Nature's Laboratory of Agricultural Chemistry

THE

CHEMISTRY OF AGRICULTURE

FOR

STUDENTS AND FARMERS

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ILLUSTRATED WITH 83 ENGRAVINGS AND 1 PLATE

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PREFACE

There is at present need for a text on general agricultural chemistry which will cover the field briefly, in a logical manner, giving only the facts, and not consisting of a disconnected series of quotations and tables from the very extended literature of the subject. The need for such a text has been particularly marked in teaching large classes of students at The Pennsylvania State College. As a consequence the present book has been written. While it is intended primarily for students who have had previous training in Botany, Chemistry, Geology and Physics, it is sufficiently elementary to make it of value to any intelligent person.

Concerning some of the statements made in the text it is well known that a difference of opinion exists among authorities, but it is deemed better to present them as facts rather than to give the various arguments or to omit them altogether.

Since the raising of crop plants is the fundamental business of agriculture, and since on them depend the life and growth of animals, there is discussed first the plant, its germination, growth, and products. Then are taken up the various conditions necessary for plant growth, such as the atmosphere, soil, fertilizers, and spray materials. A short chapter on the gas engine is inserted at this point, since the increasing use of power on the farm in the raising and marketing of crops makes some knowledge of the chemistry of gasoline and carburetion important. Finally the animal is considered, together with its food, digestion, and products.

The references at the end of each chapter give the principal sources of information used in the preparation of this text. While the lists are by no means complete, they will be of help for any who desire to pursue the subject further.

The thanks of the author are due to the German Kali Works, "La Hacienda," Great Western Sugar Co., Economy Silo and Manufacturing Co., Chilean Nitrate Propaganda, American Coal Products Co., C. Tennant Sons & Co., American Cyanamid Co., and the Avery Co., for many of the illustrations. Particularly is the author indebted to Dr. M. B. MacDonald, Mr. F. P. Weaver, and Mr. R. U. Blasingame for helpful suggestions, and to Messrs. C. A. Smith and E. DeTurk for some of the drawings.

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THE CHEMISTRY OF AGRICULTURE

PART I

THE PLANT

CHAPTER I

GERMINATION OF THE SEED

The seed of a plant contains besides the growing part or embryo, food material to nourish the seedling until it can produce enough roots and leaves to be independent. The food is stored away in a very concentrated form either in seed leaves called cotyledons, which are part of the embryo, or in a special depository called the endosperm which is merely connected with the embryo. Peas and beans are good examples of seeds with food in cotyledons; corn and wheat, of those with food in endosperms. The food material in the cotyledons or in the endosperm consists of starch, oil, and protein, the relative amounts of which vary with the kind of seed. Fig. 5 shows the interior of a corn kernel and the distribution of these foods.

1. **Conditions for Germination.**—In germinating, a seed first sends out a primary root which starts down into the soil, then it puts forth toward the light a seed bud or plumule, with or without its attendant cotyledons as the case may be. Only under certain conditions, however, will a seed germinate, and these conditions are: Presence of a certain amount of *water; oxygen;* and *heat.* All three of the conditions must be

fulfilled or no growth will result. If seeds are kept dry, even though they may be in a warm place and surrounded by air which contains all the oxygen ever needed by plants, they will not sprout. They will, however, retain their vitality for a long time, several years being the ordinary maximum, although some seeds have grown after being kept fifty or one hundred years. So also, if seeds are placed in water freed from air, and kept warm, no germination results, because the water prevents oxygen from reaching the seed. Under these conditions, however, seeds will decay in a short time, due to the influence of bacteria which act in the presence of moisture, but not otherwise. This indicates the importance of planting seeds in aërated soil, not in soil saturated with water. Seeds under the latter condition will decay. And finally if seeds are supplied with sufficient moisture and are well aërated, but kept cold, no germination will occur. It is absolutely necessary that there be present sufficient water, oxygen, and heat.

2. **Water.**—The food material packed away in the cotyledons or endosperm is anhydrous and insoluble. To be transported from the cells in which it is stored to the growing root and plumule where it can be used in manufacturing new cells, this food material must be changed to a soluble form. The chemical change which makes starch, oil, and protein soluble is hydrolytic in character; that is, water is necessary to break down the insoluble molecules of stored food into soluble molecules of transportable food. Certain catalytic agents or enzymes are necessary for this hydrolytic action. There must be in addition enough water to dissolve the soluble compounds, and to keep the new cells properly distended as fast as they are formed.

A seed in the air dry condition contains about 10 per cent. of water, but to start germination there must be present about 30 per cent. The water is imbibed in part through the seed coat, but mostly through small openings where the seed was attached to the parent plant and adjacent to the embryo. This absorption or imbibition of water is apparently caused by an attraction which the contents of the seed have for water. Starch, for example, will take on water and form a weak chemical union with it, something like water of crystallization. Other parts of the seed also have an affinity for water, a sort of molecular attraction for it. This causes the water to enter the seed.

There are several factors which affect the absorption of water by the seed. Within reasonable limits the higher the temperature the more rapidly water is absorbed. This is because the attraction of the seed contents for water is increased with rising temperature, as is true of very many chemical reactions. Another factor affecting the intake of water by the seed is the amount of salts dissolved in the water. The more salts in solution, the less water is absorbed, for the salts have a counter-attraction for water and prevent its entering the seed so readily. Strong salt water or too much soluble fertilizer around seeds will prevent their germination. This is the reason why seeds do not germinate in some of the "alkali soils" of the west—there is too much soluble salt in the soil moisture. Some salts, of course, are poisonous to seed plants and so cause death, but ordinarily harmless salts, if present in excessive amounts, act only by keeping water from the seed. It is doubtful if seeds can absorb enough water from saturated air to germinate, hence direct contact with water films is necessary; and a third factor in the amount of water absorbed by seeds is the amount of seed surface in contact with water. The finer the soil particles in the seed bed, the more points of contact with the seed, and since each soil particle is surrounded by a water film, therefore the more water in contact with the seed.

3. **Oxygen.**—In forcing the roots down into the soil as well as the plumule up through the soil, and in forming compounds from which new tissue is constructed, the germinating seed requires energy. This energy is derived from the oxidation of oils, carbohydrates, and possibly of protein materials. Just as in a steam engine where oxidation of coal or wood results in various forms of energy such as heat and work, and just as in the animal where oxidation of oils and carbohydrates results in various forms of energy such

as heat, work, and formation of compounds, so in the germinating seedling oxidation of material results in the various forms of energy necessary to produce a plant. This oxidation, or respiration as it is called, requires the presence of free oxygen, and the products of combustion are carbon dioxide and water in the case of starch and sugars. In the case of oils, probably a sugar is first formed. Both oils and carbohydrates contain carbon, hydrogen, and oxygen, but carbohydrates contain a much larger proportion of oxygen than do oils. It is highly probable that intermediate products are formed in part before carbohydrates are completely converted to carbon dioxide and water. Germinating seeds, then, absorb not only water, but oxygen, and give off or respire carbon dioxide and water. The water formed in respiration remains for the most part in the cells where it is formed, and serves as solvent water or chemical water in changing insoluble compounds to soluble compounds. Temperature is a very important factor in oxidation, and within limits the higher the temperature the faster the oxidation.

Unlike ordinary chemical oxidation or combustion, respiration in seeds is not a direct union of oxygen with another substance. Variations in quantity or pressure of oxygen have little effect on the rate of oxidation, as they have in the case of true combustion. Moreover, outside of the seed, substances like starch do not oxidize except at high temperatures, and yet in the seed oxidation goes on at relatively low temperatures. Oxidation in the seed is due rather to the presence of certain catalytic agents, or enzymes, which act as aids in making oxygen unite with seed materials.

Oxidation in the seed causes loss of material, as might be expected. In corn grain, for example, it has been noted that half of the reserve food material has disappeared in three weeks, due to oxidation. Energy produced by this oxidation can be observed in the movements of root and plumule, in the formation of new compounds, and in the production of heat. A mass of seeds enclosed in a non-conducting vessel has been observed to raise the temperature 5° to 10° C. during germination. This production of heat in the germinating seed is of value in stimulating the solution of food material and, in general, in quickening the germination.

4. **Heat.**—It has been noted how temperature or amount of heat affects germination. Seeds can germinate over a wide range of temperature; some seeds, wheat, for example, will germinate at nearly 0° C., but most seeds at not less than 5° C. The upper limit of germination is about 40° C., although cucumber seeds will germinate at 46° C. Each seed, however, has an optimum temperature, and although this varies for different seeds, it is not far from 30° C. Not all of the necessary heat need come from without; vigorous respiration of the germinating seed will produce some of the necessary heat, as noted in the preceding section.

5. **Food for the Seedling.**—The insoluble compounds which supply nourishment to the growing seedling, and which furnish material for oxidation, are starch, oil, and proteins. Starch is a so-called carbohydrate, a carbon, hydrogen, oxygen compound with hydrogen and oxygen in the proportion of water. Oil is a glyceryl salt of a fatty acid, a carbon, hydrogen, oxygen compound also, but containing less oxygen than does starch. Proteins are complex compounds of carbon, hydrogen, oxygen, and nitrogen, usually sulphur, and sometimes phosphorus.[1] The chemical changes taking place in these compounds are: First, the hydrolytic action which makes them soluble; and second, the oxidation reaction which changes starch and oil ultimately to carbon dioxide and water. It was stated in Sections 2 and 3 that these reactions were brought about by certain catalytic agents called enzymes.

6. **Enzymes.**—Enzymes are amorphous substances made by living cells, but which can act independently of the living cell. They are not organized bodies, that is, they have no life in themselves. They are soluble in glycerine and in water, insoluble in alcohol, and can be obtained from living tissue by pulverization, extraction with glycerine or water, and purified by alternate precipitation with alcohol

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[1] For complete discussion of these and other plant compounds, see Chapter III.

and solution in water. Chemically they are protein-like in character, although they have never been obtained pure enough to have their constitution accurately determined. The mode of action is catalytic, that is, they start a reaction or change its rate. In most cases it is thought that a given reaction in the seed will go on by itself, but so slowly as to be almost imperceptible. A catalytic agent hastens the reaction so that the changes take place quickly. The catalytic agent suffers no permanent change by the reaction, and a small amount of catalyst under optimum conditions can cause an almost indefinite amount of chemical change. Catalytic agents are not confined to enzymes. An example of an inorganic catalyst is manganese dioxide in the generation of oxygen from potassium chlorate. Manganese dioxide comes out of the reaction unchanged; potassium chlorate is reduced to potassium chloride. The manganese dioxide serves to hasten the reaction and to make it take place at a lower temperature than if the potassium chlorate were decomposed alone. Another example is platinized asbestos in the contact process for sulphuric acid, causing sulphur dioxide and oxygen to unite easily, remaining unchanged itself.

Enzymes are specific in their activity. There are numerous classes, each one causing or hastening a particular reaction, and no other. The principal classes that are effective in changing insoluble stored food to soluble, movable foods in the seed are *amylases*, *lipases*, and *proteases*. Enzymes which cause oxidation are called *oxidases*.

7. **Amylases.**—These enzymes, commonly known as starch splitters, are the best known of the seed enzymes. Diastase is a general name for certain members of this group which occur in plants. In the presence of water and sufficient heat, and from the energy derived by oxidation, the embryo cells, for the most part, produce quantities of these diastatic enzymes which pass through the cell walls into the starch packed cells of the endosperm or cotyledons. There they cause the starch to unite with water and, after going through a series of changes, form maltose as an end product. In some cases, although not so often in seeds, dextrose is formed from maltose by another enzyme.

Apparently there is a different kind of diastase causing each change. Maltose and dextrose are soluble and diffusible. They are the forms in which carbohydrate food is transported to the growing root and plumule and utilized in the formation of new cells. Fig. 1 shows how a starch grain is gradually broken down and dissolved away by the action of diastase and water.

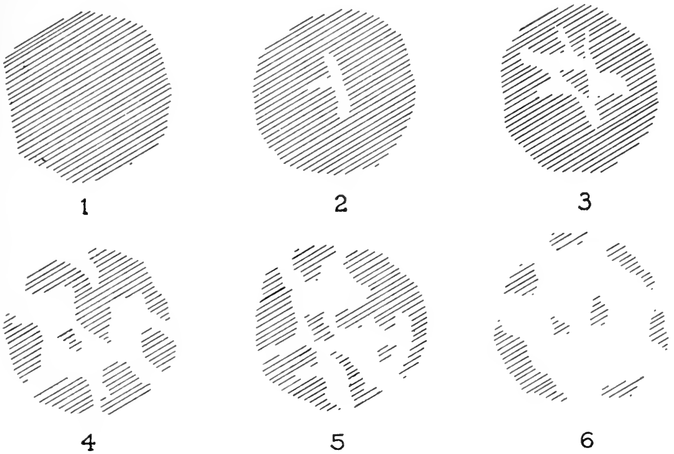

Fig. 1.—Starch grain acted upon by diastase, showing progressive solution. Much magnified. Drawing by C. A. Smith from microscopic observation.

8. **Lipases.**—There is not much known of these enzymes, except that they do exist and have the property of splitting up oil by hydrolysis. There are produced glycerine and the fatty acid or acids which were combined with the glycerine to form the oil. Glycerine is soluble and diffusible. The fatty acids are insoluble, but probably unite with such compounds as potash within the cell to form soap. From glycerine and the fatty acids, carbohydrates are formed in the growing cells, probably by oxidation.

9. **Proteases.**—These enzymes, called also protein splitters, have the power of hydrolyzing protein substances and changing them to simpler bodies such as albumoses, peptones,

amides, and even ammonia compounds. These are all soluble and diffusible. After transport to the growing points the simpler bodies are again united to form proteins.

10. **Oxidases.**—Respiration or oxidation, not being a case of simple combustion, is probably due to the activity of these enzymes which have the power of causing oxygen to unite with various compounds. Under their influence, starch and maltose are oxidized to carbon dioxide and water; oils, as well as glycerine and fatty acids, are oxidized to carbohydrates and possibly directly to carbon dioxide and water.

11. **Summary.**—A seed contains, in addition to the growing part, or embryo, a certain amount of food stored away in a compact, insoluble form. To start growth it is necessary that water be absorbed in order to supply a reagent for rendering the food soluble, and to furnish a solvent for its transport. Oxygen is also necessary to supply energy for the building of new tissue and for the work of movement. This results in the change of carbohydrates and oils ultimately to carbon dioxide and water. A certain amount of heat is necessary to aid in the absorption of water and in the oxidation. The amount of heat varies for different seeds. Food for the seedling consists of starch, oil, and protein, the relative amounts of each varying for different seeds—cereals containing large amounts of starch; cotton, flax, and nuts much oil; and legumes much protein. To make water unite with these compounds enzymes are secreted by the germinating seed, and are stimulated by the absorption of water and increased oxidation. Enzymes are not living things; they are amorphous, catalytic agents, able to act independently of the cells which produce them. Amylases hydrolyze starch for the most part to maltose in germinating seeds; lipases hydrolyze oil to glycerine and fatty acids which later unite probably with potash to form soap. Proteases hydrolyze proteins to simpler compounds, principally albumoses, peptones, and amides. For oxidation, or respiration as it is called, there are apparently necessary enzymes called oxidases, which in some cases change starch or maltose to carbon dioxide and water, and oils first to sugars then to carbon dioxide and water.

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CHAPTER II

GROWTH OF THE PLANT

As soon as the plumule rises above the surface of the soil it turns green, leaves rapidly form, and the young plant begins to live independently of the food laid up for it in the seed by the parent plant. It now obtains all the material it needs for the manufacture of new tissue from the air through the leaves, and from the soil through the roots.

I. PLANT FOOD

12. **Definition.**—Plant food is material which enables a plant to build new tissue and may still further be defined as substances supplying an element or elements by means of which a plant can carry on its normal functions of growth and reproduction. Some elements thus supplied become a constituent part of the cells. Other elements merely help in this formation of cellular substance. Plant foods may exist in forms readily taken up by the plant, in which case they are called *available foods,* or in forms not easily taken up by plants, in which case they are called *unavailable foods.* The latter must go through certain changes before they become available. To be available a plant food must be in a water soluble form.[1]

13. **Essential Elements.**—For its normal development every crop plant must be supplied with food containing the following ten chemical elements: Carbon, hydrogen, oxygen, phosphorus, potassium, nitrogen, sulphur, calcium, iron, and magnesium. Most plants contain in addition silicon, sodium, and chlorine. These latter elements have

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[1] To the botanist true plant food is material elaborated by the plant and then used in building cellular tissue. It is not material supplied from the outside. These substances might be called plant food materials. But to the agriculturist the definition in the text is the most rational and satisfactory.

not been proved essential, although in many cases plants seem to do better with them than without them. The first ten, however, are absolutely essential to the plant.

14. **Composition of the Plant.**—About three-fourths of the total weight of a green plant is water. The remaining one-fourth of dry matter is manufactured by the plant and is made up largely of fundamental organic substance containing only carbon, hydrogen, and oxygen. There is further some organic substance which includes part of the nitrogen, sulphur, and phosphorus. The remainder of the dry matter, containing potassium, calcium, magnesium, iron, and some of the nitrogen, sulphur, and phosphorus, in organic and inorganic form, is necessary for the formation of fundamental substance, although not a part of it.

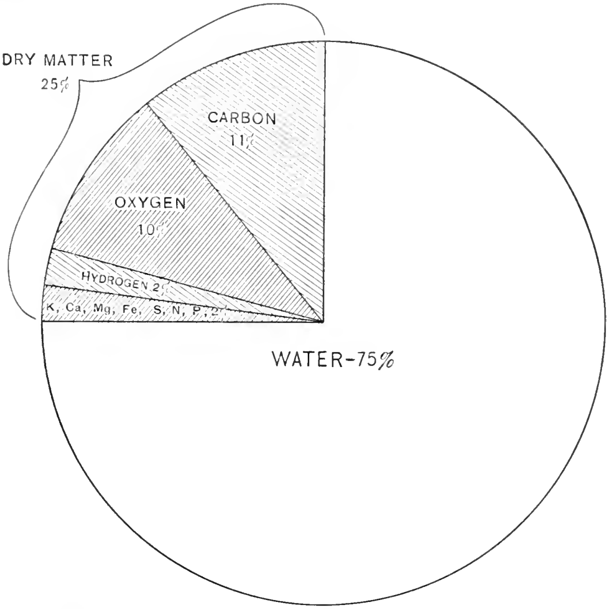


Fig. 2.—Diagram showing the distribution of water and dry matter in plants. Drawing by E. DeTurk.

Fig. 2 gives a graphic illustration of how water and dry matter are distributed in plants, and of what the dry matter is ultimately composed. The percentages are general averages of green plants.

15. **Form in which the Elements are Absorbed.**—Carbon enters the plant in the form of carbon dioxide through the leaves. Oxygen, as an element, enters the plant for the most part through the leaves, but also through the roots and stems. This is the only one of the essential elements which is taken up by the plant in the elemental form. As such, however, it is not used in making compounds, but in destroying compounds by the production of energy through the oxidation of plant substance. The same thing has been noted in the case of the germinating seed. For manufacturing plant substance oxygen is absorbed in combination with carbon as carbon dioxide, or in combination with hydrogen as water, the latter being taken up through the roots from the soil. Water also supplies the hydrogen necessary for plant life.

All the other elements enter the plant from the soil through the roots. Phosphorus, nitrogen, and sulphur are absorbed as phosphates, nitrates, and sulphates respectively of one of the basic elements, usually calcium. Potassium commonly enters the plant as carbonate or bicarbonate, but also as a salt of one of the acid elements—that is, as a phosphate, nitrate, or sulphate. Calcium and magnesium are absorbed as bicarbonate, phosphate, nitrate, and sulphate; and iron as hydrated ferric oxide.

It is to be noted that these compounds are all in a highly oxidized form. Lower oxidized compounds such as phosphites, nitrites, and sulphites are not plant foods. They are rather plant poisons. The same thing is true of other lower oxidized compounds. Ammonia may serve as a plant food in some cases, but in this form it is a base and not an acid. It is generally true, however, that nitrates are the best form of nitrogen for crop plants, and usually are the only form which can be utilized. Gaseous nitrogen of the air for legumes is a special case, and will be discussed later (Section 130).

All of the plant foods must be inorganic in nature and must dissolve in water before the plant can absorb them. It is not necessary, however, that they be very soluble. A weak solution is even better for a plant than a strong one. In the case of iron, for example, enough of the hydrated ferric oxide dissolves in the soil moisture to nourish plants, although hydrated ferric oxide is usually regarded as a comparatively insoluble compound.

16. **How Absorbed.**—As stated above, part of the plant food is absorbed through the leaves from the air and part through the roots from the soil. Considering first the absorption from the soil, it is to be noted that not all of the roots of plants spreading through the soil will absorb water and plant food. Only the very fine root hairs, located near the growing tips and extending but a short distance back of them, act as absorbers of plant food matter. The remainder of the roots is covered with a hard, corky layer which is impervious to water. Since the growing tip keeps pushing forward, the feeding ground is constantly changing.

The root hairs are long, slender, single cells. The walls are very thin, composed largely of cellulose, and are easily pervious to liquids. Lining the inside of these cells is a layer of protoplasm which serves as a regulator for the entrance and exit of water and soluble material. Under normal conditions of growth, water passes into the root hairs together with the dissolved plant food. These materials pass from cell to cell until they reach the long conducting tubes on the interior of the root and stem called tracheæ. Here the stream of liquid is forced up to the leaves and other parts of the plant. The passage of any particular plant food from cell to cell is always from the region of greater concentration *of that particular food* to the region of less concentration. Water passes into the root hairs and from cell to cell regardless of the concentration of any *one* plant food, but from the region of less *total* concentration to the region of greater *total* concentration.

17. **Selective Action by the Roots.**—The protoplasmic lining of the root hairs, as well as of other cells, exhibits a certain amount of selective action, permitting the entrance of some substances and keeping out others. To a limited

extent this means that as the plant needs this or that plant food the root hairs absorb it. For example, at any one time nitrates may pass in freely and phosphates may not. Later this proceeding may be reversed; or both may enter. On the other hand this selective action does not seem very perfect, for most soluble inorganic compounds will enter a plant even when very harmful. Still further, the protoplasmic layer may exert a sort of decomposing action on a salt like sodium nitrate, absorbing the nitrate radicle and leaving behind the sodium, combined probably as a carbonate. Or potassium sulphate may be split up, the potassium being absorbed in some other form, possibly as the carbonate, and the sulphate left behind, probably as sulphuric acid. Moreover, it prevents such cell contents as sugar and soluble proteins from passing out. In general, soluble organic compounds do not pass through the root hair wall or protoplasm in either direction. In other words, crop plants can not absorb organic compounds of the essential elements, and organic compounds such as acids are not excreted by the plant root hairs. The acid action of root hairs is due to the excretion of carbon dioxide which in water forms carbonic acid, capable of dissolving certain substances. This excretion of carbon dioxide is the result of respiration or oxidation of material within the root cells.

18. **Withdrawal of Water from the Roots.**—Under abnormal conditions, such as when the soil moisture becomes too concentrated in plant food, water passes out of the root hairs instead of into them. This extends back from cell to cell and results, if not remedied, in the ultimate death of the plant. Too much fertilizer around the roots of plants; strong brine solution, as when the ice-cream freezer is emptied on the grass; white alkali in the west; all these are familiar causes of this effect of withdrawing water from a plant, resulting in its death. This outflow of water, however, does not prevent the dissolved salts from entering the plant at the same time. In some instances the salts themselves, passing into the plant in excessive quantities, stop the vital activity of the cells. The so-called black alkali—or sodium carbonate—of the west is one of these poisonous salts, unless in very dilute solution.

19. **Function of Roots.**—Roots serve not only as an anchorage for the plant, to hold it upright and prevent its being blown down or knocked over easily, but also as ports of entry for water and plant food through the root hairs, and as "aqueducts" or water carriers for the rest of their course. The corky layer on the greater part of the roots prevents loss of water and plant food on their way up into the plant.

II. UTILIZATION OF PLANT FOOD

20. **Use of Inorganic Material.**—Unlike animals, plants manufacture carbonaceous or organic matter from inorganic raw materials. All that the plant absorbs are inorganic compounds dissolved in water. From these it makes its cells and their contents, which latter are very complex and of many different kinds. The basis of all the organic compounds in plants is composed of carbon, hydrogen, and oxygen, and is manufactured in the leaves for the most part. Energy for this chemical synthesis is derived from the sun's rays. That is, the energy of light waves is transformed into potential energy in the form of chemical compounds. Only a few of the light waves are useful in this work and of the sun's total energy only 1 to 2 per cent. is utilized.

21. **The Spectrum.**—The sun's rays are composed of many kinds of light waves, some short and some long, some visible and some not. Those that are visible can be separated by a prism into a so-called spectrum which shows the colors of the different waves from violet to red. The red waves are almost twice as long as the violet waves. It is the waves near the orange-red part of the spectrum that are absorbed and changed to potential energy.

22. **Chlorophyl.**—To absorb these light waves the plant must have chlorophyl, which is a green substance manufactured by the plant as soon as the plumule emerges into the light. It is composed of two pigments, blue and yellow, if not more. One of these pigments at least contains nitrogen and phosphorus. They may be separated by appropriate means, but their chemistry is little understood. This

chlorophyl is located in small bodies called chloroplasts, principally within the cells of the leaves (see Fig. 4, *c*). Leaves are particularly well adapted to their purpose of absorbing light waves, being broad and flat, thus exposing a large surface to the light. Moreover, they are so distributed that light can fall on them to the best advantage; as can be seen by examining the grouping of leaves on plants—a grapevine for example.

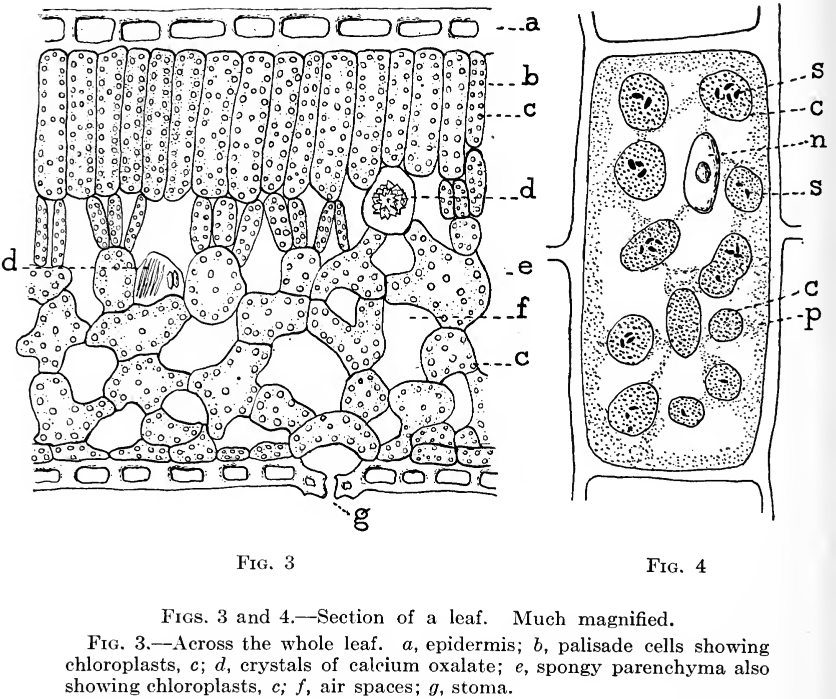


FIG. 3

FIG. 4

FIGS. 3 and 4.—Section of a leaf. Much magnified.

FIG. 3.—Across the whole leaf. *a*, epidermis; *b*, palisade cells showing chloroplasts, *c*; *d*, crystals of calcium oxalate; *e*, spongy parenchyma also showing chloroplasts, *c; f*, air spaces; *g*, stoma.

FIG. 4.—Single cell. *c*, chloroplasts; *s*, starch grains; *n*, nucleus; *p*, protoplasm. Drawing by C. A. Smith.

Chlorophyl itself does not develop in the dark. Potato sprouts, for example, that grow in a dark cellar may be of considerable size and small leaves may develop, but they are white or yellowish in color. Grass leaves that have grown under a board or stone are lacking in chlorophyl.

23. **Manufacture of Carbohydrate.**—The raw materials, combining to form the chemical compounds which store this energy, are carbon dioxide and water. The water, as has been noted, comes up from the soil through the roots and stems. The carbon dioxide enters the leaves through small openings on the under side, called stomata (Fig. 3, *g*). This gas passes into the air spaces (Fig. 3, *f*) between the cells and finally through the cell wall, dissolving in the cell sap to form carbonic acid. Under the action of the light waves absorbed by the chlorophyl, carbonic acid probably breaks up into formaldehyde and oxygen according to this equation:

$$H_2CO_3 = CH_2O + O_2.$$

The oxygen is given off through the cell walls into the air spaces and out through the stomata. The formaldehyde, dissolved in water, of course, is almost instantly condensed to dextrose, thus:

$$6CH_2O = C_6H_{12}O_6.$$

The dextrose is acted upon by an enzyme which subtracts water from it and forms starch (Fig. 4, *s*), thus:

$$n\ C_6H_{12}O_6 - n\ H_2O = (C_6H_{10}O_5)n.$$

Starch is usually the first visible compound formed in this process of photosynthesis, as the process of chemical synthesis by means of light is called. In some cases, however, the dextrose is changed to sucrose. This process of starch manufacture goes on during the day only. No synthesis takes place in the dark.

24. **Transfer of Carbohydrates.**—Starch in the leaf is only the temporary form of manufactured material. During the day carbonaceous matter is synthesized more rapidly than it can be removed, and the cells would be clogged with soluble food if it were not changed to an insoluble, concentrated form for temporary storage. At night when no car-

bonaceous matter is being formed, the starch is acted upon by amylases and is changed probably to dextrose. It is thus passed from cell to cell by diffusion through the cell walls and plasmatic linings until it passes out of the leaf into the main conducting channels of the plant. These channels are the so-called sieve tubes located outside of the tracheæ, or passages for the upward current of water and plant food.

Dextrose moves to that part of the plant needing new material, such as newly expanding leaves, growing tips, flowers, or roots. At these points other changes take place in the dextrose. It may be reconverted into starch for storage, or into cellulose for cell walls, or into oils, or into any other of the numerous plant compounds.

25. **Amount of Carbohydrate Synthesized.**—Averaging the results of several experiments, it can be said that during daylight on a bright day one square meter of leaf surface manufactures about one gram of carbohydrate material in one hour. For an acre of corn about the time of tasseling, there is manufactured about 170 pounds of carbohydrate in one day.

26. **Respiration.**—As has been shown, the manufacture of carbohydrates is brought about by the energy of light waves, and the process is called photosynthesis. The manufacture of all other products is brought about by the energy released on the oxidation of plant material, and the process is called chemosynthesis. Oxidation or respiration is common to the growing plant just as it is to the germinating seed, although not to so great an extent. It is dependent on the activity of oxidases in the presence of oxygen. This results in the production of carbon dioxide and water, and a consequent loss of plant substance. In other words the leaves of plants are not only taking in carbon dioxide through their stomata, making carbohydrates with water and giving off oxygen, but they are also absorbing oxygen, oxidizing carbohydrates, producing water, and giving off carbon dioxide. The gain of plant substance through photosynthesis, however, is much greater than the loss through respiration, for it is obvious that a growing plant gains in weight of dry

matter. It does not lose weight. Experiments have shown that the material assimilated may amount to thirty times that lost by respiration.

27. **Products of Respiration.**—The gases of respiration, oxygen and carbon dioxide, can pass from cell to cell by diffusion, being dissolved in water and transported like other soluble compounds. The greater part of these gases, however, exists in the intercellular spaces which have access to the outer air through the stomata on the leaves, and the lenticels in the bark and roots. The oxidation of material liberates in the plant several forms of energy. First, heat is generated to a noticeable extent in germinating seeds, flowers, and buds, though for the most part it is dissipated by radiation, plants having a much larger radiating surface in proportion to their mass than do animals. Second, work results, such as movements of various organs; of the entire plant; or of protoplasm within the cells. Food is also transported. Third, chemical energy is developed by the formation of new compounds, by the solution of some, and by the precipitation of others.

28. **Intermolecular Respiration.**—In addition to ordinary respiration which takes place only in the presence of free oxygen, there occurs, especially under conditions where oxygen is wanting, a process of oxidation at the expense of other molecules by their reduction. That is, energy for certain processes may be derived by a reaction between molecules in the same cell, resulting in the temporary release of oxygen from one of them. This may be called intermolecular respiration. The products of such oxidation are, besides carbon dioxide and water, ethyl alcohol, higher alcohols, acids, aromatic compounds, and even hydrogen. This sort of oxidation, it must be remembered, means as much reduction as oxidation. Where one molecule gains an atom of oxygen another molecule loses it. Plant cells, however, cannot live for any length of time by means of intermolecular respiration alone. All crop plants must have free oxygen for their development.

29. **Manufacture of Oil.**—Particles or films of oil seem to be a necessary constituent of plant cells and this material

is made from carbohydrates—probably dextrose. Since oils contain less oxygen than dextrose or other carbohydrates, the process must be one of reduction—possibly a result of intermolecular respiration.

30. **Manufacture of Protein.**—By far the most important chemical work done by the plant is the making of proteins, the most complex compounds known. Just how these compounds are manufactured from raw materials is not thoroughly understood. Starting with carbohydrates—probably dextrose—nitrates, sulphates, and sometimes phosphates, the cells of plants build up a compound which in no way resembles its constituents. The nitrogen and sulphur are no longer in the oxidized condition, in fact, just the reverse. In other words, the nitrates and sulphates are reduced, possibly to ammonia and free sulphur. Then they are combined with carbon, hydrogen, and oxygen from carbohydrates to gradually build up the complex protein. One of the first nitrogen compounds to be formed seems to be an amino-acid. It has been suggested that nitrates and sulphates are reduced by carbohydrates, as a result of intermolecular respiration, whereby the carbohydrates are oxidized in part to oxalic acid. This acid unites with the bases of the reduced nitrates or sulphates, namely, calcium, potassium, or sodium. Later the soluble oxalates of potassium and sodium are changed to insoluble calcium oxalate. (Fig. 3, *d*). This excess of calcium may possibly be furnished by calcium phosphate, since the phosphoric acid radicle is used in making some proteins. The remainder of the oxidized carbohydrates, in the form of some other acids, may unite with the ammonia to form amino-acids. A number of these amino-acids uniting together with sulphur and sometimes phosphorus gradually construct a protein.

Proteins are made to a great extent in leaves, but their formation is not restricted to the leaves. Other parts of the plant make these compounds from the raw materials. Light is not directly essential for their formation. The necessary energy is derived from oxidation of carbohydrates and is a chemosynthesis as in the case of oils. The presence of carbohydrates is, of course, required since they are the source of carbon for the proteins, and inasmuch as formation of carbohydrates depends on light, protein synthesis takes place usually more rapidly in the light.

31. **Transfer of Oil and Protein.**—Just as starch is rendered soluble and transported throughout the plant to parts needing new material, so are oils and proteins changed. Lipases and proteases are not confined to the seeds. They exist anywhere in the plant that oil and protein splitting is essential. Oils are hydrolyzed to glycerine and fatty acids, the latter to soap just as in the seed. Proteins are hydrolyzed to simpler compounds such as albumoses, peptones, amides, etc. It is not known whether the breaking down of proteins goes through the same changes in reverse order as the synthesis, but possibly it does. The course of dissolved oils and proteins through the plant is the same as that of dextrose, or dissolved carbohydrates.

32. **Functions of Carbohydrate, Oil, and Protein.**—For respiration and the consequent production of energy in the plant, carbohydrates are principally used. Oils and proteins, however, may serve this purpose. For the manufacture of cell walls, carbohydrates are employed. As was seen in Section 24, soluble material like dextrose is changed to cellulose. For the manufacture of protoplasm, and as storage material for the crop of the following year, all three kinds of material are important.

33. **Protoplasm.**—The substance which plays the most active role in all of these chemical changes, and which must be constantly renewed in old cells and increased for new cells, is protoplasm (Fig. 4, *p*). Its appearance is not the same in different cells but in general it is a more or less soft, spongy, slimy, granular mass, practically colorless, and suspended in water. Embedded in it are always the nucleus or real seat of life, and varying with conditions, chloroplasts or chlorophyl cells, particles of starch, droplets of oil, and many other substances of more or less temporary nature. The approximate chemical composition of the dry matter of protoplasm is as follows:

50 to 66 per cent. proteins.
25 to 17 per cent. oils and carbohydrates.

25 to 17 per cent. organic acids, particularly amino-acids, organic bases, and mineral salts of potassium, magnesium, calcium, and iron.

34. **Seeds.**—In providing for a continuation of itself the following year the plant has several ways of storing up food to be used before new roots and leaves can provide bodily substance for the new plant. Sooner or later crop plants bear seeds which contain carbohydrates, oils, and proteins, all in the most concentrated and dehydrated form. Carbohydrates occur in the form of starch (Fig. 6, *c* and *d*); and proteins occur in the granular or crystalline form usually called aleurone grains (Fig. 6, *b*). The oils are packed away as minute drops (Fig. 6, *f*). There is little water present in the seed (Sections 2 and 98), and but little space is occupied by the food materials. During the formation of seeds most of the plant activities are devoted to the solution and transportation of material from the leaves and stems, where it has been temporarily lodged, to the seeds, where it is changed to the insoluble form and packed away. Dextrose is dehydrated and made into starch, or reduced and made into oils; in some cases largely starch, as in cereals, in others largely oils, as in cottonseed. Peptones and albumoses are dehydrated and made into proteins.

35. **Roots, Bulbs, and Tubers.**—Some plants do not bear seeds the first year, but go into a resting stage for a time and the following year produce seed. These are the so-called biennials. To get a start the second year they must have a store of material from which to build new plant substance before roots and leaves can do their work. Consequently they form enlarged fleshy roots, like the beet; underground stems or tubers, like the potato; or enlarged stalks called bulbs, like the onion. In these storage organs the carbohydrates, oils, and proteins are not usually packed away in a dry, concentrated form. In the beet carbohydrates take the form of sucrose; in the onion, of dextrose, but in the potato, of starch. Oils and proteins are not present to any extent. If the latter are present, however, they occur not as aleurone grains, but in a more hydrolyzed form, even

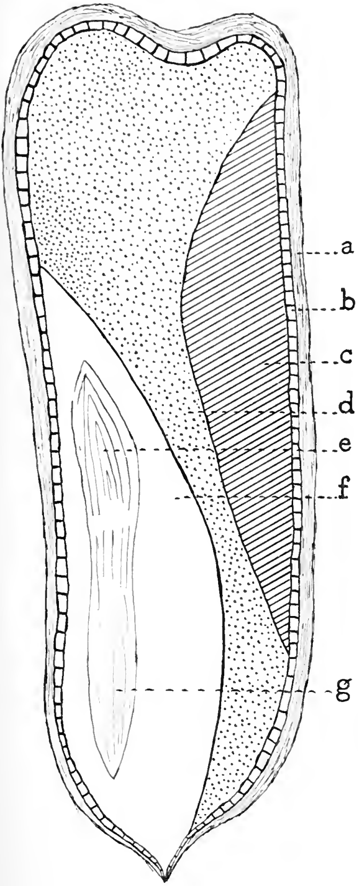


FIG. 5

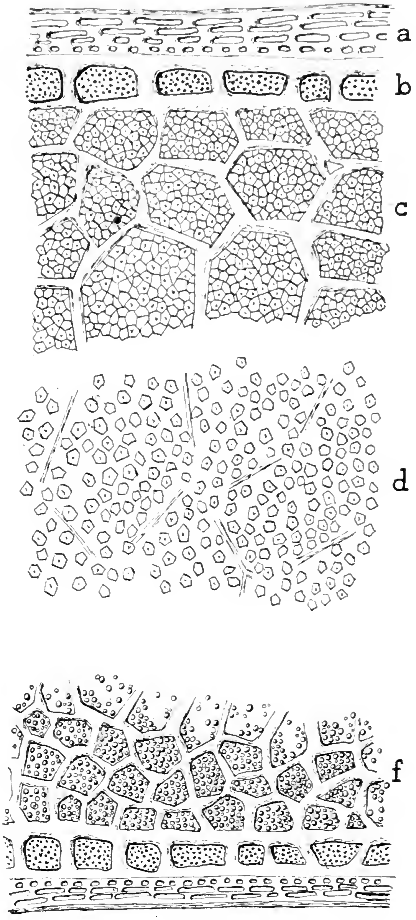


FIG. 6

FIGS. 5 and 6.—Section of corn kernel.

FIG. 5.—Across the whole kernel. Magnified. *a*, epidermis; *b*, layer of cells containing protein; *c*, hard starch cells; *d*, soft starch cells; *e*, plumule; *f*, cotyledon or "germ;" *g*, primary root.

FIG. 6.—Detail of various parts of kernel. Much magnified. *a*, epidermis; *b*, cells containing protein or aleurone grains; *c*, hard starch cells; *d*, soft starch cells; *f*, cells containing oil drops. Lettering to correspond to Fig. 5. Drawing by C. A. Smith.

amides, etc. Another class of plants is called perennials, which live on from year to year, bear seeds from time to time, and also maintain life by means of succulent storage organs. Trees are plants of this kind. Their reserve carbohydrates and other material are stored just under the bark in the so-called cambium layer.

III. FUNCTIONS OF THE ESSENTIAL ELEMENTS

36. **Value of a Study of These Functions.**—In the previous discussion of plant growth something has been stated about how the principal plant constituents are manufactured, but only in part has been noted the specific function played by each of the essential elements in this process.

A study of the physiological function of each of the essential elements is of practical importance in the proper feeding of a crop with fertilizers. It is possible by judicious feeding to produce special, desirable results, and the more facts known about the effect of fertilizers, the more economically can they be applied. As yet our knowledge of the subject is not very extensive, although some progress has been made.

37. **Carbon.**—This element is the principal constituent (45 per cent.) of the dry matter of plants. All of the compounds manufactured by plants contain carbon. Every naturally occurring organic compound owes its carbon content directly or indirectly to the activity of plants. Whether these compounds are tissues of the animal body, or coal and oil in the earth, all of them are originally from plants. Animals use as food either other animals or plants, and thus directly or indirectly are dependent on plants as the source of carbon. Coal and oil in the earth are decomposed remains of plants. The very numerous "coal tar derivatives" were originally plant compounds, decomposed in part by heat and pressure within the earth, in part by the chemist.

38. **Hydrogen.**—This is another of the elements which is an essential constituent of plant compounds. Every organic compound in plants, except neutral oxalates, contains hydrogen. And yet in spite of its wide distribution, plants average only

6.5 per cent. of hydrogen. This is because of its extreme lightness, being the lightest of all the elements.

39. **Oxygen.**—This element is second to carbon as a constituent of the dry matter of plants, occurring to the extent of 42 per cent., and entering into the composition of most plant compounds. In addition it is necessary for respiration, or for the oxidation of material, which results in energy for the growing plant (Section 26). Combined with hydrogen it forms water which may be considered here with respect to its physiological functions, although it is not an element.

40. **Water.**—This compound serves a variety of purposes in the plant. (*a*) It provides a medium in which plant food is dissolved and by which food can be transported throughout the plant. (*b*) It is a reagent which helps break down insoluble compounds to form soluble compounds (Sections 2, 24, and 31). (*c*) By filling the cells and pressing against their walls, it gives rigidity to the plant structure and keeps it erect. This filling out of the cells is called "turgor." (*d*) By its evaporation from the leaves, water reduces the temperature of plants and thus prevents overheating due to the sun's rays.

41. **Phosphorus.**—(*a*) As a necessary constituent of some proteins phosphorus is required for the building up of certain plant compounds. Cell nuclei, for example, contain phosphorus. Hence this element is necessary for cell division and new growth. (*b*) It stimulates the growth of seedlings markedly. This is to be noted in the practice of drilling a soluble phosphate with corn. Although they did not know it, it was also the cause of better corn growth when the early New England Indians planted a dead fish in each hill, and so advised the Pilgrims. (*c*) Phosphorus is important in the ripening of grain. A plentiful supply hastens maturity and also increases the yield of grain over straw or stover (Fig. 7). (*d*) A plentiful supply of available phosphorus in the soil increases root growth. This increase in root growth is important for crops, especially during a dry season when a generous root system permits plants to get subsoil water more easily. This fact has been noticed particularly in the

growth of cereals in South Australia. (*e*) Plenty of phosphorus reduces the content of nitrogen in seeds of grains.

FIG. 7.—Effect of phosphorus on seed development. Corn. The shock on the right came from a phosphate-treated plat. (Soils Department, Wisconsin Station.)

42. **Potassium.**—(*a*) For the manufacture of carbohydrates, potassium is necessary. It seems probable that the condensation of formaldehyde to dextrose takes place only in the presence of some potassium compound, organic in nature. (*b*) For the hydrolysis of starch, potassium seems necessary, possibly forming a suitable solution in which the amylases can best act. (*c*) The presence of potassium is necessary for the production of cellulose, since it gives rigidity to stems. A lack of potassium is shown in

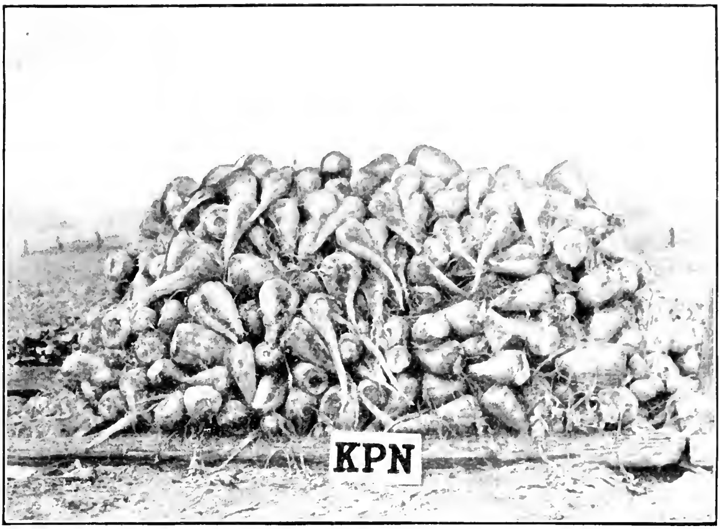


FIG. 8

FIG. 9

FIGS. 8 and 9.—Effect of potassium on development of roots containing carbohydrate. Sugar beets. KPN, potassium, phosphorus, nitrogen. PN, phosphorus, nitrogen.

weak, brittle stems, where there is insufficient cellulose for the cell walls. Potassium helps the plant to resist attacks of fungous diseases such as the rust. Fungous hyphæ can not readily penetrate strong cell walls. (*d*) It serves also to cause good leaf development. (*e*) It gives enlarged yields of potatoes, which are a starchy crop. (*f*) It also increases the yield of sugar in beets (Figs. 8 and 9). This is very well illustrated at the Rothamsted Station, England, where a mangold crop fertilized with nitrogen and phosphorus produced 1594 pounds of sugar, but when fertilized with potassium, in addition to nitrogen and phosphorus, produced 4446 pounds. (*g*) Potassium also is the base which neutralizes or partly neutralizes the acids produced during plant growth.

43. **Nitrogen.**—(*a*) Nitrogen is a necessary constituent of all proteins, and proteins play a very considerable part in the formation of protoplasm, chlorophyl, and many other compounds (Section 33). (*b*) It is important in the growth of new tissue, such as stems and leaves (Fig. 10), producing a bright green color in the leaves (effect on chlorophyl). In case an excess is present such a vigorous growth of foliage is produced as to delay maturity of the seed. The ripening of the seed is a process of translocation of food material which does not take place while active assimilation and vegetative growth are going on. This effect of delaying maturity is just the opposite of the effect of phosphorus which hastens it. (*c*) Excess of nitrogen also causes such rapid vegetative growth that the stems are weakened, and lodging in the case of grain may result. Apparently the cells of the growing stem are multiplied more rapidly than proper cell walls can form, and large cells with weakened walls result. (*d*) In the case of leafy crops, such as lettuce and cabbage, or of a stem crop like celery, this excess of nitrogen is advantageous. Seeds are not wanted. (*e*) This effect of too much nitrogen on growth renders plants susceptible to disease. Wheat crops over-stimulated with nitrogen are liable to rust. Greenhouse crops which are always grown on soils rich in nitrogen are peculiarly sensitive to diseases. Shrubbery and young trees which have been forced too

rapidly with nitrogen are also more easily attacked by fungi. The cause is due not only to a cell wall less resistant to the passage of the fungous hyphæ, but also in all probability to a change in the composition of the cell sap which is more favorable to the growth of the fungi.

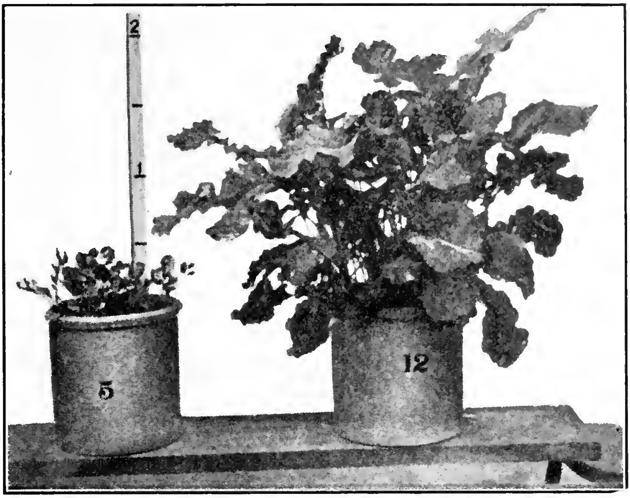


Fig. 10.—Effect of nitrogen on leaf development. Rape. Jar 5, no nitrate. Jar 12, nitrate. Wisconsin Station.

44. **Sulphur.**—(*a*) This is a necessary constituent of most proteins. (*b*) It is also a part of some of the flavoring oils in mustard, onion, cabbage, and horseradish.

45. **Calcium.**—(*a*) Like potassium, calcium has some part to play in the solution and transportation of starch, probably by forming a proper medium for the activity of the amylases. (*b*) It also takes part in the development of strong cell walls, and numerous root hairs. (*c*) It serves as a base to precipitate oxalic acid which is formed during respiration and some other activities (Section 28), and which is poisonous to the plant if allowed to accumulate. Crystals of calcium oxalate occur frequently in plants (Fig. 3, *d*).

(*d*) It is also supposed to be a necessary constituent of the proteins of the cell nuclei.

46. **Iron.**—This element is necessary for the manufacture of chlorophyl, although not a constituent part of the chlorophyl compound. Plants which fail to absorb iron, or which do not absorb enough to keep pace with growth, produce white leaves, a diseased condition known as *chlorosis*.

47. **Magnesium.**—(*a*) The production of chlorophyl is dependent on magnesium, which is a necessary constituent. (*b*) Protein formation is helped by this element, and particularly in the assimilation of phosphorus. (*c*) The formation of seeds is also dependent on the activity of magnesium, possibly as a carrier of phosphorus in the plant.

48. **General Distribution in Seed Crops.**—The staple crops in agriculture are the grains, typical seed plants, which are of value both for their seeds and for their stems and leaves. The distribution of the essential elements, and particularly of the fertilizing elements, in such plants is of importance, not only in connection with their physiological functions, but also with respect to their use on the soil and their economic value. Carbon, hydrogen, and oxygen need not be considered.

Taking the mature plant as harvested, it is to be noted that *phosphorus* and *nitrogen* move to the seeds during ripening to such an extent that there are two to three times as much phosphorus and nitrogen in the seeds as in the leaves and stems. *Potassium* and *calcium*, on the other hand, being necessary parts of the assimilating mechanism, remain in the stems and leaves where two to three times as much potassium, and nearly eight times as much calcium, are found as in the seeds. *Sulphur* is more evenly distributed, being a trifle more in the stems and leaves than in the seeds, except in the corn plant. *Iron*, being necessary for the formation of chlorophyl, is found in the leaves and stems to a greater extent than in the seeds. *Magnesium* is more evenly distributed, with a trifle more in the seeds than in the stems and leaves of most grains except corn.

For the distribution of fertilizing constituents in fruits and vegetables the reader is referred to Table III, Chapter IV.

The commercially valuable part of these crops differs with the kind of plant, thus making any general discussion impossible. For example, the apple, pear, squash, and pumpkin are raised for the fleshy seed coverings; celery and rhubarb for their thickened stems; the carrot and beet for their thickened root; and spinach and lettuce for their leaves.

49. **Summary.**—For the normal growth and development of crop plants, a certain amount of plant food is required. Plant food may be defined as a substance supplying one or more elements necessary for normal plant activities. The essential elements are ten in number, being carbon, hydrogen, oxygen, phosphorus, potassium, nitrogen, sulphur, calcium, iron, and magnesium. There are also used silicon, sodium, and chlorine to a considerable extent. Three-fourths of a green plant is water; the other fourth is mostly carbon and oxygen with lesser amounts of hydrogen and the other elements.

The plant foods are absorbed as inorganic, water soluble compounds only, except oxygen which is partly absorbed in the elemental form. Carbon is absorbed as a gas, carbon dioxide; hydrogen and oxygen, as water. The remaining seven essential elements are absorbed as salts of their several basic and acid radicles.

The root hairs situated near the tip end of the growing roots serve as ports of entry for the dissolved material. These soluble compounds pass from cell to cell by osmosis until they reach the tracheæ where they are forced up through the stem to the leaves which are the seat of manufacture of plant material. In the leaves there are chlorophyl bodies which absorb certain orange-red light waves from the sun and change the radiant energy of the sun into potential chemical energy of carbohydrate compounds. Carbon dioxide and water are combined to form formaldehyde, then dextrose, and usually starch which is the temporary storage form of manufactured organic material in the leaf.

For transport to various parts of the plant needing building material, the starch is hydrolyzed by enzymes and water to dextrose, and carried by osmosis to the needed point.

Here it may be changed into cellulose for cell walls, or starch, sucrose, and oil for storage, etc. Some of the carbohydrates are used as material for oxidation or respiration, just as in the germinating seed. Oxygen is needed for this process. Carbon dioxide and water are the products of respiration. Energy is released, and heat, work, and chemical compounds result. All the plant activities of chemical change and reproduction are dependent on respiration. In some cases, and possibly quite generally even under normal conditions, there is a so-called intermolecular respiration whereby one molecule is oxidized at the expense of another which is reduced. This respiration results in the production of such compounds as acids and alcohols in addition to carbon dioxide and water. Energy is set free by this process also.

Probably as a result of this intermolecular respiration oils are formed. They are at least made from carbohydrates—dextrose largely—and contain less oxygen. They are storage forms of food material. Proteins are built up from carbohydrates, probably by a partial oxidation of them and consequent reduction of nitrates and sulphates. These are combined to form amides, albumoses, peptones, and finally proteins. Phosphorus, or rather the phosphoric acid radicle, is sometimes included in the protein molecule. Protoplasm—the seat of cell life and activity—is largely protein with some oil, carbohydrate, and mineral water.

The seeds are the means of reproduction and contain the embryo and the stored food for the embryo. This food has been moved at maturity from the various parts of the plant where it was made or temporarily stored, and converted by enzyme action into a very concentrated anhydrous form of protein, oil, and starch. Some plants do not produce seeds the first year; others live on from year to year, and in these cases the food is not anhydrous but is usually in hydrated forms like sucrose or dextrose.

The various essential elements have special parts to play in the phenomenon of plant growth. Carbon, hydrogen, oxygen, nitrogen, sulphur, and phosphorus at least are essential constituents of plant tissue. The other elements, potassium, magnesium, iron, and calcium, serve largely as aids in the manufacture and transport of food material. They are no less necessary than the others but act more in the nature of catalytic agents, not appearing in the final product. They form a proper medium for enzyme action. As a rule, in seed crops like the grains, phosphorus and nitrogen appear more largely in the seeds than in the stems and leaves where calcium and potassium predominate. Sulphur, iron, and magnesium are more evenly distributed.

REFERENCES

See References at end of Chapter I.

CHAPTER III

PLANT COMPOUNDS

In the preceding chapters several plant compounds have been discussed with reference to their uses in the plant, their method of formation, and some of the natural changes that take place in them. Besides these few compounds already mentioned there are a very large number produced during the growth of plants. Some plants form one kind, some another. Many of the compounds have no value commercially, and no *known* value physiologically. Some are evidently merely by-products, whereas others undoubtedly serve some useful purpose to the plant. Since many of these compounds are of great importance to the human race, it is necessary to know something of their properties and uses outside of the plant. In the following discussion only those plant compounds which are of known physiological importance to the plant, and particularly those which are of economic importance to mankind, will be considered. For convenience the various compounds will be grouped as follows:

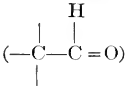
I. Carbohydrates
II. Fixed Oils and Waxes
III. Volatile Oils and Resins
IV. Nitrogenous Compounds
V. Organic Acids and their Salts

I. CARBOHYDRATES

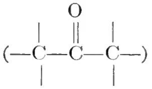
50. **General Definition.**—The most abundant group of organic compounds is that of the carbohydrates or saccharides, comprising about 75 per cent. of the dry matter of plants. Popularly, a carbohydrate is defined as a compound containing carbon, hydrogen, and oxygen, with the

hydrogen and oxygen in the same proportion as in water; or, a compound of carbon and water, thus: Dextrose = $6C+6H_2O$. This definition, while not exactly correct, will hold in a majority of cases and serves very well to distinguish the group. The exceptions to this statement are principally in the case of acetic acid, whose empirical formula is $C_2H_4O_2$, but whose graphic formula is CH_3COOH, showing the acid or carboxyl group; and lactic acid, $C_3H_6O_3$, but otherwise written $CH_3.CHOH.COOH$.

A carbohydrate may be defined more accurately as a compound containing *always* one or more hydroxyl (OH) groups, and *usually* either an aldehyde



$(-\underset{|}{\overset{|}{C}}-\overset{\overset{H}{|}}{C}=O)$ or ketone



$(-\underset{|}{\overset{|}{C}}-\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{|}{C}}-)$ group.

The presence of the aldehyde group indicates that the carbohydrate is easily oxidized, whereas the presence of the ketone group usually, though not always, indicates that the carbohydrate is not easily oxidized. The principal carbohydrates contain carbon atoms to the number of six or a multiple of six. The carbohydrates are divided into two general classes, the *Sugars* including the monosaccharides and disaccharides; and the *Non-Sugars* or *Polysaccharides.*

51. **Sugars.**—As a class the sugars are colorless, odorless, crystalline compounds, soluble in water, and, ordinarily, sweet in taste. Their most characteristic property is that of optical activity, that is, they rotate the plane of polarized light either to the right or to the left.[1] The simple sugars,

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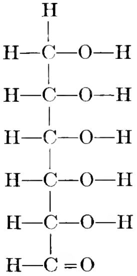
[1] *Optical Activity:* An ordinary ray of light is supposed to consist of particles vibrating in every direction at right angles to the direction of the ray. When such a ray is passed through a properly cut crystal of Iceland spar called a Nicol prism, it is separated into two rays, one of which is reflected out to one side of the prism, and the other passes through, its particles now vibrating in only one plane. This ray is said to be polarized, and substances which have the power of rotating this plane of polarized light in one direction or the other are said to be optically active, either dextrorotatory (+) or levorotatory (−) as they turn the plane of polarized light to the right or to the left. The amount of rotation depends on the specific property of the substance and the number of molecules through which the light passes. The amount of rotation can be measured, and by

or *monosaccharides,* contain from two to nine carbon atoms, and are named according to the number of carbon atoms in the molecule: Dioses, trioses, tetroses, etc. Each molecule consists of a single "sugar" group of atoms. The only important monosaccharides are the hexoses, or sugars containing six carbon atoms, $C_6H_{12}O_6$. Dextrose and levulose are the best examples of hexoses. The *disaccharides* are formed by the condensation of two molecules of a monosaccharide with the elimination of one molecule of water. Each molecule of a disaccharide, then, consists of two single "sugar" groups of atoms. Sucrose and maltose are the principle disaccharides found in plants.

52. **Dextrose, Glucose, Grape Sugar.**—$C_6H_{12}O_6$, graphically:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H—C=O} \end{array}$$

calculation the percentage composition of sugar or other substance can be determined in a solution. The instrument is called a polariscope, or, since it is used mostly for the determination of sugar, a saccharimeter. It consists essentially of a tube containing at one end a polarizing prism which polarizes a ray of light from some source, and an analyzing prism at the other end mounted on a revolving disk graduated into degrees. Between the two prisms is a trough in which may be placed a tube, closed at both ends with glass, containing the solution to be examined. The polarized light if undisturbed passes through the analyzer and illuminates the field of vision through an eye piece. If the ray is rotated by an optically active substance, the light does not pass through the analyzer and the field of vision is darkened. If the analyzer is now rotated to the right or left, as the case may be, just as much as the substance rotates the polarized ray, the field of vision will again be brightly illuminated. There are many modifications of this polariscope tending to increase the accuracy of observation, but the principle is the same in all of the instruments. For comparing the rotatory power of different substances, there is used the term *specific rotation* which is the amount of dextro- or levorotation of plane polarized sodium light caused by a solution 10 cm. long, each cubic centimeter of which contains one gram of substance, at a temperature of 20° C.

This constitutes what was termed a single "sugar" group of atoms, hence, monosaccharide. It is found free in nature in all parts of the plant, but for the most part it occurs associated with an equal quantity of levulose in such sweet fruits as grapes, cherries, and pears. It is also found in onions, as has been mentioned. Dextrose occurs as glucosides[1] in combination with different kinds of compounds such as alcohols, acids, and aldehydes, which hydrolyze naturally under the action of enzymes to form glucose and the other compounds. It is formed in nature (Section 23) by the condensation of formaldehyde in the leaf, and by hydrolytic enzyme action on such storage forms of carbohydrates as starch and sucrose (Section 24).

Physiologically dextrose is the usual transport form of carbohydrates, but occasionally it is the storage form, as in the onion. Dextrose is a nearly white solid, easily soluble in water and in hot alcohol, insoluble in ether, crystallizes as a hydrate, $C_6H_{12}O_6.H_2O$, from water, and as an anhydride from alcohol (Fig. 11). It is not as sweet as ordinary sugar. It is dextrorotatory, from which fact it gets the name dextrose, "right sugar." The specific rotation of ordinary dextrose is +52.5°. Since it contains the aldehyde group it is easily oxidized to various compounds. This oxidation is measured by the equivalent reduction of what is called

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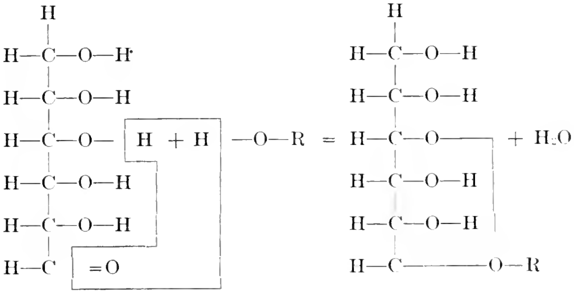
[1] The formation of a glucoside can best be seen from a graphic formula:



R represents the alkyl group of an alcohol, acid, aldehyde, or ketone.

Fehling's solution[1] and this reduction of Fehling's solution is a characteristic reaction for dextrose. Dextrose also unites with calcium hydroxide and barium hydroxide to form compounds which might be called "dextrates" or "dextroxides," $C_6H_{11}O_6.CaOH$ and $C_6H_{11}O_6.BaOH$.[2] They

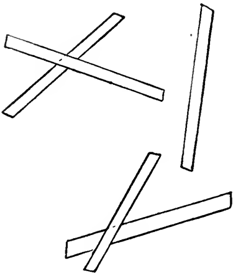


Fig. 11.—Crystals of anhydrous dextrose. Magnified. Drawing by C. A. Smith.

