# A COURSE OF PRACTICAL WORK IN THE CHEMISTRY OF THE GARDEN

D.R.EDWARDES-KER









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# PRACTICAL AGRICULTURAL CHEMISTRY

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# A COURSE OF PRACTICAL WORK IN THE CHEMISTRY OF THE GARDEN

FOR TEACHERS AND STUDENTS OF HORTICULTURE GARDENING AND RURAL SCIENCE

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## CHEMISTRY OF THE GARDEN

## CHAPTER I

#### THE CHEMISTRY OF PLANTS

THE ash obtained by ignition of leaves and other parts of plants represents the mineral constituents that have been obtained from the soil during the life of the plant. The ash contains calcium (lime), potassium, iron, carbonates, sulphates, phosphates, etc., and in those cases in which it is obtained in quantity (*e.g.* bonfire ashes), is of value as a fertiliser.

#### EXPERIMENT I. Preparation of Plant Ash.

Some leaves or other portions of plants are placed in a porcelain basin, and heated over a Bunsen burner. Steam is at first produced from water in the material, and then charring occurs owing to the burning of the dry matter. The heating is continued until all blackness due to the presence of unburnt carbonaceous matter disappears, and the greyish or white residue of plant ash is allowed to cool and used for the next experiment.

## THE CHEMISTRY OF PLANTS [CHAP.

## EXPERIMENT 2. Chemical Examination of Plant Ash.

(a) Some of the ash is dissolved in a very small quantity of concentrated hydrochloric acid. The effervescence noticeable is due to the presence of *carbonates* in the ash.

(b) Some of the solution so obtained is diluted with its own volume of water, and then treated in two portions with potassium ferrocyanide and potassium thiocyanate respectively. In the first case a blue precipitate, in the second a red coloration, show the presence of *iron*.

(c) To some of the solution of the ash in hydrochloric acid is added a few drops of barium chloride solution. The presence of *sulphates* is indicated by the production of a white precipitate of barium sulphate.

(d) Some of the original ash is dissolved in a little concentrated nitric acid, some ammonium molybdate solution added, and the whole boiled. A canary-yellow precipitate shows the presence of *phosphates*.

(e) To a solution of the ash in dilute nitric acid is added some silver nitrate solution. The presence of *chlorides* is indicated by the white precipitate of silver chloride.

The presence of the above constituents, and, in addition, nitrogen, which is lost during the process of ignition, may be shown directly in plants without incineration.

## I.] CHEMICAL ELEMENTS IN PLANTS

## EXPERIMENT 3. Detection of Chemical Elements in Plants.

(a) *Carbon.* Some leaves are cut into pieces, placed in a test-tube, and granulated copper oxide added. A cork provided with a delivery-tube is placed in the end of the tube, and the contents are then heated over a Bunsen burner. Carbon dioxide will be produced, as shown by passing the gases evolved into lime water contained in another test-tube, when the lime water will become milky.

 $C + 2CuO = CO_2 + 2Cu$ 

(b) Nitrogen. Some pea-meal, or other plant material finely chopped, is mixed with twice its bulk of soda-lime and heated in a test-tube. Under these conditions the nitrogen-containing bodies give ammonia, the presence of which can be demonstrated by holding a piece of red litmus paper in the gases evolved at the mouth of the test-tube.

(c) *Phosphorus*. A few crystals of potassium nitrate (saltpetre) are heated in a test-tube until they melt, and many successive small portions of pea-meal added on the point of a knife. After each addition of material the nitrate should be heated until all action is at an end. The mass is then allowed to become quite cold, after which it is dissolved in warm water and the solution obtained divided into two portions. To one is added nitric

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## 10 THE CHEMISTRY OF PLANTS [CHAP.

acid and ammonium molybdate, and the mixture warmed. A yellow precipitate indicates phosphate that has been formed from phosphorus-containing bodies in the pea-meal.

(d) Sulphur. The second portion of the solution obtained is treated with hydrochloric acid and barium chloride, the formation of a white precipitate showing the presence of sulphate produced from sulphurcontaining bodies in the peas.

The presence may be shown in plants of many substances which are destroyed during the process of ashing or ignition with potassium nitrate. Starch, sugar, cellulose (fibre), gum and other similar *carbohydrates* containing no nitrogen and built up by the plant from the carbon dioxide of the air, and *proteins* or nitrogenous bodies formed from carbon dioxide in conjunction with nitrates obtained from the soil, are examples of such compounds. The value of plants as human and animal foods depends largely upon the presence of these bodies.

## EXPERIMENT 4. Detection of Sugar.

Some carrots, raisins, or ripe fruits (plums, apples) are cut up and boiled with water in a flask for some little time. The sugars are thereby extracted together with other water-soluble constituents, and their presence may be shown by boiling some of the aqueous extract with Fehling's solution,<sup>1</sup> when a brick-red precipitate of cuprous oxide,  $Cu_2O$ , will be obtained.

<sup>1</sup> See Appendix.

## I.] STARCH AND CELLULOSE

Starch exists in plants in the form of granules, which vary in size and shape according to the plant in which they are produced.

