

## Abstracts from American and Foreign Journals.

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*A Chemical Study of Vegetable Albinism, Part II, Respiration and Transpiration of Albino Foliage*, A. H. CHURCH (1880, 1).—In this paper the author has sought to determine "The exact relation of equal areas of white and green foliage to carbon dioxide, oxygen and moisture." White foliage has not the power of decomposing carbon dioxide, either in strong daylight or actual sunshine; but adds largely to the normal amount of that gas in the air, thus behaving like flower petals. The plants experimented upon were *Cyperus alternifolius*, *Acer negundo*, *Ilex aquifolium*, *Hedera helix* and *Alocasia macrorrhiza*. The first of these gave indecisive, and the last yielded the best, results. When the otherwise white leaves contained green patches, these were "stopped out" by painting with collodion. The leaf-stalks placed in tubes containing recently boiled, distilled water, cooled out of contact with the air, were arranged under a bell-jar, so that the air from the leaves could be made to pass through a Pettenkofer's absorption tube containing baryta water.

The loss of water suffered by albino leaves, as compared with green ones, was also studied, using white and green holly leaves. When these were placed in water, the green leaves gained 1.55 per cent., and the white ones 0.29 per cent.; while without water, the white leaves lost 6.54, and the green ones, 10.26 per cent. of their original weight, in 3½ hours under the same circumstances.

*On Alpha-methylhydroxysuccinic Acid, the Product of the Action of Anhydrous Hydrocyanic Acid upon Ethylacetoacetate*, GEORGE H. MORRIS (1880, 6).—The author of this paper has gone over the work of Demarçay, who describes this body as oxypyrotartaric acid. The acid and its salts were prepared, the acid reduced with fuming hydriodic acid, and the products of its dry distillation examined.

The acid was prepared by heating a mixture of two parts of pure ethylacetoacetate and one part of anhydrous hydrocyanic acid, in sealed tubes for three days, at 100°; heating the resulting product on a water bath till hydrocyanic acid was expelled, and then boiling with dilute hydrochloric acid till the decomposition was complete. The acid was finally purified by treatment with ether, precipitation of the

coloring matters with basic lead acetate, evaporation of the ethereal solution, and drying over sulphuric acid in a vacuum. So obtained, the acid was a crystalline mass, very deliquescent, easily soluble in alcohol and ether, and crystallizes from these solvents in star-like groups of needles. It melts at  $108^{\circ}$ , and decomposes at a higher temperature. The barium, calcium, potassium, silver, lead and copper salts of this acid, are described by the author. The free acid gives no precipitate with neutral or acid lead acetate, but is completely precipitated by the basic acetate. A solution of a neutral salt of this acid gives a precipitate with basic lead acetate, and also with silver nitrate; but with neutral lead acetate, or barium hydrate, it gives no precipitate.

The conclusion drawn from the action of fuming hydrylic acid upon this acid is, that pyrotartaric acid is first formed, which under the influence of hydrylic acid, splits up into either butyric or isobutyric acid, and carbon dioxide.

By dry distillation it was found that the acid decomposed at about  $140^{\circ}$ , carbon dioxide, with a little carbon monoxide, and an acid, watery liquid, being the products. When the acid had been heated to  $200^{\circ}$ , and the evolution of gas had ceased, the temperature was raised to  $210-215^{\circ}$ , and a yellow oil distilled over. When the oil ceased to come over, nothing but a black, coaly residue remained. The watery distillate contained acetic acid and methylic alcohol. The yellow oil proved to be citraconic anhydride, giving silver and lead salts identical with those formed from known citraconic acid.

*Contributions to the History of Putrefaction, Part I*, C. T. KINGZETT (1880, 15).—The details of a number of experiments upon putrefaction are given, and also the results of the action of potassium permanganate upon organic bodies, both fresh and in various stages of decomposition. The experiments prove that putrefaction can begin and proceed in the absence of oxygen, as such. In some experiments the putrescible solutions used slightly more oxygen, from potassium permanganate, after a time than at the start, and some of them used less. Finally, in the putrefactive process there comes a time when the activity of the agencies at work diminishes, and finally ceases.