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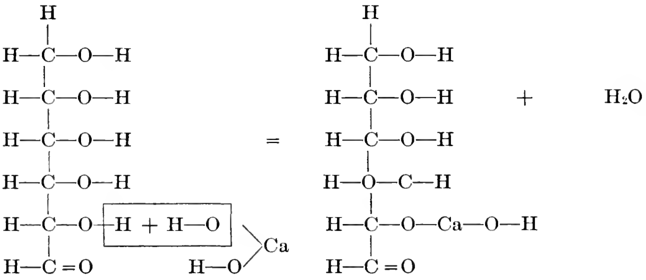
[1] Fehling's solution is made by mixing equal parts of a solution of copper sulphate with a solution of sodium potassium tartrate (Rochelle salts) in sodium hydroxide. The sodium hydroxide forms copper hydroxide which dissolves to a deep blue color in the sodium potassium tartrate. The copper hydroxide in solution is the reacting compound. It is reduced according to the following equation:

$$2\,Cu(OH)_2 = Cu_2(OH)_2 + H_2O + O.$$

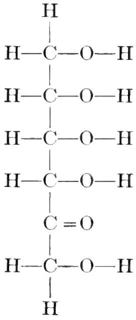
On boiling the solution the yellow cuprous hydroxide, $Cu_2(OH)_2$, changes to the brick red cuprous oxide and water, $Cu_2O + H_2O$. The amount of red precipitate is a measure of the amount of dextrose in solution.

[2] Their formation can be best illustrated graphically. The exact location of the hydroxyl group which combines with the base is not known, but the one chosen will at least illustrate the reaction:



are soluble in water but insoluble in alcohol. Dextrose is easily changed, or fermented, by fungi and bacteria to alcohol and carbon dioxide; to lactic acid; and to butyric acid, carbon dioxide, and hydrogen. Pure dextrose can be made by the hydrolysis of starch or sucrose with dilute hydrochloric acid, and recrystallization from hot alcohol. Commercial glucose is made in this country by boiling cornstarch under pressure with hydrochloric acid, neutralizing the acid with sodium carbonate, and clarifying the liquid with bone charcoal. The product is sold as a thick, amber-colored liquid containing 30 to 40 per cent. of dextrose, the rest being dextrins and other impurities. By boiling the mass longer more dextrins are converted to dextrose and a crystallizable product containing 70 to 80 per cent. dextrose is obtained. Glucose is used largely in making candy, jellies, preserves, table syrup, etc.

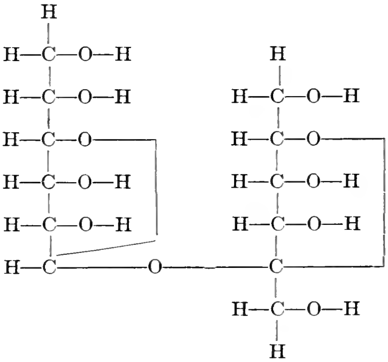
53. **Levulose, Fructose, Fruit Sugar.**—$C_6H_{12}O_6$, graphically:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{C=O} \\ | \\ \mathrm{H—C—O—H} \\ | \\ \mathrm{H} \end{array}$$

This constitutes another single "sugar" group of atoms. Levulose is found in plants, particularly the sweet fruits, and nearly always with dextrose. Honey is almost wholly a mixture of levulose and dextrose. Levulose is formed naturally by the enzyme hydrolysis of sucrose, or artificially by hydrolysis of sucrose with dilute hydrochloric acid. In either case there are produced equal quantities of dextrose and levulose. Physiologically it probably plays the same role as dextrose. Levulose is a white solid, crystallizable with considerable difficulty, very soluble in water and in hot alcohol. It is much more strongly levorotatory than dextrose is dextrorotatory, the specific rotation being —92.5°. Hence it is called levulose, "left sugar." It is sweeter than dextrose. Although it does not contain an aldehyde group it is easily oxidized, that is, it reduces Fehling's solution. Levulose forms compounds with calcium hydroxide and barium hydroxide—"levulates"—insoluble in water and in alcohol. It is fermented by fungi and bacteria like dextrose. One way to make it is to boil sucrose with hydrochloric acid and thereby change the sucrose to dextrose and levulose. On treating the cold solution with an excess of calcium hydroxide, the crystals of calcium levulate are precipitated and can be filtered. On decomposing the precipitate with oxalic acid, and concentrating the filtered solution, levulose will crystallize out. Aside from its use as a food in fruit and honey, where it occurs naturally, levulose has no economic importance.

54. **Sucrose, Saccharose, Cane Sugar.**—$C_{12}H_{22}O_{11}$, graphically:



This constitutes a double "sugar" group of atoms or the union of two single groups. Hence it is a disaccharide. It is very widely distributed in plants, being found particularly

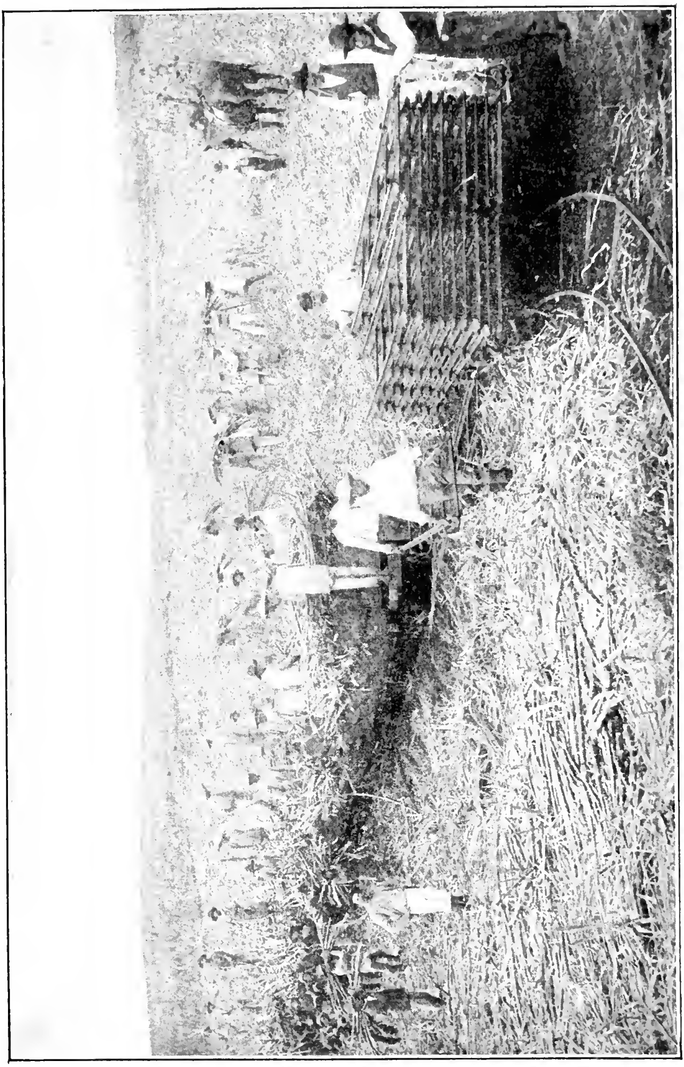


FIG. 12.—Harvesting sugar cane in Hawaii.

in sweet fruits, stalks of corn and sugar cane, in seeds, roots, bulbs, and the sap of maple, birch, and other trees. Sugar cane and sugar beets are the principal sources of sucrose, the former containing about 20 per cent., the latter, 15 per cent. Fig. 12 illustrates the harvesting of a crop of sugar cane, and Fig. 41 a growing crop of sugar beets. From the physiological point of view, sucrose is a storage form of carbohydrates, particularly in roots and tubers such as beets and sweet potatoes, it being formed in all probability by a condensation of dextrose and the elimination of water.

Sucrose is a colorless solid, crystallizing in large, clear crystals (Fig. 13). As it is usually purchased, it consists of very small crystals, the mass of which appears white due to reflected light. It is easily soluble in water, slightly soluble in hot absolute alcohol, more easily soluble in dilute alcohol, insoluble in ether and in cold absolute alcohol. It is dextrorotatory, the specific rotation being +66.5°. Its sweetness is too well known to need description.

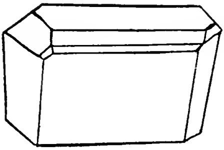


Fig. 13.—Crystal of sucrose. Natural size. Drawing by C. A. Smith.

Sucrose does not reduce Fehling's solution, that is, it is not easily oxidized. It melts at about 160° C. From 170° up to 190° C. it decomposes, by losing water, to a mixture of unknown condensation products, the mass turning brown in color and having a peculiar, agreeable flavor. Caramel is the name given to the material. Caramel is soluble in water, reduces Fehling's solution, and is used to a large extent as flavoring for candy and ice-cream.

Under the action of an enzyme called invertase, sucrose hydrolyzes to equal parts of dextrose and levulose.[1] This is the way it changes naturally in plants. Artificially, sucrose can be hydrolyzed by boiling with a dilute mineral acid like hydrochloric, the products of this acid hydrolysis being the same as with invertase. The mixture of levulose and dextrose thus produced is known as *invert sugar*, because the levorotatory power of levulose is greater than the dextrorotatory power of dextrose, the net result being levorotation. The specific rotation of invert sugar is −20°.[2] Fungi and bacteria containing invertase change sucrose to dextrose and levulose, and can then ferment to the usual products of alcohol, carbon dioxide, etc. It is not directly fermentable in most cases.

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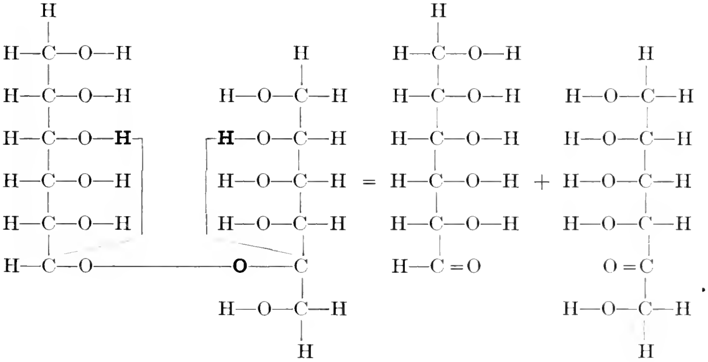
[1] The hydrolytic change of sucrose into equal parts of levulose and dextrose is shown best by the graphic formula, and illustrates very well the glucoside-like character of the sucrose molecule. (See footnote on page 53.) In fact it may be considered a "levulo-glucoside," or "levulin."



Sucrose. Dextrose. Levulose.

The hydrogen and oxygen of water enter the sucrose molecule as indicated by the heavy letters, and the molecules of dextrose and levulose result.

[2] The specific rotation of levulose is − 92.5° and of dextrose is + 52.5°, but that of invert sugar is not − 40°, but − 20°, since specific rotation is the angular rotation of a column 10 centimeters long which contains 1 gram of substance in 1 cubic centimeter (footnote p. 52), and 1 gram of invert sugar consists of $\frac{1}{2}$ gram of dextrose and $\frac{1}{2}$ gram of levulose, thus giving only $\frac{1}{2}$ the angular difference between the specific rotations of levulose and dextrose.

With alkalies and alkaline earths sucrose forms saccharates, or "sucroxides," those of calcium being the most important. There are three compounds with calcium: Monocalcium saccharate, $C_{12}H_{21}O_{11}.CaOH$; dicalcium saccharate, $C_{12}H_{20}O_{11}.2CaOH$; tricalcium saccharate, $C_{12}H_{19}O_{11}.3CaOH$. The monocalcium compound is readily soluble in water, the tricalcium compound difficultly soluble. The latter is used commerically in the separation of sucrose from beet molasses. The molasses is treated with freshly burned lime. The resulting precipitate of tricalcium saccharate is filtered, washed with cold water and decomposed by carbon dioxide in aqueous suspension. The reaction is as follows:

$$C_{12}H_{19}O_{11}.3CaOH + 3CO_2 = C_{12}H_{22}O_{11} + 3CaCO_3.$$

Many other saccharates are also formed, such as those of iron, aluminium, nickel, and copper. Those of iron are used medicinally.

Pure sucrose is prepared by precipitating it from a solution of commercial sucrose with cold, absolute alcohol, and washing the fine crystals with absolute alcohol. Commerical sucrose is made from sugar cane by squeezing out the juice in mills, clarifying with lime to remove impurities, evaporating the filtrate, and finally crystallizing out the sucrose. Fig. 14 shows the interior of a sugar factory where the cane juice is being evaporated. Further solution, treatment with lime and bone black, and recrystallization yields the pure granular sugar (sucrose) of commerce. Brown sugar is obtained by evaporating to dryness the mother liquor from which no sucrose will crystallize. Brown sugar originally contained some caramel because the evaporation of the syrup was carried on in vats heated by a free flame, and part of the material, being overheated, caramelized. Modern evaporators are steam-heated vacuum pans, and thus caramelization is avoided.

From the sugar beet, sucrose is made by slicing the beets and soaking them in water, thus allowing the sucrose to diffuse gradually out of the beet cells. The concentrated juice is clarified and purified much as in the case of sugar cane juice. Beet sugar is exactly the same as cane sugar, although when first made methods of purification were not perfect, and the admixed impurities made its quality poorer than that of cane sugar.

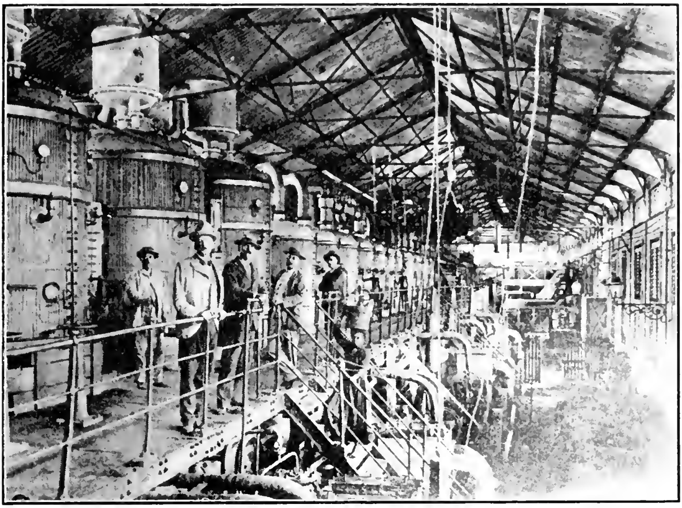
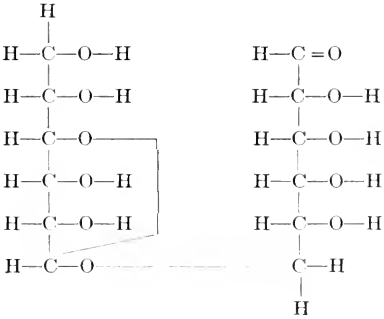


FIG. 14.—Boiling cane juice in a sugar factory at Guadaloupe.

The various uses of cane sugar are too well known to need description.

55. **Maltose, Maltobiose, Malt Sugar.**—$C_{12}H_{22}O_{11}$, graphically:



This constitutes another double "sugar" group. It is one of the most widely distributed sugars in plants, but since it is never a storage form of carbohydrates it is not found in any quantity, as are the other sugars. It is one of the transition forms from starch to dextrose, and is formed to a large extent in the germinating seed (Section 7). Of itself, however, it may serve as a transport form of carbohydrate without undergoing a change to dextrose. It is a white, crystalline solid, readily soluble in water; slightly soluble in cold alcohol; not as sweet as sucrose. It is dextrorotatory, the specific rotation being +138°. Maltose reduces Fehling's solution, since it belongs to the aldehyde group. Under the action of an enzyme called maltase, it is hydrolyzed to dextrose, one molecule of maltose beraking up into two molecules of dextrose.[1] It is also hydrolyzed to dextrose on boiling with a dilute mineral acid like hydrochloric. Maltose ferments only as it is hydrolyzed to dextrose by enzymes in the fungi and bacteria. It forms compounds with alkalies and alkaline earths, but they are of no importance.

Maltose is prepared by treating starch paste with malt extract (Section 7) at 60° C., and extracting the maltose thus formed with successive portions of hot 87 per cent. alcohol, finally evaporating and allowing it to crystallize. It is

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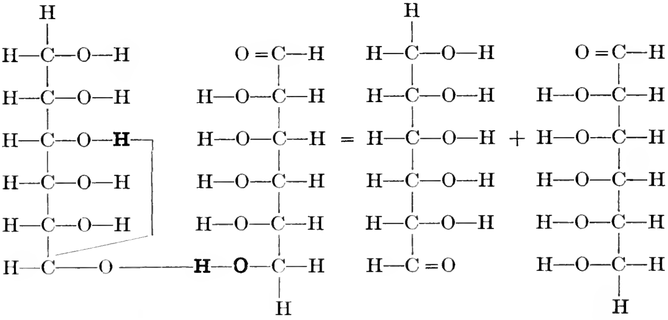
[1] As in the case of sucrose this hydrolytic change shows the glucoside-like character of maltose, it being a "gluco-glucoside," or "glucolin." Thus:



Maltose Dextrose Dextrose

recrystallized from hot methyl alcohol, after purifying with bone black.

It has no commercial use by itself, but it exists in malt and malt products which are made from germinating barley (Section 99, *a*). It also occurs mixed with dextrin (Section 57) as a thick syrup or solid.

56. **Non-sugars or Polysaccharides.**—These compounds are usually colorless or white, odorless, and amorphous, with little or no taste, and insoluble in water and in alcohol. They are formed by the condensation of a great many molecules of a monosaccharide with the elimination of water, thus:

$$n\ C_6H_{12}O_6 - n\ H_2O = (C_6H_{10}O_5)\ n.$$

Each molecule consists of a large number of single "sugar" groups. Starch and cellulose are the principal polysaccharides.

57. **Starch.**—$(C_6H_{10}O_5)_{200}$(?). The exact graphic formula is not known. Starch occurs in all parts of the plant as a storage form of carbohydrate material, being a condensed anhydride, and insoluble. It occurs to a great extent in seeds and tubers as follows:

Crops.	Approximate per cent. starch.
Corn	62
Wheat	64
Oats	54
Rice	70
Potatoes	20

Starch occurs in plant cells in the form of very small, white grains, the size and shape of which vary with the plant which manufactures it. Figs. 15 to 19 show various kinds of starch grains, and it is to be noted that those of the potato are comparatively large, while those of rice are very small. The size varies from about 0.002 mm. to 0.2 mm. in diameter. These grains are composed of very thin cellulose walls, with contents of powdery material called granulose or amylose. They are insoluble in cold water, alcohol, and ether, but on treatment with boiling water the cellulose envelope ruptures and the escaping granulose dissolves in the water to form a more or less gelatinous solution,

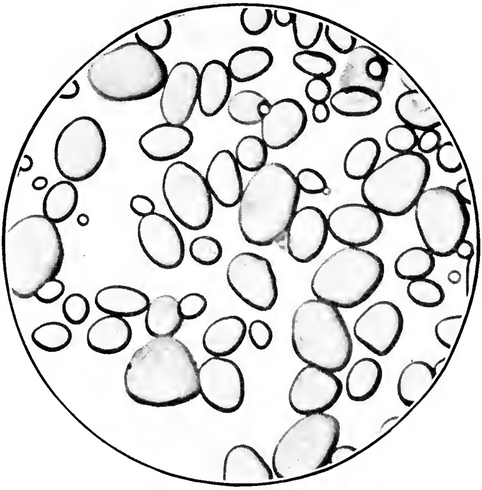


Fig. 15.—Potato starch.

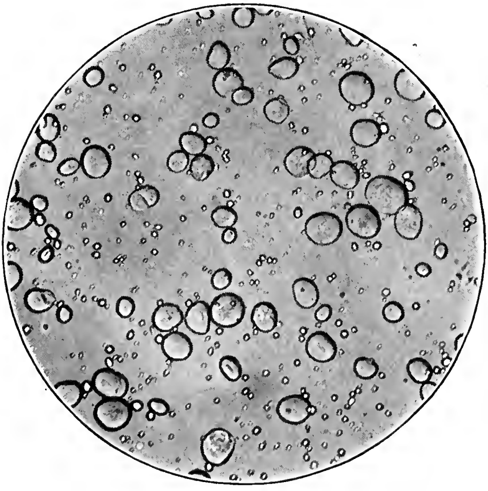


Fig. 16.—Wheat starch.

slightly cloudy from the insoluble cellulose walls. This semisolution is called starch paste. It is strongly dextro-

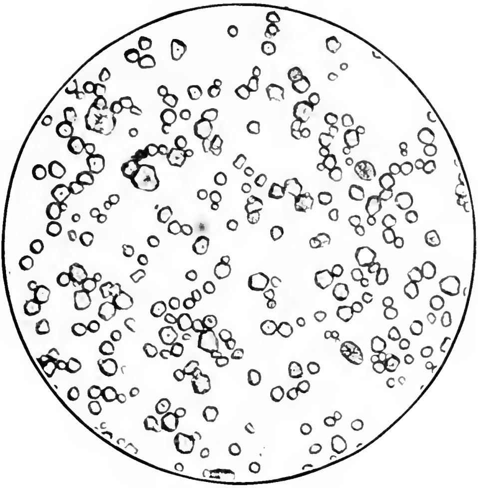


Fig. 17.—Corn starch.

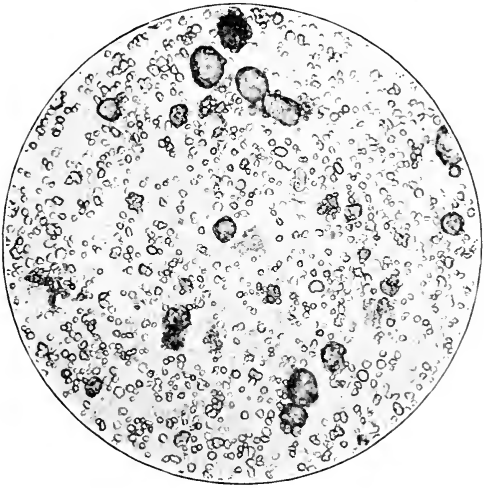


Fig. 18.—Oat starch.

rotatory, and will not reduce Fehling's solution. Its most characteristic reaction is to turn blue in the cold with a solution of iodine (in alcohol or potassium iodide). The compound formed is supposed to be $(C_{24}H_{40}O_{20}I)_4.HI$, which breaks up on heating, but which reforms again when the solution is cooled down.

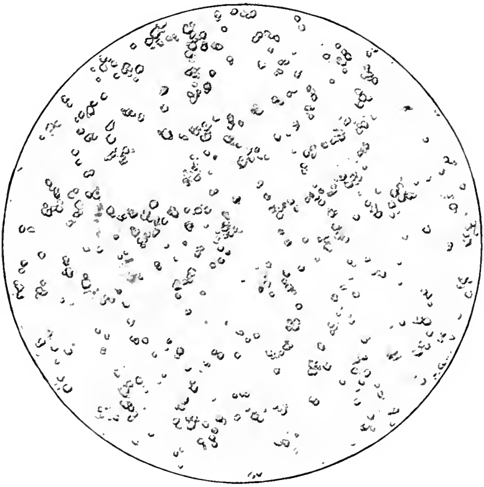


Fig. 19.—Rice starch.

Figs. 15 to 19.—Starch grains. Bureau of Chemistry, United States Department of Agriculture.

Under the action of enzymes, diastase for example, starch hydrolyzes to maltose (Section 55), thus:

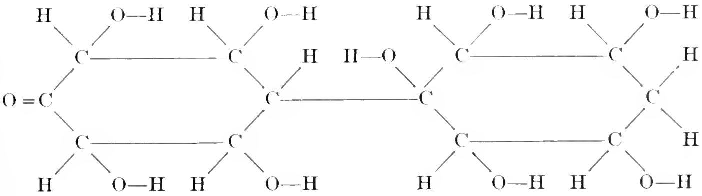
$$2(C_6H_{10}O_5)n + nH_2O = nC_{12}H_{22}O_{11}.$$

In so doing, however, it passes through a series of hydrolytic compounds, named successively: Amylodextrin, colored blue by iodine; erythrodextrin, colored red by iodine; achroodextrin, not colored by iodine; maltodextrin, not colored by iodine; maltose, not colored by iodine. These various dextrins differ from starch in containing a smaller number of $C_6H_{10}O_5$ groups in their molecules. They are colorless, soluble in water to a gelatinous consistency, and dextrorotatory. They can also be made from starch by roasting it in ovens with about 0.2 per cent. nitric acid to 110°–170° C., and dissolving out the so-called *Dextrin* or *British Gum*, which is used in the textile industries for thickening colors, as mucilage on stamps, envelopes, etc.

On boiling starch with mineral acids such as hydrochloric or sulphuric, the same hydrolytic changes take place except that maltose is still further changed into dextrose.

Commercial starch is prepared from corn by grinding and separating the starch from the other material by gravity in water; from potatoes by scraping or pulping, filtering off the fiber, and washing to separate the starch. It is used for a great variety of purposes, such as for food in puddings, for laundry work, for sizing in paper and textiles, for cosmetics, etc.

58. **Cellulose.**—$(C_6H_{10}O_5)_1$ (n greater than 200). The graphic formula is not well understood, but the following has been assigned to it as the unit group which occurs a large number of times:



Cellulose comprises about one-half of the dry matter of plants.[1] It forms their framework, being the chief constituent of cell-walls and supporting fibers. Usually it occurs in combination, either weakly chemical or physical,

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[1] Different plant materials contain the following approximate amount of cellulose:

	Per cent.
Wood	60
Straw	40
Seeds (including husks)	15
Roots	10

with so-called "encrusting substances" derived from it, such as lignin and pentosans. In the pure form it occurs naturally only in the cotton plant as a mass of seed hairs, and in a very few other plants. As has been stated (Section 24) it is derived from dextrose by dehydration, thus:

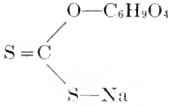
$$nC_6H_{12}O_6 - nH_2O = (C_6H_{10}O_5)n.$$

Its function is to provide a somewhat elastic, but fairly rigid envelope for plant cells. Where heavy walls are needed and heavy weights are to be supported, as in trees, these walls become "lignified" or thickened, filling the cell almost completely. This thickened part forms the encrusting substances mentioned above.

Physically, cellulose is a white, amorphous or fibrous solid, insoluble without decomposition in all solvents. Cuprammonium hydroxide solution (cf. Section 216, I, c), called Schweitzer's reagent, dissolves cellulose to a thick, viscous, dark blue liquid in which the cellulose exists as a complex compound with the copper and ammonia. From this solution it may be reprecipitated in the amorphous form by acidification with hydrochloric or sulphuric acid. A strong solution of zinc chloride in concentrated hydrochloric acid also dissolves cellulose to a complex compound from which it may be recovered on treatment with alcohol. Cold, concentrated sulphuric acid dissolves cellulose. In so dissolving it is changed to a cellulose sulphuric acid compound from which the cellulose can not be recovered. On diluting such a solution and boiling it, the cellulose is hydrolyzed to dextrose.

If cellulose is treated with a cold solution of sodium hydroxide stronger than 10 per cent., a compound is formed which has a formula something like this: $C_{12}H_{18}O_{10}Na_2$. On washing with water the cellulose is regenerated as the hydrate, $C_{12}H_{20}O_{10}.H_2O$. If cotton cloth is stretched on a frame and treated in this way there is obtained a cloth of silky appearance called "mercerized cotton." The treatment results in a shrinking of the cotton fibers, and a resultant gloss if the cloth is kept taut during the shrinking process.

If the above mentioned soda-cellulose is treated with carbon disulphide a compound is formed called "viscose," which is soluble in water to a viscous liquid. On spontaneous decomposition in the air, viscose loses carbon disulphide and sodium hydroxide. The former disappears by volatilization and the latter may be washed out. A hard, transparent, vitreous mass of cellulose is left. This is called "viscoid" or "cellophane" and finds a variety of uses. On treating cotton with nitric and sulphuric acids there are obtained, according to conditions, a hexanitrate of cellulose, $C_{12}H_{14}O_4(NO_3)_6$, or a tetranitrate of cellulose, $C_{12}H_{16}O_6(NO_3)_4$. The former, insoluble in alcohol and ether, is known as guncotton, the explosive; the latter, soluble in alcohol and ether, is called pyroxylin or soluble cotton. The solution of pyroxylin in alcohol and ether is known as collodion which finds a variety of uses in surgery as a dressing for wounds, and in photography for making films. If pyroxylin is intimately mixed with camphor, celluloid results.



The thick viscous solutions of cellulose in ammoniacal cupric hydrate, of viscose, and of collodion, all serve as materials for making artificial silk. By squeezing the thick liquid through exceedingly fine holes, and winding the resulting filaments into a thread, a lustrous imitation silk is made after regenerating the cellulose. In the case of the ammoniacal copper hydrate solution the cellulose is formed by treating the threads with dilute sulphuric acid and washing; in the case of viscose, by simple drying and washing; and in the case of collodion by denitrating with alkaline sulphides.

Under proper conditions cellulose will unite with acetic acid to form a tetra-acetate $C_6H_6O(C_2H_3O_2)_4$, soluble in nitrobenzol. On evaporation of the solvent there is formed a transparent film that is used for photographic purposes. It is also a superior insulating material for electric wires.

From the above discussion it can be seen that cellulose has both acid and basic properties, since it forms compounds with bases like sodium and copper hydroxides, on the one hand, and with nitric and acetic acids, on the other. On the whole, however, it is exceedingly inert, resisting all ordinary decomposition and decay. It is not fermentable. It finds its chief use on account of this decay-resistant property in the manufacture of rope, cotton cloth, linen cloth, paper, and other articles, all of which are made of cellulose from different sources.

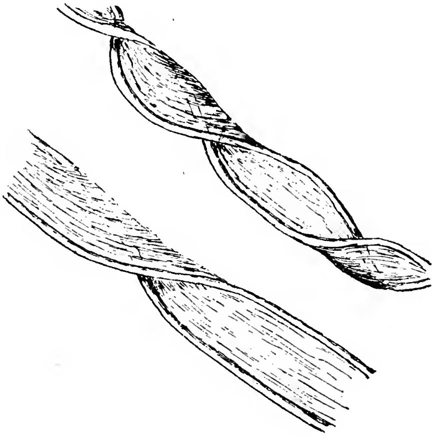


Fig. 20.—Cotton fiber. Magnified. Drawing by C. A. Smith.

Cotton fiber (Fig. 20) is the purest form of cellulose, but even that must be treated with alkali, acid, alcohol, and ether to remove impurities attached to it, such as proteins and fats. In the case of flax used for linen and hemp used for rope, various processes are employed to free the crude cellulose fibers from their encrusting substances. In making paper from wood, the lignin and other impurities are dissolved away by a weak caustic soda solution (Soda Process), or an acid sulphite solution (Sulphite Process). The remaining cellulose fibers, which by the way are much shorter than cotton and linen fibers, are sized, loaded, and matted into paper of various kinds. If unsized paper, that is, pure, matted, cellulose fibers, are dipped in fairly strong sulphuric acid for an instant and then plunged into water, the cellulose assumes a tough, parchment-like texture, and is used as a substitute for sheep skin. This material is called "amyloid," since it is starch-like in character, giving a blue color with iodine.

59. **Lignin and Pentosans.** — These "encrusting substances" are derived from cellulose apparently, but differ from it in chemical composition. Lignin contains less oxygen than cellulose, and in addition has methyl (CH_3) groups present. It is soluble with decomposition in hot dilute alkali, acid sulphite, and some other solvents. It is easily decomposed by chlorine and bromine. It forms a large part of the woody fiber of trees, and hence its name, lignin. Pentosans are compounds of the general formula $(C_5H_8O_4)n$ which are hydrolyzed by acids to pentoses, $C_5H_{10}O_5$. *Xylan* and *araban,* hydrolyzing to xylose and arabinose, are examples. Pentosans form some 10 per cent of the dry matter of coniferous trees and 20 per cent. of deciduous trees.

60. **Inulin.**—$(C_6H_{10}O_5)_6$. This carbohydrate occurs naturally as a storage form of carbohydrate in the roots of such plants as dandelion, dahlia, and chicory. It is derived undoubtedly as are the other anhydride forms of dextrose by a dehydration process: $6C_6H_{12}O_6 - 6H_2O = (C_6H_{10}O_5)_6$. It is a white, crystalline substance easily soluble in water, insoluble in alcohol. It does not reduce Fehling's solution, and is levorotatory. It hydrolyzes under the action of dilute mineral acids and of the enzyme, inulase, to levulose. It is not fermentable.

61. **Gums.**—These are amorphous substances of unknown composition, but are probably glucosides of organic acids. They are soluble in water, or at least gelatinize in it, insoluble in alcohol, and hydrolyze with acids to hexoses and pentoses. *Gum arabic,* used in making mucilage, and various *wood gums,* are examples.

62. **Pectins.**—Pectins are amorphous, white substances found in most fruit juices, soluble in water, but insoluble in alcohol. By enzyme action they are derived from insoluble pectose which gives hardness to unripe fruit. The pectins in turn are changed to pectic acid by enzymes as the fruit ripens, and the calcium salt of pectic acid is what makes the juice of fruits like apples, plums, and grapes, solidify to a jelly.

II. FIXED OILS AND WAXES

63. **General Definition.**—The name oil is given to liquid substances which are characterized by their slippery or greasy feel, and by the fact that they leave a grease spot, or permanent translucent spot on paper. The properties are the same whether the oils are the so-called mineral oils, hydrocarbons occurring naturally in the earth, or are vegetable oils, called fixed oils or fats, or are volatile oils also found in plants.

The fixed oils are always esters of glycerine and fatty acids, or glycerides of fatty acids. Glycerine being a trihydric alcohol can combine with one, two, or three monobasic fatty acids, and most fixed oils are mixtures of compounds of glycerine with more than one fatty acid. The name oil usually signifies a liquid compound, fat being the name usually given to a fixed oil which is solid at ordinary temperatures. When found in plants the fixed oils are sometimes called vegetable oils to distinguish them from the so-called animal oils which are found in animals. The present discussion will be confined to fixed oils of plants, or vegetable oils, although the general characteristics are the same for both classes of fixed oils.

64. **Properties.**—Fixed oils when pure are colorless or pale yellow. When impure they are frequently darker in color, sometimes even greenish in shade from the presence of small amounts of chlorophyl. With few exceptions they have no particular odor or taste. They are lighter than water, their specific gravity varying from 0.875 to 0.970.

They will not distill unchanged. On heating they decompose into various compounds depending on the temperature. They are insoluble in water and in cold alcohol, somewhat soluble in hot alcohol, easily soluble in ether, chloroform, carbon tetrachloride, carbon disulphide, and other volatile solvents. They "saponify" on treatment with alkaline hydroxides, that is, they break up into glycerine and the alkaline salt of the fatty acid, called a soap (Section 66). They hydrolyze to glycerine and fatty acids on treatment with steam, and also under the influence of lipases (Section 8).

They are found for the most part in the seeds of plants, where they serve as reserve material for respiration, or from which to make carbohydrates (Sections 8 and 32). Fixed oils are, however, found in all living cells of plants and apparently play a necessary part in the functioning of protoplasm.

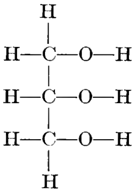
The fixed oils are "drying" or "non-drying" in character. That is, on exposure to the air some of them absorb oxygen and harden more or less, while others remain perfectly liquid. This is a property of the fatty acid radicle. The non-drying oils on exposure to the air slowly become rancid, that is, oxidation takes place, helped by the action of bacteria, which gives the oils a disagreeable smell and taste, and makes them acid to litmus. This is due to the formation of free fatty acids with some other products.

65. **Methods of Extraction.**—An old way of extracting fixed oils from seeds and other plant substances was to crush them and boil with water. The oil rising to the top could be skimmed off. Another way is to extract the oil with volatile solvents which can later be distilled off, leaving the oil behind. This process, however, is expensive and the product contains other compounds which dissolve out in the solvent and remain as impurities in the oil.

The most common method is to clean and decorticate the seeds (remove the husks), place them in bags and squeeze the oil out by heavy presses. The first expression is made in the cold which gives a better quality of oil. The pulp is then expressed hot and more oil is obtained, but it is not so pure. The material remaining is called "press cake," and when ground is sold for cattle food and fertilizers.

66. **Soap.**—The saponifying property of fixed oils is made use of in the manufacture of soap. If potassium hydroxide is used a soft soap results, if sodium hydroxide, a hard soap. Both kinds are soluble in water, but the potash salt of the fatty acids is a soft substance, whereas the soda salt is a hard substance. The oil or fat is boiled with the alkali until saponification is complete. If a hard product is being made, the soap is separated from the resulting glycerine and the excess of alkali by the addition of common salt. The soap is insoluble in this solution, and can be separated, further treated, and made into cakes.

67. **Glycerine.**—From the residue after the removal of soap, glycerine may be obtained by special processes including purification by distillation under reduced pressure. Glycerine is a thick, oily liquid, hygroscopic, miscible with water in all proportions, and has a very sweet taste. Its formula is $C_3H_5(OH)_3$, graphically:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-O-H} \\ | \\ \mathrm{H-C-O-H} \\ | \\ \mathrm{H-C-O-H} \\ | \\ \mathrm{H} \end{array}$$

It is used in the manufacture of nitroglycerine and dynamite; as a solvent in confectionery on account of its hygroscopic qualities which keep candy soft; in printing inks, etc.

68. **Classification of the Fatty Acids.**—The drying property of oils depends on the existence of double bonds in the fatty acid radicle; or to express it in another way, on the existence of unsaturated carbon atoms which readily take up oxygen. On this basis the fatty acids of the fixed oils may be classified as saturated or unsaturated compounds as follows:

(*a*) Saturated Fatty Acids.—$C_nH_{2n+1}COOH$. Stearic acid, $C_{17}H_{35}COOH$, melting point 69° C.

$$CH_3.(CH_2)_{16}.COOH$$

Palmitic acid, $C_{15}H_{31}COOH$, melting point 62° C.

$$CH_3.(CH_2)_{14}.COOH$$

(*b*) UNSATURATED FATTY ACIDS.—(1) *With one double bond*, $C_nH_{2n-1}COOH$. Oleic acid, $C_{17}H_{33}COOH$, melting point 14° C.

$CH_3.(CH_2)_7.CH:CH.(CH_2)_7.COOH$

(2) *With two double bonds,* $C_nH_{2n-3}COOH$. Linoleic acid, $C_{17}H_{31}COOH$, melting point below $-18°$ C.

$CH_3.(CH_2)_6.CH:CH.CH:CH.(CH_2)_6.COOH$

(3) *With three double bonds,* $C_nH_{2n-5}COOH$. Linolenic acid, $C_{17}H_{29}COOH$, liquid at ordinary temperatures.

$CH_3.(CH_2)_5.CH:CH.CH:CH.CH:CH.(CH_2)_5.COOH$

The presence of more than one double bond in the fatty acid is necessary for a true drying oil of commercial value. One double bond in the acid radicle does not absorb oxygen readily enough—does not harden sufficiently.

The glycerides are named according to the fatty acid radicle, thus: Olein for a glyceride of oleic acid, palmitin, for one of palmitic acid, stearin for one of stearic acid, etc.

In the above classification it is to be noted that palmitic and stearic acids are solid at ordinary temperatures, and oils containing a large proportion of these acids are solid at ordinary temperatures. They are called fats. The other acids mentioned are liquid at ordinary temperatures and oils containing them are usually liquid. This property of being solid is more or less characteristic of the saturated group, and of being liquid more or less characteristic of the unsaturated group, although not exclusively so. Some acids of the first group are liquid at ordinary temperatures, and some acids of the second group are solid.

In most cases the plant fixed oils are liquid and contain a larger proportion of the liquid fatty acids than do animal fixed oils which are called fats. The latter contain as a rule more stearic and palmitic acids.

Oils containing oleic acid have a slight drying power. Those containing linoleic and linolenic are much better "driers." The "drying," it should be remembered, is an oxidation process, resulting in the formation of a hard, resinous compound, and not a desiccation which is the case in true drying. Non-drying oils may be used as lubricants, but drying oils are not suited for this purpose, since the "drying" would make them lose their lubricating qualities.

69. **Some Common Fixed Oils.**—(*a*) CASTOR OIL is a thick, viscous, transparent, colorless or slightly yellow oil of disagreeable taste. It is pressed from the seeds of the castor bean which contain about 50 per cent. of oil, and is composed of small amounts of stearin but principally of ricinolein, the latter being the glyceride of ricinoleic acid, a hydroxy-acid with one double bond, $C_{17}H_{32}OH.COOH$. It is used in medicine; for making soap; and as a lubricant for heavy machinery, since it is very viscous and does not "dry" appreciably.

(*b*) CORN OIL is a pale yellow, fluid oil, with a smell of corn meal. It is composed mostly of olein and linolein and is a semi-drying oil. It is derived by pressing the germs which have been removed from corn kernels previous to the manufacture of starch (Fig. 5). It is used largely in making soap, oil-cloth, and as an adulterant of edible oils. The press cake is an excellent cattle food.

(*c*) COTTONSEED OIL, when purified, is a straw colored, pleasant tasting oil, composed of palmitin, stearin, olein, and linolein. It is made from husked or decorticated cotton seeds by pressure when hot, and the resulting oil, 18 per cent. yield, is clarified. By cooling below 12° C. the solid fats, palmitin and stearin, separate out and can be obtained by pressing. "Cottonseed stearin" is used in making butter substitutes, such as oleomargarine. The original oil is used as a substitute for olive oil and to adulterate olive oil, but principally in soap making. The press cake is used for cattle food.

(*d*) LINSEED OIL is obtained by cold pressing or hot pressing the seeds of the flax plant (Fig. 26 shows a field of flax in blossom). The seeds contain from 30 to 40 per cent. of oil. The cold pressed product is clear and yellow, containing less solid glycerides and hence is a better drying oil. It is also used as a food in some countries, whereas the hot pressed oil is brown and unfit to use as a food. The pressed oil is allowed to stand for some time to allow impurities to settle, and it is also further purified and bleached. It contains about 58.5 per cent. isolinolenin (isolinolenic acid has the same empirical formula as linolenic acid, but a different structural formula), 13.5 per cent. linolein, 13.5 per cent. linolenin, 4.5 per cent. olein, and 10 per cent. of solid glycerides, stearin, palmitin, and myristin (from myristic acid, saturated, $C_{13}H_{27}COOH$).

Linseed is the principal drying oil and has been used for hundreds of years in the paint and varnish industry. Its usefulness lies in the fact that a thin layer of it dries or oxidizes to a hard, transparent, more or less glossy skin which serves as varnish when uncolored or as a paint when mixed with pigments. If linseed oil is boiled first it dries more quickly on exposure to the air. Also if the oil is boiled with "driers" such as lead oxide, lead resinate, manganese borate, and manganese resinate, the drying process is hastened, probably by the metallic salts acting as catalytic agents in the oxidation. Raw, or unboiled oil is used for making soap, some kinds of paints and varnishes, and for rubber substitutes by "vulcanizing" with sulphur or sulphur monochloride. The boiled oil is used for paints, printer's inks, oil-cloth, linoleum, etc.

The oxidation process which drying oils undergo develops considerable heat. Cotton waste or similar material soaked in linseed oil has been known to take fire spontaneously, the loose mass of material preventing the radiation of the heat which gradually increases to the "flash point."

Press cake from hot pressed linseed oil makes an excellent cattle food. The cold pressed cake is more apt to poison cattle due to the presence of a hydrocyanic acid glucoside which is acted upon by an enzyme in the presence of water with consequent hydrolysis to hydrocyanic acid and glucose. The former is the poison. Hot pressed cake on the other hand has had the enzyme destroyed by heat and no hydrolytic action takes place, the glucoside itself being harmless.

(*e*) OLIVE OIL is made by pressing the fruit pulp and the seeds. The cold pressed oil from the former is the better grade and is employed as a condiment. The oil expressed hot from the original cake and from the seeds is less pure and is used for lubricating purposes and soap making. The color of the oil varies from a pale yellow to a greenish or brownish shade. It contains about 72 per cent. olein and 28 per cent. palmitin. Thin films dry slowly. Cotton seed oil is the principal adulterant.

(*f*) PEANUT OIL is obtained from peanuts, and is a light greenish-yellow oil, although colorless when refined. It is used as an adulterant for olive oil, as a salad oil under its own name, and for making butterine and soap. It contains olein, linolein, palmitin, stearin, and some less known glycerides.

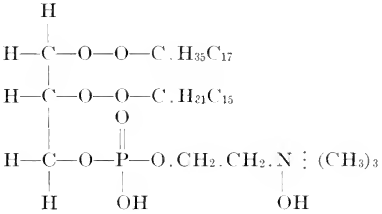
(*g*) RAPESEED OIL OR COLZA OIL is obtained from rapeseed by hot pressing. The purified oil is light colored and used as a condiment under the name of colza oil, rape seed oil being applied to the darker colored oil which is used as a lubricant and to some extent as a burning oil. Both kinds, containing mostly olein, stearin, and brassin, are very viscous, and on exposure to the air, become gummy, but do not dry.

(*h*) SUNFLOWER OIL is obtained from the seeds of the sunflower. It is pale yellow and of pleasant taste, being used in cooking. Less pure grades are used for soap making and as an adulterant for linseed oil, although it does not dry as quickly. It is composed of olein, palmitin, and linolein principally.

70. **Waxes.**—These compounds are allied to the fixed oils in that they have many of the properties of oils, and are esters of fatty acids, but the acids are combined with monohydric alcohols of high molecular weight, and not with glycerine. In the plant they serve as a protective waterproof coating on the stems, leaves, and fruit of many plants. The "bloom" on plums is a wax. The surface of corn stalks and sugar cane is covered with a thin layer of wax. The waxes may be liquid or solid and are found in animals as well as in plants.

Carnauba Wax is the principal plant wax. It is a very hard substance, usually of sulphur yellow color and obtained from the leaves of a certain kind of palm tree in Brazil by scraping the surface of the leaves, melting and collecting it in boiling water. It is an ester of so-called myricyl alcohol, $C_{30}H_{61}OH$ and cerotic acid, $C_{25}H_{51}COOH$ and some other similar esters. It is used in making candles, polishing pastes, and phonograph cylinders.

71. **Lecithin.**—While this compound is not a wax or fat, it is allied to them in chemical composition. It is an ester of glycerine and choline with a fatty acid and phosphoric acid. Its formula may be as follows:



$$\begin{array}{llllll}
 & \mathrm{H} & & & & \\
 & | & & & & \\
\mathrm{H}- & \mathrm{C} & -\mathrm{O}-\mathrm{O}-\mathrm{C.H_{35}C_{17}} & & & \\
 & | & & & & \\
\mathrm{H}- & \mathrm{C} & -\mathrm{O}-\mathrm{O}-\mathrm{C.H_{31}C_{15}} & & & \\
 & | & \quad\quad\ \mathrm{O} & & & \\
 & | & \quad\quad\ \| & & & \\
\mathrm{H}- & \mathrm{C} & -\mathrm{O}-\mathrm{P}-\mathrm{O.CH_2.CH_2.N} \vdots \mathrm{(CH_3)_3} & & & \\
 & | & \quad\quad\ | \quad\quad\quad\quad\quad\quad\ | & & & \\
 & \mathrm{H} & \quad\quad \mathrm{OH} \quad\quad\quad\quad\quad \mathrm{OH} & & &
\end{array}$$

This would be called a stearo-palmito-phosphate of glycerine and choline. Other fatty acids may replace the two given. It is a yellowish-white, waxy substance, soluble in alcohol, and other organic solvents. In water it forms an opalescent emulsion or solution. Since it contains certain fat radicles, a reduced nitrogen group, and phosphoric acid, it may be useful in the formation of fats or of proteins. It is found in cereal grains, peas, and beans, to a larger extent than in other plants, although present in most plant cells.

III. VOLATILE OILS AND RESINS

72. **General Definition.**—The name oil signifies a liquid having certain characteristic properties as noted in Section 63, but the *volatile* oils, also called *essential* or *ethereal* oils, are less greasy in character than the fixed oils, and are volatile on exposure to the air; so that the spot they leave on paper will disappear in time. Chemically they are of several different kinds of compounds, to be noted later (Section 75). They are to be found free or as glucosides

in all parts of plants, except in the seeds where the fixed oils predominate. The glucosides hydrolyze under certain conditions with the help of enzymes to glucose and the volatile oil. The volatile oils apparently serve no true physiological function in plants, being for the most part by-products or end products in metabolism. They frequently serve as valuable helps to the plant, however, in attracting insects whereby fertilization is effected; or as a repellent to keep off harmful insects.

73. **Properties.**—Volatile oils are usually colorless or yellow when fresh, but darken on standing. They have very characteristic odors and tastes and are valuable commercially for these properties. Most of them are lighter than water, varying in specific gravity from 0.850 to 0.990, although a few are less than 0.850 and many of the more common oils are heavier than water. They will for the most part distill unchanged, especially under reduced pressure. They are slowly volatile at ordinary temperatures, hence the distinction in names between the fixed oils, which are not volatile, and the volatile oils, which are like their name. Their boiling points are rather high. Volatile oils are insoluble in water, although many of them dissolve to a slight extent, imparting the characteristic odor and taste to the water. They are readily soluble in cold alcohol as well as in hot alcohol, and in ether, chloroform, carbon tetrachloride, and carbon disulphide. They are also miscible in all proportions with fixed oils. Only those which are esters saponify.

74. **Methods of Extraction.**—There are several ways of obtaining the volatile oils for commercial use:

(*a*) BY EXPRESSION, very much as in the case of the fixed oils.

(*b*) BY DISTILLATION WITH WATER OR STEAM whereby the crushed material to be extracted is either boiled with water or has a current of steam passed through it. The volatile oil is carried over with the steam and condensed. The oil and water can easily be separated because of their insolubility in each other and because of the difference in their specific gravities.

(*c*) BY HYDROLYSIS AND DISTILLATION.—Some oils occur as glucosides not only of the oil but also of other compounds. Occurring with them in the plant is an enzyme which under favorable conditions of moisture and temperature acts on the glucosides, forming in addition to glucose the volatile oil and the other compound if it is present. Commercially the oil is obtained by crushing the material in water, allowing the enzyme to act, and distilling off the oil.

(*d*) BY SOLUTION IN A FIXED OIL, such as olive oil or lard. The product is used as a perfumed oil or an unguent.

(*e*) BY EXTRACTION WITH A SOLVENT much more volatile than the oil. The solvent is removed by distillation. This method is applicable only for such oils as have high boiling points.

75. **Classification.**—The volatile oils as obtained from plants are not single chemical compounds, but are very frequently mixtures of several chemical individuals, and the difficulty often experienced in obtaining an extracted oil which resembles the original is due either to a failure to obtain every compound, or to obtain them in the proper proportions. Each oil, however, generally has one principal compound to which are due most of the odor and taste. For convenience, these compounds may be classified into three groups:

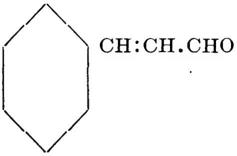
(*a*) CARBON-HYDROGEN COMPOUNDS.—These oils belong to that class of hydrocarbons called terpenes—ring compounds which have a general formula, $C_{10}H_{16}$, or a multiple thereof. They may be terpenes proper, $C_{10}H_{16}$, or sesquiterpenes, $C_{15}H_{24}$.

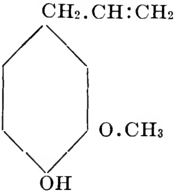
(*b*) CARBON-HYDROGEN-OXYGEN COMPOUNDS. — These compounds may be alcohols, aldehydes, or ketones of the aliphatic or carbocyclic series, or esters of any of the alcohols and acids.

(*c*) CARBON-HYDROGEN-SULPHUR COMPOUNDS.—In addition these compounds sometimes contain nitrogen. They are usually organic sulphides, or thiocyanates. The oils containing oxygen or sulphur have much stronger odors and flavors than the terpenes, and are more useful for these properties than are the commoner terpenes.

76. **Some Common Volatile Oils.**—(*a*) OIL OF BITTER ALMONDS.—This oil is benzaldehyde, C_6H_5CHO, occurring in the almond kernel as a glucoside of hydrocyanic acid and benzaldehyde, called amygdalin. The fixed oil is first expressed, and the cake is crushed, soaked in water until the enzyme, emulsin, hydrolyzes the glucoside to benzaldehyde, hydrocyanic acid, and dextrose. The mixture is then distilled. Hydrocyanic acid is a very powerful poison and care must be taken in the distillation. Moreover, the distillate must be carefully freed from hydrocyanic acid before use. Apricot and peach seeds also contain amygdalin and most of the commercial oil of bitter almonds is obtained from the former. It is a white liquid when pure, heavier than water, and is used in making dyes and for flavoring purposes.

(*b*) OIL OF CINNAMON.—This oil consists mostly of cinnamic aldehyde and eugenol, represented below,

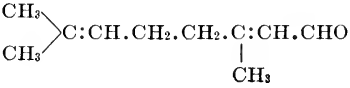




with some other compounds. It is obtained by distillation from the bark of the cinnamon tree, and is a yellow oil, heavier than water, and is used in flavoring, for perfumes, and in pharmacy.

(*c*) OIL OF CLOVES.—This oil is practically all eugenol with a little sesquiterpene. It is obtained from the dried, unopened flower buds of the clove tree, growing in the East and West Indies. It is a yellow oil, heavier than water, and is used in pharmacy, perfumery, and for flavoring.

(*d*) OIL OF LEMON.—This is mostly a terpene, limonene, $C_{10}H_{16}$, with less than 10 per cent. of citral,

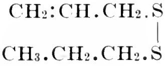


$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle C{:}CH.CH_2.CH_2.\underset{\displaystyle CH_3}{\underset{|}{C}}{:}CH.CHO$$

to which the odor is due, and many other compounds such as terpenes, alcohols, aldehydes, and esters. It is obtained from the rind of lemons either by rupturing the oil cells over a sponge, or rolling in a vessel lined with spikes, or by distillation, or expression. The two latter methods do not yield as good an oil as the sponge method. It is a pale yellow oil, lighter than water, and its uses are the same as for clove and cinnamon oils.

(*e*) Oil of Mustard.—This oil is chiefly allyl isothiocyanate, $CH_2{:}CH.CH_2.N{:}C{:}S$, with some carbon disulphide and allyl cyanide. In nature it occurs in the seeds of black mustard as a glucoside of potassium acid sulphate and allyl isothiocyanate, called potassium myronate which is hydrolyzed by a naturally occurring enzyme when water is present. The seeds are first expressed for the fixed oil, then treated with water, and digested in the cold when the enzyme myrosin converts the glucoside into glucose, potassium acid sulphate, and allyl isothiocyanate. The latter is then distilled off. It is a colorless or a pale yellow oil, heavier than water, with pungent odor and burning taste. It is used in medicine largely.

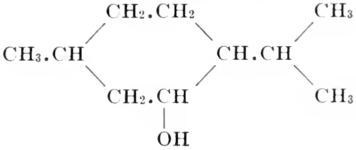
(*f*) Oil of Onion consists principally of allyl-propyl-disulphide,



$$\begin{array}{r} CH_2{:}CH.CH_2.S \\ | \\ CH_3.CH_2.CH_2.S \end{array}$$

and some other sulphides. It is obtained by distillation from onions. It is not of much value commercially, but is the compound which gives to onions and garlic their characteristic odor and taste.

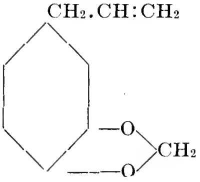
(*g*) Oil of Peppermint contains a great number of different compounds in small amounts—terpenes, alcohols, esters, acids, and aldehydes, but principally menthol, a closed-chain compound but not a binzine compound:



This is a white, crystalline solid at ordinary temperatures and can be obtained from peppermint oil by freezing. It is used in medicine. The peppermint oil itself is obtained by steam distillation of the peppermint plant and is a pale greenish-yellow oil which darkens on standing. It is lighter than water and is used in medicine and for flavoring to a very great extent.

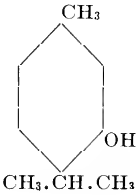
(*h*) Oil of Roses, called attar or otto of roses. This oil is composed of geraniol, $C_{10}H_{17}OH$, and citronellol, $C_{10}H_{19}OH$, both open-chain or aliphatic alcohols. There are also some esters and paraffins present. It is obtained by distillation of roses which are grown for the most part in Bulgaria and Roumania, "the rose garden of the world." It is a pale yellow oil, lighter than water, with a very delicate odor. Attar of roses is very high priced and is frequently adulterated with geranium oil which resembles it somewhat.

(*i*) Oil of Sassafras consists of safrol,



and a number of terpenes, etc. It is obtained by distilling the root bark of the sassafras tree which is very common in the United States. It is usually a reddish-yellow liquid, heavier than water, and is used for scenting cheap soaps and in flavoring. It is one of the cheaper oils.

(*j*) Oil of Thyme is chiefly thymol,



and carvacrol, isomeric phenols. The former is obtained from thyme oil, and is used as an antiseptic. It is a crystalline solid. The other constituents of thyme oil are esters,

FIG. 21.—The proper way to collect crude turpentine. Forest Service, United States Department of Agriculture.

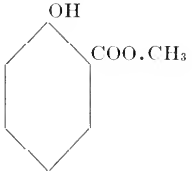
hydrocarbons, etc. Thyme oil is yellowish-red when impure, due to action of the phenols on the iron stills; and light yellow when pure. It is lighter than water; used in medicine, and as a cheap perfume for soaps. It is distilled from the leaves and flowers of an herb that grows largely in Spain and France.

(*k*) Oil of Turpentine is a terpene, usually pinene, $C_{10}H_{16}$, with some other isomers. It is obtained by steam distillation of the resinous exudate of the long-leaf pine tree. This sticky liquid which flows from cuts in the trees is composed of a resin, colophony (Section 78, *b*), and an essential oil which is volatile with steam. The resin is left in the still. The turpentine, which is lighter than water, is drawn off and sold as oil or spirits of turpentine. Figs. 21 and 22 illustrate the process of collection and distillation of turpentine. The best grades come from this country and France. Russia produces some oil of poorer quality. It is a colorless, mobile liquid with a faint, pleasant, ethereal odor when pure. On standing there is formed an oxidized compound, probably an aldehyde, which is said to give

Fig. 22.—Distilling turpentine. Forest Service, United States Department of Agriculture.

turpentine its peculiar, pungent odor. It dissolves sulphur, rubber, phosphorus, and resins. It burns with a very smoky flame, and on exposure to the air it absorbs oxygen, and hardens, much like the drying oils. For this reason it is used very largely in making paints and varnishes. It is also employed to some extent in medicine.

(*l*) OIL OF WINTERGREEN is practically all methyl salicylate,



It is distilled from the wintergreen plant, or teaberry, and from the bark of the sweet birch, both native to America. The oil is yellow, heavier than water, and has a very pleasant taste and odor. It is used in pharmacy to conceal the taste of nauseous drugs, as a medicine, and for flavoring. Since methyl salicylate can be prepared synthetically, the artificial product is largely sold in place of the true oil.

77. **Resins.**—These compounds are yellow or brown solid substances, more or less transparent, brittle, and found as natural or induced exudations from plants. Some of them are supposed to be derived by oxidation of terpenes. Their function in plants may be to serve as a protective coating for wounds and cuts. This prevents evaporation and decay until new cells can be formed to permanently cover the wound. As resins ooze out of the plant, usually from special tubular "resin ducts," they are sticky, thick liquids, but on exposure to the air they change either by oxidation or evaporation of some natural volatile solvent, like an essential oil. Resins are insoluble in water, soluble as a rule in alcohol and in other organic solvents. They decompose on heating away from the air, and burn with a smoky flame. Their chemical composition is very complex, some of them consisting mostly of esters, others of acids, and still others of uncertain compounds classed under the name of *resenes*. In addition to being of a complex nature

when purified, they frequently occur in nature as an exudate mixed with gums and called *Gum-resins,* which emulsify with water; with volatile oils called *Oleo-resins,* which are softer than the resins proper; and with volatile oils together with benzoic or cinnamic acid, in which case they are properly called *Balsams.*

78. **Some of the Common Resins.**—(*a*) AMBER is a fossil resin found mostly on the shore of the Baltic Sea, frequently buried in the earth. It is the hardest resin known, varying in color from yellow to black, sometimes clear and transparent, sometimes cloudy. Chemically amber consists of acids and esters. On heating in a retort above 287° C., it melts and decomposes, forming water, succinic acid, a little volatile fatty acid, oil of amber, and some other compounds. The succinic acid and oil of amber are used in pharmacy. Amber is used mostly for ornamental purposes, although formerly it was employed in the manufacture of the more expensive varnishes.

(*b*) COLOPHONY OR ROSIN is the solid residue remaining after oil of turpentine (Section 76, *k*) has been distilled off. It occurs naturally as an exudate with turpentine from certain pine trees. It is a brittle, yellow to brown solid, chemically consisting largely of an acid. It unites on boiling with sodium or potassium hydroxide to form a deliquescent substance called resinate used in making soaps and for sizing paper. On fusing with manganese or with lead oxides it forms resinates soluble in linseed oil and used as driers in making varnish. On dry distillation colophony breaks up into hydrocarbons, acids, and aldehydes. Commercially two products are obtained—*rosin spirit,* boiling at 80° to 250° C. and *rosin oil,* boiling at over 300° C. Rosin spirit is a colorless liquid composed of hydrocarbons, and resembling oil of turpentine for which it is used as a substitute. Rosin oil is a heavy, viscid liquid, colorless to brown, composed mostly of high boiling point hydrocarbons. It is used in making rosin-grease by mixing with milk of lime, for lubricating axles, and for making printer's ink. Colophony or rosin itself is used in making varnishes, in pharmacy, and in the preparation of resinates, rosin spirit, and rosin oil.

(*c*) COPAL is a name applied to a number of valuable resins. Some are obtained from living trees in Java, Sumatra, and the Philippines. Others are found as fossils in west Africa, Madagascar, and East Indies. Copal resins may be white, yellow, red, brown, or brownish black. The softer varieties are the recent resins and are readily soluble in the usual solvents. The harder kinds are the fossil resins and are practically insoluble in the usual solvents until they have been melted and partly decomposed, when they dissolve in hot turpentine or linseed oil. The latter copals are the more valuable. They are complex in composition, consisting largely of acids and resenes. They are used in making the better grades of varnish.

(*d*) DRAGON'S BLOOD is found in Sumatra, and is a clear, deep red resin composed of resenes and esters. It is soluble in alcohol and ether, and is used in making red varnishes.

(*e*) LAC OR SHELLAC is either a secretion of the lac insect or produced from the plant sap by the sting of this insect on the twigs of certain East Indian trees. It is sold in sticks as "stick lac;" melted, purified, and poured on cold surfaces to cool in thin plates as "shellac;" or poured into moulds to form "button lac." It is pale orange or red when pure, much darker when impure. The red shade is due to a dye secreted by the insect. Bleached shellac is made by passing chlorine through a solution of lac in alkali. This precipitates white lac which is melted and pulled. It is soluble in alcohol and alkalies, partly soluble in ether. Lac is composed of resenes and acids. It is used extensively in varnishes, for stiffening hats, as a constituent of sealing wax, etc.

(*f*) MASTIC AND SANDARAC are similar resins found in Africa and Australia, occurring in the form of "tears" or "solid drops" of rather yellow, translucent material. They are partly soluble in alcohol and turpentine, completely soluble in ether. They are composed of acids, resenes, and bitter principles, probably alkaloids. They are used in varnishes and pharmacy, in the latter for tooth cements and plasters.

79. **Some of the Gum-resins.** (*a*) ASAFETIDA is found on the roots of certain plants in Thibet and Turkestan in the form of tears and masses. It is usually yellowish or brownish

in color, and has an unpleasant garlic odor and bitter characteristic taste. Asafetida is composed of about 25 per cent. of gum and the rest resin ester with a little volatile oil and some other compounds in small amounts. Its use is restricted now largely to veterinary practice, although it is used to some extent in India and Persia as a flavoring agent in sauces.

(*b*) Frankincense or Olibanum is found on certain trees in Arabia and Africa as yellow-brown tears, with aromatic odor. It is composed of resin, gum, some volatile oil, and bitter principle. It is used somewhat in pharmacy, but more generally in preparing incense,

(*c*) Gamboge is found on trees in the East Indies as an orange-red substance which is soluble in alcohol. It is composed of an ester, an acid, and a gum. It is used in medicine and as a pigment.

