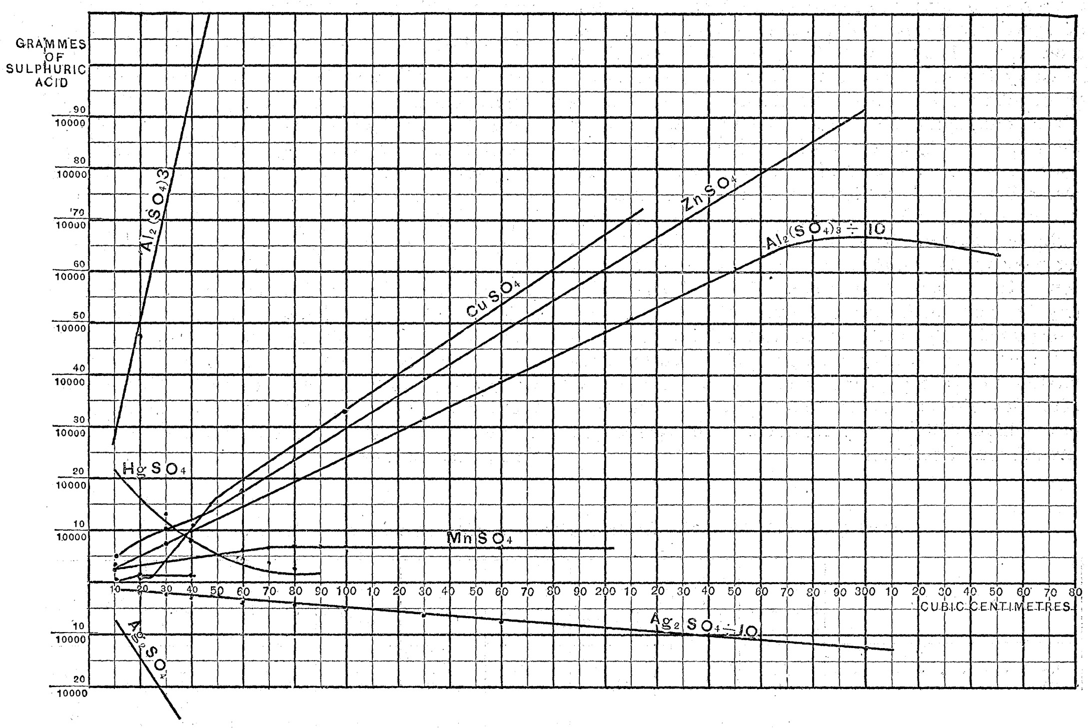
Sainte Claire Deville has called attention to apparent chemical changes which a salt may undergo by the mere fact of solution, and that such changes may increase in extent with the mere addition of water. He concludes that there is no absolute distinction between solution and chemical union; that the difference is rather of degree than of kind. From this point of view, a salt in dissolving has its particles separated much as if it were vaporized by heat, and the heat units necessary to perform this sort of vaporization are taken from surrounding bodies. As the heat absorbed increases with the degree of dilution, it will eventually become sufficient to dissociate into its elements a salt dissolved in a suitably large quantity of a neutral solvent, such as water.

Assuming that salts tend to dissociate by solution, and are decomposed when sufficiently diluted, we should expect them to break into simpler molecules first, and, of course, along the lines of least resistance. We may take three views of the possible condition of a salt dissolved in a small quantity of water — as, for instance, one molecule of sodic sulphate in two molecules of water: 1. That it is attached to the water by a sort of physical adhesion, which may be represented by $[Na_2\,SO_4\ ,\ 2H_2\,O]$. 2. That the water and salt are united in a new group which acts as a compound molecule so long as the amount of the solvent is small; this might be $[2\,(Na\,OH)\ ,\ H_2\,SO_4]$, the comma indicating a molecular as distinguished from an atomic union. 3. That we have in these cases a certain quantity of different kinds of matter held momentarily in equilibrium, but ready to form definite combinations when the external forces change. The last view would be expressed by $[Na_2\,H_2\,SO_6]$, and does not require that Na be combined with H, S, or SO_4.

The heat of combination between $H_2\,SO_4$ and 2Na OH is less than that in the formation of sodium hydrate starting with metallic sodium and water, or of sulphuric acid starting with SO_3 and water. Therefore, in the group $Na_2\,H_2\,SO_6$, the line of least resistance probably passes through where the comma is placed in the arrangement $[2\,(Na\,OH)\ ,\ H_2\,SO_4]$. Then the first stage of dissociation will be the appearance of free sodium hydrate and free sulphuric acid. The change will be partial for finite ratios between quantities of the salt and the water, and should gradually increase with augmented dilution to a point where free acid can be shown quantitatively.