These experiments have a direct bearing on the oxygen process of water analysis, and show that the amount of oxygen that a water takes up from potassium permanganate, even if it contains organic matter, does not give any idea of the degree of decomposition such organic matter has undergone.

**Notes on Manganese Dioxide**, C. R. ALDER WRIGHT and A. E. MENKE (1880, 22).—The experiments described are a continuation of the "Second Report on Some Points in Chemical Dynamics," published in the *Journal* (1878, 504). Manganese dioxide was prepared according to the following methods:

1. By the action of nitric acid upon potassium permanganate.
2. From manganese superchloride by precipitating with water.
3. By the action of sulphuric acid on potassium permanganate.
4. By the action of sulphur dioxide on potassium permanganate.
5. By the action of alcohol or glycerine on potassium permanganate.
6. By the action of potassium permanganate on manganese sulphate.
7. Manganese superoxide prepared by the action of air and caustic potash upon manganese chloride.
8. Manganese dioxide precipitated by bromine in presence of potassium acetate.
9. Manganese dioxide from manganese nitrate by heat.

From an examination of the preceding products, the authors arrive at the following conclusions: The manganese dioxide prepared by precipitation is a hydrate ( $\text{MnO}_2 \cdot \text{H}_2\text{O}$ ) which loses its water at ordinary temperatures. Neither at ordinary temperatures, at  $100^\circ$ , nor at  $210^\circ$ , does this hydrate become anhydrous. At ordinary temperatures, and at  $100^\circ$ , there is no material loss of oxygen; but at  $210^\circ$ , oxygen is slowly given off. The substance made by heating manganese nitrate does not lose oxygen thus.

Hydrated manganese dioxide, prepared in presence of potassium salts, invariably carries down more or less potash.  $\text{K}_2\text{O}$  varies from 2.50 to 14.85 per cent. of the dry manganese dioxide. And when the precipitation takes place under such conditions, that not much potash (or other metallic oxide) can be carried down, a deficiency of oxygen is noticeable in the precipitate  $\text{MnO}$  being carried down.

The precipitate formed by reducing potassium permanganate with sulphur dioxide, alcohol or glycerine, contains much less available oxygen than corresponds to the manganese present.

The substance formed by heating manganese nitrate to  $160^\circ$  is free from combined potassium, even if much potassium nitrate is present.

Hydrated manganese dioxide, heated for a long time in hydrogen, loses all or nearly all the potash, leaving green  $\text{MnO}$  behind.

Manganese monoxide, prepared by heating in hydrogen, but not long enough to expel all the potash, frequently oxidizes spontaneously in ordinary moist air; while that free from potash does not so oxidize.

Manganese chloride is sensibly volatile in a stream of hydrochloric acid gas, at a red heat.

***The Comparative Value of Different Methods of Fractional Distillation***, FRED. D. BROWN (1880, 49).—The author divides the methods of fractional distillation into two classes; those in which the vapors are passed through layers of the condensed liquid are called *washing methods*, and those in which the vapors are cooled by coils kept at a given temperature, are called *cooling methods*.

Distillations of mixtures of carbon disulphide and benzene were conducted in an apparatus called a dephlegmator, by which the vapors were washed; and also in a flask containing a tube to hold a thermometer, and having a lateral branch bent upward to hold another thermometer, and this branch again having a lateral tube to conduct the vapors to the condenser.

After reducing the results obtained from these two apparatuses to a common form, and also those obtained by distillation from a retort, and from a flask with T-piece without the upward bend, the author represents the results in a diagram of curves. From these curves it appears that the simple T-piece used to insert the thermometer, had considerable influence on the distillation; that both the dephlegmator and cooling tube gave better results than the retort and the flask with simple T-piece; and finally, that the distillation with cooling tube bent upward was rather better than with the dephlegmator.

The author also experimented upon the effect of rapidity of distillation on the results, using a special form of dephlegmator. By distilling a mixture of carbon disulphide and benzene, it was found that the slower the distillation, the more carbon disulphide was in the distillate.

Experiments made with a coil apparatus capable of being maintained at a given temperature, showed "that when the still head is maintained at a temperature equal to the boiling point of the most volatile compound in a mixture, that compound alone, or nearly alone, passes over into the condenser." By using this apparatus, the author has separated benzene from commercial benzene, and always in a nearly pure state.