(*d*) Myrrh is found on a shrub growing in Arabia and some other eastern countries. It occurs in reddish-brown lumps of oily fracture, fragrant odor, and bitter taste. It is composed of resin, gum, bitter principle, and volatile oil, being used in medicine and in making incense.

80. **Some of the Oleo-resins and Balsams.**—(*a*) Benzoin is a balsam and comes from Sumatra and Siam, that from the latter place being of the better quality. It occurs in tears or masses usually reddish brown in color, having a very pleasant, aromatic odor, and is soluble in alcohol. Benzoin consists of a volatile oil, benzoic acid esterified with a resin alcohol, and some other compounds. It is used in medicine as an antiseptic and in perfumery.

(*b*) Canada Balsam is incorrectly named, for it is not a true balsam, since it contains no benzoic or cinnamic acid. It is an exudate from the balsam fir, and is a thick liquid, yellowish in color, clear and transparent, with very high refractive index, hardening on exposure to the air. It is composed of a volatile oil and two resins, and is used in medicine, in preparing flexible collodion, and in mounting microscopic specimens.

(*c*) Crude Turpentine is the thick, viscous, yellowish liquid which exudes from cuts in pine trees, usually the long-leaf pine, in the United States. This material is collected in boxes made in the trees or better in cups hung on the trees. Fig. 21 shows the best modern method for collecting crude turpentine. The first year's flow called "virgin dip" is the best. "Yellow dip" is the yield of subsequent years, and "scrape" is the hardened material which is scraped from the trees. This last is the poorest of all. The crude turpentine is placed in copper stills and distilled with steam to separate the volatile oil of turpentine (Section 76, *k*). Colophony or rosin is left in the still (Section 78, *b*). The oleo-resin itself has no value except as a source of oil of turpentine and rosin. Fig. 22 illustrates the distillation of turpentine.

(*d*) TOLU comes from South America as a nearly solid mass, yellow-brown in color, of aromatic odor and taste. It contains both benzoic and cinnamic acids, probably united with resin alcohols, and in addition a few other compounds. It is largely used in medicine.

81. **Compounds Similar to the Resins.**—(*a*) RUBBER OR CAOUTCHOUC.—Many trees contain besides the so-called sap and other liquids, a milky juice called latex, flowing in special elongated cells or tubes. The function of this latex may be to carry food material in an emulsified form, or to serve as a protection when the tree is wounded. It oozes out of cut surfaces, hardens on exposure to the air, and serves to keep out water and bacteria just as do the resins (Section 77). This latex is an emulsion of fats, waxes, resinous substances, and proteins in a watery fluid. Certain trees, more particularly in South America, contain in the latex minute liquid drops of a hydrocarbon, having the general formula of a terpene, $C_{10}H_{16}$, but supposed to be a chain compound and not a ring compound like a terpene. These drops coagulate on exposure to the air. In practice this coagulation is hastened by the smoke of burning palm-nuts, or by the addition of salt water, wood-ash lye, or alum. The resulting mass forms the crude rubber of commerce. To obtain the latex the trees are cut and the latex gathered much as is maple sap in the United States. The pure hydrocarbon is nearly white when fresh but darkens on exposure

to the air. It is soluble in chloroform, benzine, and toluene, and is rendered hard and brittle after a time by oils. Chlorine, bromine, and strong acids destroy it. The commercial material is practically black from smoke and dirt, containing in addition to the rubber proper, or the hydrocarbon, some fat, waxes, and proteins, which were originally in the latex. In addition there are chips, bark, and dirt of various kinds accidentally present or intentionally added.

The crude material is ground and washed, and for use must be treated with sulphur, metallic sulphides, or metallic oxides. The pure rubber is very sticky, but on heating with 5 to 10 per cent. of sulphur it loses its stickiness, becomes more elastic, and is the usual form of soft rubber from which so many articles are manufactured. When heated with antimony pentasulphide it forms "red" or "antimony" rubber. Red antimony trisulphide is formed, the rest of the sulphur uniting with the rubber. If the pure rubber is heated with 25 to 30 per cent. of sulphur, it forms on cooling a hard, hornlike mass, called ebonite, or hard rubber, which finds a great variety of uses too well known to need mention. The sulphur may form a chemical compound with the hydrocarbon or it may be merely a physical mixture of sulphur and hydrocarbon.

(*b*) GUTTA PERCHA.—This material is somewhat similar to rubber, occurring in the latex of certain East Indian trees. It is obtained and washed like crude rubber and is then a fibrous white to brown mass, tough and inelastic when cold, softening greatly on heating. It is soluble in carbon disulphide, chloroform, and warm benzine. In composition it is a mixture apparently of a hydrocarbon, C_5H_8, and two resins which are oxygenated bodies. It is a very poor conductor of electricity and finds its principal use as insulating material for wires, etc.

(*c*) CHICLE is also a product of the coagulated latex of certain South American trees, and is used in the United States in the manufacture of chewing gum. It is composed of a true gum soluble in water, resins, the hydrocarbon of gutta percha, mineral constituents, and some other compounds. The purified insoluble portion is used for making chewing gum.

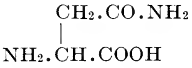
IV. NITROGENOUS COMPOUNDS

82. **Nitrates and Ammonia.**—There is always present in growing plants a certain amount of nitrates that have been absorbed by the plant roots. In some plants the amount may be 1.5 to 3 per cent. of the dry weight, but this is exceptional. They are present only until the synthetic processes are able to convert them into other compounds. This is shown by the fact that as a rule most of the nitrates are in the root, less in the stem and leaves, and none in the seed. Nitrates are present only as they are absorbed by the roots. Plants do not form nitrates from other compounds of nitrogen. Ammonia is sometimes present in small amounts as an absorbed constituent, for some plants can use ammonium salts as well as nitrates in the manufacture of proteins. Moreover, it may occur as a decomposition product of protein hydrolysis (Section 9), or as an intermediate product in the synthesis of proteins (Section 30).

83. **Amides and Amino-acids.**—It has been shown in discussing the hydrolysis of proteins to facilitate their transportation, and also in describing the synthesis of proteins from raw materials (Section 30), that some of the intermediate compounds are amides or amino-acids. Amides, sometimes called acid amides, are organic acids in which the hydroxyl of the carboxyl group is replaced by NH_2, a common amide being acet-amide, CH_3CONH_2. Acids having more than one carboxyl group may have one or all of the hydroxyl groups replaced by NH_2. They are, as a rule, crystalline substances and more or less soluble in water. They are basic in character, forming salts with acids. An amino-acid, sometimes called amido-acid, is an organic acid in which one of the alkyl hydrogen atoms is replaced by NH_2. A common one is amino-acetic acid, $CH_2(NH_2)COOH$, or glycocoll. The amino-acids as a group are crystalline substances soluble in water. They will unite with acids to some extent on account of their amine group and with bases on account of their carboxyl group.

Apparently the formation of these compounds is in most cases transitory; they are merely intermediate products, existing in but small amounts at any one time. There are a number of these amides and amino-acids found in plants, but the more common ones, and ones which illustrate these compounds very well, are as follows:

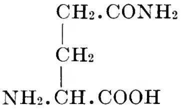
(*a*) Asparagine is found in considerable quantities in pea and bean seedlings,



$$\begin{array}{l} \quad\;\, CH_2.CO.NH_2 \\ \quad\;\;\, | \\ NH_2.CH.COOH \end{array}$$

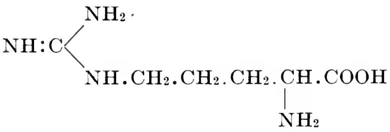
It is also called amino-succinamide.

(*b*) Glutamine occurs to a large extent in cucumber and other seedlings. It is the monamide of amino-glutaric acid,

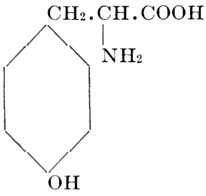


$$\begin{array}{l} \quad\;\, CH_2.CONH_2 \\ \quad\;\;\, | \\ \quad\;\, CH_2 \\ \quad\;\;\, | \\ NH_2.CH.COOH \end{array}$$

(*c*) Argenine occurs largely in coniferæ or trees of the pine order, and possesses a more complicated structure than the others mentioned,



(*d*) Tyrosine is an amino-acid of the carbocyclic series, found in many plants,



84. **Proteins.**—It has already been stated (Section 5) that proteins are compounds containing carbon, hydrogen,

oxygen, and nitrogen, usually sulphur, and sometimes phosphorus. They are the most complex compounds known, and probably the most important, since they are a necessary constititiuent of every living cell, whether plant or animal, and compose most of the dry matter of animals except the bones. Moreover, plant proteins are important not only to plants themselves, but also to animals, since the latter are dependent for the most part on the ready-made proteins of plants for their own body nitrogenous compounds. The name itself is significant, being derived from a Greek word signifying "preëminent."

The composition of proteins is about as follows: Carbon, 50 to 55 per cent.; hydrogen, 6 to 7.3 per cent.; oxygen, 19 to 24 per cent.; nitrogen 15 to 19 per cent.; sulphur, 0.3 to 2.5 per cent., and phosphorus, if present, 0.4 to 0.8 per cent. A protein molecule is known to be exceedingly large, the atomic weight of different proteins being estimated at from 4000 to 16,000 in round numbers. A formula which has been proposed for zein—an example of a typical plant protein—will give some idea of the complexity of the molecule:

$$C_{230}H_{362}O_{65}N_{58}S.$$

Most of the knowledge of proteins is based on studies of the animal proteins. Plant proteins in general, however, are very similar, although not so numerous.

The various proteins differ somewhat in solubility, some of them being soluble in water, others in dilute alcohol, others in salt solutions, and still others in very dilute acids and in alkalies. Strong acids and alkalies dissolve proteins on heating, but with decomposition. On heating with strong sulphuric acid the nitrogen of proteins is converted to ammonium sulphate, from which ammonia can be evolved with sodium hydroxide. This is the basis of the quantitative estimation of proteins (Section 95). They are built up from a series of amino-acids or their derivatives from which ammonia is easily split off. On hydrolytic decomposition they generally break down into amino-acids.

For the most part proteins are noncrystallizable, belonging to that peculiar class of compounds called colloids. Solutions of proteins are levorotatory. One of the commonest tests for a protein is to dissolve it in concentrated nitric acid which gives a yellow color, turning to orange on the addition of ammonium hydroxide. This is known as the xanthoproteic reaction—or "yellow protein" reaction. Chemists are familiar with the fact that strong nitric acid stains the skin yellow. This is due to the action of nitric acid on the proteins of the skin.

Some of the proteins in solution are precipitated unaltered by saturating the solution with sodium chloride, ammonium sulphate, or magnesium sulphate, a process called "salting out;" others are thrown down in a changed form by metallic salts; while still others are precipitated as insoluble salts by tannin. No single reaction is common to all proteins. According to their properties proteins have been classified into some eighteen groups which serve to distinguish them and aid in their study.

85. **Alkaloids.**—These are plant compounds containing nitrogen and possessing strongly basic properties. They differ from the other organic bases, like amines and amides, in being more complex in structure (the exact formula is unknown in most cases) and more basic in reaction. They differ from the proteins in being less complex. Their most characteristic property is their very powerful physiological action on animals. They are strong medicines or strong poisons. As a rule, they are colorless or white, crystalline solids, and contain oxygen in addition to carbon, hydrogen, and nitrogen. Nicotine is an exception being a liquid and containing no oxygen. Most of the alkaloids are only slightly soluble in alcohol. They dissolve in acids with the formation of salts. From their solutions they are as a rule precipitated by tannin, phosphomolybdic acid, and some other reagents. In the plant they occur in the bark of the stem or root, in seeds, and in the fruit rind. Their function is not definitely known, being considered by some authorities as end products of metabolism—waste compounds stored where they are most easily removed; other authorities, however, claim that alkaloids are intermediate or transitory compounds necessary

for the growth of the plant. They do not occur in all plants, being confined for the most part to the poppy and legume families. They occur as salts of malic, oxalic, succinic, tannic, or some other plant acid, and are extracted by dissolving out these salts with appropriate solvents, and separating the alkaloid from the acid. Ordinarily this is done by using a mineral acid like sulphuric or hydrochloric, since it is in this form that the alkaloids are used commercially; for example, quinine sulphate, cocaine hydrochloride, etc.

86. **Some of the Common Alkaloids.**—(*a*) Atropine, $C_{17}H_{23}O_3N$, is a white crystalline solid with a bitter, acrid taste and is very poisonous. It is used as the sulphate for spasmodic affections, and for dilating the pupil of the eye. Antidotes are emetics, tannin, or charcoal.

(*b*) Caffeine or Theine, $C_8H_{10}O_2N_4$, is a white, silky solid with bitter taste. It occurs in tea and coffee in combination with a complex organic acid, the compound being soluble in water and is hence extracted when tea and coffee are treated with water for beverages. The alkaloid, occurring to the extent of 1 per cent. in coffee and 2 per cent. in tea, exerts the stimulating effect of these drinks. In addition, however, there are also extracted tannin (in tea only), volatile oil of tea or of coffee, gum, and dextrin, all of which serve to modify the effect of the alkaloid. Pure caffeine is used in medicine as a stimulant, and to cure somnolence.

(*c*) Cocaine, $C_{17}H_{21}O_4N$, is a colorless, crystalline solid with bitter taste, and producing numbness. Used medicinally usually as the hydrochloride, $C_{17}H_{21}O_4N.HCl$, it is a local anæsthetic. It is, however, a dangerous drug to use. Antidotes are morphine, alcohol, ammonia, and applications of ice to the head.

(*d*) Morphine, $C_{17}H_{19}O_3N$, occurs in colorless, shining crystals, with bitter taste, and is used in medicine ordinarily as the sulphate $(C_{17}H_{19}O_3N)_2.H_2SO_4$. It is the chief constituent of opium which is obtained from the unripe seed capsules of the poppy (Fig. 23). Morphine is one of the most valuable narcotics known, but it is a very dangerous drug to use on account of its habit-forming properties and its general harmful effect on the mind and body when the habit is once formed. Antidotes to morphine poisoning are potassium permanganate, tannic acid, and emetics.

FIG. 23.—The cultivated variety of the opium poppy.

(*e*) NICOTINE, $C_{10}H_{14}N_2$, is a colorless liquid turning brown on exposure to the air, with acrid taste. It is one of the most virulent poisons known. In small doses it has been used in medicine as a sedative. It is found in tobacco, varying in amounts from 1 to 8 per cent. The pleasant as well as the exceedingly disagreeable effects of smoking and chewing tobacco are probably ascribable to nicotine. In the impure form it is used as an insecticide.

(*f*) QUININE, $C_{20}H_{24}O_2N_2$, is usually a white, amorphous powder, although it can be obtained in silky needles, and has a very bitter taste. It is used in medicine as the sulphate, $(C_{20}H_{24}O_2N_2)_2.H_2SO_4$, being particularly efficacious in malaria, and as a tonic and stimulant.

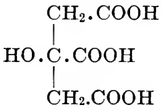
(*g*) STRYCHNINE, $C_{21}H_{22}O_2N_2$, is a white crystalline powder, with very bitter taste, and is a powerful poison. It is used in medicine in very small doses as a nerve stimulant. Antidotes are potassium permanganate, emetics, and sedatives.

(*h*) THEOBROMINE, $C_7H_8O_2N_4$, is a white crystalline powder of bitter taste. It is the active principle of chocolate and cocoa, occurring to the extent of about 1 per cent. in the cocoa bean. It is used medicinally to some extent, its effect being similar to that of caffeine.

V. ORGANIC ACIDS AND THEIR SALTS

87. **General.**—In discussing the various plant compounds, it has been found that there are a large number of organic acids present in one form or another. The fixed oils (Section 63) are glyceryl salts of various fatty acids of high molecular weight; some of the volatile oils (Section 75) are esters of organic acids both of the chain and carbocyclic series; some of the resins (Section 77) are composed largely of very complex acids or their salts; alkaloids (Section 85) exist in combination with organic acids of various kinds. But in none of these cases do the acids display the properties which are usually ascribed to them, namely, that of a sour taste and distinctly acid reaction. There are, however, in many plants, chiefly in the fruits, acids which respond to these tests. As mentioned in Section 28, acids may be in part at least the products of imperfect oxidation, or intermolecular respiration. They may be in part waste products (compare oxalic acid below), or they may serve some definite, physiological function.

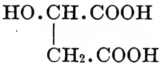
88. **Some of the Common Organic Acids.**—(*a*) CITRIC ACID,



$$\begin{array}{l} CH_2.COOH \\ | \\ HO.C.COOH \\ | \\ CH_2.COOH \end{array}$$

is found in the free state in lemons, limes, currants, gooseberries, cranberries, etc. It is obtained from lemons and limes for commercial purposes, and is used in medicine and for calico printing. It forms large rhombic crystals with one molecule of water of crystallization, and is soluble in water and in alcohol. On boiling with lime a tricalcium salt is precipitated.

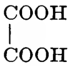
(*b*) MALIC ACID,



$$\begin{array}{l} HO.CH.COOH \\ | \\ CH_2.COOH \end{array}$$

occurs free in unripe apples, grapes, gooseberries, and in many other fruits; as the acid potassium salt in some cherries and rhubarb; and as the acid calcium salt in mountain ash berries. It is prepared from the latter, and used to some extent in medicine. It forms deliquescent crystals, soluble in alcohol. The normal calcium salt is insoluble in alcohol.

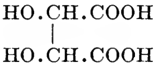
(*c*) OXALIC ACID,



$$\begin{array}{l} COOH \\ | \\ COOH \end{array}$$

is found in very many plants, frequently as the insoluble calcium salt in the form of crystals (Fig. 3, *d*). It occurs as the soluble acid calcium salt as well as the soluble acid potassium salt in sorrel and rhubarb. It forms monoclinic, efflorescent prisms with two molecules of water of crystallization. It is soluble in water and alcohol.

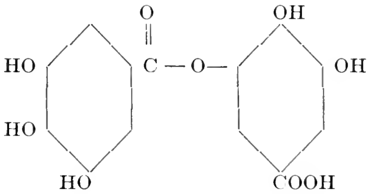
(*d*) TARTARIC ACID,



$$\begin{array}{l} HO.CH.COOH \\ | \\ HO.CH.COOH \end{array}$$

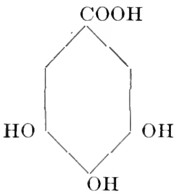
is found as the acid potassium salt in grapes; and as the acid potassium and acid calcium salts in pineapples. When grapes are made into wine, crude acid potassium tartrate, called "argol," is precipitated in the vats. When purified it is called "cream of tartar." If it is treated with sulphuric acid and recrystallized, tartaric acid is produced. The neutral calcium salt is insoluble in water. The acid potassium salt is soluble in water but practically insoluble in alcohol. Tartaric acid crystallizes in large monoclinic prisms, soluble in water and in alcohol. The sodium potassium tartrate is Rochelle salts, and potassium antimonyl tartrate is tartar emetic, both of which are used in medicine.

(*e*) Tannic Acid, commonly known as tannin, is extracted from gall nuts (Section 89, *i*), and forms usually a light, yellowish-buff, amorphous powder or small scales, soluble in water and in alcohol, insoluble in ether, and of acid reaction. It has an astringent, sour taste, precipitates some proteins, notably gelatine (Section 230), and forms a blue-black precipitate with ferric salts. Its formula is:



digallic acid

On boiling with dilute mineral acids it hydrolyzes to two molecules of gallic acid:

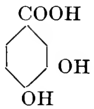


Tannic acid is used in making inks with ferric salts and as an astringent in medicine.

89. **Tannins.**—These are a group of compounds found in various plants, and in all parts of plants, namely, roots,

bark, stem, leaves, flowers, and fruit. They derive their name from the fact that they will tan hides to make leather. They are obtained by extracting the various materials with water and contain in addition to the tannins soluble carbohydrates, coloring matter, gums, and other water soluble materials. In fact their value frequently lies partly in the extractive material other than the tannins.

Chemically they are very complex and not well known. Some of them contain digallic acid (Section 88, *e*); some contain compounds of gallic acid with dextrose, as glucosides; while others contain various acids derived from gallic acid or from protocatechuic acid,



Their properties are about the same as those of tannic acid. The property of precipitating gelatine makes them valuable for tanning hides, and that of precipitating metallic salts, for dyeing. Their principal use is in tanning hides, in calico printing, dyeing, and making inks.

The following are a few of the principal kinds of tannin-containing materials:

(*a*) Root of Canaigre, a beet-like plant, growing in south-western United States, and Mexico. It contains 30 per cent. of tannin.

(*b*) Wood of Quebracho, a tree from South America, containing 24 per cent. of tannin; and of Catechu or Cutch, an Indian tree.

(*c*) Wood and bark of Chestnut, containing 8 to 12 per cent. of tannin, and of Hemlock, 10 to 14 per cent. of tannin. Fig. 24 shows hemlock bark and logs being collected for tanning purposes.

(*d*) Bark of Oak, containing 5 to 15 per cent. of tannin; and of Mangrove, a West African tree, 9 to 30 per cent. of tannin.

(*e*) Leaves of Sumach, containing 15 to 30 per cent. of tannin; and of Gambier, an Indian shrub.

(*f*) Fruit of Divi-Divi, a West Indian tree, containing 30 to 50 per cent. of tannin; and of Myrobalans, an Indian and Chinese tree, 20 to 40 per cent. of tannin.

(*g*) Acorn cups, called Valonia, of a certain kind of oak, containing 25 to 35 per cent. of tannin.

(*h*) Dried sap, called Kino, from Indian and African trees, containing 75 per cent. of tannin.

Fig. 24.—Hemlock bark and logs to be used for tanning. (Rhoads.)

(*i*) Galls, or Nut Galls, a diseased excrescence on certain Persian and Turkish oak trees, caused by the sting of an insect. Galls contain 60 to 75 per cent. of tannin. Tannic acid is the purified form of tannin extracted from these galls.

90. **Summary.**—The various plant compounds are classified as Carbohydrates, Fixed Oils and Waxes, Volatile Oils and Resins, Nitrogenous Compounds, and Organic Acids and their Salts. Carbohydrates comprise 72 per cent. of the dry matter of plants. They are compounds of carbon, hydrogen, and oxygen in which hydrogen and oxygen are in the same proportion as in water. They, furthermore, always contain one or more hydroxyl groups and usually

an aldehyde or ketone group. Carbohydrates are divided into two classes, the Sugars and the Non-sugars.

The principal sugars contain either one unit group of six carbon atoms, called monosaccharides, like dextrose and levulose, or two unit groups, called disaccharides, like sucrose and maltose. The sugars are soluble crystalline compounds, of sweet taste. Dextrose is dextrorotatory; that is, it turns the plane of polarized light to the right. It reduces Fehling's solution and forms glucosides which are condensation products of dextrose with an alcohol, aldehyde, or ketone. Levulose is levorotatory; that is, it turns the plane of polarized light to the left. It also reduces Fehling's solution. Sucrose is dextrorotatory and does not reduce Fehling's solution. It is hydrolyzed by an enzyme called invertase, or by dilute mineral acids, to equal quantities of dextrose and levulose. This mixture of sugars is called invert sugar, because its rotation is to the left, or is inverted from that of sucrose. This is due to the fact that the levorotation of levulose is stronger than the dextrorotation of dextrose. Maltose is dextrorotatory and reduces Fehling's solution. It is hydrolyzed by an enzyme called maltase, or by dilute mineral acids, to dextrose, one molecule of maltose changing to two molecules of dextrose. The hydrolysis of sucrose and maltose shows the glucoside-like character of these disaccharides.

The non-sugars, or polysaccharides, contain an unknown number of unit groups of the monosaccharides. They are non-crystalline, tasteless, and insoluble in cold water. Starch is composed of cellulose-covered grains which split in hot water and form a semisolution called starch paste. It turns blue with iodine, does not reduce Fehling's solution, and hydrolyzes with diastase to maltose, and with dilute mineral acids to dextrose. Cellulose is much more complex in structure than starch. It unites with alkalies like sodium hydroxide, and with acids like nitric and acetic. The soda cellulose treated with carbon disulphide is soluble in water from which the cellulose is regenerated in different physical form by spontaneous decomposition. The resultant material can be used for a variety of purposes on account of its transparency and homogeneity. Cellulose hexanitrate is an explosive; cellulose tetranitrate dissolves in alcohol and ether to form collodion; or mixes with camphor to form celluloid. In its original form, as obtained from cotton, trees, or flax, cellulose finds many uses as for cloth, paper, etc.

The fixed oils are glyceryl salts of the higher fatty acids. They may be liquid or solid, and drying or non-drying, depending on the character of the fatty acid radicle. The drying property is due to the presence of one or more double bonds in the fatty acid molecule, whereby oxygen is absorbed and the oil hardens. These oils decompose on heating, are insoluble in water and in cold alcohol, but are soluble in hot alcohol, ether, and in other volatile organic solvents. They hydrolyze with steam to glycerine and the fatty acids. On treatment with caustic alkalies they "saponify" to a soap and glycerine. The fixed oils are used as foods, for making soap, and for lubricants.

The volatile oils are never glyceryl salts of fatty acids but may be hydrocarbons; or acids, aldehydes, ketones, and esters of either the aliphatic or carbocyclic series; or may contain sulphur and nitrogen in which case they are sulphides and thiocyanates. They distill unchanged, are insoluble in water, but soluble in cold as well as in hot alcohol and in ether. The volatile oils are used for flavoring, perfumery, and in medicine.

The resins are solid substances supposed to be derived by oxidation of hydrocarbon volatile oils, and are acids, esters, or resenes. They decompose on heating away from the air, and are soluble in alcohol and in ether. They are principally used in making varnishes.

Rubber, gutta percha, and chicle are similar to resins. The uses of rubber are too well known to need comment. Gutta percha is an excellent insulating material for electric wires, and chicle is used in making chewing gum.

The nitrogenous compounds are: First, nitrates and ammonia, which are either transitory compounds taken up by the roots, or in the case of ammonia are synthetic or hydrolytic products of proteins. Second, amides and amino-acids, which are intermediate compounds formed in the synthesis or hydrolysis of proteins. Third, proteins which are the chief nitrogenous compounds in plants and are necessary constituents of every living cell, whether plant or animal. They are very complex, and are of various properties, though generally colloidal in character. Fourth, alkaloids which are nitrogenous bases of powerful physiological effect on animals.

The organic acids and their salts, besides those mentioned before as constituents of fixed oils, volatile oils, and resins, are noticeable in fruits for their acid taste. Tannic acid is an exception. It is the chief constituent of tannin which is a complex substance found in various plants, and used for tanning hides and in dyeing.

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CHAPTER IV

CROPS

The so-called crop plants—those plants which are of value to the farmer—owe their importance to certain of their constituents. For example, the grains are valuable for the starch, fixed oils, and proteins, which they contain; potatoes for their starch; nuts for their oils; peas and beans for their proteins; and beets for their sugar. Since most of the ordinary crop plants are raised almost entirely as food for stock or for man, it is of interest to know something of the amounts, not only of the valuable, but also of the useless food constituents in the various crops.

The determination of the different individual plant compounds discussed in Chapter III involves considerable difficulty, and although many of the determinations can be made with accuracy, the time consumed is very great even if only a partial analysis is made. For scientific stock feeding it is only necessary to know the amount of all the carbohydrates that are reasonably digestible; the amount of those carbohydrates which are indigestible; the amount of total protein material; of total oil; and of total mineral matter. Consequently there is employed a method which serves to differentiate the classes of constituents rather than the compounds in each class.

The determinations are more or less conventional and in some cases only approximate, but on the whole they are reasonably accurate. This general method of analysis is known as the "Weende Method" since it was the method employed at the Weende Experiment Station, Germany, by Dr. W. Henneberg, and reported by him in 1864. With some modifications it is still in use. A very brief description of the following determinations will help to make clear the meaning of terms which are referred to very frequently in any discussion of foods.

I. CROP CONSTITUENTS AND THEIR DETERMINATION

91. **Water or Moisture.**—This is the loss in weight of the material which takes place when it is dried at the temperature of boiling water, a little under 100° C. usually, and in an atmosphere of hydrogen or in vacuo. If the temperature is lower, not all of the water will be driven off; if it is higher, organic compounds begin to break up and the results will be high. It is necessary to make the determination in an atmosphere of hydrogen or in vacuo, because many crops contain "drying" or "semidrying" oils, which would absorb oxygen if dried in the air, and the results for moisture would be incorrect.

92. **Crude Fat.**—This constituent is obtained by extracting the dried material with dry, alcohol-free ether. The extract is dried carefully at the temperature of boiling water to remove the ether, and then weighed. If water is present in the sample, or if it is present in the ether, or if alcohol is present in the ether, there is danger of dissolving some of the carbohydrates and ash constituents. Crude fat consists of fixed oils, volatile oils, waxes, resins, chlorophyl, and other pigments, if present, and possibly some other ether-soluble compounds. This accounts for the fact that it is called *crude* fat, for it is an approximate method at best, although in most of our crop plants the constituents other than fixed oils are very small in amount.

93. **Crude Fiber.**—The material which has been dried and extracted with ether is boiled first with dilute sulphuric acid, then with dilute sodium hydroxide with a thorough washing after each treatment. The amount of acid and alkali, as well as the strength and time of boiling are very carefully regulated. By drying and weighing the residue, igniting and weighing the remaining ash, the difference in weight will give the crude fiber which consists of cellulose, lignin, and possibly some proteins. The treatment with acid and alkali is supposed to remove all soluble sugars; starch which is hydrolyzed to dextrose and washed out; proteins which are hydrolyzed and removed; and any other constituents rendered soluble by these reagents.

94. **Ash.**—By burning the material and continuing to heat it until all the organic matter has been destroyed, the weighed residue will constitute the ash or the mineral constituents of the plant substance. These mineral constituents will not occur in the ash in the same form as in the plant, for the bases which were originally united with organic acids will be present in the ash as sulphates, phosphates, silicates, and carbonates. Sulphur and phosphorus in proteins will occur here as sulphates and phosphates of the bases. Silica, which may or may not have been present in the plant in organic combination, will occur in the ash as silicates. The excess of inorganic basic elements over inorganic acid elements will be present in the ash as carbonates. The ash residue from the crude fiber determination will not serve in this determination, since much of the inorganic material has been removed by the treatment with acid and alkali.

95. **Crude Protein.**—By using a well known method for the determination of total nitrogen (Section 84) and multiplying the result by 6.25 the percentage of crude protein is obtained. This is based on the assumption that proteins contain on the average 16 per cent. of nitrogen. The assumption is only approximately correct. This method, however, does not take into consideration the presence of nitrogen in other than protein form. In some cases there is a considerable amount of this non-protein nitrogen which is of importance in feeding. Consequently it is customary in most cases to determine the so-called "*Albuminoid Nitrogen*" or protein nitrogen and calculate this to proteins. The method is based on the fact that proteins are precipitated by copper hydroxide, whereas amides, ammonia, and nitrates are not. After washing the precipitate of proteins and copper hydroxide the total nitrogen is determined and the result multiplied by 6.25 as before. The difference between the total nitrogen and protein nitrogen, is multiplied by 4.7 and called amides, on the assumption that amides are asparagine and contain 21.2 per cent. of nitrogen—a very broad generalization.

96. **Nitrogen-free Extract,** or **Digestible Carbohydrates.**—This is merely the difference between 100 per cent. and the

sum of all the other constituents. It comprises starch, the sugars, and any other compounds not determined elsewhere. Most of the analyses now in use give this determination only, but it is customary, at present, however, in most work of a careful nature, to make separate determinations of sucrose; of reducing sugars, such as dextrose, levulose, and maltose; of starch; and of the pentosans.

II. CLASSIFICATION AND ANALYSES OF CROPS

97. **Classification.**—The classification of crops is always more or less arbitrary, particularly so since the popular names for kinds of crops differ from the scientific names. For example, the botanical term for the matured ovary and its contents is fruit, no matter whether the part of the plant in question belongs to corn, or walnut, or apple, or pumpkin. Popularly the term fruit is restricted to those soft, fleshy seed coverings of the apple, pear, and similar plants.

In the present classification an attempt has been made to arrange the crops in the main according to the part of the plant from which the money value is obtained, and with some regard for popular terminology. The Seed Crops are those which are raised primarily for the seeds themselves, and they are subdivided into Grains, Legumes, and Miscellaneous. The stems and leaves of the ripe grains are also included here for comparison.

The Fruit Crops are those which are raised for their fleshy seed coverings and are particularly sweet.

The Stem and Leaf Crops or the Fodder Crops are those which are used only for the stems and leaves. In some cases, corn fodder, for example, the crop may be used when green as fodder, or when ripe as a seed crop. The composition of these crops is given at the time of cutting, not when cured for hay. For the latter see Section 104, and Table IV.

The Vegetable Crops are all those "garden crops" which are popularly called vegetables. They are valuable for their succulent or juicy parts, and may be conveniently subdivided into Stem Vegetables, Leaf Vegetables, and Fruit

Vegetables. It is to be noted that potatoes are classed with the Root Vegetables, although they are really underground stems, not roots.

98. **Analyses.**—Table I gives the percentage composition of a number of crops in each class. Table II gives the yields in pounds per acre of each crop as a whole, and of the several constituents of each crop. Table III gives the percentage composition of these same crops in the three chief fertilizing constituents—nitrogen, phosphoric acid, and potash.

TABLE I.—PERCENTAGE COMPOSITION OF CROPS

SEED CROPS

Grains.	Water.	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Barley:						
Seed	10.9	2.4	12.4	2.7	69.8	1.8
Straw	14.2	5.8	3.5	36.0	39.0	1.5
Corn:						
Seed	10.6	1.5	10.3	2.2	70.4	5.0
Stover	22.8	4.9	5.5	25.6	39.9	1.3
Oats:						
Seed	11.0	3.0	11.8	9.5	59.7	5.0
Straw	9.2	5.1	4.0	37.0	42.4	2.3
Rye:						
Seed	11.6	1.9	10.6	1.7	72.5	1.7
Straw	7.1	3.2	3.0	38.9	46.6	1.2
Wheat:						
Seed	10.5	1.8	11.9	1.8	71.9	2.1
Straw	9.6	4.2	3.4	38.1	43.4	1.3
Legumes.						
Cowpea	14.8	3.2	20.8	4.1	55.7	1.4
Soja Bean	10.8	4.7	34.0	4.8	28.8	16.9
Miscellaneous.						
Cotton Seed	10.3	3.5	18.4	23.2	24.7	19.9
Flax Seed	9.2	4.2	22.6	7.1	23.2	33.7

FRUIT CROPS

	Water.	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Apples	84.6	0.3	0.4	1.2	13.0	0.5
Blackberries	86.3	0.5	1.3	2.5	8.4	1.0
Cherries	80.9	0.6	1.0	0.2	16.5	0.8
Currants	85.0	0.7	1.5	12.8		..
Grapes	77.4	0.5	1.3	4.3	14.9	1.6
Peaches	89.4	0.4	0.7	3.6	5.8	0.1
Pears	84.4	0.4	0.6	2.7	11.4	0.5
Raspberries, black	84.1	0.6	1.7	12.6		1.0
Strawberries	90.4	0.6	1.0	1.4	6.0	0.6

TABLE I—PERCENTAGE COMPOSITION OF CROPS—(Continued)

STEM AND LEAF CROPS

	Water.	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Alfalfa, green	71.8	2.7	4.8	7.4	12.3	1.0
Alsike clover, green	74.8	2.0	3.9	7.4	11.0	0.9
Corn fodder, green	79.3	1.2	1.8	5.0	12.2	0.5
Orchard grass, green	73.0	2.0	2.6	8.2	13.3	0.9
Red clover, green	70.8	2.1	4.4	8.1	13.5	1.1
Timothy, green	61.6	2.1	3.1	11.8	20.2	1.2
Alfalfa, hay	8.4	7.4	14.3	25.0	42.7	2.2
Alsike clover, hay	9.7	8.3	12.8	25.6	40.7	2.9
Corn fodder, cured	42.2	2.7	4.5	14.3	34.7	1.6
Orchard grass, hay	9.9	6.0	8.1	32.4	41.0	2.6
Red clover, hay	15.3	6.2	12.3	24.8	38.1	3.3
Timothy, hay	13.2	4.4	5.9	29.0	45.0	2.5

VEGETABLE CROPS

	Water.	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Stem vegetables:						
Asparagus	94.0	0.7	1.8	0.8	2.5	0.2
Celery	94.5	1.0	1.1	3.3		0.1
Rhubarb	94.4	0.7	0.6	1.1	2.5	0.7
Leaf vegetables:						
Cabbage	91.5	1.0	1.6	1.1	4.5	0.3
Lettuce	94.7	0.9	1.2	0.7	2.2	0.3
Onions	87.6	0.6	1.6	0.8	9.1	0.3
Spinach	92.3	2.1	2.1	0.9	2.3	0.3
Root vegetables:						
Beets	87.5	1.1	1.6	0.9	8.8	0.1
Carrots	88.2	1.0	1.1	1.1	8.2	0.4
Parsnips	83.0	1.4	1.6	2.5	11.0	0.5
Potatoes	78.3	1.0	2.2	0.4	18.0	0.1
Turnips	89.6	0.8	1.3	1.3	6.8	0.2
Fruit vegetables:						
Cucumbers	95.4	0.5	0.8	0.7	2.4	0.2
Squash	88.3	0.8	1.4	0.8	8.2	0.5
Tomatoes	94.3	0.5	0.9	0.6	3.3	0.4
Watermelons	92.4	0.3	0.4	6.7		0.2

It also gives the yields of these constituents in pounds per acre. This latter part of the table illustates the distribution of these essential elements as discussed in Section 48. The seed and fodder crops are reported as harvested; the fodder crops also as cured. Fruit and vegetable crops are reported on the edible portion only, except for blackberries, currants, asparagus, spinach, and tomatoes which are reported as purchased. The yields of the fruit and vegetable crops have also been calculated to the edible portion, except in the cases just mentioned. In the case of the analyses of nitrogen, phosphoric acid, and potash, all crops are reported as harvested, except cherries, peaches, and squash, which are reported as edible portion. Here the yields of only these two crops are calculated on this basis, otherwise as harvested.

Table II—Yield of Crops (In Pounds per Acre)

SEED CROPS

Grain.	At harvest.	Dry matter.	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Barley (35 bushels):							
Seed	1,680	1,497	40	208	46	1,173	30
Straw	3,000	2,574	174	105	1,080	1,170	45
Corn (50 bushels):							
Seed	2,800	2,503	42	288	62	1,971	140
Stover	2,500	1,930	122	138	640	998	32
Oats (40 bushels):							
Seed	1,280	1,139	38	151	122	764	64
Straw	1,800	1,634	92	72	666	763	41
Rye (20 bushels):							
Seed	1,120	990	21	119	19	812	19
Straw	2,200	2,044	70	66	856	1,025	27
Wheat (20 bushels):							
Seed	1,200	1,074	22	143	22	862	25
Straw	2,000	1,808	84	68	762	868	26
Legumes.							
Cowpea (20 bu.)	1,200	1,022	38	250	49	668	17
Soja Bean (20 bu.)	1,200	1,070	56	408	58	345	203
Miscellaneous.							
Cotton Seed . .	850	762	30	156	197	210	169
Flax Seed . . .	560	509	23	127	40	130	189

FRUIT CROPS

	At harvest.	Dry matter.	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Apples . . .	18,750	2,888	56	75	225	2,438	94
Blackberries . .	3,000	411	15	39	75	252	30
Cherries . . .	3,800	726	23	38	8	627	30
Currants . . .	4,000	600	28	60	512		..
Grapes . . .	6,000	1,356	30	78	258	894	96
Peaches . . .	30,750	3,260	123	215	1,107	1,784	31
Pears	27,000	4,212	108	162	729	3,078	135
Raspberries . .	2,850	453	17	48	359		29
Strawberries . .	5,700	547	34	57	80	342	34

STEM AND LEAF CROPS, CURED

Alfalfa . . .	10,000	9,160	740	1,430	2,500	4,270	220
Alsike clover . .	5,000	4,515	415	640	1,280	2,035	145
Corn fodder . .	20,000	11,560	540	900	2,860	6,940	320
Orchard grass .	4,000	3,604	240	324	1,296	1,640	104
Red clover . .	5,000	4,235	310	615	1,240	1,905	165
Timothy . . .	5,000	4,340	220	295	1,450	2.250	125

Table II—Yield of Crops—(Continued)

VEGETABLE CROPS

	At harvest.	Dry matter.	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Stem vegetables:							
Asparagus	4,000	240	28	72	32	100	8
Celery	8,000	440	80	88	264		8
Rhubarb	12,000	672	84	72	132	300	84
Leaf vegetables:							
Cabbage	25,500	2,167	255	408	281	1,147	76
Lettuce	12,750	676	115	153	89	281	38
Onions	21,600	2,678	130	346	172	1,965	65
Spinach	10,000	770	210	210	90	230	30
Root vegetables:							
Beets	13,440	1,680	148	215	121	1,182	14
Carrots	10,000	1,180	100	110	110	820	40
Parsnips	12,000	2,040	168	192	300	1,320	60
Potatoes	9,600	2,083	96	211	38	1,728	10
Turnips	12,600	1,310	101	164	164	856	25
Fruit vegetables:							
Cucumbers	10,625	489	54	85	74	255	21
Squash	9,000	1,053	72	126	72	738	45
Tomatoes	24,000	1,368	120	216	144	792	96
Watermelons	9,744	741	30	39	652		20

Table III—Fertilizing Constituents of Various Crops

	Percentage composition.			Pounds per acre.		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O
Barley:						
Seed	1.75	0.75	0.50	29.4	12.6	8.4
Straw	0.60	0.20	1.10	18.0	6.0	33.0
Corn:						
Seed	1.65	0.65	0.40	46.2	18.2	11.2
Stover	1.04	0.29	1.40	26.0	7.3	35.0
Oats:						
Seed	2.00	0.80	0.60	25.6	10.2	7.7
Straw	0.60	0.20	1.25	10.8	3.6	22.5
Rye:						
Seed	1.70	0.85	0.60	19.0	9.5	6.7
Straw	0.50	0.30	0.85	11.0	6.6	18.7
Wheat:						
Seed	2.00	0.85	0.50	24.0	10.2	6.0
Straw	0.50	0.15	0.60	10.0	3.0	12.0
Cowpea	3.10	1.00	1.20	37.2	12.0	14.4
Soja bean	5.30	1.80	2.00	63.6	21.6	24.0
Cotton seed	3.15	1.25	1.15	26.8	10.6	9.8
Flax seed	4.35	1.60	0.95	24.4	9.0	5.3
Apples (fruit)	0.05	0.02	0.10	12.5	5.0	25.0
Blackberries (fruit)	0.22	0.06	0.23	6.6	1.8	6.9
Cherries (fruit pulp)	0.17	0.04	0.20	6.5	1.5	7.6
Currants (fruit)	0.30	0.12	0.30	12.0	4.8	12.0
Grapes (fruit)	0.15	0.07	0.30	12.0	5.6	24.0

TABLE III—FERTILIZING CONSTITUENTS—(Continued)

	Percentage composition.			Pounds per acre.		
Peaches (fruit pulp)	0.08	0.04	0.20	24.6	12.3	61.5
Pears (fruit)	0.05	0.02	0.10	15.0	6.0	30.0
Raspberries (fruit)	0.20	0.10	0.25	6.0	3.0	7.5
Strawberries (fruit)	0.15	0.06	0.25	9.0	3.6	15.0
Alfalfa (green)	0.60	0.15	0.50	60.0	15.0	50.0
Alsike clover (green)	0.50	0.12	0.30	25.0	6.0	15.0
Corn fodder (green)	0.41	0.15	0.33	82.0	30.0	66.0
Orchard grass (green)	0.45	0.15	0.55	18.0	6.0	22.0
Red clover (green)	0.55	0.13	0.50	27.5	6.5	25.0
Timothy (green)	0.50	0.25	0.75	25.0	12.5	37.5
Asparagus (young shoots)	0.35	0.10	0.25	14.0	4.0	10.0
Celery	0.25	0.20	0.75	25.0	20.0	75.0
Rhubarb	0.10	0.04	0.35	20.0	8.0	70.0
Cabbage (head)	0.30	0.10	0.40	90.0	30.0	120.0
Lettuce	0.25	0.08	0.45	37.5	12.0	67.5
Onions	0.23	0.09	0.22	55.2	21.6	52.8
Spinach	0.50	0.15	0.25	50.0	15.0	25.0
Beets	0.25	0.10	0.50	42.0	16.8	84.0
Carrots	0.23	0.13	0.53	28.8	16.3	66.3
Parsnips	0.22	0.20	0.65	33.0	30.0	97.5
Potatoes	0.35	0.15	0.50	42.0	18.0	60.0
Turnips	0.25	0.10	0.45	45.0	18.0	81.0
Cucumbers	0.10	0.06	0.20	12.5	7.5	25.0
Squash (edible portion)	0.22	0.08	0.05	18.0	7.2	4.5
Tomatoes	0.20	0.07	0.35	48.0	16.8	84.0
Watermelons	0.17	0.06	0.30	40.8	14.4	72.0

III. CROP CHEMISTRY

99. **Seed Crops.**—As a class the seeds of the seed crops are relatively low in water, about 10 per cent. During the process of seed formation the soluble sugars are transported to the seed where dehydration takes place in the deposition of starch. This extra water is eliminated during the drying or curing of seeds. The same change of hydrolyzed compounds to dehydrated compounds takes place in the case of proteins (Section 34). The leaves and stems of seed crops are also low in water inasmuch as they have dried out and are practically dead before they are harvested. The seeds are low in ash, much lower than any other part of the plant. Considered from the standpoint of plant economy the seeds need very little of the mineral elements. Food for the seedling is ready made in the seed, only needing

solution to make it immediately available. By the time the seedling rises into the light where it can begin the manufacture of food, the roots have begun to absorb from the soil necessary quantities of inorganic elements for the synthetic processes. Straw and stover, on the other hand, are high in ash which consists largely of the unessential element silicon together with lime and potash. The stems and leaves, it will be remembered (Section 48), are the seat of synthetic processes requiring the help of mineral elements.

Compared to other crops, seeds are high in crude protein, crude fat and nitrogen-free extract, or carbohydrates, as would be expected, since these are the stored foods for the next generation. The carbohydrates are chiefly starch. Straw and stover, on the other hand, are very high in crude fiber, which goes to make cell walls and strengthening fibers, not living matter.

(*a*) GRAINS.—Considering the grains separately, it is to be noted that *barley seed* is of importance chiefly for its nitrogen-free extract—starch—and the very active starch splitting enzyme, diastase, which is produced on germination. These are made use of in the malting of barley and the subsequent "mashing." Barley grains are soaked in water and allowed to germinate. This results in the evolution of heat (Section 3) and the production of diastase in large quantities. All seeds during germination produce diastase of some kind to dissolve the starch (Section 7), but barley diastase is particularly active. When the sprouts have well started they are killed by heat and removed, appearing on the market as "malt sprouts," a feeding stuff. The barley grains, now called malt, are still very rich in starch but have in addition quantities of diastase The malt is next heated with water when the diastase converts the starch to maltose, a process called mashing. Diastase can act on the starch of other grains as well as on that of barley, and in brewing it is used for the hydrolysis of large amounts of corn starch. The maltose is removed in solution, and fermented with yeast, producing beer. The grain that is left behind is sold as "brewers' grains" for feeding purposes. The presence of much protein in the seed interferes with the malting process.

Corn seed is rich in starch and fat. The starch is used as such, or converted into glucose (Section 52). The fat is extracted and forms corn oil (Section 69, *b*). Sweet corn contains a considerable portion of its carbohydrate in the form of sucrose. Corn is low in ash.

Oat seed is higher in crude fiber and ash than the other grain seeds due to its very considerable hull. It is correspondingly lower in digestible carbohydrates. The proportion of fat is also high, being equalled only by that of corn.

Rye seed has a relatively low protein content like corn seed, and is low in fat like barley.

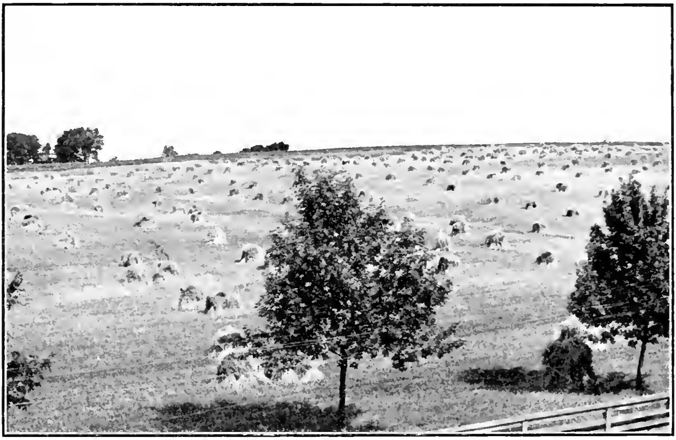

Fig. 25.—Seed crop: Wheat. Agronomy Department, Pennsylvania Station.

Wheat seed (Fig. 25) has no particularly noticeable constituent as far as percentage goes. Its starch is the chief constituent of flour and one of its proteins deserves particular mention in this connection. It is a protein called gliadin, to which wheat flour owes its stickiness or tenacity when mixed with water, and on which the baking qualities depend, serving to keep the baked loaf light. Carbon dioxide formed by the yeast puffs out the sticky mass into many minute cells, the gliadin giving tenacity to the cell walls. If it were not for the gliadin the mass would be solid and hard. This is the case with flour from other grain seeds containing no gliadin,

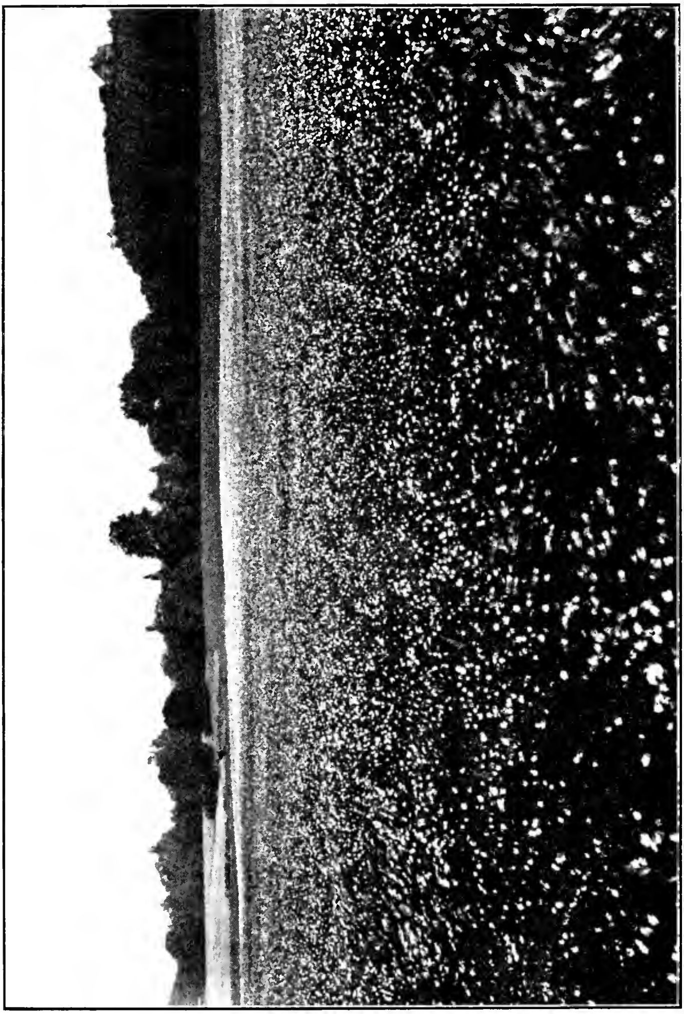

Fig. 26.—Seed crop: Flax.

or at least not enough to give good baking quality to bread made from them.

The straws from these grains are not as a class very digestible, except possibly barley and oats. The ash is high in silica and potash.

(*b*) LEGUMES.—These seeds are particularly high in protein and correspondingly low in carbohydrates. The soja bean contains considerable fat.

(*c*) MISCELLANEOUS.—*Cotton Seed and Flax Seed* (Fig. 26) are very high in fat and are used for the oil which can be expressed from them (Section 69, *c* and *d*). The press cake is used as a feeding stuff and fertilizer on account of its high nitrogen content. These seeds are also high in fiber and very low in carbohydrates.

100. **Fruit Crops** (Fig. 27).—These crops are remarkable for the extremely large amounts of water which they contain. A pound of peach pulp or of strawberries, for example, contains more water than a pint of milk. It is this water content which makes fruit such a valuable addition to the ordinary forms of food. The dry matter of fruits contain, in some cases about as much protein as the grains, in most cases more crude fiber, in many cases more nitrogen-free extract. When the fruit is green, the nitrogen-free extract consists largely of starch, which is converted to such soluble sugars as sucrose and dextrose during ripening. There are also present in the nitrogen-free extract some acids or acid salts. Certain volatile flavoring oils are included in the crude fat. The ash of fruits is very largely basic in character and this makes fruit very valuable as a food. Potash is an important constituent, being necessary for the ripening process.

101. **Stem and Leaf Crops**.—These crops when green are high in water which is largely eliminated during the curing process (Section 103). The dry matter of these crops is high in ash and crude fiber, but low in nitrogen-free extract and fat. They are not so high in crude fiber as the straws of the grains, partly because they are cut before so much of the starch and other digestible carbohydrates are changed to crude fiber. The ash is rich in lime and potash, but not much

silica is present. The changes that take place during the curing process, or haymaking, are discussed later (Section 103).

FIG. 27.—Fruit crop: Apples.

102. **Vegetable Crops.**—These crops, like the fruits, are very high in water.

(*a*) STEM VEGETABLES as a class are the highest in water content of all the crops, over 94 per cent. Of the dry matter, nitrogen-free extract is the largest in amount, although compared to the grain seeds this constituent is smaller; ash, protein, fiber, and fat all being larger in amount. It is the bases in the ash which make the vegetables an important class of foods.

(*b*) LEAF VEGETABLES (Fig. 28).—These do not differ much in composition from the stem vegetables. Stems and leaves have been classed together in the other crops.

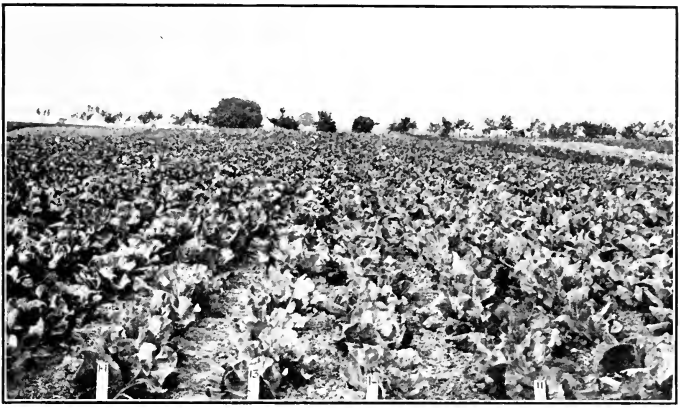

FIG. 28.—Leaf vegetable crop: Cabbages. Horticultural Department, Pennsylvania Station.

(*c*) ROOT VEGETABLES (Fig. 29).—Of these the beets are noted for their sugar content, especially the sugar beet which runs about 15 per cent. sucrose. Potatoes are much the highest in nitrogen-free extract of any of the vegetables, and this is mostly starch.

(*d*) FRUIT VEGETABLES.—As would be expected these run lower in ash than the other vegetables, although on a dry basis this constituent is higher than it is in grain seeds. The ash is largely potash. Crude fiber is less, fat is higher.

103. **Hay.**—Stem and leaf crops, or fodder crops as they are customarily called, do not keep well unless cured or preserved in some way. One of the common methods is to make hay out of them. The usual hay crops are timothy and clover, although many other grasses and legumes, par-

ticularly alfalfa (Fig. 30), are grown for this purpose. Whatever the crop, the principle is the same, namely, to cut the crop when it is in the best condition for making a valuable hay, and to dry it or cure it.

Fig. 29.—Root vegetable crop: Potatoes.

104. **Chemical Changes in Making Hay.**—As noted in Table I, the fodder crops range in moisture content from 60 to 80 per cent., whereas hay runs from 8 to 15 per cent., except in the case of cured corn fodder which contains

42 per cent. of water. In addition to a mere desiccation of the crop there are changes which take place in the various constituents. Table IV gives the changes that take place

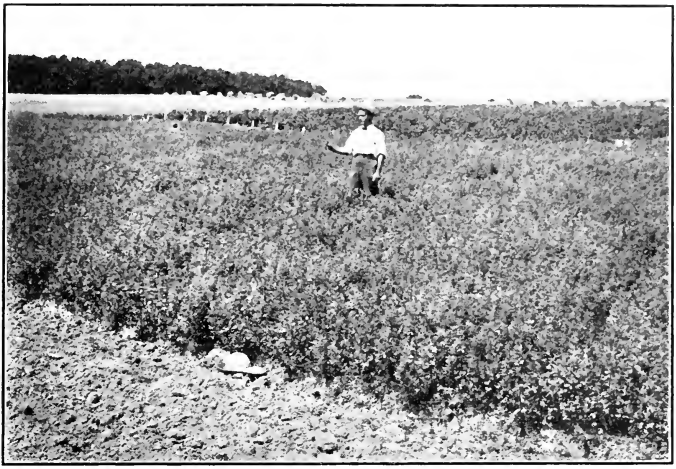

FIG. 30.—Hay crop: Alfalfa. Agronomy Department, Pennsylvania Station.

TABLE IV.—CHANGES IN COMPOSITION DURING HAYMAKING (Calculated to Dry Basis)

	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Alfalfa:					
Green	9.6	17.0	26.3	43.6	3.5
Hay	8.1	15.6	27.3	46.6	2.4
Alsike clover:					
Green	7.8	15.3	29.2	44.0	3.7
Hay	9.3	14.2	28.4	44.9	3.2
Corn fodder:					
Green	5.6	8.8	24.1	58.9	2.6
Cured	4.7	7.8	24.7	60.1	2.8
Orchard grass:					
Green	7.4	9.6	30.4	49.3	3.3
Hay	6.7	9.0	36.0	45.4	2.9
Red clover:					
Green	7.2	15.3	27.8	45.8	3.9
Hay	7.3	14.5	29.1	45.2	3.9
Timothy:					
Green	5.4	8.0	30.7	52.8	3.1
Hay	5.1	6.8	33.5	51.7	2 9

during the making of hay from alfalfa, alsike and red clovers, orchard grass and timothy, and in the curing of corn fodder. The figures are all reduced to the dry basis so that they may be compared. It is to be noted that a loss occurs uniformly in the crude protein content, in nearly every crop in ash and crude fat, whereas there is little change in the nitrogen-free extract, and an increase in the crude fiber in nearly every instance.

The drying of the crop is of the greatest importance in haymaking, for the presence of large quantities of water will promote the activities of fermentative bacteria, that is, the hay will rot. This rotting is in large measure an oxidation process caused by the action of bacteria. Moisture is necessary for the life of the bacteria, and changes take place which render the hay unfit for use as food. This bacterial oxidation sometimes raises the temperature considerably, occurring when the stack is not ventilated sufficiently, and the heat is not conducted away. Moreover, too moist hay encourages the growth of molds which destroy the value of a hay as food.

During the drying process some changes take place, probably of an enzyme nature, whereby compounds like volatile oils develop, thus giving flavor and palatability to the hay. This process undoubtedly continues to some extent in the mow or stack.

The time of cutting hay is of importance. It must be remembered that the stems and leaves are the valuable portion. They should be harvested when they contain as much valuable digestible constituents as possible, and yet give as great a yield as is consistent with the other factors. In the later stages of growth the proteins, fats, and carbohydrates are moved to the seed. The stems and leaves are exhausted of these constituents and at the same time are provided with more cell wall material or crude fiber. The seeds of grasses and of the hay legumes are very small and are easily shaken off when dry. In this way there would be lost the most valuable part of the food, were the hay to be made from mature crops.

Again, in such crops as alfalfa most of the protein is in the leaves. If the plant matures before cutting, the leaves become brittle and are easily knocked off, and in this way protein is lost. Also as a plant grows older, and the seeds form, the ash elements which are of value to stock are gradually lost from the plant, largely by being exuded on the surface of the leaves and washed off by rains. In addition, the older a fodder crop gets, particularly timothy, the less protein and fat, and the more crude fiber and nitrogen-free extract there are in the dry material (See Table V).

Table V.—Changes in the Composition of Timothy During Growth

(Pounds in 100 of Dry Matter)

	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Before bloom, headed . . .	7.7	11.3	26.3	50.9	3.8
In full bloom . .	5.7	7.9	29.9	53.6	2.9
Just after bloom .	5.7	7.1	30.9	53.2	3.1
In seed, nearly ripe	5.7	6.6	30.7	54.2	2.8

If cut too early, on the other hand, the crop will be too small and not a maximum amount of inorganic material will have been absorbed by the plant. In fact all of the constituents will be small in amount. Although the time of cutting hay will vary with the crop and the purpose to which it is to be put, and will also depend somewhat on weather and other conditions, the proper time, in general, to cut hay crops is when they are beginning to bloom. Later, of course, a larger yield will be obtained but the quality will not be as good, and the palatability and color will not be as desirable.

The proper methods of curing and storing hay are not to be considered in a work of this kind, but there is one practice which should be mentioned here. Some farmers have a habit of mixing salt or lime with the hay in stacking, with the idea of preserving it, especially if it has been necessary to stack the hay a little wetter than usual. Salt and lime may prevent the action of bacteria and fungi to some extent, although no definite information is available. Certainly stock like salted hay, but that is on account of the salt. Lime, on the other hand, does not improve the taste of the hay. The value of either of these materials as a preservative is very questionable.

105. **Silage.**—Inasmuch as haymaking is in large measure a drying process the resulting material is dry, and for general feeding purposes a certain amount of more succulent food is desirable. Silage answers this purpose. It is usually made from corn, but sometimes mixtures of corn and cowpeas, corn and soja beans, oats and vetch are employed. Those crops which do not field cure or dry readily are best employed for silage. Corn is particularly well adapted for this purpose because of its succulence and also because it is an economical crop to use, for the more mature it becomes the better is its composition from a feeding point of view. Hay, on the other hand (Section 104), becomes less digestible, containing less ash, protein, and fat, and more crude fiber. The corn crop not only increases in weight with maturity, but also improves in quality, containing more crude fat and nitrogen-free extract, much less crude fiber, and not very much less ash and crude protein (See Table VI). The material for silage is cut fine and packed tightly in an air-tight receptacle, called a silo (Figs. 31 and 74). The object is to keep the material away from the air as much as possible. Since it is a moist substance the presence of air will hasten bacterial action and cause putrefaction.

TABLE VI.—CHANGES IN THE COMPOSITION OF CORN DURING GROWTH

(Pounds in 100 of Dry Matter)

Date of harvest.	Ash.	Crude protein.	Crude fiber.	Nitrogen-free extract.	Crude fat.
Aug. 15, ears beginning to form	9.31	14.94	26.47	46.63	2.65
Aug. 28, a few roasting ears	6.51	11.71	23.31	55.49	2.98
Sept. 4, all roasting ears	6.19	11.36	19.69	59.74	3.02
Sept. 12, some ears glazing	5.57	9.58	19.33	62.59	2.93
Sept. 21, all ears glazed	5.92	9.23	18.59	63.30	2.96

106. **Chemical Changes in Silage Making.**—Decomposition occurs to some extent. Some of the sugars, usually dextrose in corn, are fermented by yeasts to alcohol, and the alcohol is changed by acetic bacteria to acetic acid. Lactic bacteria

convert part of the sugar into lactic acid. There are also small amounts of butyric and some other acids formed, the total acidity amounting to not more than 2 per cent. nor usually less than 1 per cent. It is sometimes stated that these acid changes are due not to bacteria but to intermolecular respiration in the plant cells. Whether caused by bacteria or intermolecular respiration, the accumulation of acid stops the process, thus accounting for the maxmium of 2 per cent. acid.