For the present occasion, advantage was taken of the circumstance that in some neutral salts the bases have less power to turn litmus blue than the acids have to turn it red; and also, that in certain other salts the converse is true. Thus the power of the hydrates of zinc, iron, and copper, to turn litmus blue, is quite feeble; while the power of the mineral acids to redden litmus is very great. On the other hand, the hydrates of the alkaline metals are singularly powerful in turning litmus blue. Now, if the power of the base to produce the blue is not the exact quantitative counterpart of the acid to produce red, the difference of color-producing power must increase in proportion as the solution becomes more dilute, if the theory of dissociation is well founded.

The method of experiment may be briefly stated. A series of test tubes was prepared, holding respectively one, two, three, four, etc., portions of sulphuric acid; and each was then diluted with litmus solution to an equal amount. The tubes thus filled presented a series from neutral purple to decided red. This formed a scale of colors for reference. Saturated solutions were prepared of the sulphates of Zn, Cu, Pb, Ag, Ca, Na, Hg, Mn, Al, and Fe, and $Zn\ Cl_2$. To each of these solutions, enough litmus solution was added, in a series for each salt, to exactly correspond in amount with the sulphuric-acid tubes. As each tube of a dissolved salt was prepared, and also as it was successively diluted with increasing amounts of litmus, it was compared with the tubes in the color-scale, by looking across the two tubes, until its corresponding tint was found. A complete record of these correspondences was made; and it furnished the means for constructing a diagram, in which the results are plotted in curves.



The following were the chief results: $Ca\ So_4$ and $Na_2\ So_4$ each continued to act as a neutral salt, without effect on the litmus throughout the range of dilutions. $Ag_2\ SO_4$ was the only salt which changed the solution to a blue. The results with $Fe_2\ (SO_4)_3$ and $Fe\ SO_4$ were unsatisfactory because of a dirty precipitate, but both made the litmus red. $Zn\ Cl_2$ presented a similar difficulty. There is a doubt about the result with $Hg\ SO_4$, and some obscurity about the greatly diluted solutions of $Al_2\ (SO_4)_3$ and $Cu\ So_4$.

On account of instability of color, probably caused by oxidation, a fresh color-scale had to be prepared every day, and the mixtures were made under a film of paraffine.

These experiments seem to indicate that: 1°. Sulphates of the alkali metals, except silver, are strictly neutral under all degrees of dilution. 2°. Sulphates of the $R.\ SO_4$ type, where R is a dyad metal, show an amount of dissociation proportioned to the degree of dilution. 3°. Aluminic sulphate, and other double triads, are not neutral when concentrated. When diluted they soon become strongly acid. When the dilution exceeds a certain limit, they lose acid at a decreasing rate.

Suggestions for computing the speed of chemical reactions.

BY R. B. WARDER OF CINCINNATI, O.

THIS paper urges a thorough discussion of data upon the subject indicated in its title, for the following reasons: 1°. To discover and investigate the causes of certain discrepancies between published observations and current theories. 2°. To obtain more definite information as to the nature of certain reactions and the conditions determining their speed. 3°. To afford numerical data for a fuller study of relations between the speed of reactions and other physical constants. 4°. To suggest fruitful lines for further research in chemical dynamics.

As instances of the need of such discussion, the determinations by Professor Menschutkin, of the speed and limits of the etherification of the several alcohols and acids, give numbers for the initial speed of reaction in one hour which are not proportional to speeds during the first minute. Prof. L. Meyer in his *Dynamik der atomen* passes very lightly over both the theory and the observations of speed during a reaction.

The prevalent theory of the action of mass is expressed, $\frac{du}{dt} = k\,u\,v \ldots$ in which the differential expresses the rate of change in any substance, u and v represent the masses taking part in the change, and k is a constant. Some observations by Ostwald and others indicate that some modifications of this theory are needed. Determinations of the speed of reaction require special care, both to measure time in relation to mass, and to control temperature and other conditions. The chemical section of the Ohio mechanics' institute has recently undertaken some work of the sort, and invites co-operation.

The following provisional system is suggested: for volume, one cc.; for mass, the chemical equivalent expressed in mg.; and for time, one hour. The unit of speed would be the transformation of unit of each active body per unit of volume and time. Possibly the comparison of the constants of speed or of chemical affinity with those of heat, electricity, etc., could be better made from the unit of one second or 1,000 seconds. At least two observations of time and two of mass are required, and preferably several, to determine the limits of error. Determinations which do not accord with the hypothesis that diminished speed and diminished product vary in the same ratio, need special investigation. In reciprocal reactions, some of the ratios may be combined with constants of speed already determined. By bringing all the facts into systematic order, these data can be made of use for comparison in other physical-science fields. The paper concludes with an extended bibliography of the subject, which will be very serviceable to workers in this branch of research.