***On the Influence Exerted upon the Course of Certain Chemical Changes by Variations in the Amount of Water of Dilution***, M. M. PATTISON MUIR and CHARLES SLATER (1880, 60).—The authors have determined by a number of experiments, the influence of variations in the quantity of water in the system,  $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 + x\text{H}_2\text{O}$ ; and also in the reaction,  $\text{BaCl}_2 + \text{K}_2\text{C}_2\text{O}_4 = \text{BaC}_2\text{O}_4 + 2\text{KCl}$ . In the first case they find, that the amount of chemical change in a given

time decreases regularly as the amount of dilution increases; and suppose that the chances of collision between the molecules of sodium carbonate and calcium chloride are decreased, the greater the number of inactive water molecules interposed.

In the second case, the same conclusions were drawn from the same circumstances; but when the temperature of the vessel in which the change proceeded, was decreased, it was found that the amount of chemical change in the same time, is retarded to a proportionately greater extent by a large than a small quantity of water of dilution. And when the change is allowed to proceed for a long time, there is the same irregularity in the action of the diluting water. The same results are obtained when the temperature is allowed to rise to  $16^{\circ}$  or  $18^{\circ}$ .

The authors ascribe this increased retarding action of large masses of water, to the formation of hydrates of barium chloride, and consider the cryohydrate as the most important. At moderate temperatures, this cryohydrate has least chance to form, and there results a regular action in the water of dilution. But at low temperatures, cryohydrate tends to form, and being produced in the presence of a large mass of one of the products of its own dissociation, it is stable. The greater the mass of water, the greater the stability of the cryohydrate, other conditions being constant.

The authors think that the irregularity in the amount of chemical change in the barium system with various masses of water, is due to a state of strain between its parts; and the principal forces are, the force tending to produce cryohydrate molecules, the force tending to split up these molecules, and the force tending to separate the the chemically active molecules of the system.

The paper is illustrated with a number of diagrams of curves, showing the amount of chemical change under various circumstances.

*On the Influence of Temperature upon the Decomposition of Barium Chloride by Potassium Oxalate in Aqueous Solution*, M. M. PATTISON MUIR (1880, 78).—The solutions used, and the methods employed, were the same as in the preceding paper. The influence of temperature begins to be felt when 300 c.c. of water of dilution are added; the increase in the amount of chemical change is considerably greater for the rise of temperature from  $3^{\circ}$  to  $20^{\circ}$ , than for that from  $20^{\circ}$  to  $80^{\circ}$ . When 600 to 700 c.c. of water are added, the increase in the amount of chemical change is very small for the first  $20^{\circ}$ , but after that the increase is rapid.

In concentrated solutions, temperature exerts very little influence on the amount of chemical change under consideration; in more

dilute solutions, an increase of  $20^{\circ}$  makes a marked increase in the amount of change; but after this the influence of temperature is regular. With yet more dilute solutions, increase of temperature causes, at first, a slight increase in the amount of chemical action. As the temperature rises, the amount of action rapidly increases, until a point is reached where increase of temperature but slightly affects the amount of chemical change. With very dilute solutions, the influence of temperature becomes very nearly regular.

*On Alpha- and Beta-Phenanthrenecarboxylic Acids, with Remarks on the Constitution of Phenanthrene*, FRANCIS R. JAPP (1880, 83).—In the preparation of calcium phenanthrenesulphonate, the author noticed that there was a relatively small yield of crystals, and much dark colored mother liquor. From the crystals, alpha-phenanthrenecarboxylic acid was obtained, by converting them into a sodium salt, distilling the latter with potassium ferrocyanide, and saponifying the nitrile obtained. The acid thus obtained has been described by the author in conjunction with Dr. Schultz (Ber., **10**, 1661); and the author gives the melting point of the purified acid as  $266^{\circ}$ , instead of  $260^{\circ}$ .