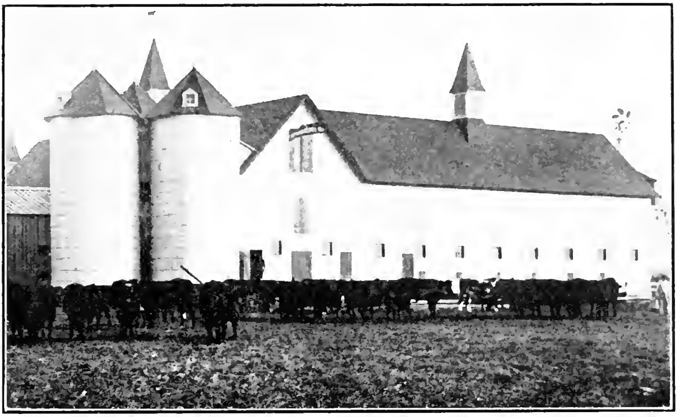

FIG. 31.—Silos.

In addition to these changes there is also a loss of protein and a formation of amides, possibly due to enzyme changes analogous to the usual hydrolytic changes of protein within the plant. Moreoever, some nitrogenous material decomposes to ammonia, which forms salts with the acids present. Crude fiber is softened and made more digestible, being partly hydrolyzed in all probability. Other compounds in the nature of volatile oils are formed, which add to the palatability of the material. There is also a complete decomposition of some of the organic material. There is oxidation to carbon dioxide and water, either by bacteria or oxidases, resulting in a loss of dry matter amounting to 10 or 15 per cent.

107. **Summary.**—The crop plants are raised for certain characteristic constituents, usually of value as food for stock or man. In scientific feeding it is necessary to know the amounts of the various food constituents in each crop, but it is a difficult and tedious process to determine each separate compound. For practical purposes it is sufficient to know the amount of each group of compounds which have food values. Consequently there is used a method which determines the following constituents in an approximate but fairly satisfactory manner:

Water.

Crude Fat, which consists of fixed oils, volatile oils, resins, waxes, and chlorophyl, if present.

Crude Fiber, which is principally cellulose and lignin.

Ash, which consists of the inorganic, or mineral elements, in the plant, although not combined in the ash as they were in the original plant material.

Crude Protein, which comprises proteins, amides, nitrates, and other nitrogenous material, unless the proteins and amides are determined separately, in which case the latter consist of all nitrogenous forms except proteins.

Nitrogen-free Extract, which consists of sugars, starch, and any other substance not determined above.

The composition and yields of the various crop plants can be found by consulting Tables I to III.

Hay consists of the leaves and stems of certain grasses and legumes which are cut about flowering time and dried or cured so that they may be preserved. The time of cutting is so adjusted that there will be a maximum crop consistent with optimum composition. The older a hay crop gets, the more crude fiber and the less crude protein, ash, and fat are present.

Some changes take place during the curing process, including the production of volatile oils or similar compounds which give additional palatability to the hay.

Silage is another form of preserved crop, and is made usually out of corn. The corn plant does not deteriorate in food value as it grows older, and fairly mature corn is cut for silage. The finely cut corn is packed tightly in an air-tight silo, since the presence of air causes undesirable decomposition. Silage is a succulent food, not dry food like hay. In making silage part of the dextrose is converted first to alcohol, then to acetic acid; part is converted to lactic acid. The total acidity is never more than 2 per cent. Proteins are converted in part to amides, and even to ammonia. Crude fiber is made more digestible, probably by hydrolysis. Compounds like volatile oils are also formed. Finally about 10 to 15 per cent. of material is lost because of complete oxidation of part of the material to carbon dioxide and water.

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PART II

FACTORS IN PLANT GROWTH

CHAPTER V

THE AIR

Of all the factors which influence plant growth, there is one over which the farmer has no control and yet one which is absolutely necessary to the life of both plants and animals. This factor is the air. It is important not only because it supplies plants and animals with certain essential elements, but also because its constituents and the changes in these constituents cause variations in climate. Moreover, the air and its constituents have a very considerable effect on the formation and decomposition of soils. It is, in short, of such vital importance to the farmer that a short discussion of its properties and constituents is advisable at this point.

108. **Height of the Air.**—If the air were of the same density throughout it would extend away from the earth for five or six miles, but since its density becomes less as the distance from the earth increases, it has been estimated that our planet is enclosed within a gaseous envelope about 200 miles thick.

109. **Pressure or Weight of the Air.**—At sea level, and at 0° C. the air exerts normally a pressure or weight of 1033 grams per square centimeter. This is 14.7 pounds per square foot or 46,100 tons per acre. The pressure diminishes with the altitude. At an elevation of about 18,000 feet the pressure is one-half that at sea-level, and at 36,000 feet about one-fourth. Since the average farm is not at sea-level it would be reasonable, then, to say that the weight of

the air on each acre is in round numbers 45,000 tons. The pressure or weight of the air, however, is never constant; it varies from day to day, from season to season, and from latitude to latitude. It is lower, for example, at the poles and at the equator than it is between these two latitudes.

110. **Properties of the Air.**—The air is usually a transparent, colorless, odorless, mechanical mixture of gases, vapor, and solids, the latter existing in exceedingly fine particles. 1000 cc. of air weigh 1.293 grams. By cooling and pressure it can be condensed to a bluish, mobile liquid, whose boiling point is about $-195°$ C. Its specific gravity is 0.9. There exist in it particles of ice from frozen water, and solid carbon dioxide. These can be removed by filtration.

111. **Water Vapor.**—Ordinary air contains varying amounts of water vapor, on the average about 1.3 per cent. by volume or 0.84 per cent. by weight. There is a limit to the amount of water vapor that the air will retain. When that limit is reached water is condensed to drops and we have rain, or snow if it is cold enough to freeze the drops. The higher the temperature the more water vapor can be held by the air. For instance, at 0° C., 1 cubic meter of air will hold 4.8 grams, whereas at 20° C., "ordinary room temperature," 1 cubic meter will hold 17.1 grams. When the air is saturated at any given temperature, a lowering in the temperature will result in precipitation. A glass of ice water "sweats," that is, moisture is condensed from the surrounding air by a lowering of the temperature below which the moisture can be retained. That temperature at which air begins to deposit water is called the dew point and, of course, will vary with the amount of water vapor present in the air. Dew is deposited at night when objects are cooled off by radiation to such an extent that their temperature is below the dew point of the surrounding air.

112. **Temperature of the Air.**—The presence of water vapor in the air modifies the temperature to a very great extent. Perfectly dry air absorbs practically no heat from the sun's rays. They pass through and warm up the earth. And in the same way at night, heat radiates from the earth, passing through dry air with but little absorption. In the

dry regions of western United States, the days are very hot. The sun's heat rays pass through the air unchecked. At night, on the other hand, it is very cool, because the heat has radiated away again. Water vapor and particles of dust in the air absorb the heat. A cloud blanket does not permit of radiation from the earth, nor does it permit much heat to pass through to the earth. On a cloudy night there is not so much danger of frost as on a clear night, since the heat is not radiated off into space so rapidly.

Air is warmed by contact with its own water vapor, or with the earth. When a surface of water is evaporating heat is being absorbed; when water vapor condenses heat is liberated. The specific heat of water is 1, whereas air is only 0.240, and the weight of a given volume of air is $\frac{1}{800}$ of the weight of an equal volume of water. Thus when a large body of water warms up one degree and evaporation takes place, a volume of surrounding air equal to 3200 times the volume of the body of water is cooled down one degree. And, conversely, when a body of water cools down one degree, the surrounding air to the extent of 3200 times the volume of water is warmed up one degree. This accounts for the modifying effect of large bodies of water on the climate of nearby land. This accounts, also, for the mild climate of western Europe which is washed by the warm Gulf Stream.

113. **Composition of the Air.**—The constituents of the air other than water vapor, which is exceedingly variable, are arranged in Table VII in the order of their amounts:

TABLE VII.—ATMOSPHERIC CONSTITUENTS

Constituents.	Per cent. by volume.	Per cent. by weight.
Nitrogen	78.03	75.51
Oxygen	20.99	23.14
Argon	0.94	1.29
Carbon dioxide	0.03	0.05
Hydrogen	0.01	0.001
Compounds of nitrogen	Trace	Trace
Bacteria	"	"
Dust, etc.	"	"

To give a striking illustration of the different amounts of the constituents of the air, a slight modification of Graham's suggestion is interesting. If the air is imagined to be separated into its several parts and these to be arranged around the earth in the order of their specific gravities, water vapor being condensed, there would be first a layer of water five inches thick, then thirteen feet of carbon dioxide, next ninety yards of argon, then a mile of oxygen, and finally four miles of nitrogen, with possibly three or four feet of hydrogen on top.

(*a*) Nitrogen.—The amount of nitrogen in the air varies but little. It is the most constant of all the constituents. It is a very inert gas, uniting with other elements only at high temperatures. It acts in the air in part as a diluent, rendering the activity of oxygen less energetic. It is the ultimate source of all nitrogenous compounds. The means by which it has been made to combine with other elements is bacterial in nature (see Section 130). By these means it is removed from the air, but is returned in small measure in the free state by the decomposition of nitrogenous organic matter, and by the burning of all kinds of fuel or other organic material containing nitrogen. The ordinary combustion of one ton of coal releases from one to five pounds of nitrogen.

(*b*) Oxygen.—This constituent, although fairly constant in amount, has been known to vary from 20.53 per cent. by volume to 21.03 per cent. Since a man consumes about 600 liters of oxygen in a day, and a ton of coal in burning consumes about 1,500,000 liters, it can easily be seen that the air of cities, which are densely populated and where much manufacturing is carried on, has a lower percentage of oxygen than the open country. And this is further emphasized by the fact that the country is where large numbers of growing plants are to be found, and in photosynthesis oxygen is given off by plants. Oxygen, as has been noted in Chapters I and II, is necessary for the germination of the seed and the growth of the plant. It is, moreover, absolutely necessary for the life of man and other animals.

(*c*) Carbon Dioxide.—Of the important constituents of the air, carbon dioxide is the smallest in amount and the most variable, with the exception of water vapor. Although normal, pure air contains about 0.03 per cent. by volume, city air contains 0.05 to 0.07 per cent., and the carbon dioxide in the air of crowded auditoriums may rise to 0.5 per cent. At night the amount of carbon dioxide is greater than during the day, due to the inactivity of plants in the dark. Since one man exhales about 550 liters of carbon dioxide daily, and a ton of coal gives off in burning about 1,500,000 liters of carbon dioxide, it is easy to account for the higher proportion of carbon dioxide in the air of cities. In the country where there are many plants and a large area of leaf surface absorbing carbon dioxide, the amount is naturally less (see Frontispiece). An acre of corn, for example, at the height of the growing season would absorb about 10,000 liters of carbon dioxide per day, and it has been estimated that an acre of forest uses up about 6000 liters per day. In addition to these compensatory changes in the amount of carbon dioxide in the air there are volumes poured into the air by some volcanoes and other openings in the earth. The decay of organic matter causes evolution of carbon dioxide; the weathering of rocks on the other hand uses up some carbon dioxide (Section 134). The amounts of carbon dioxide absorbed do not balance the amounts given off into the air. The ocean apparently acts as a regulator of the amount. When there is any increase in the percentage of carbon dioxide in the air this naturally increases the pressure of carbon dioxide on the surface of the water and some is dissolved and changed to bicarbonate of calcium. On the other hand a diminution in the amount causes a lowering in the pressure and some bicarbonate of calcium changes to carbonate again and releases carbon dioxide. In this way there is maintained a fairly uniform amount of carbon dioxide in the air.

(*d*) ARGON AND HYDROGEN.—Argon is one of the so-called rare elements. It has no agricultural bearing, and is so inert that it will unite with no other element. In fact its name means that it will not work. In addition there are several other rare gases existing in much smaller amounts, but none of them is of any importance. Hydrogen, also, although present in the air in fairly constant quantities, is of no agricultural value and need not be considered.

(*e*) Compounds of Nitrogen.—These compounds are of importance as far as they go, but the amount present is very small. They are principally oxides of nitrogen and ammonia, occurring usually, perhaps, as nitrous and nitric acids and ammonium nitrite, nitrate, carbonate, or sulphate. The oxides of nitrogen are formed from oxygen and nitrogen by lightning discharges. The intense heat in the immediate vicinity of the electric spark causes a very small part of these gases to unite. Ammonia is formed by the decomposition of organic matter, although free nitrogen is formed under some conditions (Section 129). These compounds of nitrogen can be used very well by plants after some changes in the soil, but the amount is hardly worth considering ordinarily. On the average there are about three pounds of nitrogen brought to the surface of an acre in a year by rain and snow. Occasionally this may amount to ten pounds, but very rarely.

(*f*) Bacteria.—The solid particles of the air, besides the nitrate, carbonate, and sulphate of ammonium mentioned above, consist of bacteria and dust. Bacteria exist in countless numbers in the air, invisible, but nevertheless of great importance, sometimes beneficial, sometimes harmful. The bacteria which aid in decomposing organic matter in the soil and in making nitrogen available are all carried in the air and help the farmer very materially. Moreover, the germs of many diseases are carried through the air and work considerable harm. One proof of the presence of bacteria in the air is to be found in the fact that if perfectly sterile milk is exposed to the air for any length of time it will sour, due to the lactic acid bacteria being carried to it by the air.

(*g*) Dust.—Fine particles of dust are everywhere present in the air, and consist of minute particles of organic matter, bits of cotton, pieces of hair, and fragments of minerals. There may also be pollen from flowers, and spores of fungi. These particles of dust form nuclei for the precipitation of water vapor and hence cause the formation of fog and clouds. Dustless air would contain no fog.

(*h*) Sulphur Dioxide is of very serious consequence in some places. In the western part of the United States where smelters have been erected for the treatment of sulphide ores, large volumes of sulphur dioxide are discharged into the air during the roasting of the sulphides. This has a very harmful effect on vegetation and has led to legislative action in a number of states. Not only does the gas itself harm vegetation, but its solution in rain water as sulphurous acid is poisonous. In large cities where much soft coal is burned sulphur dioxide is present in the air and this accounts in part for the weak, sickly appearance of trees and grass in such centers of industry.

114. **Summary.**—An important factor in the growth of crops is the atmosphere, not only for valuable constituents which are essential to plant growth, but also for constituents which affect the formation of soils. This atmosphere surrounds the earth to a thickness of about 200 miles and exerts a pressure of a little less than 15 pounds per square inch, or about 45,000 pounds per acre. It is a mixture of gases, vapor, and fine particles of solids, and is usually colorless and odorless.

One of the very important constituents of the air is *water vapor* which occurs on the average to an extent of about 1.3 per cent. by volume. Where the amount increases beyond the saturation point it condenses as fog, rain, or snow. The water vapor serves not only to supply water indirectly for plants, but also to regulate the temperature.

The *nitrogen* of the atmosphere is the original source of all nitrogenous compounds. It is removed from the air for the most part by bacteria, and returned when organic matter is burned. *Oxygen* is present in country air in larger amounts than in city air, because of its evolution by plants, on the one hand, and its absorption when animals breathe and fuel is burned, on the other hand. The amount of *carbon dioxide* in country and city is just the reverse of that of oxygen. Growing plants use large quantities of this gas, while breathing animals and the combustion of fuel add considerable quantities to the air. The total amount present in the atmosphere, however, is very small. *Compounds of nitrogen* occur to a very slight extent and are valuable as fertilizers as far as they go. *Bacteria* are always present in the air. Some of those which are beneficial in the soil as agents for the decomposition of organic matter, nitrification, and nitrogen fixation are carried in this way. Disease germs are also present. Particles of *dust* are of value in serving as nuclei for the precipitation of water vapor, and thus forming clouds. In some places the presence of *sulphur dioxide* is harmful.

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CHAPTER VI

THE SOIL: ORGANIC MATTER

THAT portion of the earth's crust which can support vegetation, or can raise crops, is what the farmer terms the soil. That loose mass of particles derived from rock disintegration and decay, and which covers most of the land portion of the globe is the way the geologist defines the soil. These definitions for the most part describe the same material but geological soil is not always agricultural soil, for not all loose rock particles will raise crops, and hence to the farmer are not soil.

115. **Composition of Soil.**—Soil agriculturally is composed of fine and coarse particles of rock in all stages of decomposition, of organic matter derived from decayed or decaying plants and animals, of water, of bacteria, fungi, and other forms of life, and of gases.

116. **Function of the Soil.**—Soil serves not only as an anchorage for plants, where they can spread out their roots and maintain a position which will enable them to absorb the sun's rays to the best advantage, but also serves as the source of most of those elements which are essential to the plant's growth. A perfect soil is one which maintains a reserve supply of insoluble food material that cannot be washed away; which produces enough soluble material to feed the growing crop; which is so constructed that it can supply sufficient water to the crop; which is capable of maintaining the right temperature or of warming up quickly in the spring; and which has a structure that permits of proper root movement.

117. **Soil Study.**—The study of the movements of water in the soil, of its holding capacity for water, of the arrangement of soil clusters, of the size of ultimate particles, of the relations of soils to heat, and of the various methods of

working the soil, are all important factors for the farmer to consider, but do not come within the scope of agricultural chemistry. The study of the important compounds in the soil and the changes which take place in them; in other words the chemical reactions and their causes, which directly or indirectly affect the growth of crops, do, however, comprise soil chemistry. The food of plants, from what derived, how made soluble, how retained in the soil or made insoluble, are particular points to be considered.

Plant food is derived from the rock particles and from the organic matter. Soil moisture, organic matter, bacteria, fungi, and gases are factors influencing the changes taking place in plant food. The mineral particles, and the organic matter to a small extent, supply the compounds containing phosphorus, potassium, sulphur, calcium, magnesium, and iron. The organic matter is the source of nitrogen. In taking up the subject of plant food in soils it seems best to discuss first the organic matter which has been very truthfully called the life of the soil. It is probably the most important single factor in making plant food soluble, except of course water, the solvent medium itself.

118. **Organic Matter.**—The soil is separated horizontally into two portions as it lies in the field: First, the surface soil, or sometimes called merely soil, and second, subsoil. For certain purposes, such as the scientific study of soils in comparing types, it is advisable to arbitrarily assume that the surface six, eight, or ten inches shall be the surface soil, and all below that shall be the subsoil, but the natural division lies at the place where the color of the soil changes, frequently very abruptly, almost always very distinctly, from dark to light (Fig. 32). This depth varies in different soils, sometimes lying only a few inches below the surface of the land, sometimes lying several feet below.

It is in this dark soil that crops can grow best. It frequently happens that when a light colored subsoil is turned up, crops will not grow. This may be due to several causes, but one of them at least is the absence of organic matter which gives the dark color to surface soil. Organic matter in the soil is composed of particles of roots, leaves, bark and other plant debris and fragments of animals, insects, and worms, in all stages of decomposition, ranging from their original condition and easily recognizable, down to the unrecognizable pieces and the amorphous, waxy coating on soil grains. The whole mass of soil material, which at one time or another was a part of living organisms, is called *organic matter*. Organic matter in the process of decomposition, which is changing continually and breaking down into new compounds, may be called *active organic matter*. That particular part of it which is completely decomposed, which has lost all resemblance to living matter, and which is indistinguishable among the soil grains, except that it gives the dark color to them, may be called *inactive organic matter* or *humus*.

FIG. 32.—Soil and subsoil, showing dark color due to organic matter. (Weir.)

119. **Bacteria.**—As soon as a portion of a living organism dies, whether it be a leaf, or bit of bark, or mass of roots, it is at once attacked by bacteria which are everywhere present in the soil. Inasmuch as bacteria are of such vital importance to agriculture, both beneficially and otherwise, a brief description of them is desirable.

Bacteria are one-celled plants which are composed of cell walls of protein—not cellulose—cell contents or protoplasm and enzymes, but no nucleus. They are very much like any of the simple cells in crop plants except for the absence of nuclei. These bacterial cells require soluble material which can diffuse through their walls and from which can be built up the various components of the cell wall and contents, and permit them to reproduce themselves by subdivision. The cells are small, about 1 micron (0.001 mm.) in diameter, or even smaller. Some bacteria are more or less spherical, others are rod-shaped, perhaps two or three times as long as they are wide, and some of them are spiral-shaped. They consist of about 85 per cent. of water, and of the dry matter some 8 per cent. is composed of inorganic compounds. The rest is fat, carbohydrate, and protein material largely, very much like the cell contents of any plant.

Bacteria contain no chlorophyl, hence do not make their organic food by means of the energy derived from the sun's rays. The energy they use in synthesizing compounds is derived by oxidation of various compounds, with or without the aid of free oxygen, or by intercellular decomposition, which releases energy. Many bacteria, like crop plants, oxidize organic compounds to carbon dioxide and water. Some oxidize nitrogen, sulphur, iron, and other inorganic elements (considering nitrogen an inorganic element) to nitrites and nitrates, sulphuric acid, and ferric oxide. In this way they derive energy. Others reduce highly oxidized compounds like nitrates and sulphates, using the oxygen thus derived to oxidize other compounds. And still others merely decompose compounds without any oxidation, deriving such energy, for example, as is released when dextrose is changed to lactic acid.

The material which bacteria use as food for building purposes is largely organic in nature, although there are some bacteria which live without any organic matter—that is, they use inorganic compounds entirely from which to make their cell substance. The organic material that is most frequently used is composed of the various carbohydrates, fats, and proteins of animal and plant origin. Those compounds which are insoluble are rendered soluble by the excretion of enzymes which acts hydrolytically, usually to dissolve the compound. The soluble substance then diffuses into the bacterial cell where further transformations take place.

Since enzymes act independently of the living cell which produces them, they frequently form sufficient material to kill, or at least to stop the activities of the bacteria as well as of themselves. This is true of acid- and alcohol-forming enzymes in particular. If the acid can be neutralized as fast as it is formed, or if the alcohol is further changed, the production of acid and alcohol will not cease.

Some bacteria use oxygen, while some do not. This fact goes one step further in that many of the oxygen-using, or aërobic bacteria, can not live at all in the absence of oxygen or air, and in that many of those which do not use oxygen, or anaërobic bacteria, cannot live in the presence of oxygen or air.

120. **Decomposition of Organic Matter.**—In the soil, as was stated above, are very many bacteria of all kinds. Furthermore, the conditions under which they live are very different, depending on the physical condition of the soil and on the kind of organic matter from which they derive nourishment. The principal difference, however, is the presence or absence of air. In a soil that is fairly open and aërated there are different products formed from those in a water-logged or non-aërated soil. It is not easy, however, to classify organic decomposition on this basis, for soils vary gradually all the way from those containing no air at all, like swampy lands under water, to those which are very thoroughly penetrated by the air, like loose, sandy lands.

In a general way the products of decomposition can be classified into two groups: First, those developed under aërobic conditions; and second, those developed under anaërobic conditions. Under aërobic conditions there will be produced large quantities of carbon dioxide and water, mineral salts (set free by oxidation of organic matter containing inorganic elements), and nitrates, but not much humus (Section 122). Under anaërobic conditions there will be produced small amounts of carbon dioxide and water, considerable humus, and in addition methane and hydrogen sulphide. In both cases there will be varying amounts of organic acids, alcohols, higher hydrocarbons, waxes, etc.

The classification holds only in a general way. Of course, where there is an excess of air, organic matter is largely oxidized to carbon dioxide, water, residual inorganic salts, and nitrates. As the amount of air available to the bacteria becomes less, oxidation to carbon dioxide, water, nitrates, and mineral salts, materially lessens. More acids and alcohols form, as well as more of that black, amorphous product called humus. As the air supply continues to decrease, less and less carbon dioxide and water are produced, although their formation never ceases entirely, for intermolecular oxidation sets free small quantities. The production of nitrates practically ceases in the absence of air, and products that result from reduction, like methane and hydrogen sulphide, begin to form. The reduction of one compound is accompanied by a simultaneous oxidation of another compound and the production of energy. Considerably more acids, alcohols, and waxes are formed, since intermolecular decomposition results in the formation of these compounds rather than of the completely oxidized forms. At the same time there is produced more and more of this curious, amorphous mixture called humus. In soils which are absolutely anaërobic, however, little humus is formed. In fact under conditions where no air at all is present decomposition is very slow. Organic matter is maintained in a fairly well preserved condition. In peat bogs, for example, the structure of the original plants, sphagnum moss in many cases, is not destroyed.

The bacteria exist in soils for the most part in the upper eight to ten inches, just under the surface. There are very few on top of the ground, for direct sunlight kills most bacteria.

121. **Factors Affecting the Rate of Decomposition.**—The extent to which decomposition of organic matter will take place theoretically agrees with the above classification, but the amount or rate of decomposition depends on two prin-

cipal factors: First, the number of bacteria present; and second, the kind of living matter undergoing decomposition.

(*a*) NUMBER OF BACTERIA IN SOILS.—As to the number of bacteria in soils, it will vary between very wide limits. When "number of bacteria" is mentioned it means the number of colonies of bacteria that can be cultivated from a given amount of soil in an artificial nutrient solution and subsequently counted. The supposition is that each colony is developed from a single bacterium. The numbers vary from 100,000 to 50,000,000 or even 100,000,000 per gram of soil. The average cultivated land probably contains several million per gram. The more bacteria present, the more decomposition takes place and hence a greater production of those various compounds mentioned above, namely, carbon dioxide, water, mineral salts, and nitrogenous compounds, but ordinarily less humus.

The number of bacteria is dependent on several factors, the principal ones being: Temperature, moisture, food, and reaction of the soil, whether acid or alkaline.

(1) *Temperature.*—Bacteria thrive best between 15° and 25° C., although they do live from about 0° to 40° C. Near 0° bacterial life is inactive although not dead. Above 40° the bacteria begin to die; at 100° C. most bacteria are killed, although the spores are not.

(2) *Moisture.*—It is claimed that the best moisture conditions for bacteria vary from 8 to 10 per cent. in sandy soils to 20 per cent. and even more in heavy clays. As soils dry out the bacteria for the most part merely become dormant, although some are killed outright. Excessive water tends to kill off the aërobic bacteria but encourages the growth of the anaërobes. Since for the most part the beneficial bacteria are aërobes, aëration is essential to optimum soil conditions.

(3) *Food.*—This includes of course organic matter from which most bacteria derive their sustenance. Being plants, they must have inorganic salts as well, and there are necessary such salts as sulphates, phosphates, lime, and potash compounds, derived either from the organic remains or from mineral particles in the soil.

(4) *Reaction of the Soil.*—Most beneficial bacteria require for their optimum growth a neutral or alkaline medium in which to work. The presence of an acid inhibits their growth to a certain extent. Some bacteria produce mineral or organic acids as a result of their own activities, and these acids after reaching certain concentrations not only check the growth of the bacteria which produce them, but that of other bacteria as well. If there are sufficient acid-neutralizing compounds in the soil, such as calcium carbonates, these acids are neutralized as fast as formed and bacterial life is not suspended.

(*b*) KINDS OF LIVING MATTER.—Although all portions of vegetable and animal remains are attacked by one kind of bacteria or another, and eventually can be entirely decomposed under ordinary soil conditions, some parts of these remains resist decay more strongly than others. This is due ordinarily to the few species of bacteria which can attack these parts of the plant or animal body.

Cellulose and lignin—that is, the hard, woody portion of plants—resist decay more strongly than the softer, more succulent portions. Large roots, bits of bark, particularly bark containing tannins, and wood in general, are more resistant than leaves, soft stems, and fine roots like those of grass. As a rule fats and waxes are less easily decomposed than sugars and most of the proteins. In forests, however, logs and stumps gradually decay and disappear entirely, but here the conditions for one thing are most favorable for rapid oxidation, and those bacteria and fungi which are the most active oxidizers thrive.

Most animal remains decay rapidly, but such things as the organic matter in bones, hair, or hide decompose very slowly.

122. **Humus.**—The accompaniment of almost all kinds of organic decomposition in soils is the production of a black or dark amorphous material which is called humus. It is one of the final products of decay, formed for the most part where there is insufficient oxygen to allow complete destruction to carbon dioxide and water. From the original source, whether it be root or leaf or stalk or animal, the humus is

distributed among the soil grains with considerable uniformity within certain limits. That is, it does not ordinarily extend to any great depth, nor does it extend laterally over a field with uniformity, owing to changing conditions in soil masses, but the grains themselves are fairly well covered with the humus. It must therefore have been more or less soluble in water, or in liquid form at one time or another at least, to surround the particles. Its distribution, moreover, is aided by the growth and final decay of the hyphæ or root-like hairs of certain fungi which feed on a decaying bit of organic matter. It is no uncommon occurrence to note the wide ring of darker soil surrounding a decaying root. Earthworms also distribute humus throughout the soil to a very great extent by passing soil through their bodies and drawing after themselves into their burrows particles of leaves and blades of grass. In some localities where earthworms are fairly numerous, Darwin has estimated that they work over in a year from 0.1 to 0.2 of an inch of surface soil. Ants, burrowing insects, and animals, all help to distribute organic matter and, subsequently, humus throughout the soil.

123. **Properties of Humus.**—If a dark soil containing considerable humus be first treated with a dilute mineral acid like hydrochloric, and then with ammonia, a black liquid will be obtained. The soil residue after washing is very much lighter in color, almost white in some cases. By this means the humus has been dissolved from the soil grains, although in many cases it may not be of exactly the same composition as it was in the soil. If the water is evaporated from this solution there remains a shiny black substance, rather hard and scaly, and absorptive of water. If it is burned there remains behind an ash of inorganic material.

Chemically, humus is by no means a single compound. It is a mixture, probably a mechanical mixture, of many substances. Research by the Bureau of Soils has shown that it is composed of acids, carbohydrates, fats, waxes, hydrocarbons, resins, nitrogenous compounds of various kinds, black compounds or pigments, and undoubtedly many compounds other than these few classes mentioned. Notwithstanding this great complexity, the black material has, or perhaps more correctly, these numerous compounds colored black have certain general properties which afford sufficient excuse for the term humus, and to consider them as a single kind of material in the soil.

Using the term "humus," then, in this general and popular sense, it can be said that it is composed of the same elements as are plants, except that there is more carbon and nitrogen, and less oxygen, hydrogen, and ash, or inorganic material. Table VIII gives the percentage composition of cellulose, grass, oak wood, decayed oak wood, and humus, showing the changes in composition from fresh material to humus.

TABLE VIII.—COMPOSITION OF HUMUS AND HUMUS-FORMING MATERIALS

	Cellulose.	Grass.	Oak Wood.	Decayed Oak Wood.	Humus.
Carbon	44.2	50.3	50.6	56.2	54.5
Hydrogen	6.3	5.5	6.0	4.9	3.5
Oxygen	49.5	42.3	43.4	38.9	41.5
Nitrogen	....	1.8			0.5

Results on the ash of humus are not of sufficient number for any definite statement to be made, but it can be said that whereas plants on the whole contain 6.5 per cent. ash (Section 14), humus probably does not contain more than 2 per cent. on the average. On the whole humus is insoluble in water and organic solvents.

Humus can be divided into two kinds in the soil: Acid humus, and neutral humus, both with the same physical properties.

124. **Acid Humus.**—Acid humus is formed in soils lacking sufficient neutralizing materials. It is insoluble in water, acids, and organic solvents. It combines with bases to form salts, particularly those of the alkaline earths, which are insoluble in water, and of the alkalies, which are soluble in water. By treating a soil containing acid humus—and for practical purposes this means an acid soil—with ammonium hydroxide the acid humus unites with the ammonium, the re-

sulting compound dissolving in the solution present. A dark or black liquid results. For the sake of convenience in discussing humus we can call the acid humus, humic acid, remembering, however, that it is not a single acid by any means but a mixture which acts like an acid. The compound with ammonium would then be called ammonium humate. Sodium and potassium hydroxides react like ammonium hydroxide. From a solution of alkaline humate a mineral acid like hydrochloric precipitates humic acid which separates out in black or brown flocks, drying to shiny scales.

125. **Neutral Humus.**—Where the soil contains sufficient calcium or other carbonate, humic acid is neutralized as fast as it is formed and the humus may then be said to be calcium (or other basic element) humate. This neutral humus is insoluble in water and organic solvents, unchanged by ammonium hydroxide, but partly decomposed by sodium and potassium hydroxides, forming the humates of the alkalies, soluble in water. When treated with a mineral acid like hydrochloric, the humus is decomposed, forming humic acid insoluble in water, and calcium chloride soluble in water. On further treatment of the soil with ammonium hydroxide, the humic acid forms ammonium humate soluble in water.

126. **Functions of Organic Matter.**—In considering the functions of the organic matter in the soil it should be remembered (Section 118) that there are really two kinds of organic matter: First, the active or decomposing organic matter which is constantly changing, with the production of organic acids, carbon dioxide, water, and mineral salts, and the release of nitrogen locked up in insoluble form; second, the inactive organic matter or humus, which is a more or less stable "compound" comparatively resistant to further rapid decay,

(*a*) THE ACTIVE ORGANIC MATTER serves important purposes in the production of chemical compounds active in the decomposition of mineral particles; in the formation of nitrates and soluble inorganic salts which serve as plant foods; in increasing the moisture-holding capacity of the soil; and in improving the structure of the soil.

(*b*) INACTIVE ORGANIC MATTER, OR HUMUS, serves as the reserve nitrogen supply, decomposing but slowly, and thus preventing the loss of nitrogen as nitrates by leaching. Its decomposition is ordinarily so slow that it does not serve to any great extent as a source of organic acids, carbon dioxide, and inorganic salts. Its principal function is physical, in that it improves the water holding capacity very materially; increases the heat absorption and thus warms up the soil earlier in the spring; improves the structure of the soil by loosening heavy clays, and making sandy soils more compact.

In other words, active organic matter has a decided chemical effect in the soil, while humus has an important physical effect. This distinction is not absolutely definite, but is generally true.

127. **Loss of Organic Matter.**—The active decomposition of organic matter in the soil is of vast importance to the farmer. It is not wholly a question of piling up reserves of organic matter, but rather of continually renewing the supply which is undergoing constant decomposition, thus rendering mineral particles soluble, freeing plant food from the organic matter, and making nitrogen available. In addition, of course, there must be a fair amount of humus, particularly on sandy soils, for physical reasons.

Active decomposition and loss of organic matter—and this includes humus—takes place most rapidly under intensive cultivation, proper drainage, and application of lime and commercial fertilizers. This is just what should take place, but the supply must just as surely be renewed by good applications of manure, and by plowing under grass, clover stubble, and green manure crops. Manure by its rapid decomposition does not ordinarily form humus to such an extent as do the fine, numerous roots of grass. Humus accumulates in pastures not only because of the fine roots thoroughly spread throughout the soil, but also because the soil is not cultivated and the organic matter is hence not so completely oxidized. Even very heavy applications of manure do not result in increased content of organic matter and humus, and consequently are not economical. It is better to put on reasonable applications (say 6 to 10 tons every two or three years) and supplement with hay stubble or green manure.

128. **Nitrification.**—As has been noted several times, organic matter serves as the source of nitrogen for crop plants. But before this organic nitrogen can be used by plants it must undergo a change to nitrates (Section 15), for most of the organic nitrogen is protein in character, and hence insoluble and unavailable to crop plants.

The process by which organic nitrogen is changed to nitrates, and thereby made available to crops, is bacterial in character, and is generally called *nitrification*, although it really takes place in three steps, the first called *ammonification* and the last two *nitrification proper*. Oxygen is necessary for these changes to take place, hence the importance of thorough aëration to produce nitrates from the nitrogen reserves in the soil.

(*a*) AMMONIFICATION is brought about by many of the bacteria in the soil and is caused by the proteolytic enzymes of the bacteria first breaking down the proteins into simpler compounds, and further decomposing or hydrolyzing them into ammonia among other products. Some of the bacteria producing ammonia use it as a source of nitrogenous food, others leave it merely as a by-product.

(*b*) NITRIFICATION PROPER is a distinct bacterial oxidation of ammonia to nitrous acid, and of nitrous to nitric acid. There are definitely known two kinds of organisms which oxidize ammonia to nitrous acids, and they are called nitrous or nitrite bacteria. The equation for this reaction may be expressed as follows:

$$2NH_3 + 3O_2 = 2HNO_2 + 2H_2O.$$

There is only one kind of organism oxidizing nitrous acid to nitric acid, called the nitric or nitrate bacteria. The following equation represents the reaction:

$$2HNO_2 + O_2 = 2HNO_3.$$

The amount of ammonia or nitrous acid in the soil at any one time is very small because the ammonia is changed very rapidly to nitrous acid and the nitrous acid to nitric acid.

Particularly is it difficult to detect traces of nitrous acid because the nitrous and nitric organisms work together, the latter using up nitrous acid as soon as it is formed.

It is claimed that there is one kind of bacteria which oxidizes ammonia directly to nitric acid, but its identity is not completely established.

These nitrifying organisms, the nitrous and the nitric, obtain their energy by this oxidation process, and also utilize the ammonia and nitrous acid respectively as food for growth. When this happens, as whenever bacteria use soluble nitrogenous compounds as food, some nitrogen is converted into protein and rendered insoluble and unavailable to plants until acted upon by bacteria, as in the first instance. Moreover, these bacteria utilize only inorganic food. From carbon dioxide they manufacture their cellular substances of an organic nature. The synthesis is brought about not by chlorophyl but by the oxidation of ammonia and nitrous acid. Hence organic matter is not essential for these bacteria, and in fact too much soluble organic matter interferes with their growth. This does not happen in ordinary farm soil, but is a serious matter at times in soils very intensively fertilized with manure and sewage, like greenhouse and truck soils.

It is to be noted that the free acids themselves are the products of these bacteria. In the presence of bases or basic carbonates the acids are neutralized. Since calcium carbonate is the principal base in the soil, nitric nitrogen occurs in most soils as calcium nitrate, although some of the acid is neutralized by magnesium carbonate and potassium carbonate. If there is not sufficient basic material to neutralize the acids as they are formed, the bacteria are rendered inactive or are killed by the excess of acid. Other conditions for their growth are much the same as mentioned for bacteria in general (Section 121, *a*).

129. **Denitrification.**—A process just the opposite of nitrification is denitrification, which results in a loss of nitrogen. Under anaërobic conditions and in the presence of large quantities of easily decomposed organic matter, there are several species of bacteria which can reduce nitrates to

nitrites, to ammonia, and to free nitrogen. The following equations illustrate the reactions:

$$2HNO_3 = 2HNO_2 + O_2$$
$$4HNO_2 = 2H_2O + 2N_2 + 3O_2$$
$$HNO_3 + H_2O = NH_3 + 2O_2.$$

These bacteria can live under aërobic conditions, in which case they use free oxygen for their respiration, but under anaërobic conditions they use the oxygen removed from nitrates. The oxygen, whether from the air or from nitrates, they use in oxidizing organic matter which is necessary for their growth. The denitrifiers occur in manure and on straw to a considerable extent, but are not responsible for loss of nitrogen under ordinary farming conditions. In cases of excessive applications of manure in addition to nitrates, or in greenhouses where soils are very moist and large quantities of organic matter are present, nitrates may be reduced. In any conditions where soils are compact or very wet so there is no aëration, and where excessive quantities of decomposing organic matter are present in addition to nitrates, there denitrification may occur. It is, however, not a condition that occurs frequently enough to cause anxiety over loss of nitrogen. In any event, where only nitrites and ammonia are the products, loss does not occur, for these compounds may be later oxidized back to nitrates. Only free nitrogen is a total loss.

130. **Nitrogen Fixation.**—In the discussion of nitrogen for the use of plants, it has been noted that the source of nitrogen is the organic matter of the soil, that in the decomposition processes most of it is made available but some may be lost to the air; that after entering the plant it is used in tissue building and goes largely to the seed. After the plant dies that part which is left on the field serves as organic nitrogen for bacterial decomposition again. That part of the plant which goes to feed animals returns to the soil sooner or later in the form of manure, or dead animals, or parts of animals. The nitrogen is continually travelling in a circle with some loss. So far no mention has been made of any gain.

All nitrogen in combination on the earth came at one time or another from the atmosphere. The nitrate of soda beds, coal, and many other forms, all owe their nitrogen to the air. In other words, there is and has been some natural agency for combining atmospheric nitrogen. Nitrogen gas is very inert and does not combine easily with other elements. A small portion unites with oxygen under the influence of lightning. But aside from this there exist in the soil certain bacteria which can combine nitrogen from the air with carbon, hydrogen, and oxygen, and so put it in a form that can be used. This process by which atmospheric nitrogen is fixed, or made into stable compounds, is called *nitrogen fixation*, and is probably the most important single process taking place in the soil, all things considered.

There are two kinds of bacteria which can fix nitrogen: First, those which act independently of other living things, like most of the soil bacteria; and second, those which act most energetically when living with some other plant. In both cases the bacteria derive energy for combining nitrogen from the oxidation of carbohydrates, and for their most efficient work large quantities of soluble carbohydrates, sugars probably, are necessary. The nitrogen so fixed is then used by the bacteria in part, although more is fixed than the bacteria need for their own growth.

(*a*) NON-SYMBIOTIC.—Those bacteria which act independently are non-symbiotic in character, that is, they do not live with any other plant to the mutual advantage of both. They occur in most soils apparently and are able to fix some nitrogen which is left in the soil after their death. Not very much is known about these bacteria, but it is not probable that in ordinary farming they play much part in adding nitrogen to the soil.

(*b*) SYMBIOTIC.—This class is by far the more important and is familiar to all farmers. The nodules on the roots of leguminous plants like clover, alfalfa, peas, beans, and vetch, are abnormal root growths formed to accommodate the colonies of these nitrogen-fixing bacteria which are living with the legumes to the mutual benefit of both (Figs. 33, 34, 35). The legumes supply the bacteria with soluble carbo-

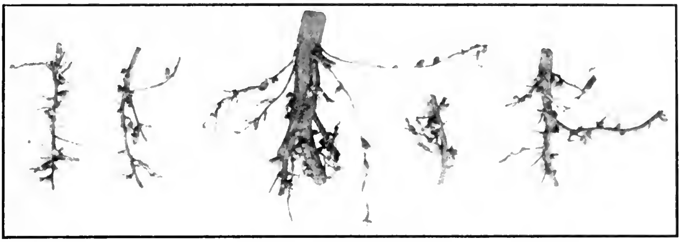

FIG. 33.—Red Clover.

FIG. 34.—Alfalfa.

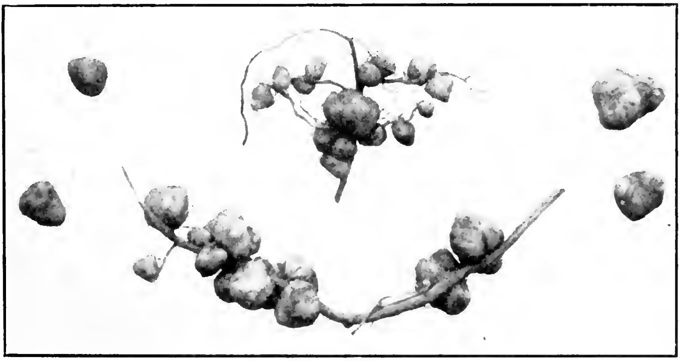

FIG. 35.—Cowpea.

FIGS. 33 to 35.—Nodules on legumes. Bureau of Plant Industry, United States Department of Agriculture.

hydrates, probably dextrose or maltose, and by the oxidation of this material the bacteria fix nitrogen obtained from the soil air through the nodules. They not only use some of the resulting compounds for their own growth but apparently pass on a large part of it for the use of the legumes. Fig. 36 shows the effect of these bacteria on clover growing in soil containing no nitrates.

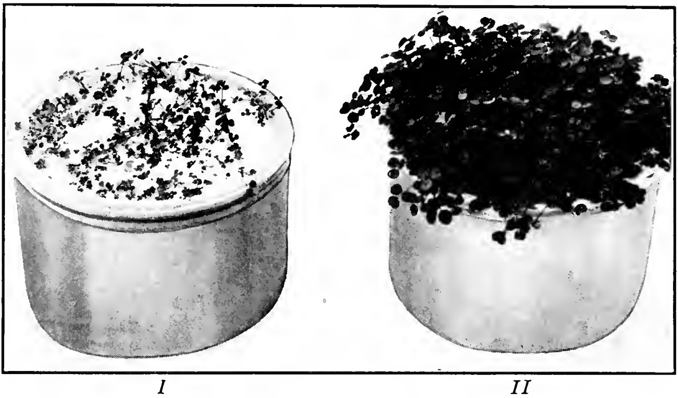

Fig. 36.—Clover growing on soil containing no nitrates. *I.* No nitrogen fixing bacteria. *II.* Supplied with bacteria. Soils Department, Wisconsin Station.

Both the bacteria and the legumes can utilize nitrates in the soil, but apparently the symbiotic relationship is better for both. The bacteria do not fix nitrogen when supplied with nitrate nitrogen, nor do the legumes accumulate the nodules to any extent when there are sufficient nitrates in the soil.

The bacteria are present in the soil to a considerable extent, and although it is claimed they can, under suitable conditions, fix nitrogen independently of legumes, they apparently do not do it readily. When legume roots are present in the soil these bacteria enter the root hairs, growing into long gelatinous threads which penetrate the various cells of the fine roots, and develop immense numbers of bacteria. Their multiplication causes the peculiar nodule formation on the young roots. On clover and alfalfa the nodules are very small like a pinhead or small bean, but on some beans and cowpeas they are very large, even reaching the size of baseballs on the velvet bean. When the legume is harvested and the roots die the nodules decompose, the accumulated fixed nitrogen going back to the soil. The bacteria remain for the most part inactive until more legumes are grown. The amount of nitrogen added to the soil by plowing under the legume crop varies considerably with the crop, season, and condition of soil, but it is safe to say that the ordinary clover crop adds 40 to 50 pounds per acre, and alfalfa 75 to 100 pounds per acre.

Although there seems to be evidence that most of these symbiotic bacteria belong to but one or two species, as a matter of practical fact they are so differentiated by habit of growth that there are several classes. For instance, the bacteria which live on alfalfa roots are not fitted to live on red clover roots, nor do the bacteria of beans live on vetch roots. Not every legume has its own special bacteria, however, for alfalfa and sweet clover can interchange bacteria; white, alsike, and red clovers apparently have the same bacteria; the vetches all seem to use the same organism.

As far as crop plants are concerned only legumes have nitrogen fixing bacteria on their roots, but there are some plants such as the alder, New Jersey tea, buffalo berry, sweet fern, and a few others which also have bacterial nodules on their roots. The importance of this fact lies in the ability of waste lands to accumulate nitrogen through the agency of wild plants.

131. **Inoculation.**—Practically all soils contain the nitrogen fixing bacteria for the common clovers, peas, and beans, so that a failure to have nodules develop on these legumes is due rather to other causes than to lack of the bacteria in the soil. For example, lime may be lacking, the soil may need drainage, too much available nitrogenous compounds like nitrates may be present, plant diseases may infect the legumes. But where a new legume is tried, such as alfalfa or serradella, and the crop fails under ordinarily beneficial conditions, it may be necessary to inoculate the soil with the proper bacteria.

This can be done by applying 200 to 500 pounds of surface soil from some field where the crop in question has produced nodules, or where a similar crop has succeeded. The soil should be harrowed in at once to prevent the sunlight from killing the bacteria. In the case of alfalfa, soil from a roadside where sweet clover grows is satisfactory. This practice of course may introduce weed seeds or plant diseases into the soil and for that reason is not always satisfactory.

It is possible to get pure cultures of the bacteria at some of the experiment stations, and from some commercial sources (Fig. 37). These cultures can be mixed with water and the seeds soaked before planting. The bacteria cling to the seeds and infect the roots when the seeds germinate. The trouble with this method is to get cultures which are fresh. Many preparations put out by commercial firms and the scheme of the United States Department of Agriculture for sending out the bacteria dried on cotton have failed because the bacteria were dead when inoculation was attempted.

Fig. 37.—Cultures for Legume Inoculation. Bacteriological Department, Virginia Station.

It must not be thought that inoculation alone is the easy way to obtain nitrogen from the air and that it will work on any crop. There are people who think it is a complete fertilizer in vest pocket form; that corn or oats can be inoculated and will gather their own nitrogen! It is not a complete fertilizer and will not help any but leguminous crops, and then only if the inoculating material contains living bacteria. The average farmer will probably never need to inoculate his legume crop. Failure to get a crop is usually due to some other cause more or less easily remedied.

132. **Summary.**—For agricultural purposes, the soil may be considered as that portion of the earth's crust which can raise crops, and is composed of fine and coarse particles or rock in all stages of decomposition, of organic matter derived from decayed or decaying plants and animals, of water, of bacteria, fungi, and other forms of life, and of gases. A perfect soil is one which maintains a reserve supply of food material and yet at the same time supplies sufficient soluble material for the growing crop. It also is in such physical condition that it can supply sufficient water to the crop and that it can permit of proper root movement. Plant food is derived from rock particles and organic matter, the former supplying the so-called mineral elements and the latter supplying nitrogen.

The top layer of soil is usually darker than the lower layers and is called surface soil, in which crops can grow best. Organic matter is defined as that part of the soil which at one time or another was a part of living organisms. As soon as an organism dies in the soil, it begins to decay by the agency of bacteria which are minute, one-celled plants that obtain soluble nutrient material for their growth by decomposing and dissolving organic material largely. They derive their energy by the oxidation of organic matter, or in some cases by the oxidation of inorganic matter. The enzymes which they secrete for the purposes of decomposing food or energy material are capable of acting independently after the death of the bacteria. There are two kinds of bacteria in general: Aërobic, or those which require free oxygen for growth, and anaërobic, which do not require free oxygen for their growth. These two classes of bacteria exist in the soil and regulate to a certain extent the manner of decomposition of organic matter. Under aërobic conditions organic matter tends to decompose completely to carbon dioxide and water, together with residual mineral salts and nitrates. Under anaërobic conditions there are less carbon dioxide and water produced, and more intermediate organic compounds, such as acids and alcohols. Sometimes even methane and hydrogen sulphide are produced. Moreover, under these conditions there is produced material which is called "humus." The rate of decomposition of organic matter is dependent on the number of bacteria present and the kind of living matter undergoing decomposition.

Humus is a black or dark colored, amorphous material, coating soil grains and giving the dark color to the soil. It is one of the final products of decay of organic matter and is a mixture of a large number of different compounds, the several properties of which, however, are sufficiently similar in some respects to permit consideration of humus as one kind of material for certain purposes. Under conditions where basic material in the soil is lacking, humus is acid in character and can be dissolved out of the soil by ammonium hydroxide which forms an ammonium compound with the so-called humic acid. Under conditions where there is sufficient basic material in the soil, humus is neutral in character and cannot be dissolved out of the soil by ammonium hydroxide until after treatment with hydrochloric acid which decomposes the neutral humate.

Of the two kinds of organic matter, the active or decomposing material is important as supplying carbon dioxide to the soil and thus aiding in the solution of mineral particles. It also sets free mineral compounds and thus supplies food to the plants. It is an active chemical agent in the soil. The inactive organic matter, or humus, is a reserve nitrogen supply, but it has more of a physical effect on the soil than a chemical one.

To render nitrogen available to plants it must be changed from its organic combination to the nitrate form, and this is accomplished by three sets of bacteria in the soil, changing protein material first to ammonia, then to nitrous acid, and then to nitric acid. This process is called nitrification. Another important kind of bacteria is the so-called nitrogen fixers, which have the power of combining the nitrogen of the air with organic matter in the soil and thus putting the atmospheric nitrogen into a form which can later be made available to crops. The nitrogen fixers live for the most part in colonies on the roots of leguminous plants and are supplied with carbohydrates by the legumes. These carbohydrates they use as a source of energy for the fixation of nitrogen. Some of this fixed nitrogen is used by the bacteria themselves and some by the legume plants.

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CHAPTER VII

THE SOIL: INORGANIC MATTER

In the previous chapter the discussion of organic matter in the soil brought out the fact that it was the immediate source of nitrogen for plants. The other necessary elements which are derived from the soil come, originally at least, from the mineral particles or inorganic portion of the soil. The organic matter in its decomposition furnishes acids which are important agents in the solution of mineral particles. Other factors in the changes of mineral particles are the gases present in the soil.

133. **Soil Gases.**—The pore spaces of a soil are filled, part of the time with gases, and part of the time with water. The latter condition happens only after a rain, and in a soil of good structure does not last very long. The water running down into the country drainage is followed by atmospheric gases. From the decomposing organic matter gases are added to those already present, and at the same time some gases are withdrawn by absorption from the soil atmosphere. Certain chemical reactions also involve changes in the composition of soil atmosphere. It has been found that nitrogen varies but little, existing in the soil in about the same proportion that it does in the air, namely 78 per cent. (Section 113).

Oxygen varies from 10 to 20 per cent., whereas in the air it runs rather constantly at 21 per cent. This difference is due to changing rates of oxidation resulting from bacterial action on the organic matter, as well as to ordinary chemical oxidation of minerals in the soil. The amount of carbon dioxide varies inversely with the oxygen content, running from about 11 to 1 per cent. As oxygen is used up in oxidizing organic matter, carbon dioxide is evolved. Ordinarily the disappearance of oxygen causes the appearance of an equal volume of carbon dioxide. Intermolecular or anaërobic oxidation is not sufficient in ordinary soils to cause much change in the composition of the soil gases. In other words the amount of oxygen and carbon dioxide together equal 21 per cent. rather constantly. In the air they amount to 21.02 per cent.

Decomposing organic matter is the principal factor in the variation in composition of soil gases, and to this cause also is due, especially in soils more or less water-logged, the presence of methane and hydrogen sulphide; but these gases are rare constituents in any ordinary soil in good condition. Other constituents are not worth considering.

As to the value of soil gases in decomposing mineral particles, it will be found later that carbon dioxide and oxygen are the most active agents. A solution of carbon dioxide in water is by far the most active solvent for minerals which the soil produces. Of course sulphuric and nitric acids which result from decomposing organic matter are more powerful reagents ordinarily, but their occurrence is very slight compared to that of carbonic acid, which though rated a weak acid is always present in large quantities in practically all soils. Decaying organic matter has been estimated to supply through bacterial action to a depth of eight inches, about 1 ton of carbon dioxide per year. When dissolved in water this makes a very respectable amount of solvent. Organic acids, together with sulphuric and nitric acids, are produced in very much smaller amounts, and being very dilute have not the effect that carbon dioxide has, although these reagents are to be reckoned with in considering mineral decomposition and solubility.

134. **Soil Solvents.**—The soil moisture which acts on the mineral particles in the soil consists primarily, of course, of water. Pure water dissolves ordinary minerals but slightly, except gypsum and sodium chloride, of which the latter occurs in normal soils more as a decomposition product than as an original mineral. In the soil, however, water is never pure. *Carbon dioxide* is always present from the decay of organic matter. Living plant roots excrete carbon dioxide due to respiration, and the soil moisture immediately around such roots is fairly well concentrated in this constituent. The growing of plants on a polished slab of marble—calcium carbonate—or on one of feldspar leaves a fine tracery of the

roots due to the solvent action of the carbon dioxide excreted. Carbon dioxide is soluble in pure water to the extent of about 1 part in 600 parts of water. The presence of soluble salts reduces its solubility.

Oxygen is very generally present in the moisture of well aërated soils, attacking minerals containing ferrous iron, like hornblende, and breaking them down with water and carbon dioxide. It is soluble to the extent of about 1 part in 20,000 parts of water.

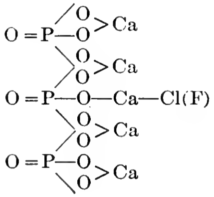
Organic Acids like acetic, butyric, and others of a more complex nature, all formed by the bacterial decay of organic matter, particularly carbohydrates, dissolve in soil water to a greater or less extent and act on many minerals.

Inorganic Acids like sulphuric and nitric, formed from sulphur and nitrogen in organic matter, serve as very active reagents. They are present, however, to a very small extent at any one time.

Soluble Salts, derived from various minerals, such as chlorides, nitrates, and sulphates, all have a greater or less effect on minerals.

135. **Soil Minerals.**—In considering the chemical changes by which inorganic plant food becomes available, it is necessary to know some of the principal soil minerals which are the source of these elements. They will be taken up and discussed in groups according to the element or elements which they supply. In addition there will be discussed the minerals of a few elements which are thought not to be essential and yet which occur very commonly in plants, or which have some effect in the soil.

(*a*) Phosphorus Minerals.—The principal mineral containing phosphorus is *apatite*, $Ca_5(PO_4)_3Cl.F$. To show its chemical structure better it may be written graphically:



It occurs in hexagonal prisms frequently of very small size, almost like needles, and green or red in color.

This compound is practically insoluble in water but under the action of water and carbon dioxide it slowly dissolves, possibly according to the following equation:

$$2Ca_5(PO_4)_3Cl + 12CO_2 + 12H_2O = 3CaH_4(PO_4)_2 + 6CaH_2(CO_3)_2 + CaCl_2.$$

Most of the phosphorus in soils, however, occurs in an amorphous, secondary form possibly derived from apatite, expressed by the formula $Ca_3(PO_4)_2$ and called tri-calcium phosphate. This compound in the presence of small amounts of carbon dioxide in water changes to the dicalcium phosphate, thus:

$$Ca_3(PO_4)_2 + 2CO_2 + 2H_2O = Ca_2H_2(PO_4)_2 + CaH_2(CO_3)_2.$$

In the presence of more carbon dioxide and water it decomposes to the monocalcium phosphate, thus:

$$Ca_3(PO_4)_2 + 4CO_2 + 4H_2O = CaH_4(PO_4)_2 + 2CaH_2(CO_3)_2.$$

Tricalcium phosphate is practically insoluble in pure water, 1 part requiring 50,000 parts of water, whereas dicalcium phosphate is soluble to the extent of 1 part in 7500 parts of water, and monocalcium phosphate, 1 part in 100 of water,

Soil water, of course, is never pure water, having always some substances dissolved in it, and these substances in solution tend to modify the above solubilities to a slight extent; but the figures serve to show the relative solubilities of the three forms of phosphate. Dicalcium phosphate and monocalcium phosphate, both of them, can be used by plants. Since carbon dioxide is so generally prevalent in soil water and can dissolve tricalcium phosphate, it is safe to say that all compounds of phosphorus with calcium are available forms of phosphorus for plant use.

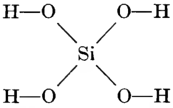
Phosphorus also occurs as more or less indefinite compounds of iron phosphate, $FePO_4$, and aluminium phosphate, $AlPO_4$, both very insoluble in water, or in water and carbon dioxide, or in any other ordinary soil solution, unless calcium is present. Where calcium bicarbonate is in solution in the soil water these phosphates are slowly changed as follows:

$$2FePO_4 + CaH_2(CO_3)_2 + 4H_2O = 2Fe(OH)_3 + CaH_4(PO_4)_2 + 2CO_2.$$

This emphasizes the importance of having calcium carbonate or lime in the soil. Aluminium phosphate acts similarly.

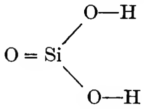
(*b*) Potassium Minerals.—Since these minerals, and in addition most of those of calcium, magnesium, and iron, belong to that principal group of minerals called silicates, it will help to understand their structure if a brief survey is made of the silicic acids from which they are derived.

Silicic Acids.—Normal or orthosilicic acid is H_4SiO_4, written graphically:



By the elimination of one molecule of water there is formed metasilicic acid, thus:

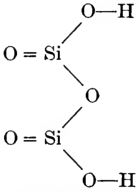
$H_4SiO_4 — H_2O = H_2SiO_3$ or:



metasilicic acid.

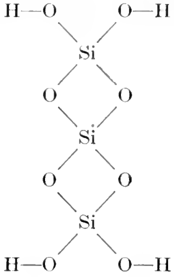
By the elimination of three or more molecules of water from two or more molecules of orthosilicic acid there are formed polysilicic acids, of which the disilicic and trisilicic acids are the commonest. They are formed thus:

1. $2H_4SiO_4 — 3H_2O = H_2Si_2O_5$ or:



disilicic acid.

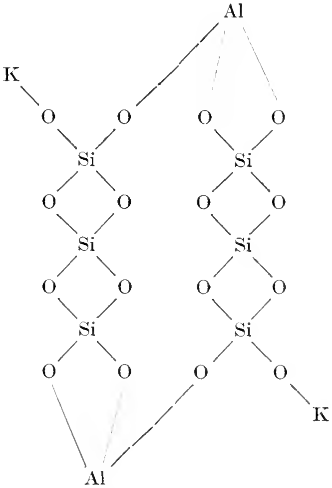
2. $3H_4SiO_4 - 4H_2O = H_4Si_3O_8$, or:



trisilicic acid.

These silicic acids are either unknown or but little known in the free condition but their salts are very common among the silicates which constitute most of the soil minerals.

The most important potassium silicate is a double trisilicate of potassium and aluminium called *orthoclase* or the *potash feldspar.* Its formula is $K_2Al_2(Si_3O_8)_2$. It is frequently written $K_2O.Al_2O_3.6SiO_2$ which shows its composition but not its chemical structure. Written graphically it is:

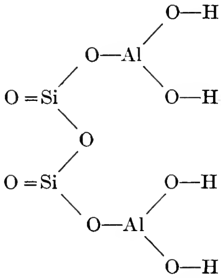


It occurs in monoclinic crystals of flesh-red, yellow, or white color. In pure water orthoclase is but very slighly soluble, but in water containing carbon dioxide it decomposes as follows:

$$K_2Al_2(Si_3O_8)_2 + CO_2 + 2H_2O = Al_2(OH)_4Si_2O_5 + 4SiO_2 + K_2CO_3.$$

Its solubility in pure water is 1 part in 37,000; in water saturated with carbon dioxide, 1 part in 4000.

From the above equation it is to be noted that the potassium goes into solution as potassium carbonate and it is this form which supplies the plant with most of its potassium. It is also to be observed that a new silicate is formed. This is a hydrated disilicate of aluminium and is called *kaolinite*, the graphic formula of which is:



It is a compact or mealy mass with greasy feel when wet, very plastic, and white, yellow, brown, red, or blue in color. This particular process of decomposition by which kaolinite is formed is called *kaolinization* and is common to very many silicates. It is one of the most important soil reactions, for not only is plant food made available by it, but in addition the soil structure is modified by kaolinite, the basis of clay. The mechanical mixture of kaolinite and silica formed in the above reaction is called *kaolin* or potter's clay. Varying amounts of silica are present, some being dissolved and washed away in the soil.

The potassium in orthoclase is also made available by another reaction due to calcium bicarbonate, thus:

$$K_2Al_2(Si_3O_8)_2 + CaH_2(CO_3)_2 = CaAl_2(Si_3O_8)_2 + 2KHCO_3.$$

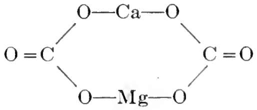
This shows the importance of having calcium carbonate in the soil. (Compare the effect of calcium bicarbonate on iron phosphate, Section 135, *a*).

Leucite is another potassium mineral which has the formula $KAl(SiO_3)_2$—a metasilicate. It occurs in translucent to opaque grains of gray to white color. The potassium becomes slowly available under the action of water and carbon dioxide.

Another potassium mineral that is very common and very familiar to nearly everybody is potash mica or *muscovite.* The thin, transparent leaves that very easily cleave are too common to need description. This is the white mica. It is an orthosilicate the formula for which is $H_2(K \text{ or } Na)Al_3(SiO_4)_3$. It might be called an acid salt since the hydrogen atoms replace bases—that is, they are true acid hydrogen atoms. It is very resistant to the action of soil reagents but does change very slowly under the action of water and carbon dioxide, allowing potassium to go into solution.

(*c*) Sulphur Minerals.—The principal sulphur mineral is gypsum or land plaster, $CaSO_4.2H_2O$. It is soft, white, granular, or compact, sometimes silky and fibrous. Occasionally it is crystalline. It is soluble in water to the extent of 1 part in 400. On being heated to 130° C. it loses one molecule of water and becomes "plaster of Paris," which has the power of reabsorbing the lost molecule of water and "setting" to gypsum again. This property is made use of in making casts, etc. There is another sulphur mineral called *anhydrite* which is $CaSO_4$. This is more or less common.