Twelve months of lysimeter record at the New-York agricultural experiment station.

BY E. L. STURTEVANT OF GENEVA, N.Y.

The lysimeters were described. They are boxes of peculiar construction, containing selected samples of soils in layers. The relative percolation of rainfall through these different soils, and the evaporation, are determined by observations of the instrument. The results are summarized as follows: Sod land allowed 11.68 of the rainfall to percolate; soil of which the surface was simply bared allowed 25.88 per cent percolation; the cultivated soil passed 37.93 per cent. The evaporation from the first of these was, of course, 88.32 per cent; from the second, 74.12; from the third, 62.07; the sum of percolation and evaporation being held to account for the entire rain-fall.

The composition of American wheat and corn.

BY CLIFFORD RICHARDSON OF WASHINGTON, D.C.

This paper gave an account of results obtained by the author in his work as first assistant chemist of the U. S. department of agriculture. More than 200 analyses of wheat, and 100 of corn, have been made during the last ten years under his supervision. It appears that while our wheats are of somewhat lighter weight, they contain less water, about the same ash, more oil, less fibre, and less albumen, than the foreign wheats. Among our wheats, only those from Colorado, Dakota, and Minnesota equal the European in albuminoids and in size of grain. The wheats of the Atlantic states are poor in nitrogen. Corn, compared with wheat, contains twice as much oil, less starch, more water and fibre, and less of albuminoids. The following table gives a condensed statement of the wheat analyses: —

Average percentage of nitrogen, albumen, etc., in wheats of the world.

COUNTRIES.	No. of analyses.	Per cent of nitrogen.	Per cent of albumen.	Highest albumen.	Lowest albumen.	Weight of 100 kernels.	Highest weight.	Lowest weight.	Authority.
Russia	24	3.12	19.48	24.56	10.68	–	–	–	Laskowsky.
Russia	5	2.34	14.63	16.56	14.24	3.610	5.350	2.000	Von Bibra.
North Germany	25	2.24	14.00	18.26	9.80	4.498	5.400	4.000	" "
South Germany	13	2.17	13.56	17.76	10.21	4.485	7.000	2.875	" "
Germany	–	2.11	13.19	–	–	–	–	–	Kühn.
Germany	–	2.08	13.09	–	–	–	–	–	Wolff.
Spain	8	2.10	13.13	15.29	11.26	4.270	5.125	3.275	Von Bibra.
France	–	2.08	13.00	–	–	–	–	–	Reiset.
Scotland	14	2.01	12.56	–	–	4.680	5.200	4.250	Von Bibra.
Australia	2	1.60	10.00	–	–	–	–	–	" "
Egypt	5	1.47	9.19	9.92	8.75	5.540	–	–	" "
All but Russia	176	2.29	13.65	19.10	5.33	–	–	–	Koenig.
America	254	1.92	12.00	17.15	8.05	–	5.924	1.830	Various.
America, except Colorado	163	1.86	11.62	16.63	8.05	3.532	5.079	1.830	"
Colorado, 1881	33	2.14	13.40	15.94	11.19	4.833	5.924	3.851	Richardson.
Colorado, 1882	12	2.09	13.06	14.88	11.55	4.299	4.670	3.976	"
Minnesota	12	2.05	12.79	17.15	10.85	3.354	3.699	3.116	"
Michigan	38	1.92	12.00	14.47	9.13	4.116	–	–	Kedzie.
Missouri	10	1.83	11.44	12.44	10.50	3.502	3.867	3.098	Richardson.
Oregon	7	1.46	9.17	10.63	8.05	4.800	–	–	"
Atlantic States	56	1.79	11.18	14.00	8.93	3.057	4.628	1.830	"
Pennsylvania	23	1.80	11.25	12.78	9.45	3.211	4.063	2.526	"
North Carolina	21	1.67	10.46	12.43	8.93	3.782	4.628	2.780	"
Alabama	17	1.82	11.32	13.65	9.80	3.137	4.647	2.011	"

The sotol, a Mexican forage plant.

BY CLIFFORD RICHARDSON OF WASHINGTON, D.C.