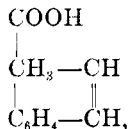
From the dark colored mother liquor, mentioned above, the author has prepared beta-phenanthrenecarboxylic acid, which is isomeric with the alpha compound. The mother liquor was treated with sodium carbonate until alkaline, then filtered from calcium carbonate, and evaporated to dryness. The dried sodium salt was mixed with potassium ferrocyanide, and distilled. The nitrile obtained was yellow, transparent, viscid, and became like butter after some days. It was saponified with alcoholic potash, and boiled until ammonia ceased to be evolved; and the new acid separated by acidifying with hydrochloric acid, as a dirty white precipitate. 2 kilos of commercial phenanthrene gave 80 grms of the crude acid. By making the sodium salt of this acid, and repeatedly crystallizing, the white acid was obtained by treatment with hydrochloric acid.

Beta-phenanthrenecarboxylic acid is soluble in alcohol, ether, and glacial acetic acid, almost insoluble in water. It melts at  $250$ – $252^{\circ}$ . The author's formula is  $C_{15}H_{10}O_2$ , for the acid;  $C_{14}H_9CO_2Na + 5H_2O$ , for the sodium salt; and  $(C_{14}H_9CO_2)_2Ba + 6H_2O$ , for the barium salt.

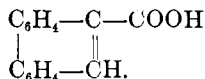
The beta-phenanthrenecarboxylic acid obtained as above, gave phenanthrene on heating with soda-lime; and the quinone obtained from the phenanthrene by oxidation, dissolved without residue in acid so-

dium sulphite. By oxidizing the new acid with chromic acid in acetic acid solution, phenanthrenequinone was obtained.

From the above and some previous results of the author, he considers the following points of theory: Since alpha-phenanthrene-carboxylic acid yields phenanthrenequinonecarboxylic acid on oxidation, the carboxyl group remaining intact, the formula of alpha-phenanthrenecarboxylic acid is



and, since beta-phenanthrenecarboxylic acid gives phenanthrenequinone on oxidation, eliminating the carboxyl group, the latter must be attached to one of the carbon atoms united with quinonic oxygen in the quinone. This would make the formula of beta-phenanthrenecarboxylic acid,



After reviewing much past work done on this subject, the author considers that phenanthrene consists of three benzene nuclei, one of which shares four adjacent carbon atoms with the two others—one ortho pair with each.

**On some Derivatives of Phenylacetic Acid.** P. PHILLIPS BEDSON (1880, 90).—NITRO-DERIVATIVES. Phenylacetic acid, when nitrated, yields two isomeric derivatives, the para and the ortho.

1. *Paranitrophenylacetic acid* is soluble in hot water, from which it crystallizes in long needles; it is sparingly soluble in cold water, and easily in alcohol and ether. The formula found is  $\text{C}_8\text{H}_7\text{NO}_2\text{O}_3$ . When oxidized with potassium bichromate and sulphuric acid, it yields paranitrobenzoic acid.

*Methylparanitrophenylacetate*,  $\text{C}_6\text{H}_4\text{NO}_2\text{CH}_2\text{CO}_2\text{CH}_3$ , crystallizes from alcohol, and melts at  $54-55^\circ$ . *Ethylparanitrophenylacetate* also crystallizes from alcohol, and melts at  $62-64^\circ$ .

*Paramidophenylacetic acid*,  $\text{C}_6\text{H}_4\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$ , is prepared by the reduction of the parinitro acid by tin and hydrochloric acid. It melts at  $199-200^\circ$ , with decomposition. Analysis gave  $\text{C}_8\text{H}_9\text{NO}_2$  as the formula.

2. *Orthonitrophenylacetic acid*. When crystallized from hot water, white needles are obtained, which melt at  $137-138^\circ$ . Analysis gave the following as the composition:  $\text{C}_8\text{H}_7\text{NO}_3\text{CH}_2\text{CO}_2\text{H}$ . When

boiled with potassium permanganate this acid yields ortho-nitrobenzoic acid. Upon reduction it gives oxindol.

3. *Bromo-derivatives.* Bromophenylacetic acid is prepared by treating phenylacetic acid and mercuric oxide suspended in water, with the calculated quantity of bromine in small quantities, keeping the mixture cool. When the reaction is complete, excess of caustic soda is added, and the filtrate from the mercuric oxide is treated with hydrochloric acid; the bromo-acid separates out as a precipitate, and, after washing, is crystallized from alcohol. These crystals melt at  $76^{\circ}$ . The alcoholic mother liquors yield an acid with a higher melting point, and give a barium salt from which crystals are obtained, which yield the acid on treatment with hydrochloric acid.