(*d*) Calcium Minerals.—Aside from apatite and gypsum which contain calcium there are a number of important calcium minerals. By far the most common is *calcite,* $CaCO_3$. This occurs as white or yellowish, transparent crystals of many shapes, but the amorphous variety known as limestone is the commonest, and is too well known to need description. It occurs pure, and with magnesium, when it is called *dolomite,* $Ca.Mg(CO_3)_2$:



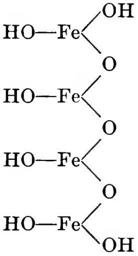
Calcium carbonate is soluble in pure water only to the extent of 1 part in 20,000, but when the water contains carbon dioxide to saturation the calcium carbonate is soluble to the extent of 1 part in 1000 of water, being changed to the acid carbonate, thus:

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

This form of calcium is the most important in the soil, although some of the more soluble silicates supply small amounts of this element.

Anorthite or the *lime-feldspar* is an orthosilicate of calcium and aluminium, $CaAl_2(SiO_4)_2$, which slowly decomposes under the action of water and carbon dioxide to kaolinite and calcium bicarbonate.

(*e*) IRON MINERALS.—Iron occurs largely as the hydrated ferric oxide, $Fe_2O_3.xH_2O$, in surface soils. There are a number of minerals of this kind, of which *limonite* is the most common. It is an amorphous, loose to compact, yellow or brown mineral, occurring fairly well disseminated in soils. Its formula is $Fe_4O_3(OH)_6$, graphically:



Limonite is derived from silicate minerals containing iron, *hornblende* for example. This occurs in columnar and granular crystals of green, brown, or black color. It is a metasilicate of any two or sometimes more of the following bases: Calcium, magnesium, iron, and aluminium. The iron may be ferrous or ferric. Under the action of water and carbon dioxide, carbonates or bicarbonates of the bases are formed, except ferric iron which is set free as such, usually in the hydrated form and becomes limonite or similar minerals. If the iron is ferrous it is changed to carbonate first but oxidizes almost instantly, if in aërated soils, to the hydrated oxide. If, however, the decomposition takes place in subsoils and in water-logged soils, ferrous carbonate may remain as *siderite*, $FeCO_3$. Iron compounds give the yellow, red, and brown color to soils when it is not masked by humus. A phosphate mineral is *vivianite*, $Fe_3(PO_4)_2$, a bluish-green, earthy mass.

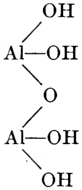
(*f*) MAGNESIUM MINERALS.—Some of the magnesium in soils is derived from dolomite, already mentioned under the calcium minerals. There are also many silicates containing magnesium, hornblende, already mentioned, and *biotite* or black mica, an orthosilicate of aluminium, magnesium, hydrogen, and potassium, thus: $(H \text{ or } K)_2(Mg \text{ or } Fe)_2Al_2(SiO_4)_3$. This mineral is similar to muscovite or white mica, except as to color, which is dark green or black.

(*g*) SILICON MINERALS.—All of the silicate minerals contain silicon, of course, but *quartz*, or SiO_2, is the only one to be considered here. It is, next to feldspar, the most common mineral in the earth's crust and occurs in many varieties and all colors from transparent and white to red, blue, green, and brown. Small quantities of impurities give the color to it. Ordinarily, however, it is a hard, brittle mineral, clear to white, and in hexagonal crystals of all sizes, although frequently amorphous. Sandstone and quartzite are massive varieties of quartz. It is ordinarily very insoluble, but some varieties dissolve appreciably to the silicic acids.

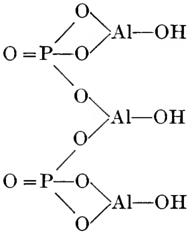
(*h*) SODIUM MINERALS.—Common salt, or *halite*, NaCl, is the most familiar mineral of both sodium and chlorine, but it does not occur to any extent in agricultural soil, being confined to beds located in many parts of the world. *Albite*, or the *soda feldspar*, is a silicate mineral of soda and is the counterpart of orthoclase, being $Na_2Al_2(Si_3O_8)_2$. It occurs in white granular masses or plates. Its solubility is similar to that of orthoclase.

(*i*) CHLORINE MINERALS.—*Halite* mentioned above is the only one of importance. There is very little chlorine in soils ordinarily.

(*j*) ALUMINIUM MINERALS.—The feldspars and many other silicates contain aluminium, and these break down as noted above to kaolinite, which is an aluminium mineral. In addition there are *bauxite*, $Al_2O(OH)_4$,



rounded grains or clay-like masses, white or yellowish in color; and *wavellite*, $Al_3(OH)_3(PO_4)_2$,



radiating crystals occurring in hemispherical masses.

136. **Factors of Solubility.**—From the above discussion of the solubilities and decomposition products of soil minerals it might be thought that solution was easy and the reactions fairly simple. But it must be emphasized that under actual conditions the reactions only approximate those indicated. That is, only a part of any mineral actually decomposes as far as stated. Reactions are not complete, and while in the case of a feldspar, for example, some potassium carbonate and kaolinite are formed, and formed continually although slowly, much of the mineral remains unaltered and some of it decomposes only partly. Intermediate compounds are formed. Other compounds interfere and react with the original mineral or with its decomposition products. Much more so is this true of more complex minerals.

Temperature has a decided effect on these reactions in the soil. The higher the temperature the more active the decomposition of most solvents except carbon dioxide. This compound is less soluble in warm water than in cold. Then, too, the amount of water; the movement of water, which latter removes decomposition products and exposes fresh surfaces to the action of the solvents; the size of soil particles; the arrangement of soil particles; all have a decided effect on the rate and amount of decomposition. Some minerals like feldspar decompose fairly readily, others, like mica, decompose with considerable difficulty. And again, small minerals like apatite may be enclosed within other minerals, like quartz, for example, and soil solvents cannot touch them. All these factors, of course, are in addition to the amount of organic matter, the rate of its decomposition, and the number of bacteria.

To sum up, then, the decomposition of mineral particles in the soil, while it appears rather simple, is in reality dependent on many factors which are only more or less controllable by the farmer. But if he understands the ordinary progress of favorable decomposition, he can modify his controllable factors accordingly. He can cultivate, maintain the supply of organic matter, and look after drainage or irrigation as the case may be.

137. **Absorption.**—From what has been said it might be thought that when once a plant food becomes soluble it undergoes no further change, and if not taken up at once by the plant is in danger of being leached from the soil. The danger of leaching is by no means as great as might be expected, and any given plant food element undergoes a great many changes before it meets its final fate in the plant or in the drainage water. Compounds are constantly going into solution or being made available, and going out of solution or being made unavailable. Compounds are also held in the soil by physical means. In other words the soil not only makes plant food available from its reserve stores, but it in large measure prevents them from being removed from the soil by leaching. This process of retention of soluble salts or of elements in soluble compounds is called *absorption,* or sometimes fixation. The latter is not so good a name since it may be confused with nitrogen fixation which

is a very different process (Section 130). Absorption, as barely indicated above, is of two kinds, chemical and physical.

138. **Chemical Absorption.**—Some elements are retained in the soil by a chemical reaction which changes the element from a soluble compound into an insoluble compound. This may take place by double decomposition and subsequent precipitation, or by simple precipitation. When, for example, potassium sulphate or potassium carbonate in solution in the soil moisture comes in contact with an insoluble compound containing calcium, such as a silicate or a humate, there is an interchange of bases, the potassium remaining as the silicate and the calcium leaching away as the sulphate or carbonate (bicarbonate would be the soluble form), thus:

$$CaAl_2(Si_3O_8)_2 + K_2CO_3 + H_2O + CO_2 = K_2Al_2(Si_3O_8)_2 + CaH_2(CO_3)_2.$$

Or take a compound like monocalcium phosphate. It is precipitated by calcium bicarbonate or iron hydroxide as an insoluble phosphate, thus:

$$CaH_4(PO_4)_2 + 2CaH_2(CO_3)_2 = Ca_3(PO_4)_2 + 4H_2O + 4CO_2$$

and

$$2Fe(OH)_3 + CaH_4(PO_4)_2 + 2CO_2 = 2FePO_4 + CaH_2(CO_3)_2 + 4H_2O.$$

In some cases the reaction occurs directly between a solid and a compound in solution. In other cases two substances in solution react and an insoluble precipitate results. In one case it is an exchange of bases, and in this connection it must be noted that other bases than potassium and calcium exchange places in this way. Sodium, magnesium, and ammonium exchange with one another and with potassium and calcium. In the other case it is the formation of an insoluble salt of an acid.

There is still another case where the base of a salt is absorbed and the acid radicle left behind as an acid. There is no exchange of bases. For instance a hydrated silicate like kaolinite in the presence of a salt like potassium sulphate and water will absorb the potassium, probably to form a potassium silicate, and leave sulphuric acid. This applies to salts like the chlorides and sulphates more particularly.

Other things being equal it has been found that there is a difference in the ability of one base to replace another. Potassium will replace magnesium and be replaced by ammonium in turn. Sodium will replace calcium and be replaced by magnesium. In other words, the order of replacing power beginning with the strongest is: Ammonium, potassium, magnesium, sodium, calcium. Each element will replace any of those following it and be replaced by any of those preceding it. In the case of acid radicles, those which form insoluble compounds the most readily are the ones absorbed the quickest. Phosphates of calcium (tri) and of iron and aluminium are insoluble. Calcium phosphate forms soluble acid phosphates, but the others do not dissolve easily. Carbonates of calcium and magnesium are insoluble, but form soluble bicarbonates very readily. Sulphates, except of barium, are rather soluble. Chlorides and nitrates, particularly the latter, are all readily soluble and hence do not form compounds which can be retained chemically.

But a part at least of the above discussion seems to be at some variance with what has been said in Section 135 about the solubility of soil minerals. The fact is that under some conditions elements are rendered soluble and under other conditions the same elements are rendered insoluble, *even when the reacting substances are exactly the same,* and this difference of reaction depends on the active mass of the reacting substance. This is called the law of mass action.

139. **Mass Action.**—To illustrate this important chemical law, the equations for the solubility of phosphorus and for the fixation of phosphorus may be written together thus:

$$Ca_3(PO_4)_2 + 4CO_2 + 4H_2O \rightleftharpoons CaH_4(PO_4)_2 + 2CaH_2(CO_3)_2.$$

This is called a reversible reaction, for it will go in either direction depending on the active mass of the reacting substance. Tricalcium phosphate continues to go into solution as long as the supply of carbon dioxide is continuous, and the monocalcium phosphate or calcium bicarbonate is removed from the solution. In the soil, decomposition of organic matter supplies carbon dioxide. Growing root hairs or diffusion may remove the soluble compounds. The reaction, then, continues to go from left to right, and phosphorus is made soluble.

But suppose the supply of carbon dioxide diminishes, organic matter for some reason does not decompose very rapidly or not at all; or suppose no plant removes the soluble phosphate; or suppose that a solution of monocalcium phosphate passing through the soil comes in contact with considerable calcium bicarbonate, or, more than all this, suppose fresh supplies of calcium bicarbonate are being continually added to the solution from other places; under these conditions, then, the reaction goes from right to left and phosphorus is absorbed or fixed in the soil. Of course, in all cases there must be enough water present to allow of reactions in solution.

Starting with a fixed amount of the reacting substances the reaction will proceed in a direction dependent upon the masses until an equilibrium is reached, or until the masses on one side of the equation balance in reacting velocity those on the other side. This, however, is something that rarely happens in a soil, for the composition of a solution is constantly changing. Reactions in a soil are always in a state of change. They are essentially dynamic and not static.

This reversible reaction and the resultant solubility or absorption of plant food is applicable just as well in the case of the reactions given for potassium in Sections 135, *b*, and 138, and for phosphorus and iron compounds in Sections 135, *a*, and 138.

140. **Physical Absorption.**—Compounds of the plant-food elements are retained by the soil to a greater or less extent in an unchanged form. Certain solid substances in the soil attract and hold on their surfaces compounds in solution. This process is called *adsorption* and may be defined as the existence in soil moisture (or other solutions) of two different concentrations of dissolved substances, the greater lying immediately adjacent to the surface of a solid. For example, iron and aluminium hydrated oxides have a very decided affinity for potassium sulphate. Adsorption is a purely physical phenomenon in that the compounds

held are not chemically changed. They remain in their original form, attached to the surface of the solid as by a magnet, and the amount of adsorption depends very largely on the surface exposed. Hence, the smaller the soil grains the greater the adsorption because of more surface exposed. Another factor in adsorption is the character of the solids and of the substances in solution. Some solids have greater attractive powers than others, and some dissolved substances are more attracted than others. For example, humus, hydrated iron and aluminium oxides, and hydrated silicates or so-called zeolites, have greater adsorptive powers than calcium carbonate and quartz. Potassium salts and phosphates are attracted more than sodium salts and nitrates. Plant foods held by adsorption on the surfaces of solids are available to plants if the root hairs come in contact with them. Substances absorbed chemically are not available to plants until they are dissolved again, as may or may not happen. It must be understood, however, that in no case is the whole of a substance in solution absorbed either chemically or physically. No chemical reaction is complete in the soil. Only a part of the monocalcium phosphate, for example, is precipitated as iron phosphate at any one time, but enough of it may be rendered insoluble to affect the growth of crops. Moreover, some of it is lost by leaching.

141. **Movements of Dissolved Substances.**—Having discussed how plant foods are made soluble and how they are retained in the soil after being made soluble, the question naturally arises as to how the compounds in solution move from place to place. That plant foods do move is obvious, for they are lost from soils in the drainage water and eventually are deposited in the ocean; and again they move upward, for incrustations of salts which have been lifted by the water appear on the surface of soils in arid countries.

Movement of plant food in the soil takes place in two ways: First, by the movement of water; second, by diffusion.

(*a*) MOVEMENT BY WATER.—Water moves in the soil in two ways to affect substances in solution, by gravity and by capillarity, or more properly by surface tension. When the saturation point of soils is reached, water responds to the pull of gravity which carries it downward through the pore spaces and channels in the soil. This bodily movement of water carries with it the substances in solution which are not absorbed as they go. The water may go directly down in a vertical direction or more nearly horizontally if anything like an impervious subsoil or entrapped air deflects its course. Gravitational movements cease as soon as the excess water drains off and the surface tension overcomes the pull of gravity. It is by this movement that soils lose plant foods which are not absorbed.

The surface of a liquid acts as if it exerted at all times a certain tension or pressure on the liquid below. If a drop of liquid is free to take any position, it assumes the spherical form in which the surface tension is uniform throughout, that is, it is in equilibrium. When the surface of a liquid is forced to assume various shapes, as in the case of film water covering soil particles, there is exerted an unequal tension. The more curved the surface the greater the tension. In a soil the surfaces at the top are more curved than they are lower down where the films are thicker. This means that the pull of the surface tension at the top will tend to raise water until the gravity pull balances the tension pull. As water evaporates, or plant roots absorb it, the increasing tension due to thinner films and consequent greater curvatures, draws up more water. This movement of water, of course, carries with it dissolved plant food. Theoretically this movement can take place in any direction and does under some circumstances, but under ordinary circumstances the increasing surface tension occurs on top of the soil due to evaporation, and hence the water movement is upward.

(*b*) Movement by Diffusion.—It is a property of substances, or rather of the molecules of such substances in solution, to move within the solvent from a region of greater concentration to one of less concentration in that particular compound. That is, sodium nitrate, for example, tends to move from that portion of the soil moisture where its concentration is considerable to other portions where there is little or no sodium nitrate. This movement is called diffusion, and may take place in any direction. Within the soil liquid, however, there is opposed to diffusion absorption both chemical and physical. Moreover the bodily movement of water due to gravity or to surface tension neutralizes the effect of diffusion in many cases.

As a matter of fact diffusion in soils does not play a very important part. Movements of plant foods in solution take place for the most part in a general direction up and down; up by surface tension, down by gravity, and are due to bodily movements of water containing the plant foods. Experiments have repeatedly demonstrated that plant foods in the form of soluble fertilizers show no effect laterally within a very short distance from the point of application. That is, the plant foods apparently get no chance to diffuse, for if they did the diffusion would be in every direction away from the point of application and the effect would be shown laterally from the fertilizers.

142. **Composition of Soil Water.**—From the preceding sections it has been seen what compounds exist in a soluble form in the soil moisture; how they may be soluble part of the time and insoluble part of the time, due to chemical change. The conditions affecting these various changes have been studied. In addition to this information it may be interesting to know how much soluble plant food material there is in soils. Soil water which contains the soluble compounds may be divided into two classes for convenience of study: Film water and drainage water.

(*a*) FILM WATER is the liquid in the soil which surrounds the soil grains with a thin film, and which furnishes plants with their foods. It bathes the plant roots with their nutrient fluid. Determining the amount of soluble material in this film water is a matter of great difficulty, and the results so far obtained can be considered only as roughly approximate, and even then represent but a few soils. However, it can be said that the following figures show the parts per million in a solution that probably is not far from an average soil solution:

N_2O_5	P_2O_5	K_2O	CaO
3	6	33	33

These figures have been calculated from data published by the Bureau of Soils. They show that at any one time phosphorous compounds and nitrates are present in considerably less quantity than are potash and lime. It is true that these two elements, nitrogen and phosphorus, are usually the limiting essential elements in crop production, as this might indicate; but on the other hand, if these concentrations are maintained throughout the growing season there will be enough of these foods supplied to nourish the crop. It is not at all probable that this same concentration is maintained in all soils and at all times. In fact quite the contrary. The amount of material in the film water must

Fig. 38.—Waste water. Outlet of drain tile. (Elliott.)

vary from day to day and from soil to soil, depending on daily temperature and moisture content, soil composition, texture and structure, amount of organic matter, character of the solvent, whether rich or poor in carbon dioxide and organic acids. The figures given, however, show only what have been obtained by very laborious methods from a few soils, and give an idea of the amount of concentration.

(*b*) WASTE WATER is the excess water which flows away from the soil as drainage or river water. Table IX gives average analyses of these two kinds of waste water. Drainage water is that which has been obtained from drains under cropped fields and represents that which comes directly from the soil after having passed through the soil and subsoil (Fig. 38). River water is that which flows into the sea and has travelled for long distances from its sources, being subjected to many changes after passing through the soil.

TABLE IX.—COMPOSITION OF DRAINAGE AND RIVER WATERS.

Expressed in parts per million.

(Averages of numerous analyses except N_2O_5 in the case of drainage water, which is from Rothamsted figures. There are not many analyses on this constituent.)

		Drainage.	Rivers.
Potash	K_2O	3.2	2.4
Soda	Na_2O	15.1	7.1
Lime	CaO	107.6	43.2
Magnesia	MgO	16.3	14.7
Silica	SiO_2	8.5	16.4
Carbon dioxide	CO_2	74.4	46.0
Phosphoric acid	P_2O_5	0.5	0.3
Sulphuric acid	SO_3	60.8	8.0
Chlorine	Cl	17.7	3.7
Organic matter	....	37.4	16.4
Nitric acid	N_2O_5	15.0	3.8
Total solids	....	352.6	168.6

Since the figures given for film water do not represent as many types of soil as those in Table IX, comparison between them is hardly feasible. Contrasting drainage water with river water it is to be noted that in practically every case the latter contains less of the various constituents. This is, of course, to be expected, for after the drainage water has entered an open stream and travelled considerable distances much of the soluble material is desposited. Aëration, for example, frees carbon dioxide from the solution and precipitates calcium carbonate and magnesium carbonate. Inter-reactions of bases and acids with new compounds remove many substances. Dilution of water charged with soluble material by fairly pure water reduces the concentration.

Taking up drainage water alone, it is very noticeable that potash is present in small quantities, whereas lime is present in considerable amounts; and it will be remembered (Section 138) that potassium is absorbed to a much greater extent than calcium. Soda and magnesia are present in nearly equal quantities. The acid radicles in the order of increasing amounts are P_2O_5, SiO_2, Cl, SO_3, and CO_2, with N_2O_5 probably about equal to Cl. Nitric acid, as nitrates, of course, will be present in widely varying amounts, probably more widely than any other radicle, acid or basic, and hence an average figure does not mean much. This arrangement indicates that most of the salts in solution are calcium and magnesium bicarbonates and sulphates, sodium chloride, some silicates of the alkalies, and nitrates of different bases.

It may be said for nitrates that although the nitric acid radicle is the least absorbed of all, there is not such a great loss of it from ordinary soils as might be expected. Rapid growth of crops at the time when nitrates are formed in greatest amount, and lack of moisture for nitrification later in the season when crop growth practically ceases, are two factors which tend to prevent loss of nitrates. The practice of fallowing, which fortunately is not very common nowadays, always results in a heavy loss of nitrates. Conditions are ideal for nitrification and there are no crops to remove the nitrates.

Bicarbonates and sulphates of calcium and magnesium, present in largest amounts in drainage water, are what ordinarily make water "hard," although any soluble substance may be responsible for this condition. The hardness of the water depends, of course, on the nature of the soil drained. A limestone country yields a very hard water. The bicarbonates of calcium and magnesium give a water "temporary" hardness, because they decompose easily on aëration or boiling and precipitate the carbonates. The sulphates of calcium and magnesium give water "permanent" hardness, since they are not so easily precipitated.

Of course in the case of drainage and river waters there is a very wide variation in the content of dissolved material, just as there is in the film water. A granitic or sandy country will yield water that is very "soft" or almost pure, whereas a limestone country gives just the opposite. Take two fresh water lakes in Wisconsin, for example. One—Devil's Lake—receives the drainage from a granitic region, the other—Lake Mendota—receives that from a limestone country. Table X gives the analyses of both lakes.

Table X.—Composition of Lakes.

(Expressed in parts per million.)

	SiO_2	Fe_2O_3 Al_2O_3	CaO	MgO	SO_3	Cl
Lake Mendota	1.1	0.8	40.1	42.3	10.3	2.0
Devil's Lake	2.2	0.6	4.5	1.8	6.7	8.2

143. **Soil-forming Rocks.**—To obtain some idea of the composition of a soil, it is necessary to know something of the rocks from which the soil is derived. Rocks are mineral aggregates, that is, they are composed of two or more minerals welded together either by heat or pressure. They are classified as *igneous,* formed by the cooling of molten masses; *sedimentary,* laid down by water; and *metamorphic,* changed by heat and pressure from their original forms. Knowing the rocks in a general way will give an idea of the minerals to be expected in a soil derived from any given rock, and also the character of the compounds resulting therefrom. This applies, of course, only to soils in place. Soils that have been transported by water have been sorted more or less according to the specific gravity of their various constituents and therefore do not contain all of their original minerals. It is impossible to describe all of the rocks or even the common rocks from which soils are derived, but it may suffice to mention a few characteristic soil-forming rocks.

(*a*) Granite.—(Fig. 39). This is one of the most common igneous rocks and many soils are derived from it. It is usually composed of quartz, feldspar, mica, and hornblende.

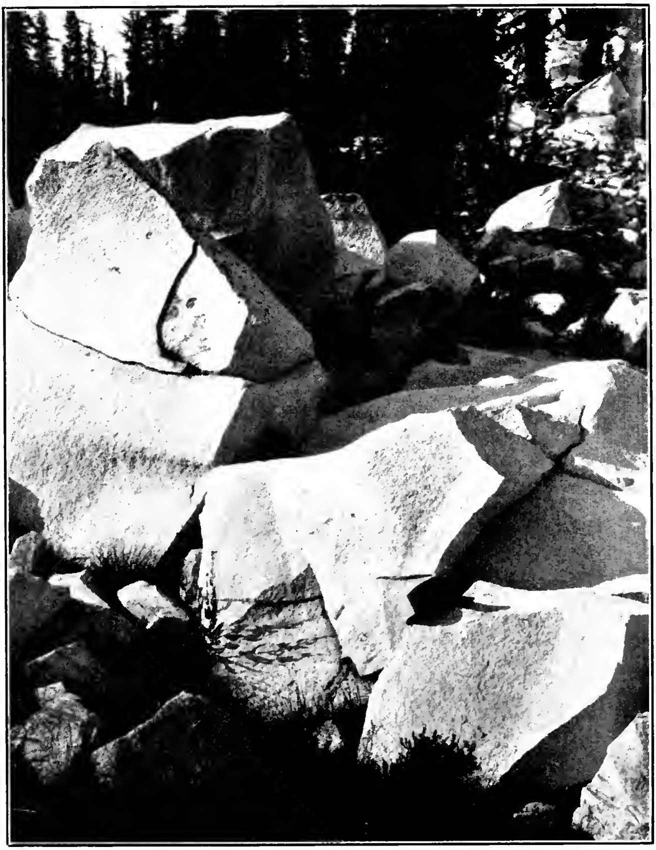


Fig. 39.—Soil-forming rock: Granite. United States Geological Survey.

The action of water, heat, and cold serve to break it down into small particles. Aided by the chemical action of water and carbon dioxide the feldspar changes in part to kaolinite and silica, or clay and potassium carbonate. Mica slowly changes to clay and carbonates of the alkalies. Hornblende forms hydrated oxides of iron and aluminium, clay, and carbonates of calcium and magnesium. Quartz changes but little except as to size of particles, these becoming small grains which form sand.

If the decomposed material is not disturbed it forms a soil of excellent texture and good composition. Apatite occurs very commonly disseminated in small crystals throughout granite, and supplies phosphorus to such a soil. All the other essential elements are present. Sorted by water, however, it separates into sand and clay soils with most of the plant foods in the clay.

(*b*) BASALTS AND LAVAS form soils which may be very sandy and barren, when silica predominates with only calcium, magnesium, and aluminium for bases; or form good soils, when bases predominate, which include potassium.

(*c*) LIMESTONE ROCKS consist for the most part of calcium carbonate (and magnesium carbonate) which is leached out very completely by the action of water and carbon dioxide (Fig. 40). There is left to form soil only a very small percentage of impurities in the form of clay. Limestone is laid down far out at sea in deep water, and there is entangled with it the finer and lighter particles of clay which have been washed out into the sea by rivers. This clayey impurity which forms soil from limestone may have been derived from granite, in which case it would be fairly rich in plant food. It may have been derived from barren basalts, in which case it would be very poor. As a rule, however, limestone soils are rich, except that they may be lacking in calcium carbonate. At first thought it seems strange that limestone soils are apt to be lacking in calcium carbonate. But soil is derived from limestone only by the solution and removal of calcium carbonate, soil material being only the impurities present in the limestone rock. Calcium carbonate is on the whole very soluble in soil water, compared to other rock constituents. Moreover, the particles composing the clay are for the most part decomposition products of silicates which may have originally contained calcium, but which have lost a large part of this constituent during decomposition.

Of course, there may be particles of limestone and calcium-containing silicates left in the soil, and these serve as sources of calcium for a time, but nevertheless, limestone soils are among the first to become acid, due to lack of calcium carbonate.

FIG. 40.—Soil-forming rock: Limestone. United States Geological Survey.

(*d*) SANDSTONES AND SHALES form sandy and clayey soils, respectively, containing more or less plant food according to their original composition and derivation, for they are secondary rocks derived from decomposition products of others. Sandstones are more apt to yield poor soils unless it happens that the binding material is of a clayey nature.

144. **Kinds of Soil.**—The number of different kinds of soil is necessarily very great, and any attempt to classify them is a very considerable undertaking. Ordinarily they are divided according to their geological origin, but they may

be classified on the basis of physical composition or of chemical composition. It is not the place here to discuss soil types and characteristics in detail, but it may be of some help to briefly discuss general soil classifications, using as a basis merely the common terms which are familiar to every farmer, and not trying to adhere rigidly to some technical basis which is of value only to the soil expert. The chemical properties of soils in every case will form the basis of the discussion. They can be discussed as: (*a*) Arid and humid soils, which will distinguish in a general way those soils which are located, on the one hand, where very little rain falls, and on the other hand, where sufficient rain falls; (*b*) sand, clay, loam, muck, and peat, names which are very commonly used and which depend on physical and chemical characteristics; (*c*) soil and subsoil, terms sufficiently plain; (*d*) alkali soils or special soils that are very important in certain arid regions of the United States particularly—an extreme type of arid soil.

(*a*) Arid and Humid Soils.—The principal chemical differences between soils in an arid or dry region and those in a humid or moist region is in the amount of available or soluble plant food. In a humid climate the soil is continually subject to leaching and fixation of soluble compounds. Decomposition takes place as indicated in Section 135. In a region of little rain, the plant food made soluble by decomposition remains in the soil for the most part as such. Decomposition of rocks takes place largely by the action of sudden extremes of heat and cold, and not to a very great extent by the solvent action of soil moisture. As a result arid soils are not only pulverulent and sandy in texture, but the soluble compounds which are formed remain in the soil. Little clay is formed from feldspars, because of lack of water for hydration. This means a coarse textured soil, as mentioned above. In other words kaolinization is not marked in arid regions. Since there is little leaching, calcium carbonate derived from limestone, or from silicate rocks by slow decomposition, is not removed from the soil and exerts its flocculent effect on what little clay is formed. Arid soils are more fertile as a rule than humid soils if water can be supplied and maintained. Fig. 41 shows the method of supplying water to such soils. The lack of organic matter is a serious drawback in arid soils, for it is easily "burned out." Decomposition is very rapid, for the pulverulent soils are naturally well aërated.

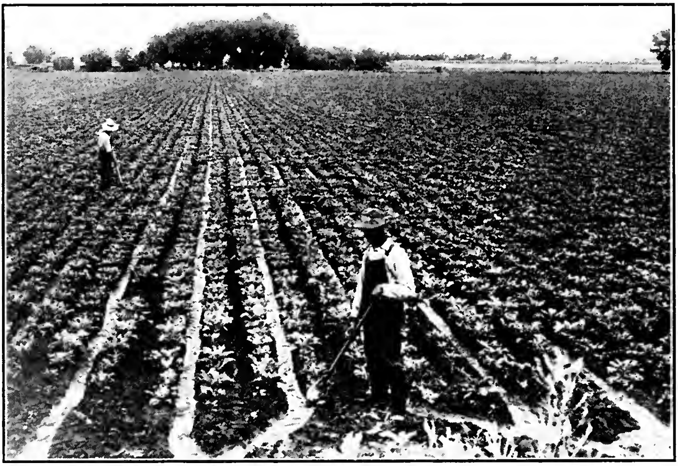


Fig. 41.—Arid soil under irrigation. Sugar beets.

(*b*) 1. *Sand Soils.*—The term sand is based on size of soil particles and not on chemical composition, although from the nature of its formation there is usually a distinct chemical composition. Technically a sand soil consists of any coarse material whether composed of pieces of lava, coral, shell, or pure quartz. Since in humid regions, however, sands are derived by the action of water and carbon dioxide on rocks containing quartz, such soils are composed largely of silica, SiO_2, since this is the least soluble of any of the ordinary minerals, and breaks up slowly largely by physical agencies. There are present in addition pieces of feldspar, mica, and hornblende. As a rule sandy soils do not contain much organic matter for the reason given above—they are too well aërated. Fig. 42 shows the effect of organic matter on such soils. In humid regions the grains are rounded from the rolling due to water movements. In arid regions the grains are angular and of any sort of material, not necessarily of silica.

FIG. 42.—Sand soil. Organic matter applied to plat on the left. Soils Department, Wisconsin Station.

2. *Clay Soils.*—Like the term sand, clay in soil nomenclature refers to size of particles, and is applied to soils, or that portion of soils, having the very finest particles, regardless of composition. It has been truly said that clay is either rock rot or rock flour. In the former case, and that is the common occurrence, clay is derived from silicate rocks by the decomposing action of water and carbon dioxide. It is largely hydrated aluminium silicate. In the latter case clay is merely very finely ground rock material made by the action of glaciers, for example, and the composition will depend on the kind of rock ground up.

3. *Loam Soils.*—The term loam does not mean much scientifically, but popularly it is a term applied to soils of good texture and well supplied with organic matter. They are sand or clay loams as they have more or less of the qualifying constituent. Their chemical composition is very general in nature.

4. *Peat Soils.*—These are composed for the most part of organic matter but little decomposed (Fig. 43). The tissue of the plants of which they are composed is still plainly distinguishable. Unless these soils are in a limestone region decomposition results in the production of a considerable degree of acidity. The mineral matter present frequently amounts to no more than 10 or 15 per cent.

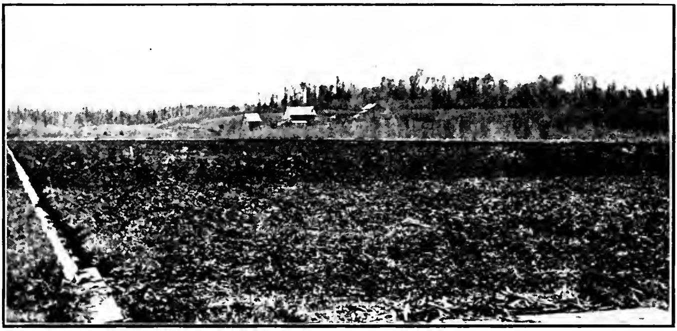


Fig. 43.—Peat soil. Soils Department, Wisconsin Station.

5. *Muck Soils.*—These are soils containing large amounts of organic matter, but which are in a more advanced state of decomposition than peats. Plant tissue is quite indistinguishable and there is very much more mineral matter present.

6. *General Composition.*—Table XI gives the approximate composition of sand, clay, muck, and peat soils in three principal constituents, nitrogen, phosphoric acid, and potash. The figures, while not applicable in every case, will at least give an idea of relative differences as they very commonly occur. The weight of the surface eight inches of sand is taken at 2,500,000 pounds, of clay at 2,000,000, of muck at 1,000,000, and of peat at 350,000.

Table XI.—Composition of General Soil Types.

Soil.	Per cent. N.	Pounds per acre.	Per cent. P_2O_5.	Pounds per acre.	Per cent. K_2O.	Pounds per acre.
Sand . .	0.05	1250	0.01	250	1.5	37,500
Clay . .	0.15	3000	0.15	3000	2.0	40,000
Peat . .	2.50	8750	0.25	875	0.5	1,750
Muck . .	0.30	3000	0.30	3000	1.5	15,000

(*c*) Soil and Subsoil.—In humid regions there is a considerable difference between the soil and the subsoil. The most striking contrast is in the amount of organic matter. In fact a common way of distinguishing between them is to note the dividing line between the dark soil and the light subsoil. It is frequently very sharply defined. This means of course that there is more nitrogen in the soil than in the subsoil. In addition there is found ordinarily more phosphoric acid and total lime in the soil than in the subsoil. There is, however, less potash, ferric and aluminium oxides, and calcium carbonate. The finer clay particles are washed down into the subsoil, which results in finer textured subsoils than soils. This fact also accounts for the greater amount of potash, ferric and aluminium oxides, and calcium carbonate in the subsoil, since these constituents are more rapidly weathered on the surface and washed into the subsoil, where they are fixed. In the soil there are more bacteria and bacterial food—organic matter—consequently there are more organic acids and carbon dioxide. The latter makes a stronger reagent of soil moisture and as a result greater availability of plant food. Being more open and porous and of better texture than subsoil, the soil is in better physical condition for crop growth. Aëration being better, all compounds are in a higher state of oxidation, iron, for example, is all in the ferric form. This is not always the case in subsoils. Iron may be in the ferrous form, and such compounds as ferrous sulphate which may be derived from the imperfect oxidation of iron sulphide or pyrites, are poisonous to plants. It very often happens that when too much subsoil has been turned up in plowing the crop is very poor. This may be due to ferrous salts, to poor texture —too compact and badly aërated—to lack of organic matter. This latter lack reduces the rate of availability of plant foods.

In arid regions there is very little difference between soil and subsoil. Organic matter extends to considerable depths, due to deep root penetration. There is no sharp, dividing line. The texture is the same throughout, lack of water causing little clay formation, and the soils are pulverulent all the way down. Weathering is uniform and production of water-soluble material is uniform. The subsoil will raise just as good crops as the soil. In many places material thrown out in excavating for the cellar of a house makes just as good a garden as the top soil.

(*d*) ALKALI SOILS.—In certain parts of the arid west, as well as of other arid regions of the world, there exist patches of so-called alkali soil (Fig. 44). They are usually barren of vegetation and are covered with white or black incrustations of soluble salts. The white salts are called "white alkali" and the black salts "black alkali." Chemically the white salts are not alkaline in character but consist largely of sodium chloride and sodium sulphate with some chlorides and sulphates of calcium and magnesium. "Black alkali" is composed largely of sodium carbonate, the solution of which dissolves from the soil through which it has passed some of the humus, thus coloring the evaporated salts black.

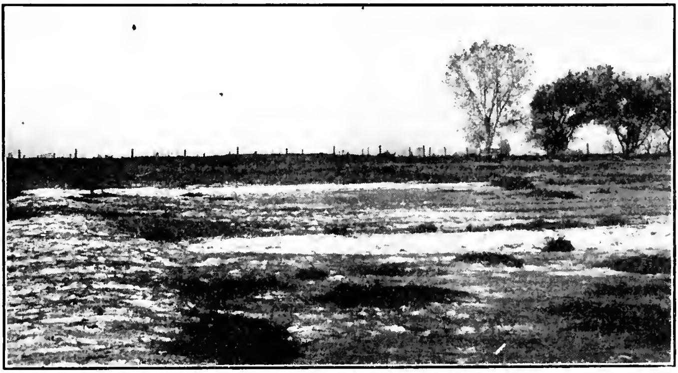


FIG. 44.—Alkali soil, showing patches of white alkali. Agronomy Department, California Station.

As was noticed in Section 144 (*a*), the soluble salts formed by decomposition of the minerals are not leached out of arid soils, and under normal conditions are spread throughout the soil and subsoil in amounts not at all injurious to plants; but when there arise conditions which permit the accumulation of a large quantity of soluble salts in one spot, then the "rise of alkali," as it is called, begins. For example, steady drainage of soluble salts from a higher region to a lower, with insufficient water to completely remove the salts in the drainage water, results in the accumulation of salts in the lower area. Where irrigation is practiced and there is used water heavily charged with salts, but not enough water to remove the salts into the country drainage, an accumulation is apt to occur. And where excessive amounts of water are used for irrigation in lands not properly provided with underdrainage, the rising water table dissolves out the soluble salts in the subsoil and brings them within capillary reach of the surface.

In any case the salts in solution in the soil water rise to the surface by capillarity and are left there by the evaporation of the water. A rain dissolves them and carries them into the soil for a greater or less distance depending on the amount of rainfall, and they return to the surface when surface tension is again established.

Many different kinds of compounds are made soluble by the decomposition of rocks, but in passing through considerable portions of soil, chemical absorption plays an important selective part. As was seen in Section 133, potassium and magnesium are retained more than sodium and calcium. Phosphates are easily retained in an insoluble form, carbonates, sulphates, chlorides less easily. As a result it is to be expected that chlorides, sulphates, and carbonates of not easily fixed bases will predominate in alkali soils, and the chloride, sulphate, and carbonate of sodium, sulphates of calcium and magnesium, and some chlorides of calcium and magnesium prevail in such soils.

White alkali is not so injurious to vegetation as black alkali, sodium sulphate being the least injurious, but both kinds are very troublesome to farmers in some arid regions. In addition to the harmful effects on crops, black alkali or sodium carbonate has the puddling effect on soils common to most alkaline solutions. Limiting strengths of these salts in sandy loam soil for cereals have been found to be about 0.1 per cent. of sodium carbonate, 0.25 per cent.

for sodium chloride, and 0.5 per cent. for sodium sulphate. On clay soils this tolerance is less. Crops vary in their ability to withstand the alkali, alfalfa, sugar beets, and radishes being better able to withstand it than the grains and celery.

Methods of reclaiming alkali soils are for the most part a matter of rotation, culture, the growing of resistant crops, prevention of evaporation, flooding, and underdrainage. Black alkali can be remedied by the application of gypsum or land plaster. This reacts with the sodium carbonate to form calcium carbonate and sodium sulphate, the former harmless and the latter relatively so.

145. **Summary.**—With the exception of nitrogen, the plant food elements are derived from mineral particles in the soil, and besides the decomposition products of organic matter, the gases in the soil have a solvent effect on these mineral particles. The composition of soil gases is somewhat different from that of the air, in that oxygen varies from 10 to 20 per cent. and carbon dioxide from 11 to 1 per cent. As oxygen is used up, carbon dioxide is evolved. Methane and hydrogen sulphide are also present, due to anaërobic decomposition of organic matter, but not to any great extent. Carbon dioxide and oxygen are the most important gases which serve as solvents for the minerals. Soil solvents, besides carbonic acid and oxygen in solution, are organic acids, inorganic acids, and soluble salts.

Phosphoric acid is made soluble by the action of water and carbon dioxide on apatite, or on tricalcium phosphate derived from it. Potash is made soluble by the action of water and carbon dioxide on orthoclase feldspar, producing at the same time kaolinite which is a hydrated aluminium silicate. The latter forms the basis of clay. Water and carbon dioxide also render soluble some potash from mica. Calcium is derived from limestone or dolomite, being dissolved in the form of the bicarbonate by the action of water and carbon dioxide. Limonite is a source of iron. Quartz is an important constituent of all soils, being the basis of sand, although, of course, it does not contain an essential element.

The soil minerals do not dissolve as completely and easily as the above statements might indicate. Reactions in the soil are never complete and while potash, for example, may continually dissolve from feldspar it is never completely decomposed. Intermediate compounds are formed. Temperature affects the solubility of soil minerals. The higher the temperature, the more active the decomposition, except in the case of carbon dioxide, which is less soluble in warm water than in cold water. Some minerals decompose very readily; others are more resistant to the action of soil solvents.

Plant food which is rendered soluble is not altogether leached out of the soil, but is retained by a process called absorption. This process may be either chemical or physical in nature. Chemical absorption is that which takes place because of a chemical reaction, and results in the formation of an insoluble compound. Sometimes the reaction consists merely of an exchange of bases by an insoluble compound and a soluble compound. At other times it consists of a reaction between two soluble compounds, resulting in precipitation. Referring to the first instance it is to be noted that, other things being equal, bases vary in their ability to replace one another. Potassium and magnesium, for example, will replace sodium and calcium. Very frequently reactions which result in the formation of an insoluble compound are the exact reverse of a reaction which results in the formation of a soluble compound, and this is due to the law of mass action, which states that the direction of a reaction depends on the active mass of the reacting substances. Reactions proceed in one way or another until the reacting masses balance one another. This equilibrium, however, is never accomplished in a soil, for the chemistry of soils is essentially dynamic in nature.

Soluble compounds in the soil are retained by physical absorption because of an attraction which exists between the surfaces of certain solids and substances in solution. This attraction results in a greater concentration of dissolved material immediately about the surfaces of solids. Physical absorption or adsorption, as it is termed, depends on the surfaces of the solids exposed and on the composition of the solids and of the dissolved substances. Adsorbed materials are available to plant roots, whereas chemically absorbed substances are not.

Plant foods move up and down for the most part in the soil, due to the force of gravity which pulls water down and to the force of surface tension which pulls water up. Diffusion is a phenomenon which affects dissolved substances in soil to a very slight extent.

Soil water may be divided into two classes: Film water, or the liquid which surrounds the soil grains and furnishes plants with food; and waste water, or water which drains away from soils. The composition of film water is not easily obtained, but to give some idea of its strength it may be stated that it varies from 3 to 33 parts per million of plant food material, containing more potash and lime than it does phosphoric acid and nitrogen. Drainage water is considerably higher in calcium and magnesium bicarbonates and sulphates, sodium chloride, and nitrates, than in any other constituents. The presence of bicarbonates and sulphates of calcium and magnesium make water "hard," the former imparting what is called "temporary" hardness because the bicarbonates are precipitated as carbonates on boiling. The latter give water what is called "permanent" hardness because the sulphates are not readily precipitated.

To obtain some idea of the minerals in a soil it is advantageous to know something of the rocks from which they are derived. Granite is one of the most common igneous rocks and is a source of many soils. It is composed of quartz, feldspar, mica, and hornblende. On decomposition it results in a soil of good texture and excellent chemical composition, containing all the plant food elements, including phosphorus which is derived from apatite disseminated in small particles throughout the granite. Limestone rocks yield light clay soils of excellent composition, but they are lacking in calcium carbonate. Sandstones and shales form sandy and clayey soils of various compositions.

Considering the different kinds of soils it may be briefly mentioned that the difference between arid and humid soils lies in the fact that lack of water in arid regions results in rock decomposition products which do not contain kaolinite or the basis of clay; kaolinite being essentially a hydrated mineral. Soluble plant food is not leached, and the soils are of good texture, needing only water for maximum production. Humid soils on the other hand are produced largely by the action of water and may contain considerable quantities of clay, with not so great an amount of soluble plant food material. Sand soils are composed of coarse particles of rock, usually of silica, but not necessarily so. They are not very fertile and do not contain very much organic matter. Clay soils consist of very fine particles of rock, largely of kaolinite. Their composition ordinarily is much better than that of sand. Loam soils are popularly soils which are of good texture and well supplied with organic matter. Peat soils consist of the undecomposed remains of organic matter and but little mineral matter. Muck soils contain less organic matter and are generally somewhat more fertile. In humid regions there is considerable difference between the soil and the subsoil. There is more organic matter, nitrogen, phosphoric acid, and total lime in the soil than in the subsoil. The other common constituents occur to a greater extent in subsoils. In arid regions there is but little difference between the soil and the subsoil. Soil is more open and porous, organic matter is distributed to a greater depth, aëration is more uniform, and the compounds are in a higher state of oxidation in the subsoils of this region than in those of the humid region. Alkali soils are those which contain excessive amounts of soluble salts. "White alkali" consists largely of sodium chloride, sodium sulphate, with some chlorides and sulphates of calcium and magnesium. "Black alkali" is partly sodium carbonate, a solution of which dissolves humus from the soil and colors the salts black. White alkali is not so injurious to vegetation as is black alkali.

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See references at end of Chapter VI.

CHAPTER VIII

FERTILIZERS

It frequently happens that soils lose their ability to raise good crops. They no longer continue to produce the high yields which are characteristic of soils functioning properly in accordance with the facts stated in the last two chapters. This failure in fertility may be due to several causes: Poor drainage, exceptionally bad climatic conditions, insufficient water, poor seed, bad physical condition, presence of fungous diseases, not enough organic matter, and lack of available plant food. Most of the conditions can be remedied by the farmer. The climatic factor is one not to be controlled except that a dry condition may be overcome by irrigation where a source of water is convenient and it is possible to ditch the land. All other factors can be supplied. In this discussion of the chemical phase of soil fertility only one factor can be considered, namely, the supply of plant food, available or total.

146. **Plant Food in the Soil.**—When it is a question of unavailable plant food, attention to such things as cultivation and the supply of organic matter will frequently remedy the deficiency; but where these factors are insufficient, or where plant foods are actually lacking, then it becomes necessary to add them to the soil.

From Table III, p. 114, showing the number of pounds of nitrogen, phosphoric acid, and potash removed from an acre by various crops, it can readily be seen that there is a steady drain on the reserve food supply in the soil, and no compensative natural return. In the case of nitrogen there is an addition of possibly 40 to 60 pounds of nitrogen in the roots and stubble of one legume crop. This is in excess of the amount removed from the soil and illustrates very forcibly the necessity of growing a legume in the rotation. And yet, compared to the total amount of nitrogen removed in the other crops of a rotation, this is inadequate to make up the loss—40 to 60 pounds returned, and 100 to 150 pounds removed.

There may be added to the soil of one field more or less fine soil blown from an adjoining field or roadway. This, of course, adds some plant food such as potash and phosphoric acid, but it is at best only "robbing Peter to pay Paul," since this plant food may in turn be lost to the next field in the same way. There is, of course, some plant food brought to the surface soil by the rise of capillary or film water, and the decay of roots and stubble may add plant food which has been brought up from the subsoil by deeply penetrating roots. But analyses show very conclusively that a long period of cropping reduces all the plant food elements. As much as one-third to one-half of the amount contained in the virgin soil has been found to disappear during 50 to 60 years of cropping with no return in the way of manure or fertilizers.

It is a well-recognized fact among farmers who have the experience of centuries to guide them that if plant food is removed it must be returned. F. H. King in his "Farmers of Forty Centuries" states that to each acre of the 20,000 square miles of cultivated land in Japan there is added annually 60 pounds of nitrogen, 32 pounds of phosphoric acid, and 48 pounds of potash. These people have been farming for centuries and are still maintaining the fertility of their soil only by a most rigorous return to the soil of the plant food elements removed.

These facts all show that sooner or later plant food must be added to the soil.

147. **Definition of Fertilizers.**—The term fertilizer is applied not only to a compound which supplies a plant food to the soil, but also to a compound which has other functions in the soil, such as neutralizing acidity, making potash available, etc. Hence, fertilizers may be defined as compounds which are added to the soil to increase the yield of crops—to increase the fertility of the soil.

148. **Direct Fertilizers.**—Compounds which supply plant food to the soil and thus have a direct action on plant growth are called direct fertilizers, and are usually compounds containing nitrogen, phosphoric acid, or potash which are the three elements most commonly lacking in soils, either because of low total content like nitrogen and phosphoric acid, or because of unavailability like potash. The addition of the other essential elements is rarely necessary, with the exception of calcium.

149. **Indirect Fertilizers or Amendments.** — Compounds which are not added primarily to supply plant food, but which cause some other plant food to become available, and which correct a harmful condition in the soil, or act as a stimulant to plant growth by other causes than merely nutritive, are called indirect fertilizers or amendments. Calcium in various forms is usually called an indirect fertilizer, although as noted in Chapter XII, calcium may frequently serve as a plant food. Sodium chloride, manganese salts, and sulphur, are all classed as indirect fertilizers or amendments.

150. **Commercial Fertilizers.**—Under this head come all those fertilizers which the farmer buys—compounds which are of great commercial importance. Compounds which are produced on the farm, such as barnyard manure or green-crop manures, are not rated as commercial fertilizers.

151. **Complete Fertilizers.**—A complete fertilizer is one which contains nitrogen, phosphoric acid, and potash. These three elements are the only ones which the farmer needs to consider as being necessary to purchase for plant food. Nitrogen and phosphoric acid exist in soils in very small amounts and are hence very likely to be lacking in sufficient quantity to nourish crops. Potassium on the other hand is rarely lacking, but is very frequently present in such unavailable form that plants cannot obtain enough for normal growth. Of the other essential elements, none is ever actually lacking in soil for the nutrition of the plant, except calcium. But since calcium is usually referred to as a soil amendment or indirect fertilizer, discussion of this element as a plant food will be postponed.

In preparing a complete fertilizer for the market the manufacturer makes use of various compounds of nitrogen, phosphoric acid, and potash in forms that are immediately soluble, or will become soluble very quickly. The farmer wants quick returns from his fertilizer and hence the various ingredients must be readily available. Chapters IX, X, and XI give the various sources of the individual elements. An almost infinite number of combinations of the different constituents can be made and the manufacturer uses many of them, with phosphoric acid, however, predominating in most of the fertilizers. In making the so-called high grade fertilizers only compounds containing the maximum amount of nitrogen, phosphoric acid, and potash are used, but even here it is not possible to manufacture a product containing very much of the essential elements. Few nitrogenous materials contain more than 15 per cent. nitrogen, or phosphate substances more than 16 to 18 per cent. available phosphoric acid, or potash compounds more than 50 per cent. potash. The rest of the product is worthless as a fertilizer, but its presence can not be helped, for it is obviously impossible to use elemental nitrogen, or phosphorus pentoxide, or potassium oxide in a fertilizer (cf. Section 209). In making low grade fertilizers, however, various diluents are used to reduce the percentage composition; diluents, however, which are harmless in themselves, although of course valueless as fertilizers. These substances are gypsum, fine, dry soil, peat (which does contain a small amount of nitrogen, although not very available), sawdust, and other dry, cheap substances. Sometimes it is necessary to add these materials to a complete fertilizer to serve as driers, for some single fertilizer ingredients, like sodium nitrate and calcium nitrate, absorb water and make the mass sticky, or cause it to cake in hard lumps and hence render it unfit for drilling purposes.

152. **Incomplete Fertilizers.**—An incomplete fertilizer is one which contains only one or two of the above named three elements. Those containing only one are frequently referred to as *single fertilizers.*

153. **Home Mixing.**—It is not necessary for the farmer to purchase ready mixed goods. He may buy single ferti-

lizers and do his own mixing before application, or he may apply them singly to the soil. Each purchaser should decide for himself which way is the best for him. There are advantages and disadvantages in the use of either form. Ready mixed, complete fertilizers are easily purchased in any quantity, with a wide variety of combinations in nitrogen, phosphoric acid, and potash, and in a fine, dry condition which will run readily through a fertilizer drill. The mixture is uniform throughout. On the other hand, they are expensive and the farmer does not know what the various ingredients are. Particularly in the case of nitrogen, the farmer does not know the source. It may be readily available and it may not, although in a majority of cases it is in a reasonably soluble form.

Home mixed goods are cheaper, the farmer knows the source of his materials, and he can apply one element at a time or only those which are necessary, without adding plant food which is not needed in order to get that which is required. On the other hand, it is not always easy to get small amounts of the separate ingredients—and this is because the manufacturer prefers to sell the single ingredients in mixed form if possible. Again, it is not always easy to get a uniform mixture and this may result in uneven yields. And finally the mechanical condition may be such that the material can not be drilled, and even otherwise must be broken up before use. This is due to absorption of moisture as above indicated.

154. **Mixtures to be Avoided.**—In mixing fertilizers care must be taken not to put together two or more substances which will cause loss of plant food or conversion to an insoluble form. Lime in any form, or basic slag and basic calcium nitrate, both of which contain an excess of lime, or wood ashes, should not be mixed with ammonium sulphate, or with organic nitrogenous materials, for loss of ammonia would occur. The same compounds should not be mixed with acid phosphate because reversion to the insoluble form takes place and the fertilizer loses its immediate value.

Unless a mixture is to be used at once it is better not to mix the basic compounds named above with sodium nitrate or with potash salts, for the latter absorb moisture and the whole mass will harden to a solid mass which requires crushing before use.

155. **Choice of Fertilizers.**—In the following discussion of various fertilizers there are considered for the most part only their effects on the plant, the soil, and on each other. Their relative value as forms of plant food is considered only on these grounds. But it must be remembered by the farmer that the economical factor should enter into the choice of a fertilizer. As a matter of scientific fact one form of fertilizer may be better than another, but its cost may be greater than the increased benefits derived from its use. With a thorough knowledge of the several forms of each element, of the effects of each crop to be grown, of the soil, and of the cost, a farmer can decide for himself which is the best kind to use under the circumstances.

156. **Summary.**—Inasmuch as one of the vital factors in crop growth is the supply of plant food in an available form, it is necessary to maintain this supply by the addition of such elements as are removed most largely and exist in the soil in small or unavailable amounts. The principal plant food elements added to the soil ordinarily are nitrogen, phosphoric acid, potash, and calcium. Substances which supply plant food are called direct fertilizers; those which affect plant food reserves already in the soil, or improve the condition of the soil in other ways, are called indirect fertilizers or amendments.

Direct fertilizers may be obtained in the complete form where all plant food elements are mixed together, or as single fertilizers, containing only one plant food element. Fertilizers can be used singly or mixed at home. There are certain advantages and disadvantages either in buying ready mixed goods or single materials and mixing them afterward.

Lime and basic materials must not be mixed with nitrogenous compounds containing ammonia or with other forms of nitrogen readily convertible into ammonia. Neither should lime be mixed with acid phosphate, since an insoluble fertilizer results. In choosing a fertilizer the farmer must take into consideration not only the form of element to use, the crop to receive the fertilizer, and the kind of soil, but he must also consider the cost.

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CHAPTER IX

NITROGENOUS FERTILIZERS

Of the various plant foods which the farmer must buy, those containing nitrogen are the most expensive. Nitrogen has usually been considered the most important element in plant nutrition, and for several reasons: It exists in the soil in only small quantities, rarely more than 0.2 per cent. It is so important in the vegetative growth of plants that frequently nitrogen is the only fertilizing constituent needed to produce large yields. In other words, the increased growth of leaves and stems gives the plant more power to forage for the other elements in the soil and so produce a greater yield. It goes for the most part to the seed, and thus, in the case of grain crops, is one of the elements that is removed from the soil. It is used by plants to a greater extent than any other element. Finally, as mentioned above, it is the most expensive, although possibly the latter fact is a result, not a cause, of its importance.

As a matter of physiological fact, of course, no one element is more important than another. All the essential elements are equally necessary for the growth of the plant; some in larger amounts than others, it is true, but not more necessary. And yet, important as nitrogen is in many ways, it is the only element which can be returned to the soil by natural means, namely, by the agency of nitrogen-fixing bacteria on the roots of legumes (Section 130). Clover, alfalfa, or some other legume, is always a part of a good rotation system. So that after all, nitrogen, except for its high cost, is not the important element for the farmer to consider.

In taking up the different forms of nitrogen on the market it is convenient to classify them according to the form of chemical combination, and this order coincides with the solubility, and roughly with the availability of the nitrogen compounds.

I. NITROGEN AS NITRATE

157. **Sodium Nitrate,** $NaNO_3$.—The best known and most important of all the nitrogen fertilizers is sodium nitrate, or more commonly, nitrate of soda, or "Chile saltpeter." Saltpeter itself is potassium nitrate which is too expensive for ordinary use as a fertilizer, although on account of the fact that it contains both potassium and nitrogen it is a plant food of great value. Nitrate of soda is a salt similar to potassium nitrate in many of its properties, and because most of the world's supply comes from Chile, it has received the name of Chile saltpeter.

Fig. 45.—Gathering caliche.

(*a*) How Obtained.—The principal deposit of nitrate of soda lies on a plateau some 3000 feet above sea-level in a region where rain falls but once in two or three years. The crude salt, called "*caliche*" (Fig. 45), is found in masses which average about 3 feet thick. On top are strata of gravel and rock several feet thick. The rock is composed largely of sand and gypsum, while the caliche contains from 17 to 60 per cent. sodium nitrate mixed with various impurities such as sodium chloride, calcium, magnesium, and sodium sulphates, some iodates and perchlorates. Dynamite is used to loosen up the masses of caliche and to break up the overlying strata. From the mines the crude material is taken to the works where it is dissolved in hot water, transferred to evaporating tanks, and the sodium nitrate allowed to crystallize out (Fig. 46). It is then dried and sacked for shipment. As it comes on the market nitrate of soda is coarsely granular material, brown, gray, or pink in color and most of it is about 96 per cent. pure, containing in addition to sodium nitrate, some moisture, sodium chloride, calcium, magnesium, and sodium sulphates. The nitrogen content is nearly 16 per cent.

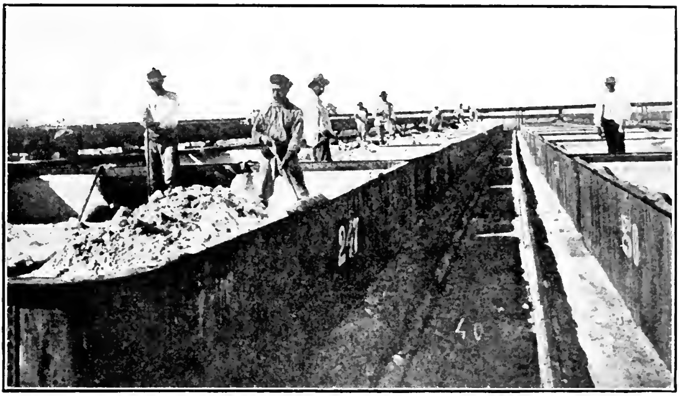


FIG. 46.—Nitrate of soda in crystallizing pans.

(*b*) AVAILABILITY.—Since nitrate of soda is very soluble, one part dissolving in about one part of water, and, moreover, since its nitrogen is in the form which plants require, it is an immediately available fertilizer. In addition to its being very soluble it is not fixed or retained by the soil to any extent, and is therefore easily lost by leaching. Consequently applications of sodium nitrate should be made a very short time before seeding, or as a top dressing.

(*c*) EFFECT ON THE SOIL.—In the soil sodium nitrate serves as an indirect fertilizer in that it reacts with insoluble potassium compounds, making the potassium soluble. Experiments have shown that sodium nitrate in this way takes the place of a potash fertilizer, in addition to supplying nitrogen to the crop. Another effect of sodium nitrate in the soil is to puddle heavy soils, if used continuously. This is because plants absorb more of the nitrate radicle than they do of the sodium. The latter unites with carbon dioxide in the soil forming sodium carbonate which deflocculates clay particles, giving the soil a very poor physical texture. This fact of its leaving a residue of sodium carbonate in the soil, however, makes sodium nitrate a valuable fertilizer on acid soils, and thus saves the calcium carbonate by supplying an additional base.

158. **Calcium Nitrate.**—Some years ago when it was thought that the Chilean nitrate beds were in serious danger of rapid exhaustion, attention was directed to methods of combining the nitrogen of the air with other elements, and so to ward off inevitable destruction when no more nitrate was to be procured! Although such a danger was very much overrated it served the purpose of stimulating invention and producing competitors for the sodium nitrate industry, a fact which will tend to keep down the price of this fertilizer, now altogether too high.

(*a*) HOW MADE.—It has been known for over a century that nitrogen and oxygen would unite if heated to a sufficiently high temperature, as by an electric spark. This fact is made use of commercially in Norway where a number of compounds of nitrogen are being manufactured, principally calcium nitrate and basic calcium nitrate. The union of nitrogen with oxygen is accomplished in a circular furnace in which the combustion chamber is an inch or so wide and about nine feet in diameter (Figs. 47 and 48). Radially in this chamber are placed U-shaped, water-cooled, copper electrodes. An alternating current produces an arc between the electrodes. A powerful electro-magnet placed at right angles to the electrodes has the effect of spreading the arc back along the electrodes, producing a flaming disk through which air is gently forced. Here at a temperature of 3000° C. some of the nitrogen of the air unites with oxygen to form nitric oxide, NO, which after cooling unites with more oxygen to form nitrogen dioxide, NO_2. The nitrogen dioxide is led up through a series of granite towers filled with crushed

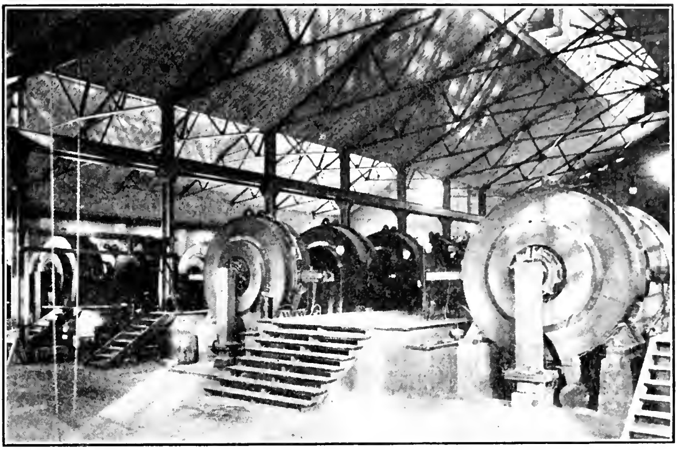


Fig. 47.—Manufacture of calcium nitrate. Interior view of furnace house at Notodden, Norway.

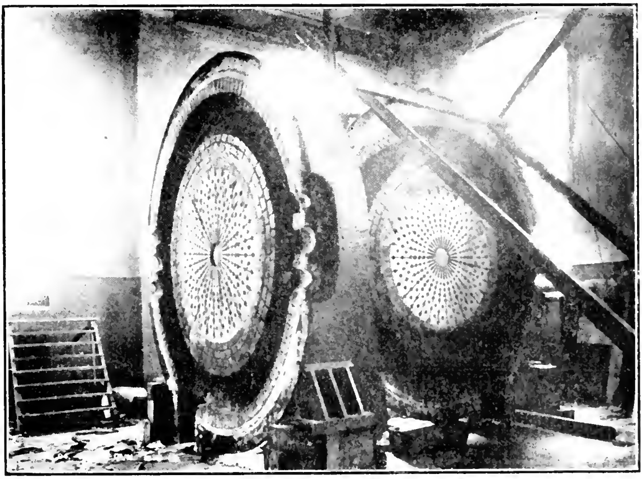
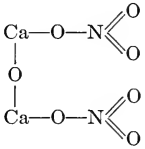


Fig. 48.—Interior of one of the furnaces at Notodden.

quartz down through which water trickles. Nitric acid is formed according to the following equation:

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

This nitric acid is neutralized by limestone and milk of lime. The resulting solution of calcium nitrate is evaporated to the proper concentration, then cooled, and the resulting product placed on the market as *lime nitrate,* $Ca(NO_3)_2$, containing about 13 per cent. nitrogen. There is also made another product called *basic calcium nitrate* by adding lime to a hot solution of calcium nitrate. This product has a formula $(CaO)_2N_2O_5$, or expressed graphically:



It contains about 10 per cent. nitrogen and does not absorb moisture to such an extent as the normal nitrate, although the special process employed in manufacturing the lime nitrate fertilizer is successful in making a product which is fairly satisfactory to handle. Pure, crystallized calcium nitrate is deliquescent and not easily handled.