#### EXPERIMENT 5. Detection of Starch.

A small potato, after washing and peeling, is grated to a pulp, and the latter tied up in a piece of linen. The bag and contents are then well kneaded under water in a beaker, whereby the fine starch granules pass through the interstices of the cloth. The turbid liquid is allowed to settle, and the water poured off from the starch. A very small quantity of the latter is transferred by a glass rod to a testtube half full of water, which is then boiled for a few minutes. After cooling, a single drop of a solution of iodine in potassium iodide<sup>1</sup> is added, the deep blue colour produced being indicative of starch. This blue colour is discharged on heating to 80° C., but returns on cooling.

Cellulose is found in largest quantity in the woody or fibrous parts of plants, and gives rigidity to the structure. The older the plant, the more fibrous and tougher is the texture of the cellulose.

# EXPERIMENT 6. Preparation and Properties of Cellulose.

Some stalks of plants, or full-grown leaves, are finely chopped, and boiled with dilute sulphuric acid for half an hour. The undissolved matter is collected <sup>1</sup> See Appendix.

## 12 THE CHEMISTRY OF PLANTS [CHAP.

on a piece of cloth, washed with hot water, and then boiled for another half-hour with dilute caustic soda solution. After washing with water, the cellulose so obtained is subjected to the following tests :----

(a) A small portion is vigorously shaken in a corked test-tube with Schweizer's reagent.<sup>1</sup> The cellulose will become disintegrated and gradually dissolved. The common solvents, water, ether, alcohol, dilute acids and alkalis, are without action on cellulose.

(b) About I c.c. of concentrated sulphuric acid is placed in a test-tube and small pellets of the cellulose dropped in at intervals, as the previous portions dissolve with shaking. When the rate of dissolution of the cellulose becomes slow, the testtube is nearly filled with water, and the solution so obtained boiled in a beaker for five minutes. A portion is then rendered alkaline with very strong (syrupy)<sup>1</sup> caustic soda solution, Fehling's solution added, and the mixture boiled. The red precipitate shows the presence of sugar that has been formed from the cellulose, the chemical structure of these two bodies being very similar. By suitable fermentation of this sugar, alcohol could be obtained, and this is the basis of the process of manufacture of alcohol from sawdust, wood pulp, etc.

 $\begin{array}{ll} C_6H_{10}O_5 + H_2O = C_6H_{12}O_6\\ (\text{Cellulose}) & (\text{Grape Sugar}) \end{array}$ 

<sup>&</sup>lt;sup>1</sup> See Appendix.

The complex nitrogenous compounds called proteins make up the "flesh" of plants, and are especially abundant in peas, beans, and other plants of the leguminous order. These plants do not, however, require excessive nitrogenous manuring on this account, as they alone of all plants possess the power of obtaining the nitrogen they require from the air (*nitrogen fixation*).

#### EXPERIMENT 7. Tests for Proteins.

Pea-meal, which contains about one quarter of its weight of a protein called *legumin*, is examined as follows :—

(a) Xantho-proteic reaction. A small quantity of the meal is heated with I c.c. of concentrated nitric acid in a test-tube until completely dissolved. To the light yellow solution is *cautiously* added syrupy caustic soda solution<sup>1</sup> until alkaline. Immediately the acidity is neutralised the colour will suddenly deepen to dark yellow or orange.

(b) *Biuret reaction*. A trace of pea-meal is dissolved in caustic soda solution with the application of heat, and to the resulting liquid after cooling is added I or 2 drops of a very dilute solution of copper sulphate. A violet colour will be produced.

(c) Adamkiewics's reaction. A little pea-meal is dissolved in glacial acetic acid with gentle heating. The test-tube containing this solution is inclined

<sup>1</sup> See Appendix.

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## 14 THE CHEMISTRY OF PLANTS [CHAP. I.

at an angle of 45°, and about I c.c. of concentrated sulphuric acid poured slowly down the inside so as to form a layer at the bottom of the acetic solution. A violet ring appears at the junction of the two liquids, the colour deepening on standing.

Many garden plants, lavender, rosemary, sage, mint, etc., contain essential oils, to which their odour and their value is due.

### EXPERIMENT 8. Preparation of Essential Oils.

Some lavender heads, or finely chopped leaves of the plants mentioned, are placed in a retort together with sufficient water. A round-bottomed flask large enough to allow the neck of the retort to reach well into it, is clamped almost horizontally, and a steady stream of water arranged to run over it. On boiling the contents of the retort, steam together with essential oil passes into the flask, and both are there condensed. The essential oil may be readily extracted by shaking the distillate with about one quarter of its bulk of petroleum ether, separating the ethereal layer, and distilling off the ether on a water-bath by means of suitable apparatus.

(Caution.—Petroleum ether should not be brought within six feet of a flame.)

#### CHAPTER II

#### CHEMISTRY OF SOILS

THE soil is the source of all the mineral constituents, and also the nitrogen, of plants. Fertile soils can hence be shown to contain phosphates, sulphates, lime, potash, magnesia, organic nitrogen, nitrates, etc.