This plant, Dasylinion texanum, grows wild and extensively on the borders of the Rio Grande and elsewhere in Texas, and in Mexico, on a rocky and gravelly soil. The plains covered with it look like a vast cabbage-field. Sheep feeding on it go without water for many weeks. Only the bulb is eaten. It is split open by the shepherd, who carries a knife for the purpose. Mexicans eat the bulb after roasting or baking it in pits. Also a liquor is obtained from it, by fermenting and distilling after roasting, called 'sotol mescal,' and possessed of highly intoxicating powers.

The plant is described in Watson's Revision of the North-American Liliaceae. About 18 per cent of sugar can be obtained from the outer husks; in the interior, more than 10.5 per cent exists; and in the whole head of the plant there is probably more than 15.5 per cent of sugars. No starch seems to be present.

A proximate analysis of the soft interior of the head gave 17 per cent sugars: 65 per cent of this soft substance in the head, when fresh, is water.

As a food-plant in dry districts, the sotol is of great value; as a fibre-producing plant, it will not be of any importance, owing to the shortness of the cells.

American butters and their adulterations.

BY H. W. WILEY OF WASHINGTON, D.C.

A series of elaborate experiments and analyses of various samples of butter, oleomargarine, tallow, and lard, have been made by Professor Wiley, chemist of the U.S. department of agriculture. The paper contained a description of Professor Wiley's method. He takes a weighed quantity of the butter, puts it in a sand-bath, and dries for two hours at 100°. The curd or caseine is determined by ignition: five grains are used for the purpose. Dry combustion in a tube is difficult and unsatisfactory: he therefore uses the moist-combustion method, with permanganate and nesslerizing. The amount of salt he considers important. It is usually determined by ignition, and weighing the residue; but he found that so much chlorine was thereby lost, that the result was not trustworthy. He washes the butter by shaking it in a separating funnel with hot water, and then determines the chlorine with standard silver nitrate and potassium bichromate as an indicator.

Professor Wiley has devised several novelties for these analyses. One of the neatest is for ascertaining the melting-point. The butter is packed in a U-shaped tube, of which one leg is longer than the other. The tube is placed upright in a vessel containing sufficient mercury to overflow the top of the tube. This vessel is placed in another containing water, and heat is applied beneath. The water, heated, in turn heats the mercury surrounding the tube, until the contents of the tube are melted. As soon as the melting takes place, the melted material leaves the tube, and floats on the surface of the mercury. Another method consisted in laying platinum wires upon the sample of butter, etc., heating the wires, and noting the heat required to cause them to disappear by sinking into the sample. These methods determined not only the melting-point of samples of butter, oleomargarine, tallow, and lard, but also of the fatty acids. But the variations in the melting-point of genuine butter are so wide, that no certain conclusion can be arrived at by comparison with melting-point of oleomargarine, etc., to test the question of genuineness. Thus it was found that first-rate butter from an Alderney cow at one time, owing to special feeding, had a higher melting-point than oleomargarine; while a few weeks later, with different food, the same cow supplied milk from which was made butter with a lower melting-point than oleomargarine.

In regard to other tests, concerning which full details were given in the paper, it may be briefly stated, that, as a general rule, the amount of caseine present in pure butter is much greater than in oleomargarine. The specific gravity of genuine butter is lower. The saturation co-efficient for the insoluble acids in the genuine butter is low, in the imitations it is high. Professor Wiley seems to place more reliance on tests for saturation co-efficient than on other methods. The soluble fatty acids in pure butter range from three to five per cent; while in oleomargarine, tallow, etc., they are either absent, or show a mere trace. The author also called attention to polarization tests. The genuine butter gives a uniform field in polarized light: oleomargarine gives a field with mottled and crystalline structure. He had made no analysis of butter known or suspected to be adulterated by mixture. He considered it unwise to decide the question of genuineness from any one of the constituents or conditions of a sample; believing that all the different tests should be brought to bear. He presented elaborate tables of analyses of different kinds of butter, etc.; specifying for each the place of purchase, name sold by, price, color, percentage of water, of caseine, of salt, specific gravity at 40°, melting and solidifying points, percentage of soluble and of insoluble acids, and the melting and solidifying points and the saturation equivalent of the insoluble acids.

The discussion respecting the analysis of butter which was brought about by this paper revolved around the question of the value of the data presented for the practical work of the determination of actual proportion of adulteration. Mr. Noyes held that the variations in pure butters in specific gravity, in melting-point, in saturation co-efficient, and in caseine, as determined by Professor Wiley, would be of little value except in cases where the adulteration was very great. Mr. Springer held that the principal constituent to be taken into account in the determination of adulteration was the amount of caseine, and that although there were some difficulties in the way of its accurate determination, they might be removed, and he should then have more faith in this than in the comparison of other data. He suggested that the accurate determination of caseine might be effected by some rapid-fermentation process by which caseine could be broken up into other organic products that could be separated by albumen. He held to this point as to caseine, because it cannot conveniently be added in the manufacture of oleomargarine; while the acids upon which the saturation co-efficient depends could readily be added as sodium compounds.