(*b*) AVAILABILITY.—Like nitrate of soda, nitrate of lime, both normal and basic, is readily soluble in water and hence immediately available to plants, it being in the form best adapted to plant use and in every way similar to nitrate of soda in effectiveness on crops. It is not readily retained in the soil and hence can be lost by leaching.

(*c*) EFFECT ON THE SOIL.—Although there is little choice between sodium nitrate and calcium nitrate as far as availability and direct effect on the plant is concerned, there is a decided choice in favor of the latter fertilizer on account of its action in the soil. It was seen that sodium nitrate, although serving to release insoluble stores of potassium and to neutralize acidity, has a tendency to deflocculate heavy soils and render them difficult to handle. Calcium nitrate on the other hand not only makes potassium available and neutralizes soil acidity, but it also flocculates heavy soils and puts them in much better physical condition. The reason chemically is analogous to the action of sodium nitrate, except that calcium carbonate is formed instead of sodium carbonate. Moreover, there is an excess of calcium in basic calcium nitrate. This residue of calcium carbonate in the soil has many other benefits which are taken up in detail in Chapter XII. Unfortunately calcium nitrate can not be obtained so readily as sodium nitrate, although when it can be purchased, it is not far from the same price as the latter.

II. NITROGEN AS AMMONIA

159. **Ammonium Sulphate.**—In addition to the nitrate nitrogen mined as nitrate of soda and manufactured as nitrate of lime, there is produced an ammonia nitrogen fertilizer called ammonium sulphate, $(NH_4)_2SO_4$, which contains about 20 per cent. nitrogen as it appears on the market. Ammonium sulphate is obtained for the most part as a by-product in the destructive distillation of soft coal. Coal contains from 1 to 2 per cent. nitrogen, of which about 15 per cent. is recoverable. In other words, from one ton of coal may be produced about twenty pounds of ammonium sulphate. For years none of this valuable material was saved, and even now not much more than one-third of the amount produced is recovered.

(*a*) How Made.—If soft coal is burned in the air all the nitrogen escapes as elemental nitrogen and cannot be recovered, but if coal is heated in closed retorts, it undergoes destructive distillation whereby coke and combustible gases are formed, the latter containing part of the nitrogen in the form of ammonia. Soft coal is treated in this way in the manufacture of coke, coal gas, or producer gas, and in any one of these processes it is possible to save the ammonia. The coke ovens have been the greatest source of loss, for in the past no attempt was made to save any of the gases, and even now not as many by-product coke ovens are in use as should be, although the coke and steel concerns are beginning to realize the advantage of saving the ammonia (Figs. 49 and 50).

Fig. 49

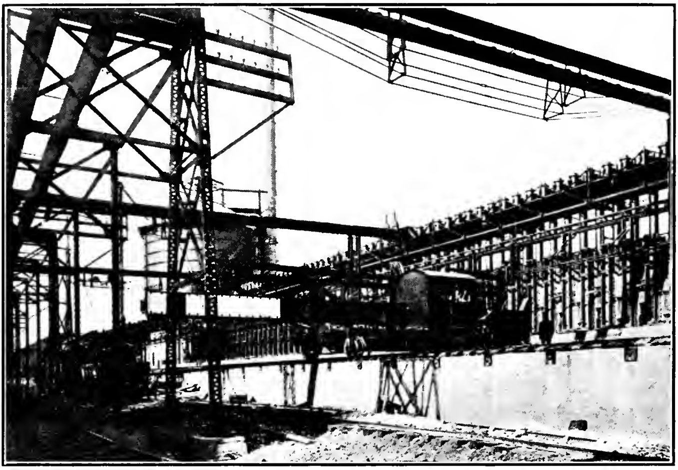
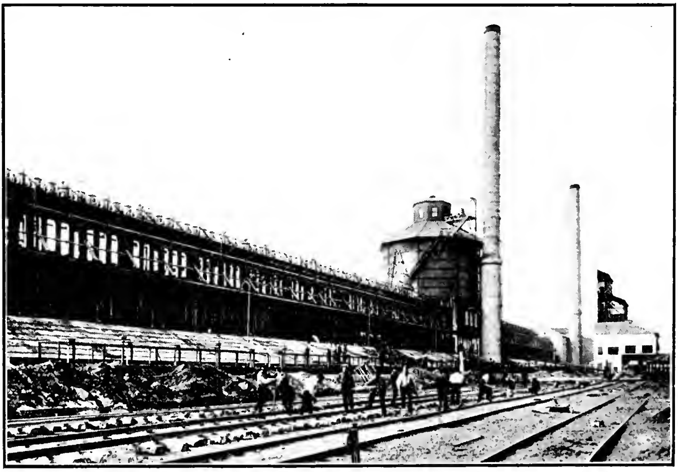


Fig. 50



Figs. 49 and 50.—Two views of by-product coke ovens.

By proper appliances the escaping gases from coke ovens or gas retorts are led through water in which the ammonia is dissolved. It is then distilled by steam with the addition of lime to break up ammonium compounds, and led into sulphuric acid. The solution of ammonium sulphate is evaporated and the white or gray salt which results is dried and sold as sulphate of ammonium, largely for fertilizing purposes.

(*b*) Availability.—Ammonium sulphate is almost as soluble as sodium nitrate, one part dissolving in about one and one-third parts of water, but for most plants it is not the best form of nitrogen. The ammonia nitrogen must first change to nitrate nitrogen which it does very rapidly in the soil by the process called nitrification (Section 128). Its ready solubility and rapid change to nitrate make it only slightly less readily available than sodium nitrate, and it is ranked as a quick-acting fertilizer. In the early spring, however, to start wheat, for example, ammonium sulphate is not good because at that time of year bacterial action is very slow and nitrification does not take place with sufficient rapidity to feed the crop. A nitrate is better under these conditions.

Ammonia nitrogen is not leached from the soil as rapidly as nitrate nitrogen, being absorbed both chemically and physically (Section 137). Ammonia, held either in other chemical combinations or absorbed by humus or hydrated silicates, is just as easily nitrified as it is in the sulphate form. Until nitrified, ammonium sulphate is not lost from the soil, but nitrification is ordinarily so rapid that ammonium sulphate is not a lasting nitrogenous fertilizer.

(*c*) Effect on the Soil.—Whereas sodium and calcium nitrates tend to produce a residual alkaline condition of the soil, ammonium sulphate tends to produce an acid condition. Long continued use of this form of nitrogen results in a very acid condition of the soil. On the fertilizer plats of the Pennsylvania Experiment Station the use of 72 pounds of nitrogen as ammonium sulphate per acre once in two years for thirty years has resulted in a soil which needs 19 times as much lime to correct the acidity as do the check plats receiving no fertilizer.

In nitrifying, the ammonia is changed to nitric acid, and sulphuric acid is set free. Both acids require bases to neutralize them, and thus there is twice as much lime or other base needed for this fertilizer as is needed for other nitrogenous materials undergoing nitrification. Lime is used up very rapidly and acidity results (Section 186).

III. NITROGEN AS AMINE OR PROTEIN

160. **Cyanamid or Lime Nitrogen.**—The utilization of atmospheric nitrogen in the manufacture of fertilizers is successfully accomplished in another way than by making calcium nitrate. The process depends on the fact that nitrogen unites with calcium carbide to form calcium cyanamide at a temperature of about 1000° C. In the soil this compound changes gradually to nitrate. This fertilizer goes under a variety of names. Cyanamid is the trade name of the American product manufactured at Niagara Falls (Fig. 51). Calcium cyanamide is a common name for it, although as a matter of fact the fertilizer contains only about 45 per cent. of this compound. Lime nitrogen is another name;

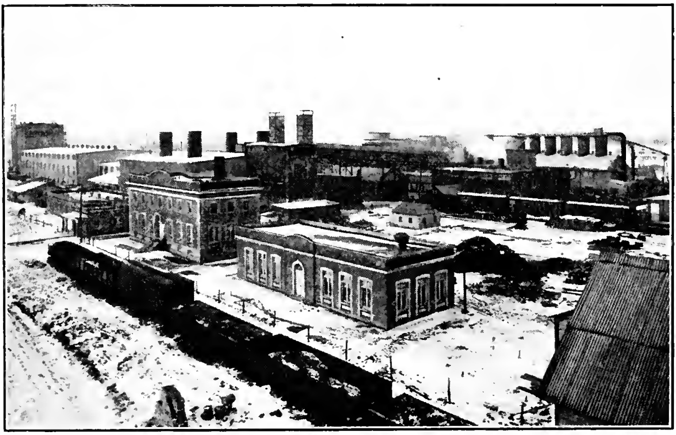


Fig. 51.—Plant of American Cyanamid Co., Niagara Falls, N. Y.

also nitrolim which is the trade name of the fertilizer sold in England.

(*a*) HOW MADE.—Calcium carbide is first made by fusing in an electric furnace a mixture of coke and lime. The reaction is as follows:

$$CaO + 3C = CaC_2 + CO.$$

The carbide is removed, cooled, crushed to a fine powder and placed in perforated steel cans set in brick ovens. A carbon rod carrying a current of electricity, and passing through the center of the can serves to heat up the carbide to about 1100° C., when union takes place between the carbide and a stream of pure nitrogen which is gently forced into the can. The reaction is as follows:

$$CaC_2 + N_2 = CaCN_2 + C.$$

Pure nitrogen is obtained by passing air over red hot copper when the oxygen unites with the copper to form copper oxide and the nitrogen alone issues from the furnace. The best process, however, is to fractionally distill liquid air. Nitrogen boils at $-195.5°$ C. and oxygen at $-182.5°$ C. The nitrogen comes off first and can be obtained very pure.

The nitrogenous product, which is really an impure calcium cyanamide, is next cooled, pulverized, and treated with water in rotating cylinders. About 30 per cent. of water is taken up, the excess of calcium oxide is hydrated, and a little carbide decomposed to acetylene and hydrated calcium oxide. The material is then pressed into bricks and before use is crushed and screened so that a granulated fertilizer is obtained which is made use of almost exclusively in manufacturing complete fertilizers. The cyanamid as it comes on the market contains about 45 per cent. of calcium cyanamide, 15 per cent. nitrogen, 27 per cent. calcium hydroxide, and 13 per cent. free carbon, besides small amounts of other constituents.

(*b*) AVAILABILITY.—The fertilizing compound in cyanamid is calcium cyanamide: $Ca=N-C\equiv N$. This compound is soluble in water but not available to plants. Before its use by plants it must be nitrified and this process takes place in five stages as follows:

First, hydrolysis to cyanamide and calcium hydroxide, helped probably by the adsorptive processes in the soil, thus:

$$CaCN_2 + 2H_2O = H_2CN_2 + Ca(OH)_2.$$

The calcium hydroxide is changed rapidly to carbonate.

Second, the hydrolysis of cyanamide with the aid of colloidal catalysts to urea, thus:

$$H_2CN_2 + H_2O = CO(NH_2)_2.$$

Third, the bacterial hydrolysis, or ordinary ammonifying process, to ammonium carbonate, thus:

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3.$$

Fourth, nitrification to nitrous acid and nitrites.

Fifth, further nitrification to nitric acid and nitrates.

Cyanamid is ranked as a fairly quick acting fertilizer, about as good as ammonium sulphate.

(*c*) EFFECT ON THE SOIL.—Cyanamid while producing nitric acid also carries considerably more calcium oxide than is necessary to neutralize this acid. The residual effect is like that of basic calcium nitrate, and is beneficial. Cases have been reported where cyanamid has harmed crops, but under ordinary farming conditions no danger from it need be feared.

161. **Dried Blood.**—By evaporating, drying, and grinding animal blood from slaughter houses there is obtained a product known as dried blood which is one of the best organic nitrogenous fertilizers. It comes on the market in two forms, red and black, the color depending on the processes of manufacture. *Red dried blood* is the better of the two, being more uniform in composition, containing more nitrogen and being more available as a fertilizer. Its nitrogen content is approximately 13 per cent. *Black dried blood* is not so pure, being often mixed with hair, dirt, and other substances which impair its value. Its nitrogen content varies greatly,

running from 6 to 12 per cent. It may also carry 3 or 4 per cent. of phosphoric acid.

The availability of the best grades of dried blood is roughly three-fourths that of sodium nitrate, although it varies with soil conditions. Its nitrogen is in the protein form and must undergo the complete process of ammonification and nitrification before becoming available. In cold, acid soils this process is not so rapid and as a result dried blood is not a good fertilizer for such soils. The nitrogen is not lost from soils since leaching cannot take place except as the protein nitrifies, and this is not rapid enough to cause loss.

Dried blood has no marked effect on the soil, except that its tendency is toward making a soil acid, it being organic in nature and the decomposition of organic matter produces organic acids. Nitrification also produces acids which must be neutralized. But it must be remembered that the natural tendency of cultivated and fertilized soils is toward acidity and this condition should not be feared. Plenty of calcium carbonate in the soil prevents acidity from appearing and liming will overcome this condition if necessary (See Chapter XII).

162. **Dried Meat, Meat Meal.**—Refuse meat from slaughter houses and packing houses, and waste from beef extract factories are first rendered, that is, steamed under pressure to remove fat, then dried and ground. Sometimes bones are mixed with the meat before rendering, and in this case, of course, the product contains phosphoric acid. The best grades of dried meat carry 13 or 14 per cent. of nitrogen, although many samples run less.

The availability of meat meal is not quite so high as dried blood, but it makes a very satisfactory nitrogenous fertilizer when rapid availability is not wanted. Its nitrogen is in the protein form and like that of dried blood is not lost by leaching. Its effect on the soil is similar to that of dried blood.

163. **Tankage.**—Besides the refuse meat there are other waste animal products that are used as fertilizers. Tendons, intestines, lungs, and hair, together with bones, horns, and hoofs are treated with steam under pressure to remove fat

and gelatine, then dried and ground. If little or no bone is present the product is called *meat tankage.* If considerable bone is present it is called *bone tankage.* Tankage is very variable in composition, sometimes containing as much as 12 per cent. nitrogen in meat tankage, and up to 9 per cent. nitrogen with 17 per cent. phosphoric acid in bone tankage.

Tankage is an excellent, rather slow acting fertilizer, its value depending, especially in the case of bone tankage, on fineness of grinding. The nitrogen is in the same form as in dried meat and the effect on the soil is the same.

164. **Dried Fish, Fish Scrap.**—The refuse material from fish oil refineries, fish salting, or canning plants is dried and ground, sometimes being treated with dilute sulphuric acid to stop decomposition and partially dissolve the bones. This fertilizer contains from 6 to 9 per cent. nitrogen and 5 to 9 per cent. phosphoric acid. Fish scrap is about as good as the better grades of tankage, though slower acting than dried blood. It contains the protein form of nitrogen.

165. **Cottonseed Meal.**—The press cake which results from the extraction of oil from cotton seed is used extensively as a fertilizer. The decorticated meal made from seeds which have had the husks removed before pressing, runs about 6 per cent. nitrogen; the undecorticated meal carries only 4 per cent. nitrogen. There are also small amounts of phosphoric acid and potash. Since cottonseed meal is an excellent cattle food, and since most of its fertilizing constituents are recovered in the manure, it is much more profitable to feed it first and use the manure as a fertilizer. But it is, nevertheless, used to a very large extent directly as a fertilizer, especially in the south. Moreover, its physical condition is such that it improves the mechanical condition of mixed fertilizers by absorbing moisture and preventing caking. Its availability is about the same as dried blood and the form of nitrogen is similar.

166. **Castor-Bean Pomace.**—This is the ground press cake from the manufacture of castor oil, and contains about 5 per cent. nitrogen with some phosphoric acid and potash. It is a good fertilizer.

167. **Leather, Hair, Wool Waste, Hoof, and Horn.**—These materials are waste products from various industries and are very slow acting, practically worthless forms of nitrogenous fertilizers when used without previous treatment. Leather, hoof, and horn are sometimes steamed or roasted and ground, and even treated with sulphuric acid, when they make a fair grade of fertilizer. Leather contains about 8 per cent. nitrogen, hair 13 per cent., wool waste 5 to 10 per cent., horn and hoof 10 to 15 per cent.

Most of these materials, however, are used by the fertilizer manufacturers in the preparation of "*base goods.*" They are treated with sulphuric acid along with rock phosphate. The nitrogen is thereby partly converted to ammonium sulphate or some more available form of nitrogen than the original non-decomposible protein form. This mixture of acid phosphate and "chamber process" nitrogenous material forms a "base" for fertilizer mixtures.

168. **Summary.**—Nitrogen is the most expensive element that the farmer has to buy, although not the most important. It occurs in various forms, nitrate, ammonia, and amine or protein, and the availability is roughly in that order. *Sodium and calcium nitrates* are the best forms for rapid action. The former occurs naturally; the latter is made from the nitrogen of the air. Both of them, aside from supplying nitrogen to the plant, act on the soil to set free potassium. Sodium nitrate has a bad residual effect on soils after long continued use. Calcium nitrate, however, has no bad effect whatever. Both tend to neutralize soil acidity.

Ammonium sulphate is very readily available since it nitrifies rapidly. The residual effect, however, is to leave the soil acid. *Cyanamid* is another manufactured product using the air as a source of nitrogen. It is an excellent fertilizer, leaving a calcium residue in the soil and thereby being of benefit.

Animal and plant nitrogenous materials are of varying availability and value. *Dried blood, tankage, fish scrap,* and *cottonseed meal* being better than *leather, hair, wool waste, hoof,* and *horn.* These materials all have nitrogen in the protein form which ammonifies and nitrifies with varying degrees of rapidity. This form of nitrogen, however, is of more lasting effect, since there is no danger of leaching as in the case of the nitrates. Their effect on the soil is not great, other than a slight tendency toward acidity due to the formation of organic acids and nitric acid during the process of decomposition and nitrification.

REFERENCES

See references at end of Chapter VIII.

CHAPTER X

PHOSPHATE FERTILIZERS

ALTHOUGH nitrogen is the most expensive fertilizing element the farmer buys and is usually considered the most important, phosphorus is actually the element which should cause him the greatest concern. The soil contains no more phosphoric acid than nitrogen, the average of good cultivated soil being not far from 0.15 to 0.2 per cent. Phosphorus is necessary for the production of seed, inducing early and full maturity. It occurs for the most part in the grain at harvest and is thereby sold from the farm, little being left in stems and leaves to be returned to the soil as litter. Finally, phosphorus cannot be added to the soil by the growth of any special crop. It is not like nitrogen which can be obtained by legumes from the exhaustless atmospheric source. Phosphorus must be purchased and added to the soil, or the soil becomes exhausted. Supplies brought up from the subsoil either by capillarity or the growth of deep rooted crops are not sufficient to add materially to the amount in the surface soil. Continued cropping and no return result in a loss of phosphorus. Phosphate fertilizers, then, are of prime importance.

169. **Raw Bone.**—Bones when fresh contain about 40 per cent. of organic matter, 53 per cent. of inorganic matter and 7 per cent. of water. The organic matter consists of fat and ossein, the latter a nitrogenous compound. The inorganic matter is mostly tricalcium phosphate, $Ca_3(PO_4)_2$. It comes on the market as raw bone-meal, and coarse ground bone, containing about 4 per cent. nitrogen and 22 per cent. phosphoric acid. The presence of the fat makes fine grinding impossible and it is not used much as a fertilizer. The fat prevents bacterial action, thus checking nitrification, and

together with the ossein protecting the phosphate from being acted upon by soil solvents.

170. **Steamed Bone, Bone-Meal.**—The fat in bone is valuable for various commercial purposes and the ossein can be converted into gelatine and glue. There are two ways of removing fat: By extraction with a solvent like benzine; or by treatment with boiling water or steam under pressure. Subsequent cooling allows the fat to solidify on top of the water, and to be removed. Steaming under pressure also converts ossein to gelatine, soluble in water. The bone that is left can be dried and easily ground fine. This material is sold as steamed bone-meal or bone-meal. The best grades contain 25 to 30 per cent. of phosphoric acid, but frequently less than 1 per cent. nitrogen. The removal of fat and ossein leaves the tricalcium phosphate in much better physical condition both for grinding and subsequent solution in the soil. Steamed bone-meal is a very excellent phosphate fertilizer and fairly available.

Bone products have had a value as a fertilizer for centuries and even now are considered by many to be superior to other forms of phosphate, consequently the temptation to adulterate bone-meal with worthless substances has been very great. This fact together with differences in method of treatment and quality of original bones makes the product one of great variation in phosphoric acid content. The figures given are average for a good product.

171. **Bone-Black.**—When bones are subjected to destructive distillation, the organic matter is largely driven off and there remains the inorganic matter and about 10 per cent. of carbon. This material is known as bone-black, or animal charcoal, and on account of its porosity and absorptive power is used after grinding for clarifying sugar solutions in sugar refineries, and for other similar purposes. But little of it is used as fertilizer in the freshly made form, most of it being first employed as above stated.

After a time it loses its absorptive or clarifying power and then is sold as a fertilizer, although the presence of the carbon prevents ready solution of the tricalcium phosphate. It contains about 30 per cent. phosphoric acid.

172. **Dissolved Bone-Black.**—If the spent bone-black above mentioned is treated with sulphuric acid, it becomes a readily available phosphate fertilizer, being converted into monocalcium phosphate which is soluble in water, whereas tricalcium phosphate is only slowly soluble in water and carbon dioxide. The reaction may be expressed thus:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

Its content of phosphoric acid is about 14 to 16 per cent.

173. **Rock Phosphate, Floats.**—Originally the name "floats" was applied to a particularly fine ground rock phosphate, so fine that it would float in the air. Now, however, the term is loosely used for any finely ground rock phosphate. Deposits of phosphate rock are found in many places. In France, Belgium, Portugal, and North Africa there are beds of greater or less thickness. The greatest source of supply, however, comes from the United States, in Florida, South Carolina, and Tennessee. Recently there have been discovered immense beds in Idaho, Wyoming, and Montana. These constitute a reserve supply of great importance since the older mines are being rapidly exhausted. In South Carolina and Florida the phosphate occurs largely as pebbles or boulders in deposits resembling gravel beds (Fig. 52). In Tennessee it occurs in veins or pockets.

The phosphorus occurs as tricalcium phosphate together with varying amounts of iron and aluminium compounds and calcium carbonate. The phosphoric acid content varies from 25 to 40 per cent., iron and aluminium oxide, 2 to 6 per cent., and calcium carbonate from 1 or 2 per cent. to 10 or 15 per cent.

As a fertilizer, rock phosphate is very slow acting when applied alone. The finer it is, the more valuable it becomes, but even very finely ground it is best used in connection with decaying organic matter. Applied to acid peat or muck soils it is especially good, and when mixed with manure gives excellent results. Opinion is divided as to its value compared to acid phosphate, even when mixed with manure. Whether or not it is as good as, or better than, acid phosphate

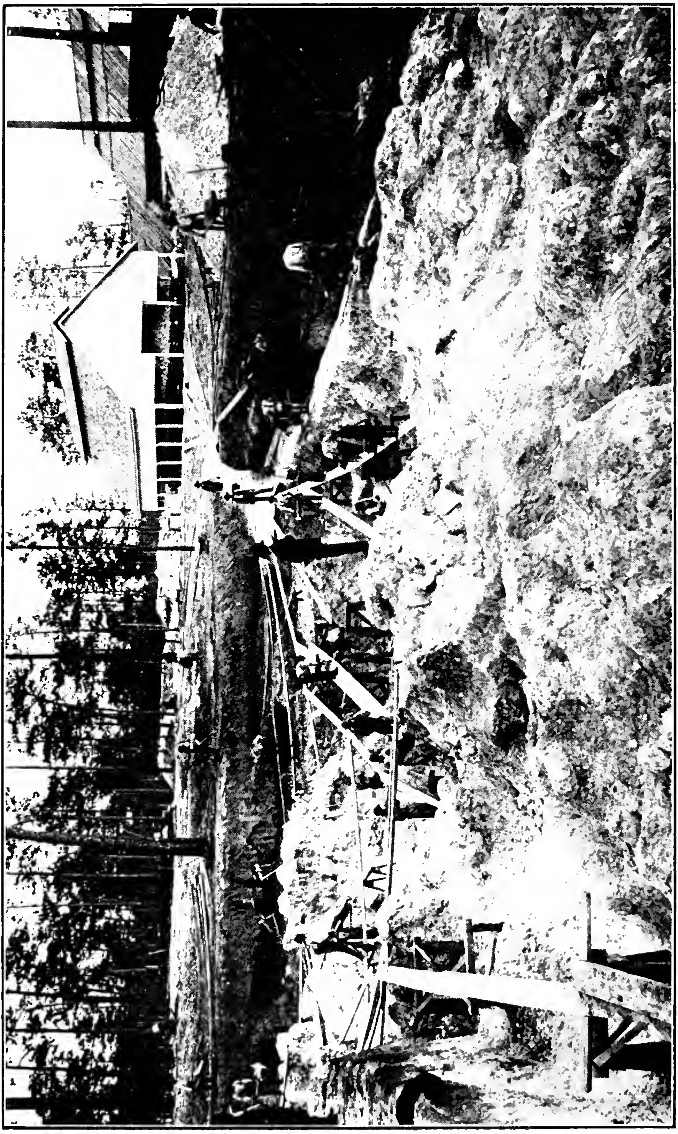


Fig. 52.—Phosphate Mining in Florida. United States Geological Survey.

when similarly mixed with manure, it is, nevertheless, a most excellent phosphatic manure. Its cheapness recommends it, as well as its high content of phosphoric acid.

The fermenting mixture of rock phosphate and manure has never showed any very greatly increased solubility of phosphoric acid under laboratory conditions of extraction, but field trials have abundantly proved that this mixture is much better than rock phosphate alone or than manure alone, showing that at least under field conditions the phosphoric acid is rendered sufficiently soluble for the growing plant.

174. **Acid Phosphate, Superphosphate.**—This is the best known form of phosphate fertilizer.

(*a*) How Made.—To make rock phosphate available it is treated with sulphuric acid which converts the tricalcium phosphate to monocalcium phosphate according to the equation given under Dissolved Bone-Black. The finely ground rock phosphate together with the right amount of approximately 65 per cent. sulphuric acid is placed in mixing chambers provided with stirrers. After being thoroughly mixed the material is dumped into "dens" where the reaction is completed. Considerable heat is developed, and the final product solidifies, due to the formation of gypsum, $CaSO_4.2H_2O$. This mass after standing for some time is crushed fine and is ready for use.

In calculating the amount of acid to use, due regard is paid to the ingredients other than tricalcium phosphate. Calcium carbonate, of course, uses up sulphuric acid and so do the iron and aluminium compounds. Iron compounds, however, interfere with the formation of a good product, if they are present in any considerable quantity—over 4 or 5 per cent. The resulting mixture is in bad physical condition due to the formation of ferric sulphate and of something like a hydrated, acid iron phosphate. It does not dry sufficiently to pulverize easily. Moreover, insoluble iron and aluminium phosphates are formed, which, of course, are worthless as quick acting fertilizers.

Acid phosphate runs from 12 to 15 per cent. phosphoric acid with 14 per cent. as the average content of available phosphoric acid. In order to prevent any possible excess of sulphuric acid it is customary to add somewhat less than the theoretical amount. This results in the incomplete conversion of all the tricalcium phosphate to monocalcium phosphate. On standing, these two compounds unite to form "reverted" or "gone back" phosphates. That is, the water soluble monocalcium phosphate starts to revert or go back to the tricalcium phosphate and forms dicalcium phosphate. Since the latter is soluble in ammonium citrate solution (Section 212), it is sometimes called citrate soluble phosphoric acid. The equation is as follows:

$$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 2Ca_2H_2(PO_4)_2.$$

Reverted phosphate is almost as available as the monocalcium phosphate.

(*b*) AVAILABILITY.—Acid phosphate is a quick acting fertilizer, readily available, and all things considered is the best form of phosphate to use under ordinary conditions.

(*c*) EFFECT ON THE SOIL.—In the soil acid phosphate reverts very quickly to dicalcium and tricalcium phosphate. Notwithstanding this reversion, which takes place before the plant obtains much of the fertilizer, acid phosphate is more readily available than tricalcium phosphate or rock phosphate for two reasons: In the first place, acid phosphate dissolves in the soil water and permeates the soil, so that when it is precipitated it is thoroughly distributed. This precipitate is much finer than any mechanically ground material and, moreover, is much better mixed with the soil. In the second place, freshly precipitated di- or tricalcium phosphate is much more soluble in water and carbon dioxide than is tricalcium phosphate, which has been formed for a long time, like the rock phosphate.

Acid phosphate is said to make a soil acid. This surely is not due to the fact that it is an acid salt, for the plant in the long run uses fully as much phosphoric acid as calcium, and usually more, so that the residual effect could not be acid. Moreover, although it may use up bases by reversion in the soil, these bases are liberated again when the phosphate redissolves in water and carbon dioxide. Some authorities claim that the acidity is due to the presence of calcium sulphate, a necessary by-product in the manufacturing process. But it is doubtful if this has any more residual acid effect than any ordinary fertilizer or than any normal soil treatment.

175. **Basic Slag, Thomas Slag.**—Basic slag is a very popular fertilizer in Germany.

(*a*) HOW MADE.—In the basic Bessemer process of making steel from phosphatic iron, devised by Thomas and Gilchrist, of England, the molten cast iron is placed in a converter lined with calcium oxide or calcium and magnesium oxides. By blowing a stream of air through the molten mass, phosphorus and silicon are oxidized and unite with the calcium to form a double, basic phosphate and silicate of calcium. The molten slag is poured off and when cool is broken up and finely ground.

(*b*) COMPOSITION.—The exact compound of the phosphorus in basic slag is not known, but there have been found crystals of so-called tetracalcium phosphate. Most of the phosphorus, however, is probably in the form of a pentacalcium silico-phosphate. These compounds may best be compared with the other compounds of calcium and phosphorus so far studied:

1. *Monocalcium phosphate*, $CaO.(H_2O)_2.P_2O_5$, found in dissolved phosphates such as acid phosphate and dissolved bone-black.

2. *Dicalcium phosphate*, $(CaO)_2.H_2O.P_2O_5$, found to some extent with acid phosphate as the so-called reverted phosphate.

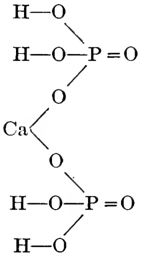
3. *Tricalcium phosphate*, $(CaO)_3.P_2O_5$, found in rock phosphate and bones.

4. *Tetracalcium phosphate*, $(CaO)_4.P_2O_5$, and pentacalcium silico-phosphate, $(CaO)_5.SiO_2.P_2O_5$.

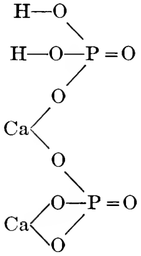
The formulas for the first three have here been modified from their usual form to bring out the differences between them and the last two.

Now to illustrate their combination graphically:

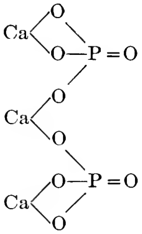
Monocalcium phosphate



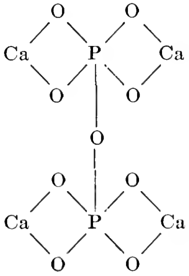
Dicalcium phosphate



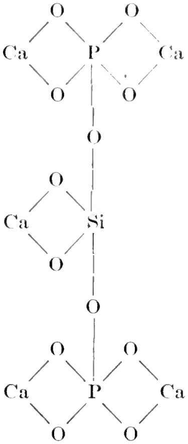
Tricalcium phosphate



Tetracalcium phosphate



Pentacalcium silico-phosphate



(*c*) Availability.—Basic slag is usually considered about one-half as available as acid phosphate, although on acid soils it is much more readily soluble and quick acting. It is considered an excellent form of phosphate. In this country its use is limited by few importations and relatively high price. Iron ores in this country are too low in phosphorus to produce a slag from steel that is valuable as a fertilizer. In Europe, on the other hand, the slags are rich in phosphorus, the phosphoric acid content running from 10 to 20 per cent.

(*d*) Effect on the Soil.—Basic slag was formerly thought to have considerable free lime, since it was basic in character and was excellent on an acid soil. As a matter of fact it contains only a few per cent. of free calcium oxide (1 to 6 per cent.). The decomposition of the basic slag in the soil, however, results in the production of calcium carbonate. The action of water and carbon dioxide produces di- or tricalcium phosphates and bicarbonate of calcium, in addition to silicic acid or free silica. In this way basic slag acts as a neutralizer of soil acidity, and an improver of soil texture. There is not, however, enough calcium carbonate resulting from an ordinary application of basic slag—say 500 or 600 pounds—to entirely correct the acidity of an ordinarily sour soil. In such an application there probably would not result more than 100 pounds of calcium oxide combined as carbonate, not enough for any immediate effectiveness.

176. **Summary.**—Phosphate fertilizers are all of them forms of calcium phosphate with varying degrees of availability depending in large measure on the form of combination. Monocalcium phosphate, found in *acid phosphate, dissolved bone-black,* and other sulphuric acid-treated phosphate products, is the most quickly available and in general the best to use. Tricalcium phosphate, found in *rock phosphate* and *bones* not treated with sulphuric acid, is the least soluble. In rock phosphate it is available only when mixed with decomposing organic matter, and is best used with manure, or on acid soils containing large amounts of organic matter.

Raw bones are unavailable on account of the presence of fat and ossein which prevent the solvent action of soil moisture on the phosphate, they themselves decomposing very slowly. *Steamed bone,* however, in the form of steamed bone-meal is a good fertilizer of fairly rapid availability. Here the fat and most of the ossein have been removed by high-pressure steam, leaving the tricalcium phosphate in a condition easily ground and readily attacked by the soil moisture. *Bone-black* has had all the organic matter destroyed by heat in the absence of air, leaving only tricalcium phosphate mixed with some carbon. After this is employed to clarify such things as sugar solutions it is used as a fertilizer to good advantage.

Basic slag is a manufactured product having the phosphorus in the tetra- and pentacalcium form, in the latter compound also united with some silica. The compounds are fairly soluble in the water and carbon dioxide of the soil, leaving a residue of calcium carbonate or bicarbonate which has a beneficial alkaline effect, especially on acid soils.

REFERENCES

See references at end of Chapter VIII.

CHAPTER XI

POTASH FERTILIZERS

THE third of the fertilizer trio is potassium or, as it is usually called, potash. The element potassium occurs in most soils to a very considerable extent (Section 144 *b*, 6), but it is frequently present in an unavailable form. Some plants, notably clover and alfalfa, require considerable potassium; and other crops also remove it to no small extent. Unlike nitrogen and phosphorus, however, potassium is not sold from the farm in any considerable amount except in hay, since it occurs for the most part in the stems and leaves of plants. These are the portions of the crop which usually remain on the farm, being fed as roughage or used as litter. In this way the potassium gets back to the soil. Its application, however, frequently results in increased yields, and it is thus an important element in fertilizers.

177. **The German Potash Deposits.**—The most important source of potassium in the world is located at Stassfurt in northern Germany where there are today over one hundred mines producing potash salts (Fig. 53). For several centuries common salt had been obtained from its salt springs and wells. About the middle of the nineteenth century deep borings revealed the presence of immense beds of rock salt at a depth of about 1000 feet. Overlying these beds of salt, however, were considerable deposits of potassium and magnesium compounds. These salts were considered worthless at the time and were thrown away, but later their value became apparent, until now the potash salts are the only ones of value. Rock salt is no longer mined at Stassfurt.

It is believed that in past geologic ages there existed here an immense inland sea which was probably fed intermittently by inrushes of water from the ocean outside.

The climate of Europe at that time was tropical and evaporation of water from this sea was consequently rapid. The

Fig. 53.—Mining potash salts at Stassfurt.

water became more and more concentrated in salts until finally the least soluble were deposited. On top of these compounds other salts were deposited layer by layer. Intermittent additions of sea water from outside caused a dilution of the water within, and deposition of salt was consequently interrupted, causing alternate layers of less soluble and more soluble compounds as evaporation went on. Geologic changes brought about finally the deposition of various sedimentary rocks and finally a layer of impervious clay which protected the soluble salts from solution in rain water.

The bottom layers of these beds are composed of anhydrite (sulphate of calcium) and rock salt. Next comes the so-called polyhalite region (sulphates of calcium, magnesium, and potassium); then the kieserite region (magnesium sulphate); and finally the carnallite region (chlorides of potassium and magnesium). The latter is a bed ranging from 50 to 130 feet in thickness, from which most of the potash salts are obtained. Due to the intermittent deposition of salts, partial solution from infiltration of rainwater, and redeposition, the layers of salts are not perfectly distinct and not always in the same order. For instance, layers of anhydrite and rock salt intersperse the other salts, together with minerals, such as sylvine (potassium chloride) and kainite (sulphate and chloride of magnesium and potassium).

178. **Muriate of Potash, Potassium Chloride,** KCl.—This is the most widely used potash fertilizer. It is manufactured from carnallite which occurs mixed with rock salt and other minerals, and contains only 9 per cent. actual potash. By dissolving carnallite in hot magnesium chloride solution, boiling, and crystallizing, there is obtained a muriate containing about 20 per cent. potash and called *Potash Manure Salt.* On further evaporation and crystallization of the mother liquor a pure carnallite ($KCl.MgCl.6H_2O$) is obtained (Fig. 54). This salt on being treated just like the crude carnallite yields the commercial muriate with one crystallization.

There are three grades of muriate on the market, 80 per cent., 95 per cent., and 98 per cent., which contain respectively 50.5 per cent., 60 per cent., and 61.9 per cent. potash (K_2O). The 80 per cent. muriate is the one usually sold, however.

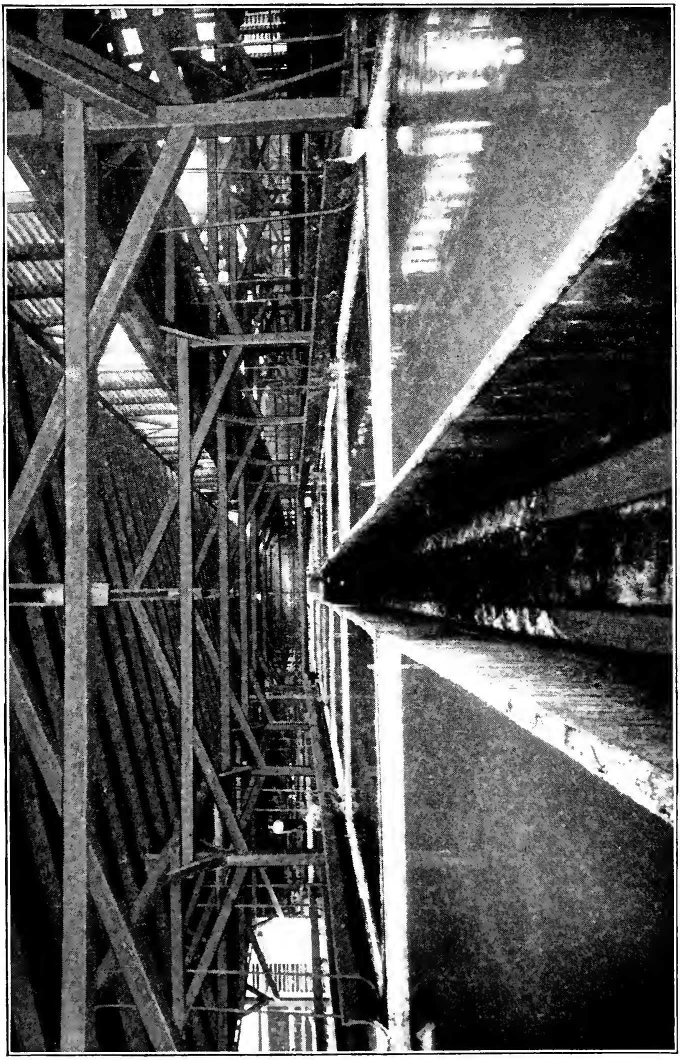


Fig. 54.—Crystallizing pans for muriate of potash.

It is very generally stated that potassium chloride affects the burning quality of tobacco and makes potatoes watery. The former is probably true, but the latter is not always the case, for excellent potatoes can be grown with the chloride, provided, however, that lime has been applied to the soil. The bad effects of the chlorine are apparently most pronounced on acid soils.

The tendency of potassium chloride is to make a soil acid (Section 186). Plants exercising their selective action remove the base, potassium, from the soil and leave the chlorine which is assimilated but little. This results in the production of hydrochloric acid which neutralizes any basic compound present in the soil, and this means usually calcium carbonate. When the reserves of base are used up the soil becomes acid. The calcium chloride thus formed is easily leached from the soil. Potassium chloride removes calcium from the soil in another way by reacting with calcium silicates to form potassium silicates and calcium chloride which is, of course, leached out.

179. **Sulphate of Potash, Potassium Sulphate,** K_2SO_4.—This fertilizer, although not used to so great an extent as the muriate, is in many respects the best one to employ. It is made by dissolving and concentrating a mixture of potassium chloride and kieserite (magnesium sulphate). There is precipitated the double sulphate of potassium and magnesium ($K_2SO_4.MgSO_4$), which is also sold under the name of *Double Potash Manure Salt,* containing about 27 per cent. potash. This double salt is further dissolved with a certain amount of potassium chloride and boiled. Potassium sulphate is precipitated. Two grades are sold, 90 and 96 per cent. pure, containing, respectively, 47 per cent., and 52.7 per cent. potash.

Potassium sulphate has no bad effects on tobacco and potatoes, and, furthermore, is not so apt to make a soil acid, since plants assimilate sulphur to a considerable extent. The whole salt is thus absorbed and no residue left. This fertilizer has an action on calcium silicates similar to that of the chloride, but the resulting calcium sulphate is not so soluble as calcium chloride, nor is it leached to so great an extent. Loss of calcium from soils is hence not so great as in the case of the chloride.

180. **Kainite.**—This fertilizer was formerly the mineral of the same name, the formula of which is $KCl.MgSO_4.6H_2O$, but at present it is merely a name for a potash fertilizer containing 12 per cent. potash, the form of the potassium and the other compounds varying considerably. The percentage of potash only is constant. Since kainite always contains chlorine in some form, it is open to the same objection as is the muriate of potash, but it is nevertheless a good low grade form of potash.

181. **Wood Ashes.**—One of the oldest sources of potash is wood ashes. When clean, hard wood is carefully burned, the potash content may run up to 8 or 10 per cent., mostly in the carbonate form. In addition there may be 1 or 2 per cent. of phosphoric acid, and 30 per cent. of calcium compounds, the calcium being in the oxide form when fresh burned, but changing to carbonate on exposure. The wood ashes now on the market are of a very inferior grade, carrying not more than 3 or 4 per cent. of potash in unleached ashes. Leached ashes, that is, ashes which have been leached to extract potash for other purposes than for fertilizers, or ashes which have been exposed to the weather and leached by rain, contain usually less than 1 per cent. potash.

Potassium carbonate in wood ashes is a good fertilizer unless too much is applied, when it has a deflocculating effect on soil grains and is poisonous to plants. This carbonate and the calcium carbonate in wood ashes are both neutralizers of soil acidity and are valuable for this purpose.

182. **Kelp and Alunite.**—The only sources of potash in the United States of any consequence are the giant kelps or seaweeds on the Pacific coast (Fig. 55), and alunite, a mineral found to some extent in Utah, and consisting of a double sulphate of potassium and aluminium. The giant kelps grow rapidly and sometimes attain a length of hundreds of feet. Dry, they contain 15 to 20 per cent. potash and their ashes contain as much as 30 to 35 per cent. potash in the form of the chloride. Alunite contains 10 per cent. potash, but can be ignited and the potash content increased to 15

per cent., or ignited and the leached potassium sulphate evaporated, when the nearly pure potash salt can be obtained.

FIG. 55.—Giant kelp.

The latter process, however, is expensive. Both kelp and alunite have given good results as a fertilizer with no treatment other than drying in the case of kelp and pulverizing in both cases. Used in this way, however, they are low grade fertilizers. Any treatment of them, however, makes the resulting product rather expensive, and so far little is being done to utilize these sources of potash. The German potash salts can be produced under normal conditions too cheaply to make other sources pay.

183. **Tobacco Waste.**—In some sections of the country the stems, stalks, and other waste from harvesting the crop and manufacturing tobacco products, can be obtained easily. If ground fine this waste makes excellent fertilizing material, being fairly available. The potash content varies from 4 to 10 per cent., phosphoric acid less than 1 per cent., and nitrogen from 2 to 4 per cent., sometimes as much as half of it in the nitrate form.

184. **Summary.**—Although potassium occurs in soils to a very considerable extent, it may be in a very unavailable form. Moreover, some crops require considerable potassium, and although it is usually returned to the farm in the straw and other litter, its application as a fertilizer sometimes pays.

Practically the only source of potash in the world is the mines at Stassfurt, Germany, where there are immense beds of potash salts formed in past geologic ages by the evaporation of sea water. The salts are chlorides and sulphates of potassium, magnesium, and calcium with sodium chloride.

Muriate of potash is made from carnallite (chlorides of potassium and magnesium) and contains about 50 per cent. potash. During the process there is obtained a so-called *potash manure salt* containing 20 per cent. potash. Potassium chloride is said to affect the burning qualities of tobacco and to make potatoes watery. It has a tendency to make soils acid, but applications of lime correct this effect and also seem to overcome the bad effects of this fertilizer on crops.

Sulphate of potash is made from potassium chloride and magnesium sulphate, and contains about 50 per cent. potash. An intermediate product called *double potash manure salt* contains 27 per cent. potash. The sulphate has no bad effects on plants and is not so apt to make soils acid as is the muriate.

Kainite is a mixture of crude salts containing 12 per cent. potash. *Wood ashes* when pure contain 3 to 4 per cent. potash in the form of carbonate and with the 30 per cent. lime, usually as carbonate, make not only an available potash fertilizer but a good neutralizer of soil acids. *Kelp* and *alunite* are low grade potash materials found in the United States, but not yet of commercial importance. *Tobacco waste* is an excellent low grade fertilizer containing also small amounts of nitrogen and phosphoric acid.

REFERENCES

See references at end of Chapter VIII.

CHAPTER XII

LIME

NITROGEN, phosphorus, and potassium compounds are direct or food fertilizers primarily. It is for their food value to the plant that they are purchased. Calcium compounds, on the other hand, are usually considered as indirect fertilizers or amendments. Calcium is, of course, an essential element in the growth of plants, but the effects of compounds of calcium on the soil, and the exploitation of these effects has given calcium an importance for other than feeding purposes. As a plant food, however, calcium is frequently necessary in soils, especially for certain crops, and it is necessary to consider calcium in this connection, without at all minimizing its effect as an amendment.

185. **Calcium Fertilizers as Plant Food.**—The total amount of calcium in soils of course varies considerably, but on the average is not as much as that of potassium—0.5 to 1.50 per cent. In many cases it may be present in part as calcium carbonate which is fairly soluble in soil moisture, but most of it is in silicate and organic form and may be very insoluble. Since calcium carbonate is so soluble, it very frequently happens that this compound is entirely lacking even in limestone soils. As a result, soils may lack sufficient available calcium for the nutrition of crops.

Some farm crops do not need very much calcium, it is true, but other crops like clover and alfalfa do need large quantities. Table XII shows the amount of calcium oxide removed by various crops. Of course, this represents the amount removed only, and not the whole amount needed, for plants at harvest do not remove as much as they need during their growth.

Table XII.—Amount of CaO Removed by Various Crops

(Expressed in pounds per acre.)

Alfalfa	212
Cabbage	95
Corn	12
Clover	90
Oats	11
Potatoes	31
Timothy	14
Tobacco	83
Wheat	8

In many cases, it is true, sufficient calcium is added in the ordinary fertilizers to feed crops. Table XIII gives the estimated amount of calcium oxide in 100 pounds of various fertilizers.

Table XIII.—Amount of CaO in Various Fertilizers

Fertilizer.	Form of Calcium.	Per cent. CaO.
Acid phosphate	Phosphate and sulphate	21
Basic slag	Phosphate, silicate, and oxide	48
Bone meal	Phosphate	27
Rock phosphate	Phosphate and carbonate	42
Wood ashes	Carbonate and phosphate	34

It may happen, however, that a fertilizer application does not add calcium and the crop becomes starved for lack of this essential element. Particularly may this be true in the case of clover and alfalfa, as mentioned above. An application of lime, then, has the added benefit of feeding the crop.

186. **Soil Acidity.**—One of the most important effects of adding lime to the soil is the neutralization of soil acidity—or to "sweeten a sour soil." This condition in the soil is very common, may occur in all kinds of soils, and in fact is the natural result of cropping. Its bad effect on crops is frequently exaggerated, some crops preferring an acid soil and even refusing to grow in neutral or alkaline soils. For ordinary crops, however, in the usual farm rotation, a soil which is neutral or slightly alkaline is preferable and should be maintained.

The primary cause of soil acidity is the production of acids or acid salts. These acids may be organic or inorganic in nature and may vary in their harmful effect on crops.

They may occur in the soil by natural changes which take place particularly when the soil is cultivated and crops grown. Or they may be the result of the application of fertilizers, in which case soil acidity may be said to be caused by artificial means.

(*a*) Natural Acidity.—When organic matter in the soil undergoes decomposition through bacterial action, organic acids are some of the intermediate products. Decomposition in the presence of air is an oxidation process, and with thorough aëration results ultimately in the formation of carbon dioxide, water, and inorganic salts resulting from the combination of mineral elements with the organic matter. Nitric acid of course is formed from nitrogenous compounds and possibly mineral acids, but before complete oxidation occurs, and especially in soils not thoroughly aërated, organic acids are formed. These acids are sometimes fairly simple, like acetic, or butyric, or oxalic, but more frequently they are very complex, and many of them unknown. In the absence of air, as in water-logged soils, acids are even more commonly produced as a result of what may be called intermolecular oxidation, where one compound is oxidized at the expense of another.

Another natural cause of acids is the removal of bases from salts by plants and by certain hydrated compounds in the soil. Plant root hairs exercise a so-called "selective absorption" in taking up plant foods (Section 17). Sulphates and chlorides, for example, are split up, the base element entering the plant and the acid radicle being left in the soil as an acid. Certain colloidal compounds like hydrated silicates and humus produce this same result, the base being adsorbed or perhaps chemically combined with the colloid. It is possible that hydrolysis takes place previous to the absortive phenomenon. This means the formation of a hydroxide of the base, and an acid, thus:

$$\mathrm{KCl} + \mathrm{HOH} = \mathrm{KOH} + \mathrm{HCl}.$$

(*b*) Artificial Acidity.—The application of ammonium sulphate results in the production of nitric acid from the ammonia by the nitrifying bacteria, and of sulphuric acid as the residue from the nitrification. Figs. 56 and 57 show the effect of such acidity on corn and oats. Figs. 58 and 59

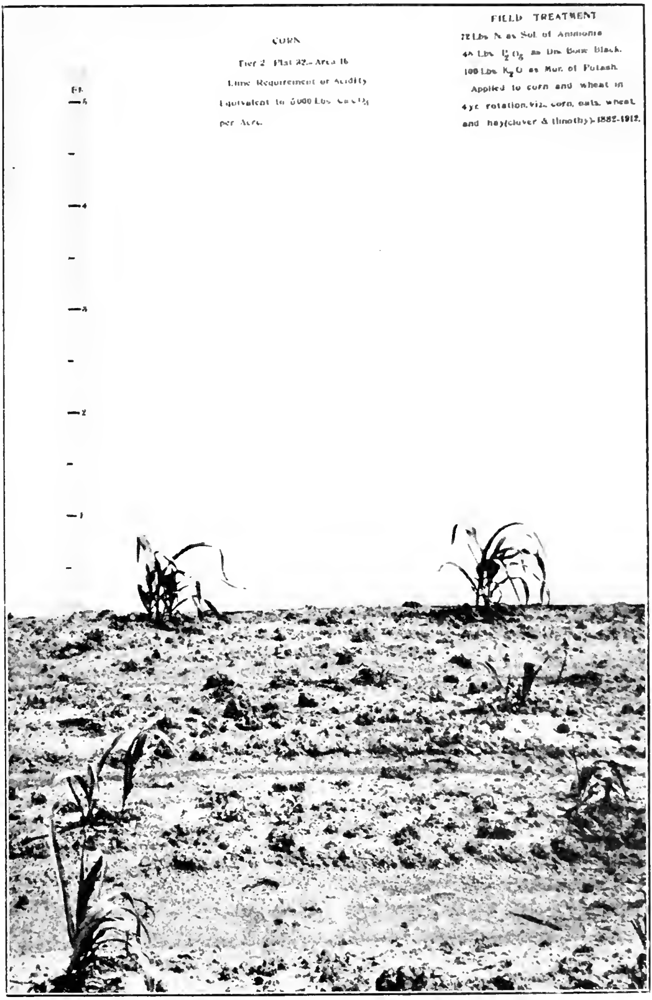


Fig. 56.—Effect of acidity resulting from use of ammonium sulphate. Corn. General fertilizer plats, Department of Agronomy, Pennsylvania Station.

show the effect of the same treatment on corn and oats, but in soil that contains enough limestone to neutralize the acidity. Sulphate and particularly the muriate of potash also tend to leave an acid residue, due to the absorption of potassium by plants or colloids and the presence of the acids sulphuric and hydrochloric. This of course is the same phenomenon described under natural acidity, except that it is more pronounced.

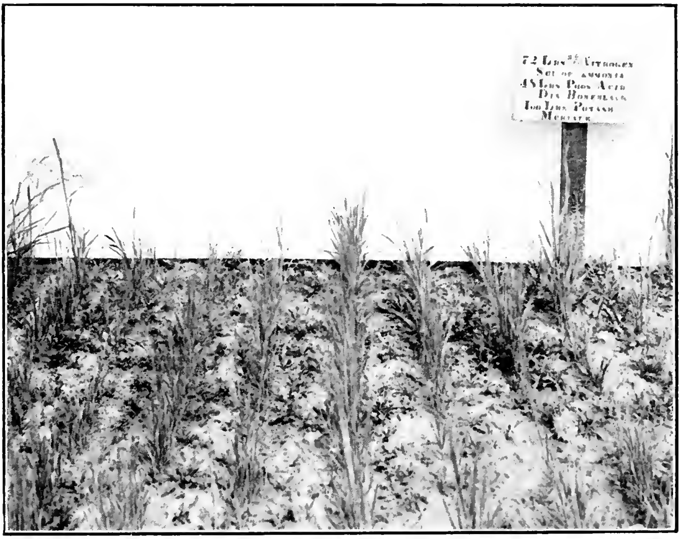


FIG. 57.—Effect of acidity resulting from use of ammonium sulphate. Oats. General fertilizer plats, Department of Agronomy, Pennsylvania Station.

Whether or not a soil becomes acid from any or all of the above mentioned causes depends on the absence or presence of sufficient bases to neutralize the acids as they are formed. In other words the causes above enumerated produce acids. The effect is noticed if insufficient bases are present to neutralize the acids (Figs. 56, 57, 58, and 59). The principal base in the soil is calcium carbonate resulting from limestone or from silicates containing calcium. Soils derived from limestone contain particles of calcium carbonate which slowly dissolve, yielding a solution which neutralizes any acids resulting from organic decomposition or selective absorption. Little calcium is as a rule present in silicate form and hence little carbonate can be produced from this source. In time all the calcium carbonate is dissolved out and then the acid condition of the soil asserts itself. This solution of calcium carbonate takes place rapidly and completely.

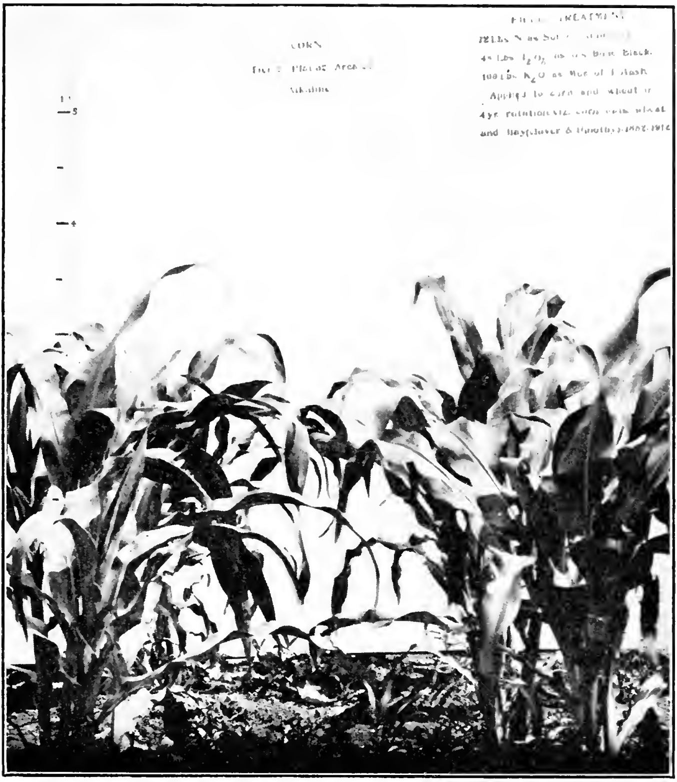


Fig. 58.—Effect of sufficient limestone in the soil to neutralize the acidity from ammonium sulphate. Corn. General fertilizer plats, Department of Agronomy, Pennsylvania Station.

On the other hand, it frequently happens that soils derived from silicate rocks containing calcium do not become acid readily. This is because the calcium is slowly dissolved out as calcium bicarbonate and but little is wasted due to leaching. Practically all of it neutralizes acids or serves some other valuable function. There is no excess at any one time and, moreover, the total amount of calcium present is very considerable.

Fig. 59.—Effect of sufficient limestone in the soil to neutralize the acidity from ammonium sulphate. Oats. General fertilizer plats, Department of Agronomy, Pennsylvania Station.

But, nevertheless, the general tendency of all soils is to lose the basic material and to produce acids from various causes. This combination of changes results in an acid or sour soil.

Virgin soils may be temporarily acid, the latter being due to the accumulation of organic matter. Cultivation will cause further oxidation and destruction of these acids and also will cause increased solution of basic material and hence neutralization of the acids.

But whatever the cause may be, permanent soil acid, as a rule, should be neutralized by certain calcium compounds, loosely called "lime."

187. **Lime.**—The chemical term lime is used for calcium oxide, CaO. Agriculturally, however, lime is any compound of calcium which will neutralize acids. The compounds having this power are the carbonate, hydroxide, and oxide.

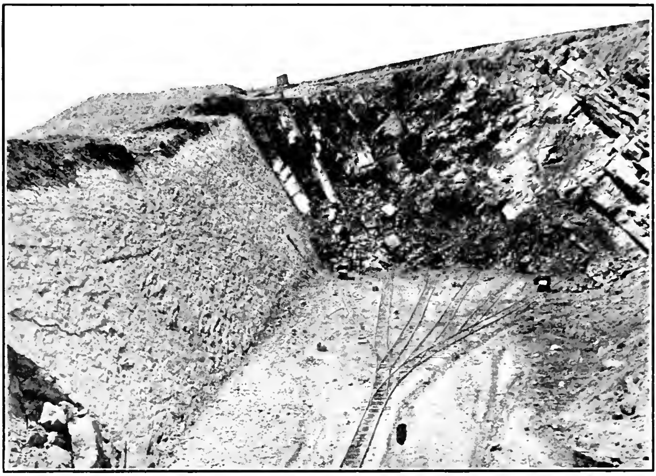


Fig. 60.—Limestone quarry. Department of Experimental Agricultural Chemistry, Pennsylvania Station.

(*a*) Calcium Carbonate, $CaCO_3$.—This form of calcium occurs in limestone, oyster shells, shell marl, and chalk, all of which when pure may contain as much as 95 to 98 per cent. calcium carbonate, but frequently contain less (Fig. 60 shows a limestone quarry). Limestone very often is composed of magnesium carbonate as well as calcium carbonate, in amounts varying from a few per cent. up to 45 per cent. When the latter content of magnesium carbonate is present the mineral is called dolomite. To be used on the soil all forms of calcium carbonate should be ground very fine, preferably so that 75 per cent. at least passes a hundred mesh sieve. It must be remembered that it is the calcium oxide content only which is of value in neutralizing acids. One hundred pounds of calcium carbonate contain fifty-six pounds of calcium oxide, or to be more in accord with the naturally occurring limestones, one hundred pounds of 95 per cent. limestone contain fifty-three pounds of calcium oxide.

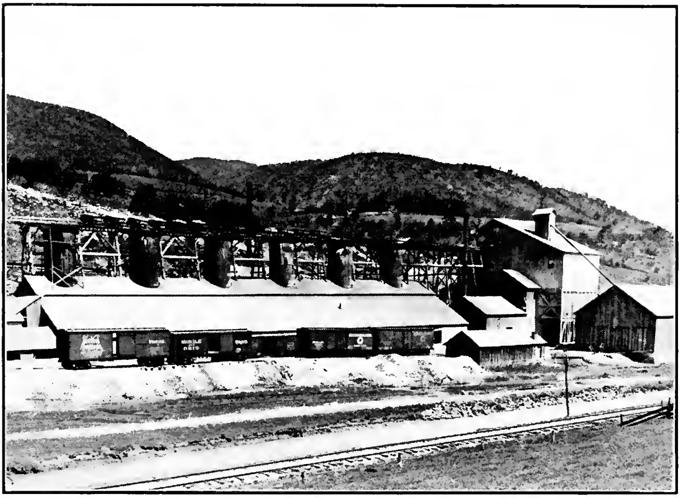


FIG. 61.—Lime kilns. Department of Experimental Agricultural Chemistry, Pennsylvania Station.

(*b*) CALCIUM OXIDE, called also BURNT LIME, STONE LIME, LUMP LIME, ROCK LIME, CAUSTIC LIME, and QUICKLIME, CaO.—This is prepared from any of the forms of calcium carbonate, although usually from limestone, by "burning," either in specially built kilns (Fig. 61) or in piles in the field. In either case the limestone is alternated with wood or coal and the latter by burning produces sufficient heat to drive off carbon dioxide from the limestone and leave calcium oxide, thus:

$$CaCO_3 + \text{heat} = CaO + CO_2.$$

If pure this form of lime is all valuable in neutralizing acids and is the most concentrated form that can be obtained.

It is in fact the only fertilizer which contains practically 100 per cent. of the valuable constituent.

(*c*) CALCIUM HYDROXIDE, SLAKED LIME, HYDRATED LIME, $Ca(OH)_2$.—When water is added to a lump of calcium oxide it swells, gives off heat, and finally crumbles to a fine, dry powder. The process is called "slaking," and the product slaked lime. The reaction is expressed thus:

$$CaO + H_2O = Ca(OH)_2.$$

The volume of the calcium oxide is increased two or three times, and the weight is increased one-third. To put it in another way, 100 pounds of slaked lime contain about 75 pounds of calcium oxide. A solution of calcium hydroxide in water is called lime water. A thin paste of the hydroxide and water is called milk of lime.

(*d*) AIR-SLAKED LIME—When burnt lime is allowed to remain exposed to the air it first takes on water and then carbon dioxide until it finally becomes calcium carbonate, thus:

$$CaO + H_2O = Ca(OH)_2.$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

A pile of burnt lime slakes first on the outside and the lumps fall apart covering the pile with fine material and filling up the interstices so as to protect the interior of the pile from rapid change to carbonate (Fig. 62). The outside changes very quickly to the carbonate. Without a chemical analysis it would be impossible to tell how much calcium oxide there is in a given lot of air-slaked lime, unless, of course, the amount of burnt lime originally present is known. The process, however, is very slow. For example, a sample taken at a depth of 4 inches from the surface of a heap exposed ten years contained 27 per cent. calcium carbonate and 37 per cent. calcium hydroxide.