## EXPERIMENT 9. Detection of Phosphates in Soil.

A small quantity of a fertile soil is ignited in a porcelain basin in order to burn off organic matter. The material is then boiled in a test-tube with a few cubic centimetres of concentrated nitric acid, and after cooling and settling, the clear liquid decanted off. Ammonia solution insufficient in amount to neutralise all the acid is added, followed by ammonium molybdate solution. On warming, the characteristic yellow precipitate indicating phosphates is observed.

### EXPERIMENT 10. Detection of Potash in Soil.

By boiling some soil with dilute hydrochloric acid in a test-tube, potash salts together with certain <sup>15</sup>

### CHEMISTRY OF SOILS

CHAP.

other compounds are extracted. The solution is filtered, the filtrate evaporated to dryness in a basin, and the residue heated to redness over a Bunsen burner. Silica and other bodies are rendered insoluble by this treatment. The cooled mass is then scraped into a test-tube, shaken with a little cold water, and the solution of potassium chloride so obtained filtered from insoluble matter. The presence of potash is shown in the clear liquid by the addition of a little acetic acid, followed by some sodium cobaltinitrite<sup>1</sup> solution, when a reddish precipitate will be obtained.

All plants excepting those of the pea and bean family (*leguminosæ*) are entirely dependent on the soil for their nitrogen. The reserve form in which this nitrogen exists in the soil is *humus*, a complex nitrogenous organic compound produced by the bacterial decay of vegetable and animal matter.

## EXPERIMENT 11. Proof of Organic Nitrogen in Soil.

A small quantity of soil is tested as in experiment 3(b) above.

## EXPERIMENT 12. Preparation of Humus.

Thirty or forty grams of a peaty soil are placed in a beaker of suitable size, and about half full of dilute hydrochloric acid. The mixture is well stirred as

<sup>1</sup> See Appendix.

#### HUMUS

long as it effervesces, after which it is poured into a piece of calico about a foot square. The corners of the cloth are gathered together, and as much liquid as possible squeezed out. The residue is returned to the beaker, well stirred with water, and the mixture again poured into the calico and squeezed dry. This process is repeated until the water squeezed out does not give an acid reaction (red coloration) with litmus paper. The solid matter which is now free from acid is once again placed in the beaker, and dilute ammonia solution added to the half-way mark. The whole is thoroughly mixed and allowed to stand for some hours, or even days, whereby the humus is dissolved out in the ammonia. The coffee-coloured liquid is then separated from the solid matter, using a piece of cloth as before, but this time the liquid portion is saved. To this liquid is carefully added strong hydrochloric acid until a bulky precipitate of humus (humic acid) is formed. This precipitate is filtered off by means of a funnel and filter paper, and a portion tested for organic nitrogen as in experiments 3 (b) and 11.

Although humus is the reserve form of nitrogen in the soil, this nitrogen is not assimilable by plants until it has been converted into nitrate by bacterial agencies. The necessary nitrifying bacteria are present in all soils, consequently all soils contain appreciable amounts of nitrates. The nitrates never accumulate in ordinary soils, as they are too rapidly removed by growing plants, and by the washing or leaching action of rain water.

### CHEMISTRY OF SOILS

[CHAP.

## EXPERIMENT 13. Detection of Nitrates in Soil.

About twenty grams of soil are shaken with 100 c.c. of distilled water, the soil allowed to settle and the clear liquid filtered off. About 2 c.c. of this filtered extract are poured into a test-tube, and a sufficient amount (3 to 5 drops) of a solution of diphenylamine<sup>1</sup> in pure sulphuric acid added to give a distinct milkiness. This milky liquid is then carefully poured on to the surface of I c.c. of pure nitratefree sulphuric acid contained in another test-tube, and the junction of the two liquids examined. A blue ring should be immediately produced, or, if the amount of nitrate present is small, will gradually develop. If there is no visible blue ring after five minutes, some of the filtered soil extract should be concentrated to a small bulk by boiling, and then again tested.

The experiment is of course valueless if there is the slightest trace of nitrates in either the sulphuric acid or distilled water used, and these reagents should be carefully tested prior to making the examination.

Nitrification is the term applied to the conversion in the soil of ammonium salts into nitrates by the agency of specific bacteria in conjunction with the oxygen of the air. Organic nitrogen (in humus, farmyard manure, shoddy, etc.) is first changed into ammonium salts by other bacterial action, nitrification of these ammonium compounds then taking

<sup>&</sup>lt;sup>1</sup> See Appendix.

#### NITRIFICATION

place. As a plentiful supply of air is required for this latter change, it is stimulated by tillage, owing to the resultant aeration of the soil.