On account of the difficulty of getting accurate results in determining nitrogen, it was thought best to use the wet-combustion method with permanganate, because a small quantity of material might be used, and there would be fewer chances for loss that otherwise occurs in nitrogen determinations that are effected by the combustion of butters.

Dr. Wheeler called the attention of the section to the use of what is known as 'cotton-seed-oil stock,' in the manufacture of oleomargarine. This, doubtless, contains considerable nitrogen, and, of course, would reduce the value of the caseine-test for adulteration. A sample was shown, supposed to contain cotton-seed-oil.

The sense of the discussion was, that it was very desirable that Professor Wiley should continue his experiments, as they are of great value; but there is yet a great deal of work to be done in the investigation.

List of other papers.

The following additional papers were read in this section:—The formation and constitution of chlordibromacrylic acid, by *C. F. Mabery* and *Rachel Lloyd.* Orthiodtoluolsulfonic acid, by *C. F. Mabery* and *G. M. Palmer.* Estimation of carbon and nitrogen in organic compounds, by *C. Leo Mees.* New forms of burettes, by *W. H. Seaman.*

PROCEEDINGS OF SECTION D.—MECHANICAL SCIENCE.

PAPERS READ BEFORE SECTION D.

A comparison of terra-cotta lumber with other materials.

BY T. B. BAKER OF MILLERSVILLE, PENN.

THE material called 'terra-cotta lumber' is made out of clay and sawdust. The investigation which formed the subject of this paper was to ascertain certain qualities of this artificial product. The paper also described the apparatus used for the tests. The results indicated that the material was 875 times as permeable to air as pine, and 135 times as brick. Air was forced by pressure of a column of water. Other tests showed that the material was four times as hard as pine, but not so hard as brick. Its grip on nails driven into it was about half that of pine. The author was careful to disclaim any intention of advertising the merits of the material, but he evidently regarded it as serviceable for the purposes for which it is intended. Specimens were exhibited.

Improvements in shaping-machines.

BY J. BURKITT WEBB OF ITHACA, N.Y.

IN the ordinary shaping-machine there are two defects, one of which is found also in the planer. The ram of a shaping-machine is a bar sliding in bearings, and carrying at one end the cutting-tool. If we represent by a the variable horizontal distance from the tool to the first bearing (or nearest end of the long bearing), and by b the variable horizontal distance from the tool to the second or farthest bearing (back end of long bearing), and by c the length of stroke, we shall have,—

Maximum value of $a =$ (minimum value of a) $+ c$.
Maximum value of $b =$ (minimum value of b) $+ c$.

In other words, the length of the ram is variable, and the spring of the ram from the work is variable, the tool springing away from its work more at the end of its stroke. This springing takes place mostly in the joint between the ram and its bearings, and cannot be wholly avoided without a change of construction. To remedy the defect, the author proposes a reversed construction of the sliding parts; the two bearings (preferable to a long bearing) to be formed on the ram, so as to make the distances a and b constant, and the long slide being part of the bed of the machine.

The second defect, which is also common to the planer, is in having a 'drop-block' which fits but indifferently between the jaws and against the bottom of its seat. From the necessity of the usual construction, the tool attached to this block will have more or less spring. The remedy is to dispense with the drop-block, and introduce an automatic motion to lift the tool on the return stroke, as has been done, the author has understood, on some large machines.

Regularity of flow in double-cylinder rotary pumps.

BY J. BURKITT WEBB OF ITHACA, N.Y.

THE speaker introduced his subject by exhibiting a number of models of these pumps from the cabinets of Cornell university, which has recently purchased copies (243 in number) of the celebrated models of the Reuleaux collection in Berlin. Class I. of this collection is devoted to these pumps. The speaker then produced and demonstrated a formula for the flow of these pumps, and showed that the regularity of flow depended upon other principles opposite to those which have been given for determining this point. The formula given for the flow was:—

$\pi[R'^2 + R''^2 - (r'^2 + r''^2)] =$ Flow for one revolution, when R' and R'' (generally equal to each other) are the extreme radii of the two revolving wheels; and r' and r'' are the radii (often, perhaps generally, variable) from the point of contact between the wheels to their centres. It was shown that the regularity of flow depends upon $r'^2 + r''^2 =$ constant. R' and R'' may be called the 'piston radii,' and r' and r'' the 'valve radii.' These pumps are