188. **Availability of Lime.**—Under the best conditions chemically pure calcium oxide is soluble as calcium hydroxide at ordinary temperatures to the extent of one part in 1000 parts of pure water. Chemically pure calcium carbonate, freshly precipitated, is very slightly soluble in pure water,

but in water saturated with carbon dioxide at ordinary temperature it is soluble as calcium bicarbonate to the extent of one part in about 1000 parts. The less carbon dioxide present, the less calcium carbonate is dissolved. Soil moisture contains small quantities of carbon dioxide. This would change calcium hydroxide dissolved in it to carbonate, a change which takes place very quickly. Further quantities of carbon dioxide would change the carbonate to bicarbonate and so dissolve it. Since carbon dioxide is being constantly produced in the soil, the change of hydroxide to carbonate and bicarbonate is fairly rapid. On account of this double change of hydroxide, it makes very little difference which form is used on soils, whether fresh slaked lime, air-slaked lime, or limestone. Burnt lime has a caustic effect on plant growth, and is said to cause rapid decay of organic matter in the soil; consequently it should be used with great care and never should be applied near seeding time. Due to a difference in physical condition, or more accurately stated, due to a difference in molecular arrangement, there is a difference in the solubility of various carbonates. Shell marl, oyster shells, limestone, is the order of solubility of these carbonates. For practical purposes, however, it may be said again that the availability of all forms of lime is

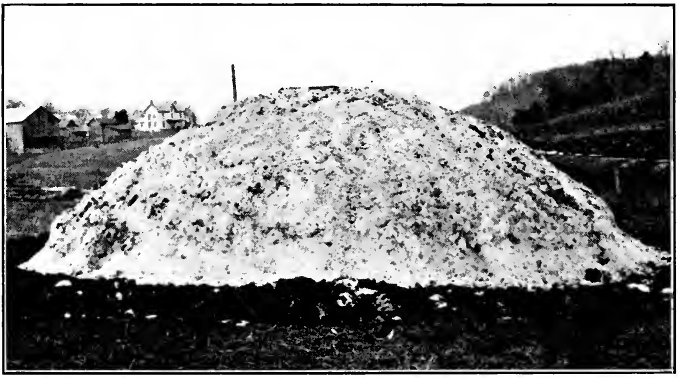


Fig. 62.—Pile of air-slaked lime. (Hibshman.)

about the same. In other words the farmer may apply slaked lime, air-slaked lime, or ground carbonate in the form of shell marl, oyster shells, or limestone, with equal results. It is the bicarbonate of lime in any event which is the active form in the soil. All that he must remember is that to get 100 pounds of calcium oxide he must use 100 pounds of burnt lime, 130 pounds of slaked lime, or 180 pounds of carbonate; of air-slaked lime he must know the calcium oxide content.

FIG. 63.—Lime and clover test. Check plat, yield of hay 980 pounds per acre. Pennsylvania Station.

189. **Effect of Lime on the Soil.**—Inasmuch as lime is for the most part a soil amendment, the changes which it occasions in the soil, and by which plants are benefited, are of great importance. No other element has such a great variety of uses in crop production, and yet it must not be considered a universal panacea for all soil ills. Figs. 63, 64, 65, and 66 show that while lime is needed to correct acidity, fertilizers also are needed.

(*a*) NEUTRALIZING ACIDS.—This is perhaps the best known function of lime, and the results are far reaching. Many acids are poisonous to plants. That is, there is a direct physiological effect, more particularly from the mineral acids and from some organic acids, oxalic for example. Then again, acids check the activity of soil bacteria. Decomposition is prevented. This means that the production of carbon dioxide is limited, and, hence, solution of soil minerals is lessened and plant food thereby diminished. Ammonification and nitrification are very seriously checked by acids and the supply of nitrogen for plants is therefore cut off. The activity of nitrogen-fixing bacteria is also

Fig. 64.—Lime and clover test. Lime at rate of 1000 pounds per acre. Yield, 1960 pounds. Pennsylvania Station.

Fig. 65.—Lime and clover test. Commercial fertilizer only at rate of 250 pounds per acre. Yield, 1560 pounds. Pennsylvania Station.

lessened by acids. Fig. 67 shows the effect of different amounts of lime on the growth of clover in an acid soil.

Fig. 66.—Lime and clover test. Lime and fertilizer. Same amounts as before. Yield, 2526 pounds per acre. Pennsylvania Station.

Fig. 67.—Pot test of lime on clover in acid soil. Amounts indicated are rates per acre, 5200 pounds $CaCO_3$ being needed to neutralize the soil according to the Veitch method. Yields from left to right: 8.7 gms.; 8.8 gms.; 7.9 gms.; 2.3 gms.; 0 gms. Department of Agronomy, Pennsylvania Station.

By neutralizing soil acids lime prevents poisoning of plants, hastens decomposition of organic matter, and increases nitrification and fixation. The fact that lime hastens decomposition is frequently charged against it. This is a great mistake, for decomposing organic matter is of very great value to crops and should be encouraged, within reason of course. Active organic matter helps to release the stores of unavailable plant food. Organic matter in the soil should be maintained so that it may be destroyed. A mere piling up of organic matter in the soil, organic matter that does not decay, is useless except for holding moisture and improving soil texture.

(*b*) MAKING POTASSIUM AVAILABLE.—Lime releases potassium from insoluble silicates and humates. Calcium takes the place of potassium in these compounds and potassium is made soluble as the carbonate.

(*c*) MAKING PHOSPHORUS AVAILABLE.—Lime also changes iron and aluminium phosphates to calcium phosphate and thereby makes the phosphorus compound soluble in the soil moisture (Section 135, *a*). Also by maintaining a supply of lime in the soil, phosphate fertilizers are prevented from changing to iron and aluminium phosphates.

It must be borne in mind that valuable as lime is in freeing unavailable potassium and phosphorus, it does not *add* either of these elements to the soil, it rather exhausts the soil. This is of course beneficial—the freeing of plant food in the soil—but additions must be made in the form of phosphate fertilizers if the supply is to be maintained.

(*d*) IMPROVING THE PHYSICAL CONDITION.—Lime also improves the structure of soils by flocculating heavy clays and binding together loose, sandy soils.

(*e*) CHECKING PLANT DISEASES.—Lime destroys some fungous diseases of plants, notably the club-root or finger-and-toe disease of cabbage and turnips.

(*f*) HARMFUL EFFECTS.—Lime, on the other hand, is favorable to potato scab. It prevents the growth of such crops as the cranberry, watermelon, blueberry, and trailing arbutus. It is not known why this is, whether they can live better on other forms of calcium than the bicarbonate or whether they prefer an acid soil. Too heavy applications of caustic or burnt lime particularly destroy organic matter to an unreasonable extent, and also will injure germinating seeds if applied too near to seeding.

190. **Use of Magnesian Lime.**—Some limestones contain magnesium, and small amounts do no harm. Large amounts up to 45 per cent. (dolomite) are questionable. When burned, such a lime slakes with difficulty, and may cause serious harm to crops if the soil to which it is applied contains an undue proportion of magnesium. Just what this proportion should be varies with the crop and depends of course also on the relative amounts of calcium and magnesium that are dissolved in the soil moisture. On the other hand, magnesian lime does no harm on soils not so well supplied with magnesium. To be safe it is better to use a grade of lime high in calcium carbonate.

191. **Calcium Sulphate, Gypsum, Land Plaster,** $CaSO_4.2H_2O$. —This material is used to some extent on soils as an amendment. It frees potassium and phosphorus from insoluble compounds, and is said to hasten the decomposition of organic matter, but it has no neutralizing effect and is not of much value. The other compounds of clacium have all these effects plus the neutralizing effect.

192. **Waste Lime.**—Lime is used in purifying coal gas and in the manufacture of sugar from beets. *Gas-lime* should be exposed to the air for some time before applying to the soil, or should be added to the soil a long time before seeding because it contains sulphides and sulphites from sulphur compounds absorbed from the gas. These compounds change to sulphates on exposure to the air and are thus rendered harmless to plants.

Lime is a waste product in the manufacture of acetylene gas, and should be exposed to the air before use to allow traces of acetylene to escape, which is harmful to seeds.

Lime from these processes is usually a mixture of hydroxide and carbonate and is valuable for agricultural purposes if it can be obtained cheap and if the content of calcium oxide is known.

193. **Summary.**—Calcium compounds as a rule are considered soil amendments, that is, their effect is on the soil and not on the plant directly. But calcium is a necessary

element in plant growth, is used by some plants, notably clover and alfalfa, in large quantities, and is frequently lacking in soils in an available form. It has a distinct value in many cases as a plant food, and lime compounds may very frequently be direct fertilizers.

Soil acidity, a condition corrected by lime, occurs in many soils and is a natural result of cultivation and cropping. Acids are produced in soils by the decay of organic matter; by the selective action of plants which removes the base from a salt and leaves the acid radicle free as an acid; and by the adsorption of the base from a salt by hydrated silicates and humus. Applications of potassium sulphate and potassium chloride intensify this action. Soil acidity results when there are not sufficient bases present to neutralize the acid. Calcium carbonate is the principal base.

Lime, properly so-called, is calcium oxide, but popularly is any compound of calcium which will neutralize an acid. Calcium carbonate and calcium hydroxide are the forms ordinarily used. Whatever the original compound may have been, the bicarbonate is the active one in the soil, and is formed sooner or later from either the carbonate or hydroxide. Hence no one compound is preferable.

Lime acts on the soil by neutralizing acids and thus hastening decomposition of organic matter, increasing nitrification and fixation of nitrogen—all bacterial processes. It also prevents the acids from poisoning plants. Lime also frees potassium and phosphorus from insoluble compounds, improves the physical condition of soils, and checks plant diseases. It causes potato scab, however, and prohibits the growth of some crops. Too heavy applications of burnt lime destroy organic matter unnecessarily and may destroy seeds if applied too near seeding.

The use of magnesian lime is not recommended. Waste lime is good if care is taken in buying and using the various forms. Gypsum is not particularly valuable.

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CHAPTER XIII

FARM MANURE

Up to the present time the fertilizers discussed have been commercial products only, and many of them inorganic materials of value only for the plant food which they contain. There is one fertilizer, however, which is produced to a greater or less extent on every farm, and which contains not only the three principal plant foods, but which also contains organic matter and bacteria, both of which are valuable to the soil. This material is the excrement of domestic animals mixed with straw or other litter. In this discussion the term farm manure will be used to describe the mixture of solid and liquid excrement of any domestic animal with the litter of whatever character. There is some tendency today to call the mixture of horse excrement and litter, stable manure; and cattle excrement with litter, barnyard manure. The term manure is sometimes applied to any fertilizing material, but this practice is more common in England than in the United States.

194. **Solid Excrement.**—The solid excrement, or feces, of an animal are the undigested portions of the food. This material has been rather thoroughly comminuted by the animal in the various processes of mastication, remastication in the case of ruminants, and of churning movements in the stomach and intestines. On account of the more complete mastication and digestion in cattle, the feces of the latter are more finely divided and more compact than those of horses. Although the constituents of the feces have not been digested and absorbed by the animal, more or less decomposition has taken place, particularly in the case of the proteins. Part of this change has occurred in the stomach and intestines due to partial enzyme action, and part in the

intestines due to bacteria. These bacteria are present in very large numbers in the voided excrement and are valuable in promoting further decomposition in the soil. Although on this account feces contain plant food that is more available than it was in the original animal food, nevertheless, it is not a quick acting fertilizer. All of the fertilizing constituents in feces have to undergo decomposition to be soluble and available to plants.

The amount of the various fertilizer ingredients in solid excrement varies with different animals. Table XIV gives the average percentage composition of the excrement of the common farm animals, horse, cow, pig, sheep, and hen. The table also gives the amount voided per year for each animal, taking the indicated weights as rough averages.

Table XIV.—Composition and Amount of Animal Excrement

Kind of animal and average weight.	Excrement.			Nitrogen per cent.	Phosphoric acid per cent.	Potash per cent.
	Kind.	Proportion per cent.	Amount voided per year, pounds per average animal.			
Horse, 1300 pounds	Solid	80	18,700	0.55	0.30	0.40
	Liquid	20	4,700	1.35	Trace	1.25
Cow, 950 pounds	Solid	70	18,000	0.40	0.20	0.10
	Liquid	30	7,600	1.00	Trace	1.35
Pig, 150 pounds	Solid	60	2,700	0.55	0.50	0.40
	Liquid	40	1,800	0.40	0.10	0.45
Sheep, 120 pounds	Solid	67	1,000	0.75	0.50	0.45
	Liquid	33	500	1.35	0.05	2.10
Hen, 4 pounds	.....	..	35	1.00	0.80	0.40

It is to be noted that the solid excrement of the horse is much drier than that of the cow, hence its decomposition is more rapid and the temperature of the mass rises very considerably. This fact is made use of in making "hot-frames" in the early spring. Fermenting horse manure is the source of heat.

195. **Liquid Excrement.**—The liquid excrement, or urine, of animals contains waste food material which has been

digested and absorbed, but which has also been utilized, broken down, and eliminated. All of the material is soluble and is quickly made available. Decomposition to inorganic forms of plant food is rapid. Table XIV also shows the relative amounts of liquid excrement.

196. **Litter.**—By litter is meant the plant residues or other materials used in stalls as bedding for animals and which becomes mixed with excrement. As a part of farm manure litter serves important functions, such as the absorption of urine, and of ammonia which escapes from excrement on decomposition. It also makes manure easier to handle and adds organic matter and plant food.

Table XV shows the number of pounds of water and ammonia absorbed per 100 pounds of litter of various kinds.

TABLE XV.—AMOUNT OF WATER AND AMMONIA ABSORBED BY LITTER

Kind of litter.	Water pounds per 100.	Ammonia pounds per 100.
Wheat straw	220	0.17
Partly decomposed oak leaves	162	. . . .
Pine sawdust	435	0.05
Peat	600	1.10
Peat moss	1300	0.86

TABLE XVI.—COMPOSITION OF LITTER

Kind of litter.	Nitrogen per cent.	Phosphoric acid per cent.	Potash per cent.
Straw	0.50	0.25	1.10
Leaves	0.80	0.30	0.30
Sawdust	0.45	0.30	0.70
Peat moss	0.80	0.10	0.17
Peat	0.85	0.18	0.08

Table XVI shows the composition of various litters in the fertilizing constituents. It is to be noted that straw, the usual form of litter, contains about as much nitrogen, phosphoric acid, and potash as does excrement, so that as far as actual plant food is concerned there is no dilution of the amount present in excrement by mixing it with the litter. Sawdust and shavings, however, which are used to a considerable extent in cities, contain much less plant food, and furthermore, they decompose very slowly in the soil, so that what plant food they do contain becomes available to a very slight extent. But sawdust and shavings are good absorbers of liquid, even better than straw, and are consequently of considerable value. They do no harm in the soil as is sometimes claimed.

197. **Mixed Excrement.**—Considering the mixture of solid and liquid excrement, exclusive of litter, it is found that the composition varies with the age of the animal and the kind of food eaten. An adult animal, working or fattening, retains not more than 5 or 10 per cent. of the nitrogen, phosphoric acid, and potash in the food. Cows giving milk, and young animals, retain from 25 to 50 per cent. of these constituents in their food. Taking the average excrement produced on the farm, it may be said to contain about 80 per cent. of the fertilizing constituents of the food eaten.

The kind of food eaten will influence the composition of excrement. If the food consists of press cake, grains, bran, or other concentrated material, the excrement will be much higher in nitrogen, phosphoric acid, and potash than if the food were roughage, or ensilage, or beets (see Table III).

198. **Farm Manure.**—This product, as mentioned at the beginning of the chapter, is a mixture of solid excrement, liquid excrement, and litter. As can be readily seen from what has been said about the causes of variation in the composition of excrement, and what is known about variation in the composition of litters, the amount of plant food in farm manure is never constant. From the discussion which follows as to the decomposition and losses of manure piles, it is to be noted that these factors also affect the composition. For purposes of rough calculation, however, it is somewhat generally agreed that the average farm manure contains about 0.5 per cent. nitrogen, 0.25 per cent. phosphoric acid, and 0.5 per cent. potash; or, to put it more plainly, a ton of farm manure contains 10 pounds of nitrogen, 5 pounds of phosphoric acid, and 10 pounds of potash.

199. **Compounds in Fresh Farm Manure.**—When first produced, farm manure contains in the solid excrement,

starch, cellulose, other carbohydrates, lignin, fat, proteins in various stages of decomposition, mineral elements combined organically, remains of intestinal juices, and other compounds. The liquid portion contains organic and inorganic salts, soluble nitrogenous compounds like urea, etc. The litter, of course, contains the usual plant compounds present in such materials.

200. **Bacteria in Manure.**—Liquid excrement when first voided contains no bacteria, but the solid excrement contains exceedingly large numbers, determinations on various excrements showing from 90,000,000 to 150,000,000 organisms in one gram of material. In addition to this, litter contains from 10,000,000 to 400,000,000 organisms. In the course of time the number of organisms diminishes as food becomes scarcer and the products of their activities increase sufficiently to kill many of them.

201. **Decomposition of Farm Manure.**—As a result of its high bacterial content, manure commences to decompose as soon as it is produced. Molds also help the decomposition. The bacterial changes which take place in it are of considerable importance and can be discussed best under two heads: Aërobic, where air has free access to the materials; and anaërobic, where air is kept out.

(*a*) Aërobic.—The most important changes taking place in manure are those affecting nitrogen. This element is present in the urine largely as urea, $CO(NH_2)_2$, which is attacked very easily by several kinds of bacteria. The action is one of hydrolysis, thus:

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3.$$

The ammonium carbonate readily breaks up on exposure to the air, as follows:

$$(NH_4)_2CO_3 \rightleftarrows 2NH_3 + CO_2 + H_2O.$$

This results, of course, in loss of nitrogen, for the ammonia escapes into the air. The reaction is reversible, and in the presence of plenty of carbon dioxide and water with no circulation of air to remove the volatile products, ammonium carbonate is not decomposed.

In the solid excrement nitrogen is present in protein forms which have resisted decomposition in the digestive tract of the animal, and hence do not decompose very rapidly in manure. In the litter the nitrogenous compounds are also proteins, and although somewhat more easily broken down than the proteins of the solid excrement, they are not decomposed very rapidly. Considering the nitrogen compounds in the solid part of the manure, it can be said that they break down in the presence of air with the formation of ammonia which escapes into the atmosphere. Moreover, in the presence of plenty of air, ammonia is further oxidized to free nitrogen. True nitrification, that is, the formation of nitrates, is not a common bacterial change in manure piles.

Aërobic decomposition results in a gradual change of carbohydrates—cellulose, starch, and pentosans—and of fats, as well as of proteins, to carbon dioxide and water, with the intermediate production of organic acids. Compounds containing potassium and other bases decompose with the formation of carbonates of the bases. Phosphorus and sulphur in proteins remain as phosphates and sulphates, or more correctly speaking as phosphoric and sulphuric acids which are neutralized by the bases present. As a matter of fact, there is an excess of alkaline carbonates in decomposing manure piles, whether the action is aërobic or anaërobic. This is evidenced by the dark liquids which may be seen draining from manure piles. This dark liquid is an alkaline extract of humus, for humus, or at least humus-like compounds, result from partial decomposition of the organic matter, more particularly where there is not much air present.

In general, aërobic decomposition of manure results in the production of considerable heat. Horse and sheep manure being more porous and drier, decompose very easily and are called "hot" manures. The manure of pigs and cattle, on the other hand, are more compact, contain more water, and hence do not decompose so rapidly. They are called "cold" manures. The loss of carbon dioxide and water from manure, of course, results in loss of weight.

(*b*) Anaërobic.—When air is not present in manure, decomposition and loss of ammonia are not so rapid. While urea may change to ammonium carbonate there is no opportunity for this compound to break up into ammonia, carbon dioxide, and water. The proteins of the solid portion are slowly changed to soluble compounds and some ammonia, but the latter is not lost to any great extent. Moreover, much of the nitrogen so changed is absorbed by the bacteria themselves and retained in the manure as insoluble compounds.

The non-nitrogenous portions of the manure are broken down into organic acids, carbon dioxide to some extent, and in addition considerable quantities of hydrogen and methane. Sulphur is likely to be changed in part at least to hydrogen sulphide. Moreover, considerable quantities of black "humus" are formed. The straw and other litter lose their original fibrous condition and become a part of the dark, fine mass of "well-rotted manure." Under anaërobic conditions the loss of carbon dioxide, water, hydrogen, and methane results in loss of weight.

202. **Molds.**—Particularly in loose, dry manure, molds develop and cause destruction of both nitrogenous and non-nitrogenous compounds. "Fire fanging" is a result of the growth of molds on horse manure, resulting in the appearance of a white, powdery coating on the material.

203. **Loss.**—The above mentioned changes are what take place under special conditions. Considering now an ordinary manure pile, such as is altogether too common even now, it will be interesting to note what happens. Such a pile is only moderately compact; loose on the outside at any rate, and exposed to the weather. Both aërobic and anaërobic decomposition take place. Urea changes rapidly to ammonium carbonate and ammonia. Proteins are changing to ammonia. Ammonia is being oxidized to free nitrogen as well as passing off into the air. Carbon dioxide and water are being formed in considerable quantities as well as some hydrogen and methane. The pile shrinks in volume, losing weight constantly. Humus-like substances form, many of which are dissolved out by a solution of alkaline carbonates

formed by the decomposition of organic compounds of potassium and other alkalies, including some ammonium carbonate. Rain leaches out these soluble compounds as well as soluble phosphates. There is consequently a decided loss of potassium and phosphorus by leaching; of nitrogen by volatilization as free nitrogen and as ammonia; and a decrease in amount of organic matter due to volatilization of carbon dioxide, hydrogen, and methane, and to leaching away of humus compounds. The most serious loss, however, is that of nitrogen, phosphorus, and potassium, and amounts under such conditions to more than half of the original content of these elements. Moreover, they are in the best form, being soluble and available to plants.

204. **Prevention of Loss.**—From the preceding discussion, it can be seen that the greatest loss of nitrogen occurs under aërobic conditions, while the loss of phosphorus and potassium and some of the nitrogen occurs only when leaching takes place. Since it is possible to retain a large part of the volatile ammonia by chemical means as well as by producing anaërobic conditions, methods of preventing loss of the fertilizing constituents can be grouped under two general heads: Mechanical and chemical.

(*a*) MECHANICAL.—Since phosphorus and potassium in the solid excrement, after being rendered soluble under either aërobic or anaërobic conditions, are only lost by being washed out of the manure pile, it is sufficient only to prevent leaching by keeping the pile under cover, or in a water-tight receptacle; or piled in such a way that leaching is reduced to a minimum. This may be accomplished by making the pile decidedly concave on top to hold the water that falls, and building the sides vertical.

Since a large part of the potassium and nitrogen are in the urine and hence soluble, it is necessary to take precautions which will prevent the urine from running off. Litter accomplishes this purpose if employed in sufficient quantities, and particularly if cut into short pieces—a practice which increases the absorptive capacity of straw two or three times. Rock phosphate sprinkled in the stalls before adding the bedding also makes an excellent absorbent material. This practice not only reinforces the manure in phosphoric acid content, but also serves to make the rock phosphate available to plants (Section 173). Three or four pounds to each animal every day for horses and cattle is a good amount to use.

In addition to the leaching away of soluble nitrogenous compounds, a large part of the nitrogen is lost by volatilization. Since this is due largely to aërobic bacterial action, combined with free circulation of air which allows dissociation of ammonium carbonate, a system which keeps the pile compact and saturated with water, or at least with carbon dioxide, will answer the purpose. This may be accomplished by compacting either in piles or pits, or under the feet of the animals by the so-called deep-stall system.

If a pile of manure is kept well packed down and thoroughly though not excessively soaked with water or surplus urine, air will not have access to the pile except on the surface, and aërobic decomposition will be reduced to a minimum. By this means nitrogen is not lost to any great extent either as free nitrogen or as ammonia.

The deep-stall system consists in allowing the manure to be compacted by the feet of animals in stalls where the manure can accumulate and be well tramped down, litter being liberally used. By this means the loss of nitrogen is reduced to about 15 per cent., but the practice is not sanitary and although used to some extent in Europe is not to be recommended. The saving of nitrogen in manure is not the only thing to be considered in caring for stock.

(*b*) CHEMICAL.—In preventing the loss of fertilizing constituents from manure by chemical means there is only nitrogen to be considered. Phosphorus and potassium are easily retained by preventing leaching and this is a mechanical means. Nitrogen, on the other hand, is volatile as ammonia and free nitrogen, hence chemicals which form non-volatile compounds of nitrogen, or which prevent complete decomposition, are employed.

1. *Gypsum, Land Plaster.*—By using gypsum, $CaSO_4$, at the rate of 100 pounds to the ton of manure, or better yet by sprinkling three or four pounds in the stall of each

animal per day and then adding litter, the ammonium carbonate is changed to ammonium sulphate, thus:

$$(NH_4)_2CO_3 + CaSO_4 = (NH_4)_2SO_4 + CaCO_3.$$

Ammonium sulphate is non-volatile, although it is soluble, and must be prevented from leaching. The advantage is that no ammonia escapes into the air. Gypsum is perfectly safe to use because it has no harmful effect on the feet of the animals. By itself it has no fertilizing effect on the soil, but after reacting with ammonium carbonate, the resulting calcium carbonate will neutralize soil acids, although there is but little present at any one time.

2. *Acid Phosphate.*—This material may be used at the rate of 50 pounds per ton of manure, but on account of its harmful effect on the feet of animals it is better to use it in the gutters or with manure after the latter has been removed from the stalls. The value of acid phosphate is two-fold. It holds the ammonia as ammonium sulphate, due to the calcium sulphate in the fertilizer. And furthermore, it reinforces the manure with phosphoric acid which is the deficient element. It is stated that acid phosphate is the most efficient holder of ammonia in use.

3. *Potash Salts.*—The muriate and sulphate of potash, kainite, or any of the salts of potash used as fertilizers, except potassium carbonate (see below), are used at the rate of 50 pounds per ton of manure. These compounds are also injurious to the feet of animals and should be used like acid phosphate. Ammonia is converted to ammonium chloride or sulphate and is non-volatile, although soluble.

4. *Sulphurous and Sulphuric Acids.*—These acids will retain ammonia as the sulphite (later changing to the sulphate) and the sulphate, but they are not to be recommended, for their acid character renders them harmful to the soil if they are not completely neutralized.

5. *Preservatives.*—To check bacterial action and thus prevent the formation of ammonium carbonate, such preservatives or antiseptics as carbon disulphide and soluble fluorides have been employed. Their use, however, should

be discouraged, for they are not only expensive, but by interfering with the activity of bacteria in manure destroy one of its most valuable functions, namely, that of supplying microörganisms to the soil.

6. *Lime Should Never be Used.*—In this connection it must be emphasized that for the preservation of nitrogen or absorption of liquid in stalls, lime should never be used. It does not hold the ammonia, but rather causes its loss by releasing it from any of its compounds. Ground limestone is not so bad in this respect as burnt lime. Wood ashes should never be used because the potassium carbonate will drive off ammonia even more readily than burnt lime. The use of lime in composting, however, is allowable, but for a different purpose if proper precautions are taken (Section 205, *c*).

205. **Methods of Use.**—There are only a few points to be brought out in a work of this kind. A more complete treatment of the subject is better suited to a discussion of special crops and methods of farming.

(*a*) Fresh Manure.—Experiments show conclusively that better yields are secured on ordinary soils from manure hauled fresh to the fields than from manure that has stood in the pile for some time even under optimum conditions. This is principally due to the fact that all the fertilizing material has been retained and that the maximum effect of bacteria in decomposing organic matter and dissolving mineral plant food has been obtained. Manure which has been hauled fresh to the fields can be spread on the surface of the soil and allowed to lie exposed without danger of loss of nitrogen, for the sun will check bacterial action directly, and also by drying the manure will thus deprive the bacteria of their necessary moisture. Fresh manure can be applied on top of the snow with success. No loss of ammonia will occur, and as the snow melts the soluble fertilizing ingredients soak into the soil. This practice, however, is not safe on frozen hillsides where there is danger of loss of these soluble compounds by being washed away over the frozen soil.

(*b*) Well Decomposed Manure.—Sometimes, however, it is not economical to spread manure at once. It may cost more to haul it fresh to the fields than the increase in crops would be worth. In such cases the application of decomposed manure should be followed at once by plowing or harrowing, or be made just before a rain which will wash into the soil ammonium carbonate previously formed. In the fresh manure ammonium carbonate has not been produced, so its loss need not be feared.

On light soils well decomposed manure has some advantages over fresh manure, since the latter would make the soil only more open and porous and would burn out quickly. The nitrogen of well decomposed manure is not so available as that of fresh manure, for much of it has been decomposed to soluble compounds and back again to proteins in the bodies of bacteria. The phosphorus and potash on the other hand are more available. On account of these facts, the action of well decomposed manure is more uniform and under certain special conditions is desirable.

(*c*) COMPOSTED MANURE.—This is a practice resorted to by vegetable growers, largely to get the manure quickly into a thoroughly decomposed and disintegrated condition. The objects are to get the manure in a fine state of division for easy mixing with the soil, and to make the fertilizing constituents more uniformly available. As mentioned before, fresh manure contains more available nitrogen than decomposed manure, and when used in large quantities fresh manure produces too great a leaf growth on roots or other similar crops, due to excess of nitrogen. The manure is piled in alternate layers with some absorbent like soil. All sorts of organic refuse can be added and sometimes bones, commercial fertilizers, and lime. The pile should be well covered with earth and kept reasonably moist. The alternate layers and covering of soil absorb ammonia which is generated freely under these conditions, particulatly if lime is present. The pile is thoroughly turned over from time to time—a practice which hastens decomposition and the formation of nitrates. The organic matter of bones in a compost heap is so decomposed that they can be easily ground. If lime is used, particular care must be exercised to keep plenty of absorbing material in the pile, and to cover it well.

206. **Manure an Unbalanced Fertilizer.**—As a complete fertilizer manure is not well balanced. It contains 0.5 per cent. of nitrogen, 0.25 per cent. of phosphoric acid, and 0.5 per cent. of potash. Proportionately expressed this is a 2–1–2 fertilizer. A common fertilizer for general farm crops is a 1–6–4 combination (Section 212), and for garden crops a 4–8–10 fertilizer is used. Manure is very deficient in phosphoric acid, and in order to obtain enough of this constituent it is necessary to apply in many cases more manure than is economically profitable. While it is possible to maintain the fertility of a soil for a long period of years, at least with no other fertilizer than manure, it is not a practice to be recommended. Manure reinforced with phosphoric acid is more satisfactory and, better yet, a judicious use of commercial fertilizers and manure, properly distributed in a rotation according to the crops, is to be recommended. It is by no means a good practice to add such excessive amounts of manure as are used in some sections of the country on tobacco land where an average of eighteen tons of manure per acre have been applied annually. Under these conditions the loss of the fertilizing constituents from the surface soil have been enormous.

207. **Value of Manure.**—The proper use of barnyard manure is something to be earnestly recommended on every farm. No other single material will do so much for the soil, and no other material is so cheap and easily obtained in most cases. Manure adds organic matter to the soil, and organic matter, it will be remembered, improves the physical condition of the soil, increases the moisture holding capacity and the temperature of soils. Moreover, organic matter is the source of carbon dioxide and organic acids which aid in making mineral compounds soluble. This is particularly true of fresh manure which decomposes easily. Manure also adds large numbers of bacteria to the soil, and the benefits to be derived from bacteria are too numerous to mention. And finally manure adds nitrogen, phosphoric acid, potash, and even calcium to the soil. Fig. 68 shows the effect of manure on a soil which does not respond to liming, although somewhat acid. It is probably the effect of the plant food in the manure which is here most important.

All these valuable properties of manure, moreover, are lasting in effect. An application of manure shows by increased yields for many years afterwards, whereas the effect

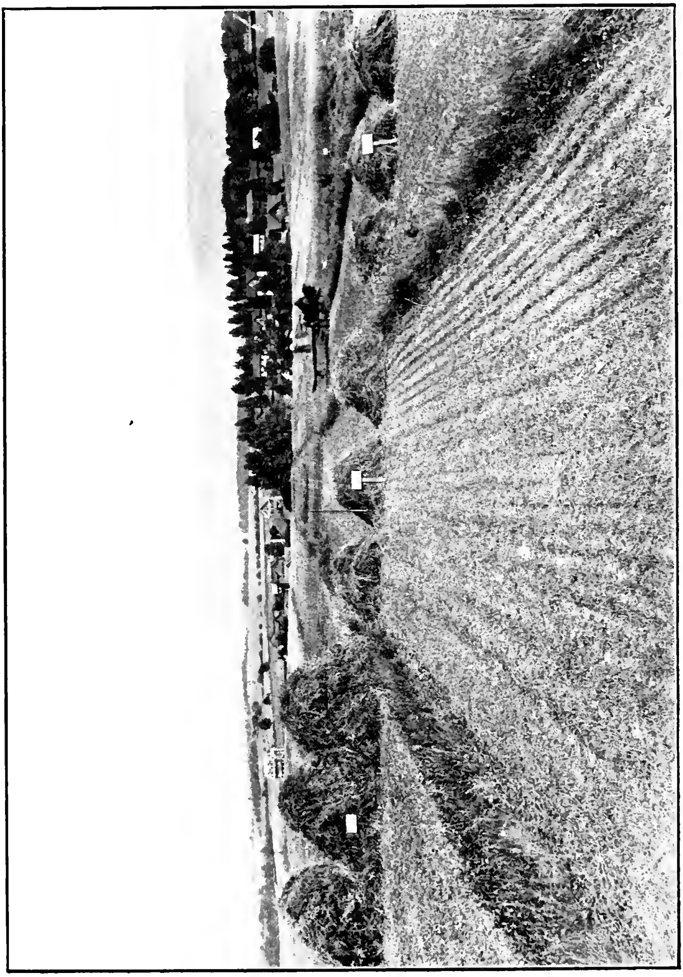

Fig. 68.—Effect of manure. Hay crop. Treatments left to right: (1) six tons of manure every two years, two tons of lime every four years; (2) two tons of lime every four years; (3) check. General fertilizer plats. Department of Agronomy, Pennsylvania Station.

of commercial fertilizers lasts but a few years at most and usually but one or two.

208. **Summary.**—One of the most valuable materials which can be used on the soil, and a material which is very generally produced, is farm manure. This is defined as a mixture of solid and liquid excrement of any domestic animal with any kind of litter. The solid excrement is the undigested portion of food eaten by the animal. The liquid excrement consists of digested material which has broken down in the process of metabolism and has been eliminated in solution. Most of the nitrogen and potash occur in the liquid excrement and practically all of the phosphorus in the solid excrement. The composition of the solid and liquid excrement varies with the kind and age of animal and kind of food eaten. In general about 80 per cent. of the fertilizing constituents in the food are recovered in the excrement. The composition of the litter or bedding affects the composition of the manure. The amount of the fertilizing constituents as a result of these various factors, and in addition, on account of decomposition and loss of material, varies a great deal, but for purposes of discussion we may consider average manure to contain 10 pounds of nitrogen, 5 pounds of phosphoric acid, and 10 pounds of potash per ton.

Due to the large number of bacteria voided in the solid excrement, and multiplying so rapidly in the liquid excrement, manure decomposes quickly. All compounds suffer change, but the most important changes are those which affect nitrogen. Under aërobic conditions proteins are changed to ammonia and even to elemental nitrogen. Urea, a constituent of urine, is changed to ammonium carbonate and ammonia dissociates and disappears. Considerable heat is produced. This fact is made use of in the case of horse manure, which is drier than cattle manure, in making "hot frames." Under anaërobic conditions, ammonia is produced but there is no opportunity for it to escape readily, and much of it is slowly absorbed by bacteria and changed to insoluble compounds again.

Under either condition phosphoric acid and potash are made soluble and easily lost if the manure pile is subjected to leaching. The cellulose and other carbohydrates are decomposed and carbon dioxide and water formed. As a result the mass loses weight very markedly. "Humus" is produced, and the litter loses its original form, the whole mass becoming short-fibered, dark-colored, and homogeneous.

The loss of nitrogen by volatilization as ammonia and free nitrogen is much greater under aërobic than under anaërobic conditions. A good way to prevent loss is to keep the manure pile thoroughly compacted and moist. To prevent loss of potash and phosphoric acid a cover to the pile is advantageous to prevent leaching. Rock phosphate in the stalls absorbs the liquid excrement and thus mechanically prevents loss of this valuable constituent of manure.

By the use of gypsum, acid phosphate, kainite, and other potash salts, except potassium carbonate, the ammonia is retained as a non-volatile though soluble compound.

By spreading manure on the fields as fast as it is formed the greatest benefit can be derived from its use, except on very light, sandy soils where well decomposed manure is preferable. Composted manure is used largely by market gardeners and is a very thoroughly decomposed manure made by mixing manure with soil, and sometimes with lime to hasten decomposition, and with commercial fertilizers to reinforce it. A layer of soil should cover such a compost heap, particularly if it contains lime, to prevent loss of ammonia.

Although manure is an unbalanced fertilizer, containing too little phosphoric acid, it is nevertheless a very necessary material for use on the soil. It supplies organic matter, bacteria, and plant food. If used in excessive amounts, however, there results great waste of fertilizing constituents, thus making it a very uneconomical material to employ. Its effect is more lasting on the soil than any other single fertilizer.

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CHAPTER XIV

SOIL AND FERTILIZER ANALYSIS

The analysis of soils and fertilizers is such an important part, both of scientific and practical agriculture, that there is necessary a brief discussion of the terms used, of the possibilities and limitations of such work, and of the immediate value.

209. **How Analytical Results are Expressed.**—It is customary in ordinary analytical work to express results in terms of the oxide of the element, thus: CaO, K_2O, Fe_2O_3, P_2O_5. This is not the form in which these elements occur, but is a convenient and conventional means of expression. In fertilizer work the elements usually determined are nitrogen, phosphorus, and potassium, and reported as nitrogen, N, phosphoric acid, P_2O_5, and potash, K_2O. Phosphoric acid is not the correct name for the oxide of phosphorus—P_2O_5—but since the oxide is the acid oxide there is some excuse for it. Furthermore, it is not consistent to express nitrogen as the element, and phosphorus and potassium as the oxides. There is a desire on the part of some chemists to express these and other results in the elemental form. It is the logical way to do, but since custom is so strong, and since most farmers and scientists think in the conventional terms, these inconsistent forms have been used here.

210. **Soil Analysis.**—The popular conception of the purpose of soil analysis is to ascertain the fertilizer deficiencies of a soil. That is, by determining in some way the amount of nitrogen, phosphoric acid, and potash, the need of a soil for any particular element can be predicted. This idea has resulted, of course, in the development of a large number of methods, and in the analyses of a large number

of soils, together with the publication of a large number of predictions. Some of these predictions have proved correct; some of them incorrect; and some of them have never been put to the proof. The difficulties in the way of determining accurately fertilizer deficiencies of a soil are so many that an analysis *alone* cannot give the information desired in a great majority of cases. Fertilizer tests in the field are the best single way to ascertain the plant food needs of a soil (Fig. 69).

The total amount of each of the several constituents can be determined accurately, and the result is a complete inventory of the plant food supply in any given soil, provided the sampling has been done carefully. It is very important to obtain a sample of soil which represents as nearly as possible the soil of the whole field in question. This information in connection with other data, such as topography, physical condition of the soil, kind of seed, cultivation, temperature, rainfall, and appearance of crop, will give an expert a good idea of the needs of a given soil.

The difficulty with this kind of analysis in interpreting plant food deficiencies is that by no means all of any particular element is available or will even become available readily. A soil may contain a large amount of phosphoric acid, but may have it in such unavailable form that plants cannot obtain enough for normal growth, and a phosphate fertilizer is actually needed. On the other hand, another soil may contain a very small amount of phosphoric acid and yet have it in readily available form. Of course, if a constituent is present in ridiculously small amounts a deficiency in that constituent may be suspected.

Various methods have been developed for determining available or readily available plant food. Strong hydrochloric acid has been used more largely than any other reagent to extract those constituents which it is assumed will be most readily available to plants. Most of the soil analyses published have been made by this method. But the results mean very little for interpreting fertilizer deficiencies. There is no accurate standard or minimum amount known, below which a fertilizer need is indicated.

The minimum varies with kinds of soils, kinds of crops, and many other factors.

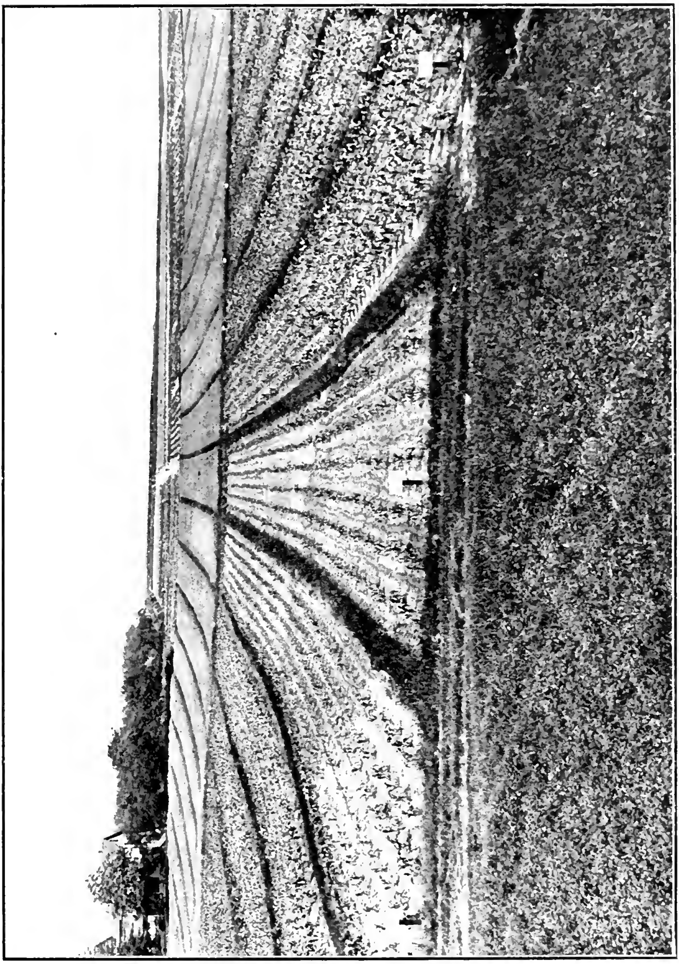

FIG. 69.—The best way to determine the plant food needs of a soil. General fertilizer plats, Department of Agronomy, Pennsylvania Station.

Numerous weak organic acids and dilute mineral acids have been proposed, and some methods seem reasonably good for certain special soils, but there are no methods of general applicability. Pure water, or water charged with carbon dioxide, might seem an excellent solvent, but against this solvent as against others for that matter, though in lesser measure, the power of chemical and physical absorption acts to prevent the extraction of plant food that may be readily available to plants in the soil. Moreover, in all these methods it is not the amount of plant food available at any one time which nourishes the crop, it is the plant food available from day to day throughout the growing season. It is the rate at which plant food becomes available that determines crop growth.

But soil analysis is of very great value to the soil chemist in determining changes which take place in the soil under certain conditions, and in comparing one soil with another, all of which work is valuable in studying the effect of fertilizers, the effect of changing physical conditions, and the effect of cropping. The knowledge so obtained can later be practically applied to help the farmer obtain better and larger crops.

211. **Lime Requirement.**—Since acidity is a very prevalent condition of many soils, and since it needs correction in most instances, numerous efforts have been made to determine the amount of acid in a soil; or, which is more direct, to determine the amount of lime necessary to neutralize acidity to a given depth. The method which has given the best results is one devised by F. P. Veitch. Equal weights of soil are treated with different amounts of lime water until one amount is found which leaves the soil slightly alkaline. Knowing the weight of soil in the sample, the weight of lime applied, and the weight of an acre of soil to the given depth, the amount of lime in pounds per acre needed to correct the acidity can be calculated. The results are only approximate at best, but the method serves to compare the relative amounts of lime needed on different soils, or on a soil under different treatments. It is not sufficiently accurate to tell a farmer just how much lime to put on a given field, although it may be a guide to the expert in determining the amount.

There are two tests for telling whether or not a soil is acid, but not how acid. One is by the use of blue litmus paper. A strip of blue litmus paper is placed in the bottom of a beaker or tumbler and on top of this a piece of filter paper or clean white blotter cut to fit the bottom of the vessel. The soil to be tested is added until the dish is half full, and is then soaked with pure water. Another beaker or tumbler is prepared the same way but no soil added. This is to test the paper and water for acids. If the litmus paper in the beaker containing the soil has turned red after standing an hour, the soil is acid, the degree of acidity depending on the amount and rapidity of coloration. At the same time the litmus paper in the beaker containing no soil must remain blue. If it turns red the paper or water contains acid and a fresh test must be made using different paper and water.

Another test is to add two or three ounces of soil to a beaker or tumbler full of dilute ammonium hydroxide, made by mixing one part of strong ammonia with five parts of pure water. After standing some time an acid soil will yield a brown or black color to the liquid, due to the solubility of the humus acids in ammonium hydroxide (Section 124). A neutral or alkaline soil will not yield a color to the liquid beyond that which will be imparted to it by the fine soil particles held in suspension.

212. **Fertilizer Analysis.**—The total amount of plant food in fertilizers can be determined accurately and, with the possible exception of nitrogen, the available material can also be determined. In buying a fertilizer a farmer wants something ordinarily which is quickly available to his crops. State laws now require fertilizer manufacturers to give the analysis with every fertilizer. This analysis usually consists of total nitrogen; water soluble, citrate soluble, insoluble, and total phosphoric acid; and water soluble potash.

There are methods which attempt to determine available nitrogen, but except for the determination of nitrates and ammonia which are satisfactory, there are no really good methods. As a matter of fact, however, a determination of total nitrogen is usually sufficient. The use of certain materials, such as hair, wool waste, and leather is not permitted by some states in making complete fertilizers unless they are treated with sulphuric acid as in the manufacture of "base goods." Their presence in the raw state can be detected with a microscope, and the farmer is thus protected against their use in this condition.

Water soluble phosphoric acid is monocalcium phosphate, $CaH_4(PO_4)_2$, citrate soluble phosphoric acid is the dicalcium phosphate, $Ca_2H_2(PO_4)_2$. It is also called "reverted" phosphate (Section 174). The name "citrate soluble" comes from the fact that it is soluble in a neutral solution of ammonium citrate. Both water soluble and citrate soluble phosphoric acid are available to plants, so that analyses sometimes give only the available phosphoric acid which includes both forms. Insoluble phosphoric acid is tricalcium phosphate, $Ca_3(PO_4)_2$.

Water soluble potash is a simple determination, and of course is that potash which is readily available to plants. The guaranteed analysis does not state whether the potash is in the chloride or sulphate form, or whether these acid radicles are present. This is sometimes important (Sections 178 and 179), and if so it would be necessary to have the fertilizer analyzed further, or to buy known materials.

In discussing fertilizers, and sometimes even in naming them, it is customary to use the percentage figures only, in the order of nitrogen, phosphoric acid, and potash. Thus, a 1–6–4 fertilizer is one which contains 1 per cent. nitrogen, 6 per cent. phosphoric acid, and 4 per cent. potash.

In expressing the results of analyses it is sometimes customary to add: "Nitrogen equal to ammonia." This gives a little higher figure and makes the fertilizer look richer than it really is, unless the purchaser is in the habit of thinking of nitrogen in terms of ammonia, the way the fertilizer manufacturers do. They buy all nitrogenous materials on the ammonia basis.

In the same way phosphoric acid is sometimes referred to as "bone phosphate of lime." Phosphoric acid is P_2O_5, bone phosphate is $Ca_3(PO_4)_2$. Hence the percentage is more than doubled by expressing the amount of phosphorus in the latter way.

Potash is sometimes called "equivalent to sulphate." This also apparently increases the amount, almost doubling the figures.

For example, a fertilizer containing 1 per cent. nitrogen, 6 per cent. phosphoric acid, and 4 per cent. potash would be expressed on the higher basis as 1.21 per cent. ammonia, 13.08 per cent. bone phosphate of lime, and 7.40 per cent. potassium sulphate, and yet it might contain no ammonia, no bone phosphate, and no sulphate of potash.

In interpreting a fertilizer analysis the farmer need pay attention only to the nitrogen, phosphoric acid, and potash, and not be led astray by the more attractive higher figures. It is only just to say, however, that most of the fertilizers now offered for sale by reputable concerns are honest goods with the guaranteed analysis well stated.

213. **Summary.**—Analyses of soils and fertilizers are usually reported in terms of the oxides of the elements, basic or acid, as the case may be. Although the use of the elements alone in reporting such work seems more logical and consistent, it is not customary for various practical reasons.

The analysis of soils for the purpose of discovering fertilizer deficiencies is not very satisfactory. Many methods have been devised, some for determining the total amount of any element present, and this can be accurately done; some for determining the amount of available material, and this can not be accurately done. Taken in connection with other information, soil analysis, more particularly of the total constituents, is of help to the expert in interpreting soil deficiencies. The value of a soil analysis is very great for the purpose of studying the changes in soils, the effect of fertilizers and crops, in comparing soils, and in special scientific work in soil chemistry. The results of this kind of work can later be applied in a practical way.

Tests for determining the amount of lime required by a soil to correct acidity are in use and one in particular is approximately accurate, although it is better fitted for comparative work than for practical application to a single soil. The use of blue litmus which turns red in an acid soil, and of ammonium hydroxide which dissolves dark organic acids from acid soils are tests which are easily applied and of value as qualitative tests.

Fertilizer analysis determines the amount of the various plant foods present in fertilizers. The methods are accurate. The results are expressed as total nitrogen; total, water soluble, citrate soluble, and insoluble phosphoric acid; and water soluble potash. There is no very good method for available nitrogen. Water and citrate soluble phosphoric acid are together termed available phosphoric acid; and of course water soluble potash is available. Other expressions may be used in stating the results of a fertilizer analysis but those mentioned are in universal use and are easily understood. Other terms only tend to confuse.

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CHAPTER XV

INSECTICIDES AND FUNGICIDES

THE treatment of plants to destroy insect pests and fungous diseases is now so important a factor in the growth of crops that a short description of the compounds and mixtures employed will be of value. No attempt will be made to describe the various insects and fungi or to give the proper treatment for each. All such details including methods of application and proper dilution of spray material should properly be taken up in connection with the propagation and growing of various plants. The present discussion will be limited to the chemistry of the more common spray materials, noting first the chief characteristics of the pests to be destroyed. Figs. 70, 71, and 72 illustrate the method and results of spraying.

214. **Insects.**—The insects which destroy crops are of two kinds: First, those which have biting mouth parts for chewing the plant tissues, such as grasshoppers, caterpillars, and cucumber beetles. Second, those which have a beak or apparatus for penetrating the skin of plant organs and sucking up the juices. They do not chew and swallow any of the tissue proper. The woolly aphis and San Jose scale are examples of these insects.

For insects which eat plant tissue, it is usually sufficient to sprinkle the surface of the leaves with a poison. This kills the insects when the poison is taken internally. The insects which do not eat tissue but suck out the plant juices are not injured by this treatment. They penetrate the skin for their nourishment and do not eat the poison on the surface. Spray materials which kill by contact are efficacious. They act by destroying the skin of the insects or by clogging up their breathing pores, or by merely repelling them.

215. **Fungi.**—Fungi are plants which have no chlorophyl and are consequently dependent on host plants for all their food. They are propagated by spores which are produced in great numbers and can be easily disseminated. When the spores germinate on some suitable host, a little tube is put forth, from which develops the mycelium. Some fungi grow mostly under the surface, the spore tube entering by the stomata or other openings in the leaf or stem. These are fungi like the brown rot and grain smuts. Other fungi grow on the surface, like the powdery mildew. Internal fungi cannot be killed after they have gained entrance to the host, but must be caught before the spore germinates, by covering the plant with a poison which kills the spore or germ tube. External fungi can be killed at any time because they are always exposed.

Fig. 70.—Spraying an orchard. Department of Experimental Pomology, Pennsylvania Station.

FIG. 71.—Unsprayed fruit. Department of Experimental Pomology, Pennsylvania Station.

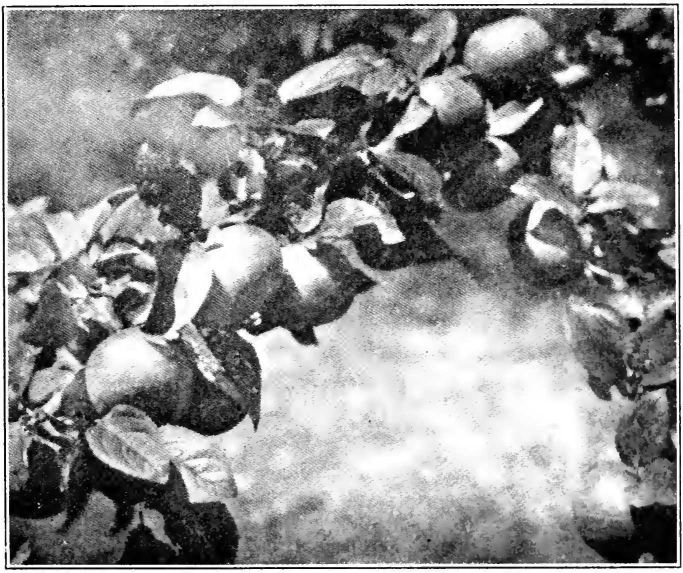

FIG. 72.—Sprayed fruit. Department of Experimental Pomology, Pennsylvania Station.

216. **Insecticides.**—These spray materials may be divided into two classes, internal, and external or contact insecticides.

I. INTERNAL INSECTICIDES

(*a*) HELLEBORE is a powder made by grinding the dried roots of the American hellebore (veratrum viride) or of the white or European hellebore (veratrum album). The active constituents are certain alkaloids, said to be some six in number.

(*b*) LEAD ARSENATE is made by mixing sodium arsenate, Na_2HAsO_4, with lead acetate, $Pb(C_2H_3O_2)_2$, or lead nitrate, $Pb(NO_3)_2$. The precipitate, depending on conditions of temperature, concentration, and methods of mixing, consists of neutral or triplumbic arsenate, $Pb_3(AsO_4)_2$, and acid lead arsenate, $PbHAsO_4$, in varying proportions. It comes on the market as a paste or powder which forms a suspension on mixing with water in the proper proportions for spraying. When eaten by insects the arsenic in the compound is fatal.

Injury sometimes results to the leaves from the use of lead arsenate. Since insoluble compounds do not harm foliage it is certain that enough arsenic from lead arsenate goes into solution to penetrate the leaves and kill the tissues. Consequently the amount of water soluble arsenic in commercial preparations of lead arsenate is limited by the national Insecticide Act of 1910 to 0.75 per cent. of water soluble As_2O_5.[1] But injury has resulted from the use of lead arsenate that came well within the law, and as a result of investigation the following facts have been discovered: Triplumbic arsenate or the neutral lead arsenate is insoluble in pure water or water containing chlorides, sulphates, or carbonates, and causes no harm to foliage. The acid arsenate, on the other hand, is slightly soluble in pure water and much more so in water containing the above named substances in solution. Injury results when hard water, or "alkali"

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[1] Determined by soaking 1 gram of lead arsenate in 1000 c.c. of carbon dioxide-free water for ten days, shaking eight times a day, and analyzing the filtrate. Water soluble As_2O_3 in Paris green is determined in the same way.

water, is used in the preparation of the spray from acid arsenate, and when, furthermore, heavy dews or fogs keep the foliage soaked with moisture part of the time, and so dissolve enough arsenic to injure plant tissue. Rain would wash off the dissolved arsenic and cause no harm. It is possible to purchase lead arsenate at present which is guaranteed to be the neutral arsenate.

(*c*) PARIS GREEN, SCHWEINFURTH GREEN, is made by boiling arsenous oxide, As_2O_3, with basic copper acetate, $Cu(C_2H_3O_2)_2.CuO$. The brilliant green precipitate is used as a suspension in spraying. Its chemical name is copper aceto-metarsenite, $[Cu(AsO_2)_2]_3.Cu(C_2H_3O_2)_2$. The arsenic content is the active poison for insects.

Leaf burning is very apt to result from the use of Paris green, due to water soluble arsenic. The national Insecticide Act of 1910 prohibits the sale of Paris green containing more than 3.5 per cent. water soluble As_2O_3.[1] In addition to this, however, the action of water and carbon dioxide will dissolve arsenic according to the following equation:

$$[Cu(AsO_2)_2]_3.Cu(C_2H_3O_2)_2 + 10H_2O + CO_2 =$$
$$6H_3AsO_3 + CuCO_3.Cu(OH)_2 + Cu(C_2H_3O_2)_2.CuO.$$

This danger is so great that it is usually customary to mix Paris green with lime or Bordeaux, the latter containing an excess of lime. The free arsenic is neutralized by the lime, thus:

$$2H_3AsO_3 + 3Ca(OH)_2 = Ca_3(AsO_3)_2 + 6H_2O.$$

Sometimes Paris green is adulterated with worthless articles like gypsum. It is easy to test for such adulteration by treating the material with strong ammonia. Paris green dissolves according to the following equation:

$$[Cu(AsO_2)_2]_3.Cu(C_2H_3O_2)_2 + 36NH_4OH =$$
$$4[Cu.(NH_3)_4.(OH)_2] + 6(NH_4)_3AsO_3 + 2NH_4C_2H_3O_2 + 22H_2O.$$

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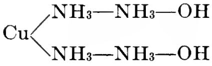
[1] See footnote, page 284.

The soluble copper compound called cuprammonium hydroxide is written graphically,



$$\mathrm{Cu}\left\langle\begin{matrix}\mathrm{NH_3{-}NH_3{-}OH}\\ \mathrm{NH_3{-}NH_3{-}OH}\end{matrix}\right.$$

and is the same thing as Schweitzer's reagent used for dissolving cellulose (Section 58). The gypsum is left as an insoluble residue. So far as adulterations go, however, the Insecticide Act of 1910 protects the farmer by limiting the minimum amount of arsenous oxide to 50 per cent.

II. EXTERNAL INSECTICIDES

(*a*) HYDROCYANIC ACID GAS is a very violent poison to man as well as to insects. The acid at ordinary temperatures is a mobile, volatile liquid, with an odor of bitter almonds and a boiling point of 26.5° C. It kills insects by entering their breathing apparatus and putting a stop to their vital functions. As used for fumigation it is prepared by treating sulphuric acid with potassium cyanide. The reaction is:

$$\mathrm{KCN + H_2SO_4 = KHSO_4 + HCN.}$$

Potassium sulphate, K_2SO_4, is not formed with the excess of sulphuric acid necessary to get the maximum evolution of gas. It is necessary to use enough water to hold the acid potassium sulphate in solution after the reaction, especially in the generators used for the purpose of producing the gas on a large scale. The best proportion of cyanide, acid, and water is a 1–1–3 formula, or 1 part potassium cyanide to 1 part of concentrated sulphuric acid (commercial concentrated acid is about 93 per cent. pure) and 3 parts of water. Much stronger sulphuric acid results in the decomposition of hydrocyanic acid and the formation of ammonia and formic acid or carbon monoxide depending on the strength of the sulphuric acid. The ammonia forms ammonium sulphate with the acid.

The use of sodium cyanide is preferable in some ways, since more hydrocyanic acid gas can be liberated from a pound of sodium cyanide than from a pound of potassium cyanide, due to the lower atomic weight of sodium. 100 parts of sodium cyanide is equal to 132 parts of potassium cyanide in theoretical effectiveness. The reaction is similar, but the sodium acid sulphate is more soluble than the corresponding potassium salt and a 3–4–6 formula is recommended.

The trouble which is sometimes experienced in obtaining good results from the use of potassium cyanide is due in part to the presence of sodium chloride. Sulphuric acid sets free hydrochloric acid, and the latter forms ammonia, later ammonium chloride, and formic acid. This reaction of course reduces the yield of hydrocyanic acid gas. It is not sufficient that the potassium cyanide have a guarantee of 98 per cent. pure, for a mixture of potassium and sodium cyanides would show 98 per cent. expressed as potassium cyanide and yet have considerably more than 2 per cent. of sodium chloride present. If possible the amount of sodium chloride present should be known, and it is recommended not to have more than 1 per cent.

Since the use of hydrocyanic acid gas is attended with great danger to the operator, extreme pains should be taken by him not to inhale the gas himself, or generate it where others may run any risk. It is altogether too dangerous to handle with impunity, and too much carelessness is displayed in its use.

(*b*) Kerosene Emulsion.—Kerosene, or coal oil, as it is sometimes called, is an excellent contact insecticide, killing by entering the pores of the insect. Used in the pure state, however, it is apt to harm vegetation, and is not much employed. It is one of the fractional distillation products from crude petroleum and consists of a mixture of paraffine or methane hydrocarbons whose boiling points lie between 150° and 300° C. Kerosene is insoluble in water and hence cannot easily be diluted, although attempts have been made to agitate the two together so as to obtain a mechanical mixture suitable for application to trees, but the mixture separates too rapidly to be satisfactory. By thoroughly agitating kerosene with a solution of hard or soft soap, there is obtained an emulsion which, when properly made, retains its permanency for at least several days.

An *emulsion* is a mechanical mixture of two liquids insoluble in each other. One is usually an oil, the particles of which are very finely divided and are held in suspension in the other which is of a gelatinous or viscous nature. The permanency of suspension is brought about partly because the particles are very small and the friction in moving through the suspending liquid is sufficient to prevent their accumulating rapidly; and partly because the suspending liquid exerts some physical if not chemical attraction for the particles, thus helping to prevent their uniting with one another. Moreover, each fine particle of oil is surrounded by a coating of the gelatinous or viscous suspending liquid and can not easily touch another particle to coalesce with it. The finer the particles of oil, the more surface exposed, and hence the greater the attraction of the suspending liquid for the oil, and the more friction in moving. Kerosene and soap solution are liquids of the character just described.

(*c*) LIME-SULPHUR BOILED is made by boiling together for about an hour, or until the sulphur is dissolved, 50 pounds of pure lime and 100 pounds of finely ground sulphur in 50 to 55 gallons of water. The lime is slaked before actual boiling is begun. When properly made there are formed the tetra- and pentasulphides of calcium and calcium thiosulphate. The exact reaction is not known, but the following is given as a possibility:

$$3Ca(OH)_2 + 11S = CaS_2O_3 + CaS_4 + CaS_5 + 3H_2O.$$

This reaction corresponds fairly well to the proportions of lime to sulphur recommended, and to the amount of sulphur in solution as thiosulphate and sulphides found by analysis.

Lime containing magnesia should not be used, for magnesium forms no compounds with the sulphur and only serves to increase the amount of sediment. Long boiling changes the thiosulphate to insoluble sulphite (Reaction 1);

oxidizes the sulphite to insoluble sulphate (Reaction 2); and the sulphide to thiosulphate (Reaction 3), with a separation of sulphur in each case except the second. Exposure to the air causes the oxidation changes to take place. The reactions are as follows:

1. $CaS_2O_3 = CaSO_3 + S$
2. $CaSO_3 + O = CaSO_4$
3. $CaS_4 + 3O = CaS_2O_3 + 2S$

The active constituents as a contact insecticide are the polysulphides which are caustic in nature, destroying the skin of insects. The more sulphides in solution, the more effective the spray; and much variation from the formula given, or boiling too long, or use of impure materials, all lessen the amount of sulphides formed.

Lime-sulphur is also a fungicide and in addition to the sulphides, the thiosulphate has value for this purpose. When sprayed on the trees and exposed to the air, the thiosulphate and sulphides oxidize as indicated in Reactions 1 and 3. The insoluble sulphite and sulphur which are formed are also useful as fungicides. The carbon dioxide of the air also breaks up lime-sulphur as follows:

$$CaS_4 + CO_2 + H_2O = CaCO_3 + H_2S + 3S$$

Injury to foliage from the use of this spray is due to the caustic effect of the polysulphides, and occurs for the most part when the sulphides occur in too great concentration or when they penetrate the surface of the leaf through cracks or stomata. Applied too thickly the drops coalesce and run to the edge where by evaporation the solution becomes sufficiently concentrated to destroy leaf tissue. Injury, however, takes place only during the early part of the application, for the longer the spray stays on the leaves the more the sulphides are broken up as described above.