## EXPERIMENT 14. Nitrification by Soil Bacteria.

A solution for the nutrition of the bacteria is made up as follows :-- 3 grams potassium phosphate. 2 grams ammonium sulphate, I gram magnesium sulphate, a trace of common salt, and 2 drops of dilute ferric chloride solution, are added to I litre of water and well shaken. One hundred c.c. of this solution are placed in each of two flasks, the mouths of which are then plugged with cotton wool. The flasks and their contents are sterilised by boiling for five minutes, and after cooling the plugs are removed. and about 4 gram of chalk, previously sterilised by heating, introduced into each. To one flask only is also added a pinch of arable soil. The two flasks are again plugged and placed in a warm cupboard. Every three or four days some of the solution is removed from each flask and tested separately for nitrates with diphenylamine and sulphuric acid. If the experiment has been carefully carried out, the liquid in the flask to which no soil was added should show no nitrate reaction for some weeks, while the contents of the other flask should give a pronounced blue ring at the first time of testing.

The presence in soil of a certain percentage of calcium carbonate (chalk), or "lime" as it is wrongly called, is of the

## CHEMISTRY OF SOILS [CHAP.

utmost importance for many reasons (see page 30), and the cropping power of many soils may be considerably increased by the application of chalk, or lime which rapidly undergoes conversion into chalk.

## EXPERIMENT 15. Detection of Calcium Carbonate in Soil.

About a gram of dry soil is placed in a test-tube, and covered with a few cubic centimetres of dilute hydrochloric acid. The mixture is shaken, and the amount of effervescence produced by the action of the acid on the chalk is observed. If there is a visible effervescence, it may be concluded that the soil contains a sufficiency of chalk. If the mouth of the test-tube has to be brought to the ear before the effervescence can be heard, an application of chalk or lime would probably be beneficial, while if no effervescence can be detected at all, the soil examined is badly in want of treatment in this direction.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$
  
(Chalk)

The water-holding capacity of soils, and consequently their ability to withstand drought, depends mainly upon the fineness of division of the soil particles; the smaller the particles, the greater the retentive power for water.

## EXPERIMENT 16. Comparison of Water-holding Capacity of Soils.

Four ordinary lamp glasses are fitted at the bottom with pieces of calico tightly stretched and

## II.] FLOCCULATION OF CLAY

firmly tied. The four vessels so improvised are filled to exactly the same height with air-dry samples of (a) coarse sand, (b) a loam, (c) a heavy clay soil, (d) a peaty soil or peat moss, in the respective cases, and they are then clamped in vertical positions over medium-sized beakers. Two hundred c.c. of water are then poured on the top of the soil in each of the glasses, and the drainings collected in the beakers below. By measuring the volumes of liquid collected when drainage is complete, a comparison of the water-retaining capacities is made.

Successful treatment of heavy clay land is one of the most difficult problems of work in the garden or field. Clay if treated or worked when in a wet condition, readily becomes sticky and "puddled," or "deflocculated" as it is scientifically termed. Such puddled clay is unworkable, and even after drying is extremely intractable and difficult to deal with. This undesirable condition can be corrected by several different agencies that bring about flocculation, such as the action of frost, or by treatment with lime, chalk, or certain salts.

## . EXPERIMENT 17. Flocculation of Clay.

A small quantity of clay is deflocculated by kneading with distilled water in a beaker, more water then being added to the sticky mass to bring it to the consistency of a thin cream after well mixing. This cream is diluted to about I litre with water, and after allowing any stones or other large particles to

settle, the turbid liquid is poured in lots of 200 c.c. into four gas cylinders.

To No. 1 is added 1 c.c. dilute hydrochloric acid.

To No. 2 is added 5 c.c. lime water.

To No. 3 is added 1 c.c. dilute caustic soda solution. While 4 is kept as a control.

The contents of each cylinder are well stirred, and are then allowed to settle. The rapidity of clearing of the columns of liquid is noted, when it will be found that the acid is strongly deflocculating in its effect, the lime water also fairly strongly so, while the caustic soda has the effect of keeping the clay particles permanently deflocculated.

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## CHAPTER 111

#### CHEMISTRY OF MANURES AND FERTILISERS

CONTINUED cropping results in an impoverishment of the soil by a gradual removal of the mineral constituents and nitrogen. The constituents on which these losses fall most heavily are nitrogen, phosphates, and potash salts, and the supply of these is kept up by the addition of fertilisers containing them. Such artificially added plant foods may be either of organic (animal or vegetable) origin, *e.g.* farmyard manure, shoddy, guanos, bone meal, in which case they add also valuable humus to the soil; or of inorganic origin, *e.g.* nitrate of soda, superphosphate, potash salts.

MANURES OF ORGANIC ORIGIN.

Farmyard manure contains nitrogen, phosphates, and potash, but varies considerably in composition. The large amount of organic matter present is converted on decomposition into humus, a substance of great value on account of the improvement it effects in the texture and water-holding capacity of soil.

## EXPERIMENT 18. Examination of Farmyard Manure.

The presence of nitrogen in farmyard manure is shown by the method used in Experiment 3 (b).

### 24 MANURES AND FERTILISERS [CHAP.

Some of the manure is dried, and then strongly ignited, the ash so obtained being tested for phosphates and potash as in Experiments 2(d) and 10 respectively.