*Parabromophenylacetic acid* is obtained by crystallizing the above acid from hot water. It melts at  $114-115^{\circ}$ . It is a monobromophenylacetic acid, with the same melting point as the parabromophenylacetic acid of Loring Jackson and W. Lowery (Ber., **10**, 1210). The formula is  $C_8H_7BrO_2$ .

*Orthobromophenylacetic acid.* The mother liquors from the barium salts mentioned above, are treated with lead acetate, and the washed precipitate boiled with dilute sulphuric acid. The filtrate from the lead sulphate gave an acid, in crystals, melting at  $103-104^{\circ}$ . Its formula is  $C_8H_7BrO_2$ . It gives orthobromobenzoic acid by oxidation with potassium permanganate; hence, it is orthobromophenylacetic acid.

These results show that the parabromophenylacetic acid described by Radziszewski, melting at  $76^{\circ}$ , is a mixture of two isomerides.

4. *Bibromo-derivatives.* A bibromo acid is made from crude bromophenylacetic acid (m. pt.,  $76^{\circ}$ ), by exposing it to sun-light in sealed tubes, with the calculated quantity of bromine, for several months. The product obtained is converted into methyl ether, as it cannot be obtained in crystals. The methyl ether is distilled under reduced pressure, and comes over at  $220-230^{\circ}$ ; it is saponified, the potassium salt decomposed with hydrochloric acid, and an acid crystallized from water. This acid has a melting point of  $114-115^{\circ}$ , and a bromine determination shows it to be bibromophenylacetic acid.

5. *Bromonitro-derivatives.* Short notices of two of these have already been published (Ber., **10**, 530 and 1637). The following facts are given, and also an account of a third isomeride.

*Parabromometanitrophenylacetic acid*,  $C_8H_8NO_2Br.CH_2CO_2H$ , crystallizes from hot water, and melts at  $113-114^{\circ}$ . It is insoluble in



cold water, but dissolves easily in alcohol and ether. By oxidation with potassium bichromate and sulphuric acid, it gives parabromometanitrobenzoic acid. Its formula is  $C_8H_5NO_2BrO_2$ . The barium salt has the composition  $Ba(C_8H_3BrNO_4)_2 + H_2O$ . It is soluble in water, and a dilute solution gives precipitates with silver nitrate, copper acetate and lead acetate.

The methyl ether gives yellowish needles, melting at  $40-41^\circ$ . Its ethyl ether has only been obtained as an oily liquid.

*Parabromometamidophenylacetic acid*,  $C_8H_3NH_2Br.CH_2CO_2H$ , is obtained by reducing the nitro acid with tin and hydrochloric acid, and crystallizes from water. It is easily soluble in alcohol and chloroform, sparingly in ether. It melts at  $133-134^\circ$ . Its hydrochlorate crystallizes in white needles, soluble in cold water.

*Alpha-bromonitrophenylacetic acid* crystallizes from water, and melts at  $167-169^\circ$ . It is soluble in alcohol and ether, and insoluble in cold water. The barium salt is soluble in hot water, and has the composition  $Ba(C_8H_3BrNO_4)_2 + 4H_2O$ . The aqueous solution of the barium salt gives precipitates with silver nitrate, copper acetate, and lead acetate.

The methyl ether forms needles melting at  $66-68^\circ$ ; the ethyl ether forms yellowish needles.

*Alpha-bromamidophenylacetic acid* is made by reducing the nitro acid with tin and hydrochloric acid. It crystallizes in needles which melt at  $167^\circ$ , with decomposition. It is soluble in alcohol and chloroform, sparingly in ether.

*Beta-bromonitrophenylacetic acid*. This is the third isomeride formed with the two preceding ones. It was obtained by extracting with chloroform the mother liquors from the nitration of bromophenylacetic acid. The extract was dissolved in glacial acetic acid, and slow evaporation gave an acid, melting at  $162^\circ$ , and crystallizable from hot water. Reduction with tin and hydrochloric acid gives bromamidophenylacetic acid, melting at  $168^\circ$ . The formula of the bromamido acid given is  $C_8H_3Br.NH_2.CH_2CO_2H$ .