Guanos are valuable fertilisers possessed of an extremely high reputation, and commanding a high price in consequence. Consisting of the consolidated dung of sea-birds, they contain when fresh both nitrogen (up to 14 per cent.) and phosphates (up to 9 per cent.). If originally deposited on islands subject to occasional rains, the more soluble nitrogenous constituents have been washed out, and the material is then phosphatic only. Fish "guano" and meat "guano" are not guanos in the true sense of the term, but are nevertheless valuable manures.

#### EXPERIMENT 19. Examination of Guano.

The colour of the material should be noted, as guanos containing both nitrogen and phosphates are grey, while the phosphatic guanos are reddish or brown. Chemical tests for nitrogen and phosphates should be applied.

Other manures of organic origin are shoddy (nitrogenous only, and especially valued for hops and fruit trees), bone meal (nitrogenous and phosphatic), dried blood (nitrogenous), steamed bone flour (phosphatic only), and rape dust (mainly nitrogenous, traces of phosphates and potash).

#### EXPERIMENT 20. Examination of Shoddy.

The points on which shoddy is valued are: (1) content of nitrogen; (2) texture. A sample of

shoddy should be examined to determine whether the material is lumpy or homogeneous, and coarse or finely divided. The best shoddies (above 9 per cent. nitrogen) are like wool in appearance, while low-grade samples (below 4 per cent. nitrogen) are generally dirty, lumpy, with little of the texture of the original wool.

FERTILISERS NOT OF ORGANIC ORIGIN.

III.]

*Nitrogenous.* Nitrate of Soda, Sulphate of Ammonia, and the new fertilisers prepared from atmospheric nitrogen, nitrolim or calcium cyanamide, and nitrate of lime.

Phosphatic. Superphosphate. Basic Slag. Potassic. Kainit. Sulphate of Potash. Potash Salts.

Nitrate of soda is a natural deposit found a few feet below the surface in Chile, Bolivia, and Peru. It is subjected to a crude method of purification on the spot by crystallisation from water. It contains 16 per cent. of nitrogen.

## EXPERIMENT 21. Examination of Nitrate of Soda, NaNO<sub>3</sub>.

(i.) A few crystals are exposed to the air for an hour or so. They rapidly become moist, and finally dissolve in the water they absorb from the atmosphere. Nitrate of soda should therefore not be stored in sacks in moist localities. (The same applies to nitrate of lime.)

(ii.) A few crystals are shaken up with water in a test-tube and will be found rapidly to dissolve. Nitrate of soda is hence speedily dissolved in the soil water, and coming into quick contact with the

## 26 MANURES AND FERTILISERS [CHAP.

plant roots, acts as an extremely rapid fertiliser. For the same reason it is washed away into the drains, if there be not already growing plants in possession of the ground ready to utilise it.

Sulphate of ammonia is a by-product in the manufacture of ordinary coal gas. Most samples are greenish in colour, and contain about 20 per cent. of nitrogen.

## EXPERIMENT 22. Examination of Sulphate of Ammonia, (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>:

(i.) A little of the fertiliser is heated in a basin or on a piece of sheet iron over a Bunsen burner. The substance is entirely converted into vapour, and no residue should be left.

(ii.) A few crystals are exposed to the air as in Experiment 21 (i.). There will be no absorption of atmospheric moisture.

(iii.) Some of the substance is dissolved in water, and will be found to do so readily. It is not so quick-acting a fertiliser as nitrate of soda, however, as it has first to undergo nitrification before it can be utilised by plants. In spite of its ready solubility it is not washed out of even fallow land, as it is held firmly by certain soil constituents.

(iv.) Some of the solution obtained is boiled with caustic soda and the smell of ammonia so produced is noticed, and tested with red litmus paper.

Superphosphate is prepared by treating certain ground

#### SUPERPHOSPHATE

III.]

mineral phosphates with sulphuric acid, whereby a large proportion of the insoluble phosphate is rendered soluble.

EXPERIMENT 23. Examination of Superphosphate.

(i.) A little superphosphate is moistened with water and tested with blue litmus paper. It will be found to be strongly acid; hence it should not be employed on sour or acid soils, or indeed on those deficient in calcium carbonate.

(ii.) Some superphosphate is shaken with water in a test-tube, the liquid filtered free from insoluble matter, and the clear filtrate tested for phosphate with nitric acid and ammonium molybdate.

Superphosphate contains a large percentage of its phosphate in the water-soluble form, hence is quick in its action. It is not washed out of soils by rain, being retained by constituents of the soil.

*Basic slag* is a by-product in the removal of phosphorus from iron in the manufacture of steel.

## EXPERIMENT 24. Examination of Basic Slag.

(i.) Some slag is rubbed between the fingers. It should be an impalpable powder, otherwise it is too slow in action.

(ii.) Some basic slag is moistened with water and tested with red litmus paper. It will be found to be alkaline in reaction, a condition due to the presence of free lime; hence basic slag is of especial value on sour, acid land.

## MANURES AND FERTILISERS [CHAP.

(iii.) Some slag is shaken up with water, the solution filtered, and the filtrate tested for phosphate as usual. It will be found that there is no watersoluble phosphate, hence the fertiliser is not so quick in its action as is superphosphate.

(iv.) A small quantity is shaken up with dilute citric acid solution, and after filtering, the solution tested for phosphate, a good indication of which will be obtained. The phosphate is therefore not entirely insoluble, although it does not dissolve in water.

Practically all the potash fertilisers on the market are derived from the natural salt deposits at Stassfurt in Germany. Kainit, the commonest in use, is marketed as mined, but sulphate of potash and muriate of potash are prepared by methods of crystallisation of the natural salts.

## EXPERIMENT 25. Examination of Kainit.

(i.) A sample of kainit is examined, and the different coloured particles picked out and placed together in small heaps. It will be evident that kainit is not a pure salt but a mixture; in fact, it contains sulphates, chlorides, salts of soda and lime, as well as of potash.

(ii.) The presence of sulphates, chlorides, lime, and potash should be demonstrated by the chemical tests that have been described.

Kainit cannot be employed as a fertiliser for potatoes if it be applied immediately before the "seed" is sown, as the

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## III.] SULPHATE OF POTASH

chlorides it contains have the effect of rendering the tubers of bad quality and waxy in texture ; for the same reason, muriate of potash is even worse, and for application at the time of sowing, sulphate of potash alone can be employed. The use of the cheaper kainit is, however, possible if it be applied some months before sowing, as the chlorides are then washed away, while the potash is retained as carbonate by the soil.

## EXPERIMENT 26. Examination of Sulphate of Potash, K<sub>2</sub>SO<sub>4</sub>.

The pure white colour of the salt is noticed, indicative of the fact that this fertiliser is a pure chemical compound and not a mixture, as is kainit. When tested for chlorides by nitric acid and silver nitrate, only the slightest opalescence should be obtained.

Incompatible Mixtures. A soil often requires manuring with regard to more than one constituent, and it is convenient to mix the separate fertilisers. Certain of the substances mentioned above cannot be left in contact without undergoing a loss of valuable constituents, and care should be taken not to make a mixture of fertilisers that deteriorates in this way.

## EXPERIMENT 27. Superphosphate and Nitrate of Soda (or Nitrate of Lime).

Equal parts of nitrate of soda and superphosphate are well mixed, placed in a stoppered bottle, and allowed to stand overnight. If the air in the bottle be tested with moist blue litmus paper next day, it will be found to be distinctly acid. This acidity

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is due to the production of free nitric acid, the evolution of which naturally results in the loss of part of the fertilising constituent (nitrate) of the nitrate of soda.

# EXPERIMENT 27. Basic Slag and Sulphate of Ammonia.

A test similar to the last is carried out with these two fertilisers, a piece of red litmus paper being employed. The alkalinity detected is due to the volatilisation of ammonia liberated by the action of the free lime in the basic slag. (Similarly, lime or chalk and sulphate of ammonia should not be mixed in practice.)

Lime and chalk, although not direct plant foods, are largely used for the treatment of soil, and should doubtless be more frequently applied than is often the case. The beneficial effect of these substances is due to several different actions :— (i.) Neutralisation of acidity, especially in those soils that tend to become sour after repeated heavy dressings of dung; (ii.) a favouring of the growth of the nitrifying and other bacteria in soils; (iii.) liberation of insoluble potash compounds, especially in heavy clay soils; (iv.) improvement in the texture of heavy land. Although both lime and chalk act similarly, the former should not be brought into contact with plants, owing to its caustic nature, but should only be applied to soil which is at the moment fallow.

## EXPERIMENT 29. Examination of Lime.

(i.) A sample of lime is sprinkled with a little water, when a considerable rise in temperature

## LIME

should be noticed, and the lime should swell up and fall to powder. This phenomenon is due to the slaking of the lime, and the quality of the latter can be roughly gauged from the vigour of the action, poor or "grey" limes showing practically no change.

> $CaO + H_2O = CaH_2O_2$ (Quicklime) (Slaked lime)

(ii.) A small quantity of the lime is boiled with strong hydrochloric acid in a test-tube. The greater the undissolved residue, the poorer the quality of the lime.

(iii.) Some lime is exposed to the air for about twenty-four hours, is then placed in a test-tube and treated with dilute hydrochloric acid. The effervescence noticed is due to the fact that the lime has been converted into chalk by absorption of the carbon dioxide of the air.  $CaO + CO_2 = CaCO_3$ . This action of course takes place in the field when lime is applied, and it might be thought that it would be more economical to employ, in the first instance, the cheaper chalk. This is not entirely so, however, as (1) the cost of carriage of lime is cheaper than for an equivalent quantity of chalk; (2) the lime on slaking falls to a fine powder which is much more easily distributed than chalk, unless the latter be finely ground; (3) lime exerts a certain sterilising action on harmful organisms in the soil, a property not possessed by chalk.

## CHAPTER IV

#### CHEMISTRY OF SPRAYS AND WASHES

WASHES and sprays of various compositions are used largely for combating the different insect and fungous pests from which fruit trees, flowers, and vegetables are liable to suffer. The sprays in general use may be conveniently considered in the following classes :—

Insecticides.—(a) Toxic washes for caterpillars and other biting-mouthed insects. Arsenic in some form or another is the poisonous constituent of most of these sprays.