*On the Specific Volume of Water of Crystallization*, T. E. THORP and JOHN I. WATTS (1880, 102).—Playfair and Joule have noticed that the volumes of certain hydrated salts are exactly equal to that of the water they contain, considered as ice. In salts less highly hydrated, this law does not hold good.

The present paper contains the results of an investigation to determine the precise relation between the specific volume of a salt and its degree of hydration. These results were obtained by taking

the specific gravity of a number of salts of different degrees of hydration. The specific volume of a salt is the volume in cubic centimeters occupied by the equivalent of the salt taken in grms. The following table gives a synopsis of the results obtained by the authors:

Hydrate.	0	1	2	3	4	5	6	7
Copper sulphate.....	44.4	54.3	67.0	80.0	.....	109.1	.....	.....
Magnesium sulphate....	44.8	55.6	67.0	.....	.....	112.4	130.8	146.6
Zinc sulphate.....	45.6	54.7	66.6	.....	.....	113.7	130.2	146.8
Nickel sulphate.....	44.6	56.5	.....	.....	.....	.....	129.0	144.6
Cobalt sulphate.....	44.7	55.2	70.9	.....	97.4	114.6	130.1	146.0
Manganous sulphate....	45.0	55.7	73.6	86.6	98.2	114.4	.....	.....
Ferrous sulphate.....	44.5	56.2	67.7	.....	100.5	.....	.....	146.7
Mean of means.....	44.8	55.5	68.8	83.3	98.7	112.9	130.0	146.1

The numbers at the head of the vertical columns indicate the molecules of water of hydration contained in the salt used, and each result is the mean of experiments by the authors and others; the figures at the foot of the vertical columns being the mean of these means.

The conclusions, drawn from the above observations, are, that the volume occupied by the several molecules of water varies with the degree of hydration. Thus for the first hydrate its mean relative value is 10.7, and the difference between the monohydrate and the dihydrate is 13.3; between the dihydrate and the trihydrate, 14.5; between the trihydrate and the tetrahydrate, 15.4, and so on for other hydrates.

**Note on the Formation of Ozone During the Slow Oxidation of Phosphorus,** HERBERT McLEOD (1880, 118).—Ozonised oxygen, prepared with a Siemen's tube, was passed through a U-tube containing sodium carbonate solution, a mixture of potassium bichromate and sulphuric acid, and potassium permanganate saturated with carbonic dioxide. In all the cases the ozone passed through even when the tube was placed in boiling water.

Corresponding experiments were made with air in which phosphorus was slowly oxidizing. After drawing the air through the U-tube with one of the above reagents, both cold and at 100°, in all cases it gave a blue color when passed through potassium iodide and starch solution.

The effect of raising the tubes to 150–200° was also tried, and the gas escaping still decomposed potassium iodide.

Since hydroxyl and ozone may be formed simultaneously by oxidizing phosphorus, the action of these bodies upon one another was examined. Some commercial peroxide of hydrogen was intro-

duced into a cylinder of ozonised oxygen, and the gas affected ozone paper even after prolonged agitation. But if the acid mixed with the hydroxyl is neutralized with sodium carbonate, or the liquid is made very slightly alkaline, the ozone is destroyed.

The author regards the above experiments as evidence that the gas formed by the slow oxidation of phosphorus, has the properties of ozone and not peroxide of hydrogen.

*On the Analysis of Organic Bodies Containing Nitrogen, etc.,*  
W. H. PERKIN (1880, 121).—After pointing out the defects of the present methods, the author describes a number of experiments to obtain a simple and effective method to attain the point in view, and finally adopts the following :

Instead of using metallic copper to stop the nitrous fumes given off when nitrogenous bodies are burned in oxygen, potassium chromate is used. It is found that this salt absorbs nitrous fumes when cold, and also when heated. It is, of course, essential that the chromate should be free from alkali. The presence of small quantities of bichromate is not harmful ; but bichromate alone does not work as well as the chromate. The chromate is granulated by evaporating the solution, and stirring the mass till dry ; or pumice stone may be saturated with the solution and dried. With uric acid the author found 6-7 inches of filled tube sufficient. The best temperature appears to be just below a dull red heat.