(b) Contact washes for aphides and other sucking-mouthed insects. As these insects live on the sap of the plants, they are naturally not poisoned by treating the plants superficially with toxic washes, and have to be dealt with by the use of sprays that either block up their breathing pores and act as corrosives (e.g. soft soap, paraffin) or exert a poisonous action on their bodies (e.g. nicotine). Quassia is also employed for the sake of the astringent and cleansing properties it possesses.

(c) Winter washes of caustic alkali for use on dormant wood. The hibernating quarters of many insects are thus removed.

Fungicides.-(d) Various copper compounds.

(e) Sulphur, either in the free form (flowers of sulphur) or else combined (liver of sulphur, lime-sulphur).

## CHAP. IV.] LEAD ARSENATE WASH

## EXPERIMENT 30. Preparation of Lead Arsenate Wash.

In 100 c.c. of water is dissolved  $\frac{1}{4}$  gram of anhydrous sodium arsenate or  $\frac{1}{3}$  gram of the crystalline salt, and in another 100 c.c. water is dissolved I gram of lead acetate (sugar of lead). The latter solution is then slowly added to the former with constant stirring, when a precipitation of insoluble lead arsenate in a finely divided form takes place.

 $_{2}Na_{3}AsO_{4} + 3(CH_{3}.COO)_{9}Pb$ 

 $= Pb_{3}(AsO_{4})_{2} + 6CH_{3}. COONa$ (Lead arsenate)

The wash so prepared when sprayed on to the leaves will rapidly kill caterpillars, but containing as it does both soluble arsenic and free acetic acid, may produce a certain amount of scorching of the foliage in some cases.

(For making the wash in quantity, use 2 ozs. anhydrous or  $3\frac{1}{2}$  ozs. crystalline sodium arsenate to 5 gallons water, and 7 ozs. lead acetate to another 5 gallons, and mix as directed.)

Soft soap is used alone in solution for combating the attacks of various insects such as aphides, while it is also employed in conjunction with nicotine and quassia in many cases, giving greater adherence to the sprays. It is also valuable for diminishing the surface-tension of water in the preparation of paraffin emulsions, and a permanent emulsion of paraffin can be prepared for use when required by melting together soft soap and paraffin to give a paraffin jelly in which the oil is in the form of an emulsion.

## EXPERIMENT 31. Determination of Lathering Power of Soap.

The value of soap when used either alone or in conjunction with other substances depends upon its lathering power, a property which varies both with the quality of the soap and the hardness of the water used. Five grams of soft soap are dissolved in dilute alcohol, and made up to 500 c.c. with distilled water. Fifty cubic centimetres of tap water are placed in a flask, and a few cubic centimetres of the soap solution run in from a burette. On shaking, no lather will generally be produced, the soap having been precipitated in the form of a curd by the calcium and magnesium compounds in the water. More soap solution is then added, the mixture being well shaken after each addition, and the procedure repeated until a permanent lather is formed. The volume of soap solution required to produce the lather is then noted.

The lathering power of soap with any certain water is generally given in pounds of soap required to produce a permanent lather with 100 gallons of water; this value can be calculated from the number of cubic centimetres of soap solution required in the above titration, thus:—

Suppose 20 c.c. soap solution were required to produce a lather. Then 20 c.c. soap solution  $\equiv \cdot 2$ 

## IV.] PARAFFIN EMULSION

grams soap, for 5 grams of soap are present in 500 c.c. of the soap solution prepared.

Hence .2 grams soap lather with

50 c.c. = 50 grams tap water, therefore  $\cdot 2 \times 20$  (=4) grams soap lather with  $50 \times 20$  = 1000 grams tap water;

or, expressed in pounds,

1000 *lbs.* tap water require 4 *lbs.* soap, 100 *gallons* tap water require 4 *lbs.* soap.

It may be generally stated that with a water of 16-20 degrees of hardness (a medium hard water), a good soap should be found to have a lathering power of from  $3\frac{1}{2}$  to 4.

As stated above, paraffin has a distinct insecticidal value, but cannot be applied in the concentrated form. It will not dissolve in water, but can be made to form an emulsion, especially in the presence of soap.

## EXPERIMENT 32. Preparation of Paraffin Soft-Soap Emulsion.

Thirty-five grams of soft soap are dissolved in I litre of water in a suitable vessel, and 100 c.c. of paraffin poured on to the surface of the liquid. By means of an ordinary garden syringe, with a "rose" nozzle containing a large number of fine openings, the paraffin layer and some of the water is sucked up, and then forced vigorously into the bulk of the liquid. This operation is performed several times, in fact

CHAP.

until there is no visible oily layer on the surface. The emulsion so prepared will contain the paraffin suspended in extremely small globules in the body of the soap solution. The emulsion cannot be kept, as the paraffin will gradually rise to the surface.

(For the preparation of the emulsion in quantity, take water, 10 gallons; soap,  $3\frac{1}{2}$  lbs.; paraffin, 1 gallon.)

EXPERIMENT 33. Preparation of Paraffin Jelly.

Fifty cubic centimetres of paraffin and 8 grams soft soap are placed in a beaker, which is then covered with a plate of glass. The covered beaker and its contents are heated until the mixture boils, and I c.c. of water is then poured in. On cooling, the liquid becomes a jelly, of which I gram is taken and stirred with 40 c.c. of water. The jelly will readily dissolve to give a liquid suitable for spraying, and, as the jelly will keep for any length of time, furnishes a convenient means of preparing an emulsion at short notice for treatment of red spider, aphis, etc.

(For preparation in quantity, 5 gallons paraffin, 8 lbs. soft soap, 1 pint water when boiling. For use, 10 lbs. jelly to 40 gallons water.)

"Bordeaux mixture" is a copper fungicide that is very largely used. Its method of preparation is due to the fact that the copper must be obtained in the form of an insoluble precipitate of sufficient fineness not to settle rapidly nor to clog the fine nozzle of the spraying machine. The presence in the mixture of any soluble copper results in a scorching of the foliage.

#### BORDEAUX MIXTURE

## EXPERIMENT 34. Preparation of Bordeaux Mixture.

Eight grams of crystallised copper sulphate are dissolved in 500 c.c. water, and the same weight of quicklime is shaken up with an equal volume of water. The copper sulphate solution is then gradually added to the other solution with constant stirring, and the mixture poured into a tall gas jar or measuring cylinder. The blue precipitate of basic copper sulphate will gradually fall to the bottom, and the longer this settling takes, the more satisfactory may be regarded the preparation.

A few cubic centimetres of the supernatant liquid are filtered, and the filtrate tested for soluble copper by adding some potassium ferrocyanide solution. The production of a chocolate precipitate must be regarded as unsatisfactory, as indicating the presence of soluble copper compounds.

(For preparation in quantity, 4 lbs. copper sulphate in 25 gallons water, and 4 lbs. quicklime in 25 gallons water.)

"Lime-sulphur" is a new fungicidal wash of American origin which is undergoing extensive trials in this country. The sulphur is in a completely soluble form, but after spraying is deposited in a very finely divided condition which has the advantage over flowers of sulphur in that it is not washed off. The successful application of the wash so as to avoid a certain amount of damage demands, however, a considerable amount of skill.

IV.]

## SPRAYS AND WASHES [CHAP IV.

## EXPERIMENT 35. Preparation of "Lime-Sulphur" Wash.

One hundred c.c. of water are placed in a litre flask or other vessel, and 50 grams of quicklime added. After well mixing, 100 grams of flowers of sulphur are added, and the whole stirred to a thin homogeneous paste. Four hundred c.c. of water are then poured into the mixture, and the solution boiled for half an hour. The orange-red liquid, consisting of a solution of polysulphides of calcium, contains a certain amount of undissolved sulphur and impurities from the lime, and should be filtered through cloth. The concentrated wash so obtained must not be exposed to the air, but should be kept in closed bottles until required. Before use, the stock solution is diluted with twenty or forty times its volume of water according to the variety of plant to be treated, the dilute solutions so obtained possessing specific quantities of I.OI and I.OO5 respectively.

(For preparation of stock solution in quantity, 10 gallons water, 48 lbs. quicklime, 96 lbs. flowers of sulphur; mix, and add 40 gallons water.)

# APPENDIX

IN most cases, the solutions mentioned in the text are prepared of any convenient concentration, and need be made of no especial strength.

Special reagents, which are required of certain definite concentrations, should be made according to the following directions :---

Fehling's solution should be made in the form of two solutions, which are mixed in equal volumes for use as required.

Solution A. 17.32 grams copper sulphate dissolved in 150 c.c. water, and the cold solution made up to 250 c.c.

Solution B. 35 grams stick caustic soda and 90 grams sodium potassium tartrate (Rochelle salt) dissolved in 150 c.c. water, and the cold solution made up to 250 c.c.

Indine in potassium indide solution. 5 grams potassium indide dissolved in 100 c.c. water and  $\frac{1}{2}$  gram indine added.

Schweizer's reagent consists of an ammoniacal solution of cupric hydroxide. 10 grams copper sulphate are dissolved in 200 c.c. water, a little ammonium chloride solution added, and then caustic soda solution in sufficient amount just to precipitate all the copper as copper hydroxide. The precipitate is collected on a piece of linen, well washed with cold water, and squeezed as dry as possible. The copper hydroxide so obtained is

#### APPENDIX

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then added to a mixture of I part strong ammonia solution and 3 parts water until no more of the hydroxide dissolves.

Syrupy caustic soda is prepared by dissolving successive quantities of solid caustic soda in water until the solution so obtained is quite viscous and treacly in consistency.

Sodium cobaltinitrite solution is prepared by dissolving a little of the salt in water as required. The solution deteriorates on keeping.

Diphenylamine in sulphuric acid is made by dissolving sufficient of the solid in *pure nitrate-free* sulphuric acid, so that a few drops of the solution obtained give a distinct milkiness when added to I c.c. distilled water.





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