Although there is some evidence that lime-sulphur is an internal as well as an external insecticide, its action in this respect is not sufficiently pronounced for general use, and it is advantageous if some internal insecticide can be mixed with the lime sulphur, so that one spraying, or series of sprayings, may be useful for biting insects, sucking insects, and fungi. Paris green is not satisfactory because it is decomposed, freeing arsenous acid and injuring foliage. Lead arsenate is the best material to use, and this in the triplumbic form. The acid arsenate is not satisfactory, on account of the formation of a soluble arsenic compound, possibly arsenic acid. The reactions which take place when lead arsenate is mixed with lime-sulphur are complex and not well known. Apparently, among other compounds, lead sulphide is formed, and there is an increase in the amount of thiosulphate and sulphite.

Some commercial preparations of lime-sulphur, particularly the dry powders which are to be dissolved in water, consist largely of sulphides of sodium or potassium. These compounds are fungicides not contact insecticides, and, furthermore, their use with arsenicals causes foliage injury due to a greater solution of arsenic acid.

(*d*) MISCIBLE OR SOLUBLE OILS.—Not only kerosene, but crude petroleum also has valuable insecticidal properties. Its use, however, like the use of kerosene in the pure state, is not possible on account of its injury to trees. To facilitate the proper dilution of these oils which can be so valuable, the so-called miscible or soluble oils have been prepared.

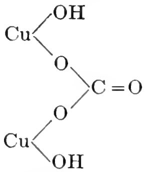
For this purpose there is made first an "emulsifier" which is essentially a soft, carbolated soap, made commonly by boiling 10 gallons of menhaden oil, 8 gallons of carbolic acid, and 15 pounds of caustic potash, then mixing with it 2 gallons of kerosene and 2 gallons of water. This emulsifier is then mixed with varying amounts of other oils such as crude petroleum, paraffine oil, rosin oil (Section 78, *b*), and more kerosene. This final solution is the miscible oil and when mixed slowly with water according to the spray requirements forms a milky emulsion that is reasonably permanent if care is used in making and mixing.

(*e*) PYRETHRUM, PERSIAN INSECT POWDER, BUHACH, is made by grinding the dried flowers of various species of the pyrethrum plant. The active constituent is a volatile oil of strong characteristic odor which can be extracted by ether. It varies in amount from 5 to 10 per cent. It is green to brown in color and on exposure to the air oxidizes to an inactive resin. This explains the necessity of keeping the powder in air tight containers, otherwise it loses its efficacy. Pyrethrum is not poisonous to man.

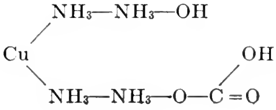
(*f*) TOBACCO.—An old remedy for certain delicate insects like plant lice has been a simple decoction of tobacco leaves or waste. The water extracts the alkaloid nicotine (Section 86, *e*) which is active in destroying insects. Besides a liquid extract, powdered tobacco and the smoke of tobacco are efficacious in some instances. The latter contains some nicotine, but in addition decomposition products which have some toxic effect. Commercial preparations are on the market, many of them containing nicotine sulphate as the active constituent. It will be remembered (Section 85) that alkaloids are basic in character and will unite to form salts with mineral acids.

(*g*) WHALE OIL SOAP.—Only the name is left of what used to be the soap made from whale oil. Now almost any kind of cheap fish oil is used and saponified with potassium or sodium hydroxide. The potash soap is soft; it is more readily soluble in hot water, and the solution does not harden when cold. It is also more penetrating and effective. One pound of soap in 4 to 10 gallons of water are the proportions ordinarily used. The sticky soap solution clogs up the pores of the insects and causes death.

217. **Fungicides.**—(*a*) AMMONIACAL COPPER CARBONATE is a solution of basic copper carbonate, $CuCO_3.Cu(OH)_2$, or



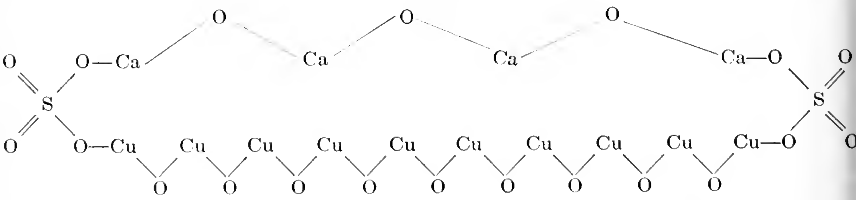
dissolved in ammonia to form cuprammonium carbonate, $Cu(NH_3)_4CO_3.H_2O$,



Dilute ammonia dissolves more copper carbonate than strong ammonia, so that it is better to use dilute ammonia in dissolving the copper carbonate, rather than to use strong ammonia for solution and to dilute it afterward. Excess of ammonia harms vegetation, hence care must be used in dissolving the copper carbonate. The soluble copper is the active fungicide and in this form is not so dangerous to foliage as is copper sulphate which is sometimes used in dilute solution.

When diluted considerably, basic copper carbonate is apt to precipitate out and in such cases an agitator can be used in the spray, although if the spray is used immediately after dilution, it can be brought on the plants before precipitation begins.

(*b*) Bordeaux Mixture is usually made by mixing equal parts of copper sulphate and burnt lime, the former previously dissolved in water, and the latter slaked and mixed with an equal quantity of water. The proportions vary with the different uses of the fungicide. Formerly the reaction was thought to be a simple one by which copper hydroxide and calcium sulphate were formed, but this is impossible. The mixture would gradually turn black if copper hydroxide were formed. Copper hydroxide, $Cu(OH)_2$, blue, changes to $Cu(OH)_2.(CuO)_2$, and finally CuO, black. The color is, however, very permanent and there is some evidence to show that the compound formed is a double basic sulphate of copper and calcium to which has been given the formula, $(CuO)_{10}.SO_3.(CaO)_4.SO_3$. Graphically it can be written as follows:



Burnt lime which has been air-slaked and hydrated lime which contains considerable carbonate are not recommended for use in making Bordeaux unless the proportion of lime is increased. Calcium carbonate does not form a compound with copper sulphate.

The active agent in killing fungi is copper sulphate, but the use of copper sulphate even in dilute solution is attended with so much danger to foliage that Bordeaux, which is a suspension of an insoluble copper salt in water, is far preferable. The bluish-white particles are distributed over the surface of leaves, and under the action of water and carbon dioxide very small quantities of copper sulphate are formed, sufficient to kill fungous spores and germ tubes. Calcium carbonate is also formed.

Under certain climatic conditions, such as long periods of damp weather, but no rain, enough copper sulphate may be formed to burn the leaves. Even under these conditions, however, the presence of an excess of lime prevents this danger. The formulas call for more lime than is necessary to form the compound with copper.

Bordeaux may be mixed with arsenicals—Paris green and lead arsenate—to good advantage so as to have both an insecticide and a fungicide in the same spray. Paris green is benefited by this mixing because the excess of lime neutralizes the free arsenous acid so readily formed in plain Paris green applications.

(*c*) CORROSIVE SUBLIMATE, MERCURIC CHLORIDE, $HgCl_2$, is a very powerful fungicide and antiseptic. Furthermore, it is very poisonous to human beings and should be used with great care. A solution of 1 part sublimate to one thousand parts of water is a common strength to employ. Since mercuric chloride corrodes metal the solution should be made up in a wooden pail preferably. Sometimes it is purchased in tablets mixed with ammonium chloride which increases the solubility of the mercuric chloride by the formation of a double mercurammonium chloride, $HgCl_2.(NH_4Cl)_2$.

(*d*) FORMALDEHYDE is a gas, CH_2O, at ordinary temperatures. It dissolves in water readily, and in commerce is sold in the form of a solution containing approximately 38 per cent. by weight. *Formalin* is the trade name of such a solution made by one German firm only. It has no advantages whatever over any 38 per cent. solution made by other reputable manufacturers. Formaldehyde may be used in the liquid form by proper solution or in the gaseous form by liberating it in a closed room. The evolution of formaldehyde may be produced by heating the solution under pressure; by simple evaporation from large surfaces; by treatment with potassium permanganate whereby part of the formaldehyde is oxidized and the heat of oxidation volatilizes the remainder; or by burning the so-called formaldehyde candles. The latter are made of paraform which is a condensation product of formaldehyde made by spontaneous evaporation of the solution. The compound is supposed to be trioxymethylene, $(CH_2O)_3$. On heating this white solid, formaldehyde is evolved.

(*e*) LIME-SULPHUR BOILED, being an insecticide as well as a fungicide, was discussed under the former head (Section 216 II, *c*).

(*f*) LIME-SULPHUR SELF BOILED is essentially a mechanical mixture of sulphur and slaked lime. It is prepared by adding, for example, 6 pounds of sulphur, finely ground, to 6 pounds of lime which has just started to slake. The mixture is stirred and more water added until the mass boils, due to the slaking lime. The boiling is continued five or ten minutes and then the remainder of the water—to equal 50 gallons in all—is added. This cools down the mass. The violent boiling has thoroughly mixed the sulphur and slaked lime and formed very little calcium sulphides. But at the strengths applied very little sulphides are desired, or leaf burning results. This is why the boiling is checked by the cold water. The mixture is of course a suspension and must be applied with an agitator. Lead arsenate and some other insecticides have been mixed with the self-boiled lime-sulphur with good results. Some chemical changes take place, due to the calcium sulphides in solution.

218. **Summary.**—The spraying of plants for the control of insects and fungi is now one of the most important phases of agriculture, particularly for horticultural crops. For

insects which eat the foliage it is only necessary to spray the leaves with a stomach poison and for this purpose the so-called arsenicals—lead arsenate and Paris green—are used. Hellebore is employed to a less extent.

Paris green is an aceto-metarsenite of copper and unless mixed with lime is apt to injure foliage because of the ease with which soluble arsenous acid is formed by the action of water and carbon dioxide in the air. *Lead arsenate* is usually a mixture of triplumbic and acid lead arsenates, although the better grades are now composed very largely of the triplumbic arsenate only. The latter does not dissolve or decompose under any ordinary conditions, whereas the acid arsenate may break up to form arsenic acid, soluble and injurious to leaves.

For insects which puncture the surface of plant leaves or stems and suck the juices, a stomach poison on the surface does no good. It is necessary to use a material which kills by contact, either on account of its caustic action, or because it enters their pores and stops up their breathing apparatus. Such external insecticides are principally hydrocyanic acid gas, kerosene emulsion, lime-sulphur boiled, and miscible oils.

Hydrocyanic Acid is a liquid at ordinary temperatures, but is volatile and exceedingly poisonous, especially to man, so it must be used with great care. It is generated by mixing potassium cyanide and sulphuric acid. If the acid is too strong, or if the cyanide contains chloride as it frequently does, loss of hydrocyanic acid occurs by decomposition. *Kerosene emulsion* is a mechanical mixture of kerosene and soap in which the kerosene is suspended in very minute globules. It will not do this in pure water. Kerosene itself is harmful to vegetation and the emulsion is a convenient way of applying it in dilute form. *Lime-sulphur boiled* is a very important insecticide and is in addition an excellent fungicide. It is a solution of tetra- and pentasulphides of calcium, and calcium thiosulphate. After application the sulphides gradually oxidize to sulphite of calcium and free sulphur; and the thiosulphate changes to sulphite and free sulphur. This formation of sulphite and sulphur increases the fungicidal value of the spray. Leaf injury is due to too concentrated a solution of the sulphides. Lime-sulphur may be mixed with lead arsenate, but unless the triplumbic form of the latter is used, leaf injury may result due to the formation of a soluble arsenic compound. *Miscible Oils* are the result of an attempt to dilute crude petroleum so that it can be used with safety to plants. The result is accomplished by making what is essentially a soft carbolated soap called the "emulsifier." This is mixed with crude petroleum, paraffine oil, or rosin oil, and a "miscible" oil is formed. When this is mixed carefully with water in any proportion a milky emulsion is produced that is reasonably permanent.

For fungi the plants must be sprayed at the proper time to kill the spores of internal fungi, or at any convenient time to kill external fungi. Copper salts make excellent fungicides, but the soluble salts are injurious to leaves, hence it is customary to use a compound of copper which is ordinarily insoluble, but which dissolves slowly enough under atmospheric conditions to kill fungi. It is only soluble compounds which are actually injurious to fungi. *Bordeaux mixture* is such a suspension. It is a complex, double basic copper calcium sulphate from which copper sulphate gradually forms under the action of water and carbon dioxide. It is sometimes harmful to vegetation on this account, especially when atmospheric conditions are aggravating and there is not enough lime present. *Formaldehyde* is a gas which dissolves readily in water and can be easily obtained in solution. From the solution formaldehyde can be generated in a number of ways and thus be used where a spray could not reach. *Lime-sulphur boiled* has been mentioned. *Lime-sulphur self boiled* is a mechanical mixture of slaked lime and sulphur with some sulphides of calcium. It is made by mixing sulphur with slaking lime and the heat of slaking boils the mass. Too long boiling forms more of the sulphides than are desirable to use at the strengths employed.

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Penna. Agr. Expt. Sta., Bul. No. 110. The Control of Insects and Diseases Affecting Horticultural Crops.

Penna. Agr. Expt. Sta., Bul. No. 115. Concentrated Lime-Sulphur Spray.

CHAPTER XVI

THE GAS ENGINE

ALTHOUGH not strictly a factor in plant growth, the gas engine has become a very important factor in farm life. For running tractors in plowing large farms rapidly (Fig. 73), in furnishing power for pumping, silage cutting, cream separating, and in moving products to market, as well as providing rapid means of locomotion for the modern farmer, the gas engine today occupies an almost essential place on many farms. On this account a short discussion of the principles of combustion, products obtained, fuels, and lubricants, should fit in at this point. The subject of gas engines is too large a one to treat from any standpoint except the chemical one and should include only such other details as may be necessary to fully understand the chemistry involved.

219. **The Gas Engine.**—The gas engine is an appliance for making use of the energy developed when a mixture of a combustible gas and air explodes. When gases explode a sudden pressure is produced. This pressure is directed against a piston-head and the movement of the piston is transmitted to a wheel by a connecting rod. In a steam engine, steam is admitted first to one end and then to the other end of the cylinder. This moves the piston back and forth and by means of the connecting rod a wheel rotates. In a gas engine a mixture of gas and air is admitted to one end of the cylinder and at the proper moment is exploded, usually by an electric spark. The pressure thus developed drives the piston to the other end of the cylinder. Gas is not exploded on the other end of the piston to drive it back, but the momentum of a heavy fly-wheel attached to the main shaft carries the piston back again. In one type of engine, the so-called "four-cycle" type, the explosion comes at every other inward movement of the piston, or once every two revolutions of the fly-wheel. It is called four-cycle because there are four strokes which complete the cycle:

An outward movement of the piston which draws gas and air into the cylinder, or intake; inward movement and explosion, or compression; outward movement and work, or expansion; and inward movement, or exhaust. In the other type, the "two-cycle," the explosion comes at every inward movement of the piston, or once every revolution of the fly-wheel. In this type the crank case is air tight, so that air and gas can be admitted to the outer end of the cylinder. A by-pass permits the mixture to go to the inner end of the cylinder for the explosion. At the outward stroke the gas and air are first compressed in the crank case and then as the by-pass is opened by the movement of the piston, the mixture is forced into the inner end of the cylinder, driving ahead of it the burned gas through a port. At the inward movement of the piston the mixture is compressed and the explosion takes place, and at the same time gas and air are drawn in to the outer end of the cylinder; then the cycle is repeated.

Fig. 73.—Gasoline tractor for plowing.

A very important part of the gas engine is the carburetor or place where the air and gas are mixed. If the fuel is a liquid at ordinary temperatures it is necessary to vaporize it before an explosive mixture can be obtained. A liquid like gasoline vaporizes very readily and it is only necessary to convert it to a spray in the carburetor. The inflowing air evaporates the fine particles of liquid and a gas mixture results. Fuels like kerosene which do not vaporize so readily at ordinary temperatures, should be heated before they are admitted to the carburetor, in order to develop maximum power.

The mechanical devices for admitting gas and air to the carburetor, for regulating the inflow of explosive mixtures to the piston, for removing the burned gas, and for the numerous other necessary steps in the development of maximum power in a gas engine cannot be discussed here. For such details the reader is referred to books on gas engines. (See reference list at end of chapter). For the present purpose, however, a brief description of fuels, their properties and sources, may not be out of place.

220. **Crude Petroleum.**—Crude petroleum is the source of gas engine fuels. It is usually a heavy, dark, oily liquid with peculiar characteristic odor, and found in porous rocks at a depth of 300 to 3700 feet below the earth's surface. The decomposition of organic matter within the earth is supposed to be the origin of it. Since petroleum is an inflammable liquid it can be used in the crude state as a fuel, but not of course in a gas engine. To obtain the greatest value from this material it is necessary to separate it into its various components. This can be readily accomplished by fractional distillation, since petroleum is essentially a mixture of paraffine hydrocarbons of very many kinds. There are other compounds in some petroleum, but in the better grades of Pennsylvania oils from which the refined products are most easily made, these compounds are present in very small amounts and need not be considered.

The paraffine hydrocarbons have as empyrical formula C_nH_{2n+2} and run from methane, CH_4, to hexacontane, $C_{60}H_{122}$, from gases through liquids to solids. The more carbon atoms in the molecule the greater the density and the higher the boiling point. Without going into the details of the distillation process it is sufficient to say that the crude petroleum is charged into large stills and heated, the various hydrocarbons coming off at different temperatures. By changing receivers at any point in the boiling as many fractions can be obtained as desired.

At first there are obtained only three or four fractions, the first one called benzine distillate or crude naphtha (sometimes light naphtha and heavy naphtha), with a density of 80° to 58° Bé.[1] Then come burning oils or kerosene with a density of 58° to 43°. Tar or residuum is left in the stills. The temperature of distillation rises gradually to 300° or 400° C. From the crude naphtha several colorless fractions are usually obtained by distilling again and purifying with strong sulphuric acid and caustic soda. The liquid to be thus treated is agitated with sulphuric acid of 66° Bé., then washed with water, agitated with caustic soda of 4° to 10° Bé., and finally washed with water. The acid and soda decompose or dissolve various impurities and coloring matters in the petroleum products other than the paraffine hydrocarbons. The spent acid which settles to the bottom is drawn off as "sludge" acid and is used in some places for making phosphatic fertilizers. The various fractions have different names, not always uniform. They are arbitrary at best, depending on the density. Some of the names are gasoline; naphtha, A, B, C, grades; benzine; petroleum ether, etc. It is not safe to buy by name for any special purpose but by specific gravity (Baumé scale) or by boiling points.

The kerosene is redistilled into two or more nearly colorless fractions, purified with acid and alkali as above described, and sold as burning oils of various "tests."[2] Many of the

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[1] Baumé. This is an arbitrary standard of density for liquids. Hydrometers are graduated for liquids heavier and lighter than water. For the former, 0° on the Baumé scale is where the instrument sinks in pure water, and 10° in a 10 per cent. solution of salt. For the latter 0° is the point to which the hydrometer sinks in a 10° per cent. salt solution, and 10° in pure water. The graduation is extended uniformly in both cases. The temperature is 17.5° C.

[2] For use in lamps particularly, kerosene must not be so volatile as to cause an explosion when the wick is lighted. This volatility or "flash point," as it is called, is regulated by law. The flash point is the temperature at which kerosene gives off enough vapor to ignite in a flash over the surface. In most of our states 110° F. is the legal flash point. Flash tests are the determinations which are made to show what the flash points are. Fire tests, also made sometimes, are the determinations which show the temperature at which the vapor will burn continuously. The fire point is usually about 20° F. higher than the flash point.

above distillations are accomplished with steam, as the steam distilled products are of better grade with less loss and less danger of decomposition in the still.

The tar left in the stills is removed and destructively distilled, yielding hydrocarbons of much higher density and greater viscosity; some even being solid at ordinary temperatures. By redistillation, washing with sulphuric acid and caustic soda, and chilling and pressing, there are obtained heavy oils used for lubricating—called lubricating and paraffine oils—paraffine, vaseline, and coke.

The very volatile products of low density are used for solvents; intermediate products for fuel; kerosene for lighting purposes; lubricating oils for machinery; paraffine for candles; vaseline for medicine; and coke for electric light carbons.

221. **Gasoline.**—Originally the name gasoline was applied to a fraction whose density was somewhere between 90° and 80° Bé., but now the product sold under the name of gasoline may be anything from 90° to 60° Bé. Most of the engine gasoline runs from 65° to 60° Bé.,[1] specific gravity 0.718 and 0.737, boiling point 120° to 150° C. It is a mixture of hydrocarbons, having no constant composition. It is possible to obtain any particular density by mixing light and heavy fractions. The same result may be secured by uniting a very light product with a very heavy one, or by uniting two of more nearly equal densities. As a result the mere specific gravity or Baumé reading of a grade of gasoline does not tell the purchaser just what he is getting. If a single hydrocarbon liquid, having a density of 65° Bé., is just suited to a certain engine, a grade of material would not be as well suited which consists of a mixture of very light hydrocarbon with very heavy hydrocarbon, the resultant density of which is 65° Bé. The lighter material would vaporize too rapidly and explode too easily, whereas the heavier portion would vaporize very slowly or too slowly to make a proper explosive mixture. In time it may be possible to buy gasoline, or

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[1] Instead of saying "65° or 60° Bé. gasoline" it is usually customary to speak of it as "65 or 60 test" gasoline.

at least a gas engine fuel, which has its constituents guaranteed, in order that the purchaser may obtain whatever grade he wants for his particular purpose. Density alone is not the best test; a fractional distillation test should also be made.

It is important in using a gas engine to have the proper amount of air mixed with the gasoline vapor. Too much air dilutes the mixture and reduces the power. Too little air does not permit of complete combustion, and this also reduces the power and causes waste of fuel. Gasoline being a mixture of hydrocarbons burns to carbon dioxide and water when there is enough oxygen present. On this account the exhaustion should not take place indoors for the large quantities of carbon dioxide eliminated are detrimental to health. The following may be taken as a typical reaction:

$$2C_8H_{18}+25O_2=16CO_2+18H_2O.$$

This means that one gallon of gasoline, assuming it to be octane, C_8H_{18}, 64.8° Bé., will require about 1180 cubic feet of air at 62° F. When insufficient oxygen is present the products of combustion are different, and include carbon. The maximum amount of heat, and consequently power, is developed only when combustion is complete.

222. **Lubricants.**—The purpose of a lubricating oil is to reduce friction between moving surfaces, and it should have sufficient "body" or viscosity not to be squeezed out from between the surfaces. Too viscous an oil will cause friction of the oil itself and reduce efficiency. A lubricating oil should not be so volatile that it will not last under the temperature to which it is subjected. The flash test is useful in determining this point. Neither should an oil have any free acid present, such as sulphuric acid if a hydrocarbon oil; fatty acid, usually stearic, if an animal or vegetable oil. The free acid corrodes the bearings.

From the tar or residuum left in the first distillation of crude petroleum there are obtained (Section 220) a series of lubricating oils which are of excellent character, and better suited for most machinery than animal or vegetable oils, though for some purposes the latter are better.

This is not the place to discuss the various grades of lubricating oils and their properties and uses, but it may be well to mention one fact and that is the necessity of using a good grade of oil especially adapted for gas engine cylinders. The contact surface of the piston in the cylinder must be lubricated, of course, and since the temperature is very high, the oil must be of a character that does not readily carbonize or volatilize under the action of heat. An oil whose density is 26° to 28° Bé., with a flash test of 400° to 475° F., has been recommended for some engines. Dealers in engines can recommend the best cylinder oil for use in their particular engine.

223. **Summary.**—The gas engine has become such an important factor in the raising and marketing of crops, and for many other purposes on the farm that a brief discussion of it, particularly in its chemical bearing, is not out of place. It is a machine in which pressure is applied to a piston head by the explosion of a mixture of inflammable gas and air. This explosion comes either every time the piston compresses the mixture by an inward stroke, or every other time. The former type is called a two-cycle engine, the latter a four-cycle engine. The mixing of gas and air is a very important part of such an engine. Gasoline is the common fuel employed, and since it is a liquid, it must be volatilized before use. This is accomplished by drawing it into the cylinder in a fine spray along with the air.

Gasoline is one of the distilled and purified fractions obtained from crude petroleum. Although properly it has a density of 90° to 80° Bé. it is more frequently 65° to 60° Bé., for gas engines. Gasoline is a mixture of hydrocarbons and may consist of few or many. It is possible to maintain a uniform density in the product by mixing different light and heavy fractions in various proportions. A mixture of very light hydrocarbons with very heavy ones does not give as efficient a fuel as a mixture of several having more nearly equal densities, even though the result is a liquid of the same density.

A proper amount of air is essential in obtaining maximum power. With sufficient air to supply oxygen the hydrocarbons are burned completely to carbon dioxide and water. With insufficient oxygen intermediate products are formed, even carbon, and maximum heat is not developed—hence not maximum power. On the other hand, too much air dilutes the mixture to such an extent that maximum power is not obtained.

Lubricants for engines are obtained, preferably from crude petroleum, and should be light or heavy depending on the purposes for which they are to be used. In gas engine cylinders where high temperatures exist it is important to use a so-called cylinder oil which will not carbonize or vaporize to any extent. Ordinary engine oil will not answer the purpose.

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PART III

THE ANIMAL

CHAPTER XVII

THE CHEMISTRY OF ANIMAL PHYSIOLOGY

The highest and most complex products of the farm are animals (Fig. 74). Directly or indirectly animals are dependent on plants for their sustenance. There are, of course, many obvious differences between plants and animals, but they are both living things that reproduce themselves. They are composed largely of carbon compounds; that is, they are organic in nature. For the proper elaboration of these compounds, a few elements are necessary. But, whereas plants absorb soluble inorganic compounds and from them build up their tissue, animals must have organic food material previously elaborated by plants. This material is taken into the animal and made soluble before being absorbed and rebuilt into animal tissue.

224. **Essential Elements for Animals.**—For animals there are needed in compound form the following fifteen elements: Carbon, hydrogen, oxygen, phosphorus, potassium, nitrogen, sulphur, calcium, iron, magnesium, sodium, chlorine, iodine, silicon, and fluorine. It is to be noted that the last five elements, while essential for animals, are not essential for plants.

225. **Composition of the Animal.**—Like the plant, the animal is composed largely of water, but not to so great an extent. The average amount of water in farm animals is not far from 50 per cent. In man it is about 70 per cent. Of the dry matter of steers 60 per cent. is carbon, 14 per

cent. oxygen, 9 per cent. hydrogen, 6 per cent. nitrogen, and 11 per cent. ash. This analysis may be taken as fairly representative. It shows (cf. Section 14) that there is a much larger proporton of carbon to oxygen in animals than

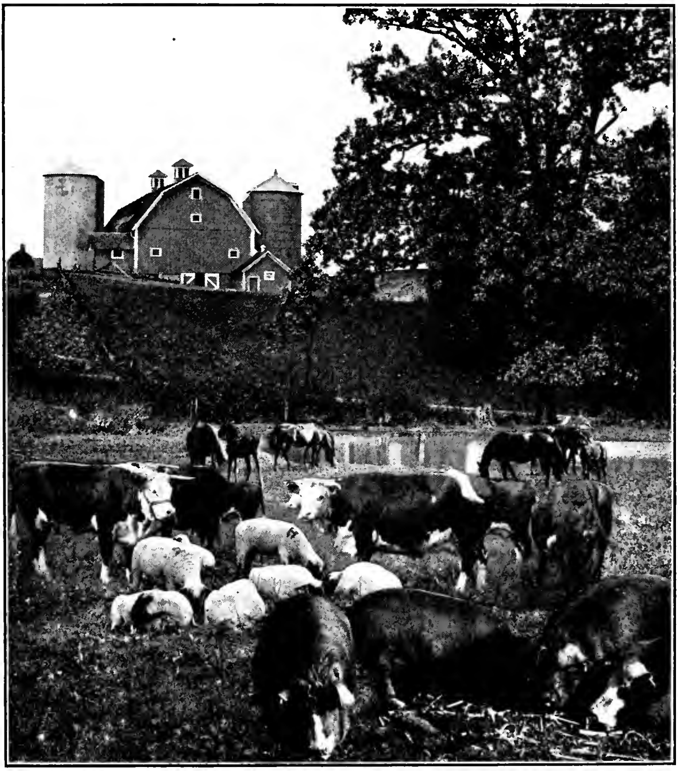

Fig. 74.—Farm animals.

in plants, and more nitrogen. This is because the dry matter of animals consists mostly of fats and proteins, whereas the dry matter of plants consists largely of carbohydrates and crude fiber. The cell walls of plants are made of cellulose, but the cell walls of animals are made of protein.

Table XVII shows the composition of various farm animals, expressed for the most part on the same basis as the composition of plants in Table I, except that there is no crude fiber or nitrogen-free extract.

TABLE XVII.—COMPOSITION OF FARM ANIMALS

Kind of animal.	Water per cent.	Fat per cent.	Protein per cent.	Ash per cent.	Contents of stomach and intestines, per cent.
Fat calf	63.0	14.8	15.2	3.8	3.2
Half fat ox	51.5	19.1	16.6	4.6	8.2
Fat ox	45.5	30.1	14.5	3.9	6.0
Fat lamb	47.8	28.5	12.3	2.9	8.5
Normal sheep	57.3	18.7	14.8	3.2	6.0
Half fat sheep	50.2	23.5	14.0	3.2	9.1
Fat sheep	43.4	35.6	12.2	2.8	6.0
Normal pig	55.1	23.3	13.7	2.7	5.2
Fat pig	41.3	42.2	10.9	1.6	4.0

In studying the animal it is necessary to know something of the various parts of the body, their general composition, functions, and the reactions taking place in them. The animal is obviously very complex in its structure and only the very general points of physiology can be touched upon. For further information the reader is referred to any good text on animal physiology. (See references at end of chapter).

226. **Bones.**—The framework of the body about which all the tissues are grouped, and which serves to give rigidity and afford protection to the more delicate and sensitive parts is composed of bones and is called the skeleton. Chemically bones are composed of protein material called osseous tissue, or ossein, permeated with tricalcium phosphate and calcium carbonate. The mineral and organic part are present in about equal proportions (Section 169). Bones are hollow to give greater strength to them, and are filled with soft material called marrow, which consists largely of fat and protein. Blood-vessels permeate the bones, and the marrow is supposed to be the source of the red blood corpuscles. Fig. 75 illustrates the appearance of bone tissue under the microscope.

227. **Muscular Tissue.**—The flesh of an animal, or muscular tissue is composed usually of bundles of cells called fibers

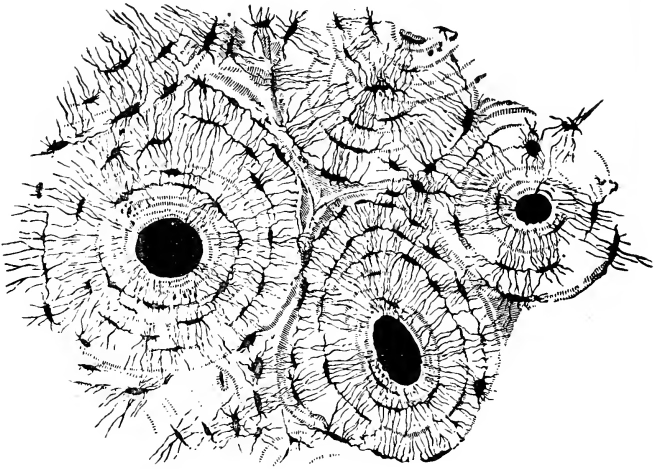

Fig. 75.—Transverse section of bone. Magnified. (Sharpey.)

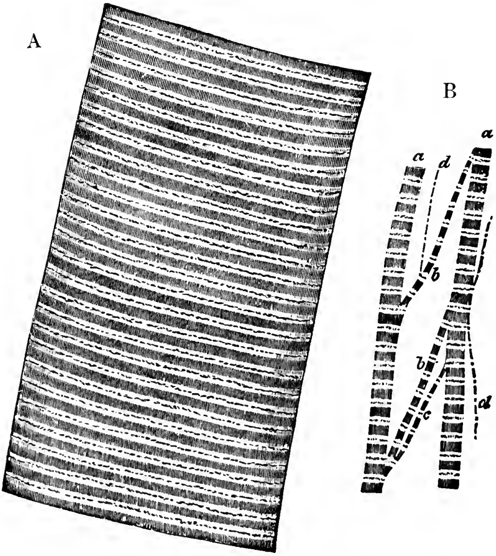

Fig. 76.—A, portion of a medium-sized human muscular fiber. Magnified nearly 800 diameters; B, separated bundles of fibrils, equally magnified; *a*, *a*, larger, and *b*, *b*, smaller collections; *c*, still smaller; *d*, *d*, the smallest which could be detached. (Gray.)

(Fig. 76). It causes motion in the animal, having the power of contracting and expanding when stimulated by the nerves. This contraction may be transmitted to the bones and cause locomotion, or may be merely a rhythmical contraction and expansion, causing the well-known movements of the heart, lungs, and other organs. The muscle substance is composed largely of proteins, but also some glycogen, dextrose, potassium phosphate, and nitrogenous extractives.[1] It is about 75 per cent. water and 25 per cent. solids. The principal protein is myosinogen, liquid in living muscle, but changing to solid myosin in dead muscle. Living muscle at rest is alkaline in character; active or dead muscle is slightly acid due to the formation of an isomer of lactic acid called sarcolactic acid. Muscles are bathed in lymph and permeated with blood-vessels. When a muscle does work, the dextrose is oxidized by the oxygen brought to it in the blood stream, and carbon dioxide is given off. Heat is also developed by this oxidation.

228. **Fatty Tissue.**—Besides the fats or fixed oils which constitute a part of all protoplasmic material, there are in animals various deposits of fat in the muscles, bone marrow, liver, and so-called adipose tissue (Fig. 77). The latter is a mass of cells each composed mainly of a large globule of fat. This adipose tissue usually lies just under the skin. Chemically fat is composed for the most part of glycerides of stearic, palmitic, and oleic acids, as in the case of plants (Section 63, *et seq.*).

229. **Epithelial Tissue.**—Epithelial tissue lines all the surfaces of the body—the skin on the outside and the mucous membrane on the inside, such as the lining of the alimentary canal and body cavities. Such epithelial cells as the hair, nails, hoofs, etc., are composed largely of a protein called keratin which is rich in sulphur. Epithelial cells of the mucous membrane are largely mucin which gives this tissue its viscid character.

230. **Connective Tissue.**—This material serves to bind together the various body parts, and composes the tendons,

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[1] Nitrogen compounds, not proteins, soluble in water.

cartilage, and such substances. Collagen and elastin are two proteins contained in connective tissue. Gelatine can be prepared from collagen by boiling it in water.

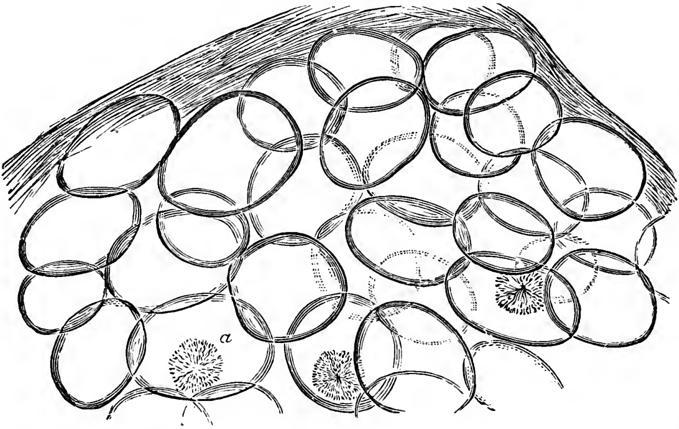

Fig. 77.—Adipose tissue, highly magnified. *a*, star-like appearance, from crystallization of fatty acids. (Gray.)

231. **Blood.**—This liquid serves to carry nutrient material to all parts of the body, supplying the various tissues with what they need for growth and repair. It also serves to carry away the waste products of metabolic activity. The blood may be compared roughly to the sap of plants in so far as it supplies soluble food material to various parts of the living organism. The sap of plants, it will be remembered (Section 16), is forced through tracheæ up the stem and into the leaves by osmotic pressure or surface tension, or a combination of both; whereas the blood is forced through a system of open canals or vessels to all parts of the animal body by the pressure of a pump which is called the heart. A rhythmic expansion and contraction of muscles around the heart pull the blood in and force it out, thus keeping up a continuous circulation of blood through the vessels. The main channels which bring blood to the heart are called veins, while those carrying blood away from the heart are called

arteries. All the tissues of the body are penetrated by a system of very fine blood-vessels called capillaries, and it is through the walls of these capillaries that the nutrient material passes and thus feeds the cells of the tissues.

Physically, blood is an opaque, red liquid consisting of a colorless solution holding in suspension several kinds of solids, one of them red in color. These red colored particles are so numerous that they give the blood a red appearance. The clear solution is called plasma. The suspended solids are red corpuscles, white corpuscles, and some other small bodies which need not be considered.

(*a*) PLASMA is a clear, transparent, colorless or slightly yellow, partly viscid liquid, consisting largely of water which holds in solution or in suspension proteins, fats, dextrose, lecithin, mineral salts, urea, uric acid, enzymes, and gases. The proteins are principally serum albumin, which is the most important constituent, and is probably the source of the body proteins. Fibrinogen is another protein, and although not present in a large amount, is very imporant. This will be discussed later under coagulation. Fats are present in minute globules. The inorganic salts are mostly sodium and potassium chlorides, carbonates, sulphates and phosphates, together with calcium and magnesium phosphates. The reaction of the blood is slightly alkaline, due to sodium carbonate and phosphate. Urea and uric acid are waste products.

(*b*) RED CORPUSCLES, ERYTHROCYTES, occur in the blood to the extent of about 5,000,000 per cubic millimeter in man. They are disk- or bell-shaped, about 7.5 microns in diameter (0.0075 mm.) and about 2 microns thick (0.002 mm.) (Fig. 78). They consist of a framework of protein material called stroma and coloring matter called hæmoglobin. The latter compound can combine with oxygen, carbon monoxide, and some other gases. It will crystallize, acts as a weak acid, and is composed of a protein called globin and an iron compound which is the real coloring matter. Hæmoglobin when combined with oxygen is called oxyhæmoglobin. The union is a weak chemical one in the proportion of one molecule of hæmoglobin to one molecule of oxygen. The union is apparently a function of the iron, one atom of iron combining with two atoms of oxygen. The oxygen can be removed by means of reducing agents, by merely passing a neutral gas like nitrogen through a solution containing hæmoglobin, or by exposure to a vacuum. Hæmoglobin is darker red, more purplish in color, than is oxyhæmoglobin, which is bright red. Blood which flows in the veins is darker in color than that which flows in the arteries, there being more hæmoglobin in the veins and more oxyhæmoglobin in the arteries. Hæmoglobin in the form of oxyhæmoglobin is the oxygen carrier of the blood. As was noted above, carbon monoxide will unite with hæmoglobin and the combination is stronger than the combination of oxygen with hæmoglobin. Hence in an atmosphere containing carbon monoxide, the oxygen is driven out of combination with the hæmoglobin and the carbon monoxide takes its place. This is the cause of carbon monoxide poisoning, since the carrying of oxygen by the hæmoglobin is a very necessary function of the blood.

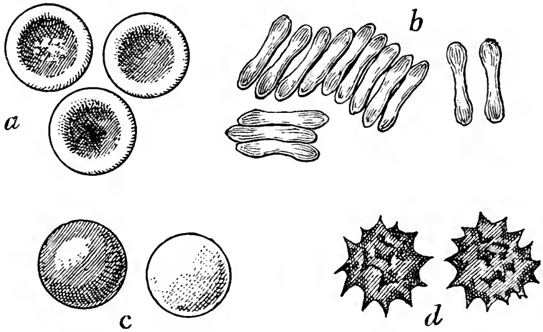

Fig. 78.—Human red blood corpuscles. Highly magnified. *a*, seen from the surface; *b*, seen in profile and forming rouleaux ; *c*, rendered spherical by water; *d*, rendered crenate by salt solution. (Gray.)

(*c*) White Corpuscles, Leucocytes, occur in the blood of man to the extent of about 5000 to 10,000 to the cubic millimeter. They are more variable in size and form than the red corpuscles, being 4 to 13 microns in diameter (0.004 to 0.013 mm.). They can move by their own processes, being somewhat amœboid in character (Fig. 79). They can pass through the walls of the capillaries and wander through the tissue fluids. These leucocytes are composed of proteins, glycogen, lecithin, fat, and phosphates. They are said to serve as blood scavengers, carrying away and absorbing undissolved substances in the blood such as bacteria. Apparently whenever a wound gives entrance to bacteria the white corpuscles swarm to that place and help to destroy them. Although this fact has not been definitely proved, it is still a reasonable belief.

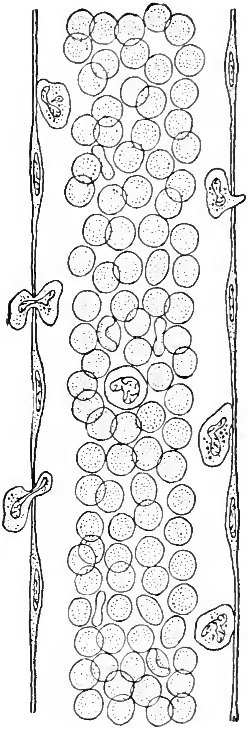

Fig. 79.—Small blood-vessel, showing how leucocytes penetrate the wall. (G. Bachman.)

(*d*) Coagulation.—On exposure to the air blood clots or coagulates, and there is formed a mass of corpuscles matted together with a fibrous substance. The cause of this clotting is not definitely known, but the theory has been advanced that an enzyme with the help of a calcium salt acts on fibrinogen, a soluble protein, changing it to fibrin, an insoluble protein. Fibrin is a white, fibrous material which entangles the corpuscles into a clot. The liquid remaining after the clot forms is called serum, and is merely plasma without the fibrinogen. By beating fresh drawn blood the fibrin can be obtained free from corpuscles. The speed of coagulation is hindered by cold, by a 10 per cent. solution of ammonium oxalate or of sodium chloride. It is hastened by heat, ferric chloride, and alum. Speed of coagulation also varies with animals. The blood of horses clots very slowly.

(*e*) GASEOUS EXCHANGE IN THE BLOOD.—Reference has been made occasionally to the fact that the blood in one way or another carries oxygen and carbon dioxide. The oxygen is necessary to oxidize dextrose and supply energy to the various tissues. Carbon dioxide is a result of the oxidation of dextrose and must be eliminated. The lungs are the seat of exchange between the oxygen and the carbon dioxide. They are a mass of tissue containing very many minute cells or alveoli surrounded by capillaries. The venous blood coming into the left side of the heart is charged with carbon dioxide. It is forced from there to the lungs where carbon dioxide is given off and oxygen taken in. This renewed blood passes then to the right side of the heart where it is discharged into the arterial system. Fig. 80 gives in diagrammatic form the circulation of the blood.

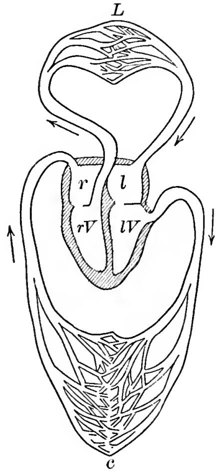

FIG. 80.—Diagram of blood circulation: *L*, lung capillaries; *c*, other capillaries; *r*, *rV*, right compartments of heart; *l*, *lV*, left compartments of heart.

The lungs contract and expand by involuntary muscular effort as they exhale and inhale air. From Table XVIII, which gives the composition of 100 volumes of inspired and expired air, it is to be noted that the inspired air is richer in oxygen than the expired air, and contains much less carbon dioxide and water.

TABLE XVIII.—COMPOSITION OF AIR

100 volumes

Inspired air.		Expired air.	
Oxygen	20.80	Oxygen	16.02
Carbon dioxide	trace	Carbon dioxide	4.38
Nitrogen	79.20	Nitrogen	79.60
Water	variable	Water	saturated
		Organic matter	trace

From Table XIX, which gives the composition of 100 volumes of arterial and venous blood at 0° and 760 mm.

pressure it can be seen that the arterial blood contains more oxygen and less carbon dioxide than the venous blood.

TABLE XIX.—COMPOSITION OF GASES IN BLOOD

100 volumes

	Arterial.	Venous.
Oxygen	20	12
Nitrogen	1 to 2	1 to 2
Carbon dioxide	40	45

The blood going into the lungs through the capillaries is charged with carbon dioxide but it does not contain its full quota of oxygen. The inspired air with which this blood comes in contact contains on the other hand an excess of oxygen and little or no carbon dioxide. Consequently, oxygen passes through the capillary walls, dissolves in the blood plasma, and then combines with the hæmoglobin to form oxyhæmoglobin. Carbon dioxide meanwhile has been carried in the blood in the form of sodium bicarbonate and dissolved to a slight extent in the blood plasma. The dissolved carbon dioxide passes through the capillary walls into the lung cells and with the reduction in the amount of dissolved carbon dioxide, sodium bicarbonate breaks up into sodium carbonate and carbon dioxide, the latter passing into the lung cells, as above described.

The blood, now charged with oxygen and containing less carbon dioxide, passes to the tissues where oxygen is needed. The oxyhæmoglobin now breaks up, oxygen dissolving in the plasma and passing through the capillaries. It oxidizes dextrose with the elimination of carbon dioxide, which passes through the capillaries, first dissolving in the plasma and then combining with the sodium carbonate to form sodium bicarbonate.

The above gaseous exchange in the lungs and in the tissues is caused by a difference in the pressure of oxygen and carbon dioxide, and is the result of mass action as can be easily seen from the following reversible equations:

$$\text{Hæmoglobin} + O_2 \rightleftarrows \text{Oxyhæmoglobin}$$

$$2NaHCO_3 \rightleftarrows Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide in the veins is under greater pressure than the carbon dioxide in the inspired air. Hence the plasma loses carbon dioxide and sodium bicarbonate breaks up. The partial pressure of the oxygen dissolved in the plasma is less than that of the oxygen in the lungs. Hence more oxygen is dissolved by the plasma and consequently a combination of oxygen with hæmoglobin takes place.

Chemically one volume of oxygen produces one volume of carbon dioxide, but in the case of animal respiration the amount of carbon dioxide evolved is normally less than the amount of oxygen absorbed. This is because some oxygen is used to oxidize the hydrogen of fat to water and to form waste products from proteins like urea. Therefore it does not appear as carbon dioxide. The ratio of carbon dioxide to oxygen is called the *respiratory quotient.*

232. **Lymph.**—The tissues of the body are all bathed in a liquid called lymph, or tissue fluid, which serves to bring nutrient material in direct contact with the tissue cells and to carry waste products away from the tissue cells. The various tissues are all in a constant state of building up and tearing down. Changes are constantly taking place. New cells are forming and old ones wearing out. The blood serves as the fluid which carries nutrient material from one part of the body to another and transports waste products of metabolism for elimination. It is carried within the walls of the blood-vessels—veins, arteries, and capillaries. Water, soluble compounds, and leucocytes can pass through the walls of the capillaries, and this fluid, which is practically blood plasma, constitutes the lymph.

Not only are the tissues bathed in lymph but the tissue spaces unite to form lymph vessels which are provided with valves at frequent intervals to prevent the fluid from flowing backward. These vessels permeate the body in every direction in a network, and combine sooner or later into the thoracic duct (Fig. 82, *th.d.*), a large lymph vessel running through the left side of the centre of the body and emptying into the venous system at the left side of the base of the neck. At intervals along the lymph vessels are enlargements called lymph glands which serve among other things as a principal source of white corpuscles.

Pressure caused by blood plasma being forced out of the capillaries, possibly contraction of lymph vessels, and particularly muscular exercise, all serve to force lymph along its vessels so that a continuous stream is poured into the veins from the thoracic duct.

Lymph being essentially blood plasma is a clear to opalescent liquid, slightly alkaline in character, containing proteins, dextrose, sodium chloride and carbonate, some other salts, white corpuscles, and a small amount of fibrinogen. It also contains oxygen and carbon dioxide dissolved in it, although part of the latter is combined with sodium carbonate. The proportion of the various constituents is not quite the same as that in blood plasma and varies from one part of the body to another according to the needs of the body.

233. **Animal Compounds.**—Many of the animal compounds are the same as those in plants, but there are some differences, enough to warrant a brief review of the subject. In this discussion, of course, no attention is paid to compounds eaten by the animal for food—only those compounds actually absorbed and utilized by the animal. For convenience in comparison, the same order will be observed as in Chapter III on Plant Compounds.

(*a*) CARBOHYDRATES.—Of the many carbohydrates known only three are of importance in the animal.

1. *Dextrose,* already described, Section 52. It is found in blood, liver, muscles, and other tissues, serving as a source of energy by its oxidation, and also as a source of fat (Section 239, *a*).

2. *Glycogen, Animal Starch* $(C_6H_{10}O_5)_n$.—It is a white, amorphous, tasteless powder, dissolving in water to an opalescent solution, and giving a dark red color with iodine. On hydrolysis with mineral acids or with amylolytic enzymes it yields dextrose. The liver is the principal repository of glycogen, containing from 1 to 4 per cent. The liver produces glycogen from dextrose, levulose, and probably galactose, the form of soluble carbohydrates absorbed. As needed by the body the liver reproduces dextrose. Glycogen is also found in the muscles to a maximum extent of 1 per cent.

Like starch in the plant, glycogen in the body is the concentrated, dehydrated form of storage carbohydrate material in the animal.

3. *Lactose.*—This is found in milk and will be described in Section 244, *a*.

4. *Cellulose* and *Crude Fiber* are not found in animals as in plants.

(*b*) Fats.—The fats are very much the same as in plants. Their general properties are the same, but there are a few animal fats and oils which deserve mention.

1. *Tallow* is the name given to certain animal fats, more or less hard in character and extracted or "rendered" from adipose tissue by melting out the fat to free it from the protein membranes. It is almost white when pure and nearly tasteless. It is composed of mixed glycerides of stearic, palmitic, and oleic acids in varying proportions, the commercial grades usually containing free fatty acids due to hydrolysis of the glycerides. Beef tallow or beef fat is softer than mutton tallow. The former is used for making oleomargarine (Section 248) and as an adulterant of lard in addition to its use as a food. The latter is employed in the making of soap, candles, and lubricants besides being used as a food.

2. *Lard* is the fat of pigs, and is obtained by rendering, as in the case of tallow. It is composed of the glycerides of stearic, palmitic, oleic, myristic, lauric, linoleic, and possibly linolenic acids.

3. *Neatsfoot Oil* is made from the feet and shin bones of cattle by boiling in water. The oil rises to the surface and is skimmed off. It is pale yellow in color, consisting chiefly of olein with some palmitin and stearin. In leather dressing and as a lubricant it finds its chief uses.

4. *Codliver Oil* is extracted from the liver of the cod, pure varieties being used in medicine, and other kinds in tanning. Its composition is very complex, containing in addition to myristic, palmitic, stearic, oleic, and erucic acids, two new acids.

5. *Menhaden Oil* is obtained from the whole body of the menhaden fish by boiling in water and expressing. It finds various uses, as in soap making and tanning.

6. *Sperm Oil* is not a true oil, being a liquid wax (Section 70), or compound of fatty acids, principally oleic, with monohydric alcohols. It is obtained from the head cavities of the sperm whale. On cooling it deposits crystals of spermaceti, a solid wax. Sperm oil is a most excellent lubricant. Spermaceti is used in making candles and in medicine.

7. *Beeswax* is the substance from which honey-comb is made, being manufactured by the bees. It is a tough, compact mass, yellow or brownish in color. It is not greasy to the touch. In composition it is a wax, containing compounds of palmitic, cerotic, and melissic acids with monohydric alcohols, and in addition some higher hydrocarbons.

8. *Volatile Oils* are not found in animals.

(*c*) Nitrogenous Compounds.—These are for the most part proteins, which differ somewhat from plant proteins. Most of the knowledge of proteins is derived from a study of these compounds in the animal. They have been classified, their properties observed and tests described, but their study is too complex and technical for a work of this kind. As occasion arises various proteins will be named and briefly described. Other nitrogenous compounds, as amino-acids and ammonium compounds, occur as transition products.

(*d*) Organic Acids are not a normal part of the animal body, except as by-products of metabolic activity, as, for example, sarcolactic acid in active muscle, and uric acid—waste material in the blood.

(*e*) Compounds of the Inorganic Elements.—In the plant inorganic compounds exist merely as transitory food materials absorbed by the roots. The so-called inorganic elements are combined organically for use by the plant either as an integral part of its tissue or as a sort of helping compound for tissue formation. In the animal, however, inorganic compounds play a very important part. They can best be taken up by elements.

1. *Compounds of Phosphorus.* — *Calcium phosphate*, $Ca_3(PO_4)_2$, exists in bones and teeth, and $CaH_4(PO_4)_2$ in the tissue fluids. In the bones and teeth it gives solidity to the organs. It is associated with magnesium phosphate, $Mg_3(PO_4)_2$.

Sodium phosphate, Na_2HPO_4, is found in all the solids and fluids of the body, giving an alkaline reaction to the latter. It is associated with potassium phosphate, K_2HPO_4, with similar properties.

2. *Compounds of Potassium.—Potassium chloride,* KCl, occurs together with sodium chloride in all the tissues and fluids of the body, being present, however, to a greater extent in the tissues than in the fluids.

Potassium carbonate, K_2CO_3, is found with potassium phosphate, which is mentioned above.

3. *Compounds of Calcium.—Calcium phosphate,* mentioned above.

Calcium carbonate, $CaCO_3$, occurs together with calcium phosphate in various parts of the body, and fulfills apparently the same functions. In the tissue fluids it occurs as a bicarbonate, $CaH_2(CO_3)_2$.

Calcium fluoride, CaF_2, is found in the bones and teeth.

4. *Compounds of Iron* are organic in nature, occurring in hæmoglobin, in the lymph, bile, gastric juice, and in the coloring matter of the eyes, hair, and skin.

5. *Compounds of Sodium.—Sodium chloride,* NaCl, is present in all the tissues and fluids of the body, particularly in the latter. The blood contains 0.6 per cent., lymph 0.5 per cent. Its function apparently is to maintain osmotic equilibrium between the cells and the fluids of the body, regulating the intake of water to the former. In pure water the tissue cells swell rapidly and die. The presence of sodium chloride in water prevents too rapid entrance of water to the cells. On this account in investigating living tissue it is customary to use a physiological salt solution which is a 0.6 per cent. solution of sodium chloride. Sodium chloride is also the source of chlorine for potassium chloride mentioned above and also for the hydrochloric acid of the gastric juice mentioned below.

Sodium phosphate, mentioned above.

Sodium carbonate, Na_2CO_3, found together with sodium phosphate, and serves also to give alkalinity to the tissue fluids. When combined with carbon dioxide it exists in the form of sodium bicarbonate, Na_2HCO_3.

6. *Compounds of Chlorine.*—*Sodium chloride* and *Potassium chloride,* mentioned above.

Hydrochloric acid, HCl, is found in small amounts in the gastric juice of the stomach where it aids in the enzyme activity of digestion.

7. *Compounds of Iodine* are found in organic form in the thyroid gland of man.

8. *Compounds of Silicon* occur in organic form in the hair.

234. **Summary.**—Animals, the highest product of the farm, are similar to plants in that they are living things that reproduce themselves, and are composed largely of organic matter. They differ from plants in many ways, one of them being the manner of nutrition. Plants absorb inorganic compounds in soluble form and from these compounds and by their help the plant tissues are built up. Animals need organic food already elaborated by plants, and are equipped with the apparatus necessary to digest and render soluble these foods before building up from them the animal tissues.

Animals need the same essential elements as do plants, and in addition sodium, chlorine, iodine, silicon, and fluorine. Animals consist largely of water, although not to so great an extent as plants, perhaps on the average not far from 60 per cent. There is a larger proportion of carbon to oxygen in animals than in plants and more nitrogen. This is because the dry matter of animals consists largely of fats and proteins instead of carbohydrates and crude fiber.

Bones are the framework about which the other tissues are grouped. They consist of about equal parts of mineral matter, mostly tricalcium phosphate and calcium carbonate, and of organic matter consisting of a protein called ossein. Bones are hollow and permeated with marrow, which is supposed to be the source of the red blood corpuscles. Muscle tissue consists of bundles of fibers which have the power of contraction and expansion, causing the various body movements. Muscle is composed largely of proteins, the principal one of which is called myosinogen, a liquid in the living muscle, but changing to solid myosin in dead muscle.

Muscles are bathed in lymph from which they derive nourishment and into which they discharge products of their activity, principally carbon dioxide resulting from the oxidation of dextrose. This oxidation results in the energy of heat and work. Fatty tissue is composed of masses of cells almost completely filled with globules of fat. Other tissues of the body are called epithelial, comprising the lining of all body surfaces. Hair, nails, and hoofs are composed largely of a protein called keratin and the epithelial cells of the mucous membranes are composed largely of a protein called mucin. Connective tissue is the name applied to that tissue which holds together the different parts of the body, such as tendons and cartilage. Collagen and elastin are two important proteins in this tissue. Gelatine is prepared from the former by boiling in water.

Blood is the liquid which carries nourishment to various parts of the body and removes waste material. It corresponds roughly to the sap of plants, but is forced through the body by the pumping action of the heart, and not by mere physico-chemical phenomena as in the case of plant sap. Blood consists of a clear, yellowish fluid which holds in suspension red and white corpuscles, the former occurring in such numbers as to give the blood a red color. The clear liquid is called plasma, holding in solution or suspension proteins, fats, and dextrose. The principal inorganic salts present in the plasma are sodium and potassium chlorides, carbonates, and phosphates. The reaction of the blood is slightly alkaline. The red corpuscles are colored by an iron compound called hæmoglobin which forms a weak chemical union with oxygen called oxyhæmoglobin. The hæmoglobin is darker red in color than the oxyhæmoglobin, the former flowing in the veins, the latter in the arteries. Hæmoglobin serves as the oxygen carrier of the blood.

The white corpuscles are somewhat larger than the red corpuscles and are able to move by their own processes, having the power of penetrating the walls of the capillaries and wandering through the tissue fluids. They serve to destroy bacteria that may gain entrance to the blood.

On exposure to the air blood coagulates, due to the formation of a fibrous material called fibrin, resulting from the action of an enzyme and a calcium salt on a soluble protein called fibrinogen. The fibrin entangles the corpuscles and forms the blood clot.

Oxygen, as has been noted, serves as a source of energy to the various tissues, the waste product being carbon dioxide. The lungs of the animal, which are a mass of tissue containing minute air cells, are the seat of the transfer of oxygen and carbon dioxide in the blood. When air is drawn into the lungs, oxygen passes through the capillaries of the blood, which surround the air cells, dissolves in the blood plasma and then unites with the hæmoglobin. At the same time, carbon dioxide dissolved in the plasma passes through the capillaries into the lungs, and sodium bicarbonate in the plasma breaks up into sodium carbonate and carbon dioxide, which dissolves in the plasma and passes out through the capillaries as before. After the blood thus charged with oxygen and relieved of carbon dioxide is forced into the tissues, oxygen passes from the plasma through the capillaries into the lymph surrounding the tissues. Oxyhæmoglobin breaks up as a result of this decrease in the amount of dissolved oxygen. Dextrose is oxidized in the tissues; carbon dioxide is eliminated in the lymph from which it passes through the capillaries to the blood plasma and combines with sodium carbonate to form the bicarbonate.

The tissues of the body are all bathed in a fluid called lymph which is derived from the blood by diffusion of the plasma through the capillaries. The tissue spaces filled with lymph unite to form lymph vessels, which permeate the body in every direction, combining sooner or later to form the main lymph channel called the thoracic duct. Lymph vessels pass through a series of enlarged bodies called lymph glands which serve among other things as the principal source of the white corpuscles. The composition of the lymph is very similar to blood plasma, containing the same compounds, although not exactly in the same proportions.

The animal compounds are somewhat similar to plant compounds, the principal difference being the carbohydrate, glycogen, which corresponds in formula to starch and serves as the reserve supply of carbohydrate in the body. Inorganic compounds serve in very many functions in the animal, whereas in the plant they are only transitory forms of food material. The animal contains no cellulose, crude fiber, or volatile oils, as do plants.

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CHAPTER XVIII

FOOD AND DIGESTION

One of the principal differences between plants and animals is the manner of food absorption. Plants must have their food dissolved on the outside before they can take it into their circulatory system. Animals can take in insoluble food and make it soluble within themselves before absorbing it into their circulatory system. For a proper understanding of the principles of feeding it is necessary to know something of the chemical processes by which foods are made soluble in the animal and of their functions after absorption.

235. **Food.**—Sherman defines food as "those substances which supply the body either with material needed for its substance, or with energy for its activities." Sometimes a distinction is made between the food of human beings and the food of animals. This is a distinction in terminology only, food of domestic animals being called *feed* as distinct from *food* which is applied to human foods only. Since the processes of digestion and the main constituents of food are the same for man as for domestic animals, no distinction will be made in this chapter, all the material considered being called food.

The tissues of the animal body are in a constant state of change, new tissue being formed, old tissue being broken down. These chemical processes of building up and tearing down are called metabolism. Food supplies the material for constructive metabolism. For the chemical changes of metabolism in general, for the production of heat and work in the animal, energy is necessary. Food supplies the necessary material for this energy, which is a result of destructive metabolism. A comparatively small part of the food required for animals is necessary in repairing and building tissue, the greater portion of the food being utilized in the production of energy.

236. **Food Constituents.**—Food in general is composed of different kinds of material, every one of which is separately digested and absorbed in the animal and which serves special functions in the body. These constituents are: Carbohydrates, fats, proteins, and inorganic salts, not to mention water which, strictly speaking, should be considered a food constituent; but since it is combined with all food constituents and since its presence is necessary for their solution and absorption, it will not be necessary to consider it separately.

237. **Digestion.**—The processes by which insoluble food materials are rendered soluble for absorption into the blood of animals are called digestion. Digestion takes place in the various parts of the alimentary canal, which consists principally of the mouth, stomach, and small intestine. There are connected with these various parts of the alimentary canal certain appendages, which are necessary for the various activities of the food canal. Since digestion occurs in three places and under three different kinds of conditions, it is advisable to separate the discussion of these processes into three parts: Salivary, gastric, and intestinal digestion.

(*a*) SALIVARY DIGESTION.—The first process is one of mastication, which serves to grind the solid food into more or less fine particles so that the digestive juices can act on them to better advantage. While the food is being masticated, there is poured into the mouth from three different glands a liquid called *saliva,* which serves mechanically to combine the fine particles of food together so that they may be more easily swallowed, and also to act chemically on some of the food constituents. Saliva is a slightly turbid, opalescent, somewhat viscid liquid which is composed almost entirely of water, but with some soluble organic matter, inorganic salts, and an enzyme called *ptyalin.* It is slightly alkaline in character, due to the presence of sodium carbonate. The enzyme ptyalin or salivary amylase is the active digestive agent in the mouth. It acts on starch, changing it first to dextrin and then to maltose. The process is hydrolytic in character and in every way is similar to the amylolytic action of diastase in seeds. The slightly alkaline character of saliva is necessary for the activity of ptyalin. It does not function in strong alkalies or acids. No other constituents are acted upon in the mouth and not all of the starch is rendered soluble. Food material, now united into a moist ball, is swallowed and passes into the stomach where the next change takes place.

(*b*) GASTRIC DIGESTION.—In man, horses, and pigs, there is but one stomach, but in the ruminants, like cattle and sheep, there are four stomachs, or at least four compartments to the stomach. Animals of this type "chew the cud," and food passes from the mouth to the first and second compartments of the stomach, is then forced back into the mouth for further mastication, and then after swallowing is passed finally through the third stomach into the fourth for final digestion. The repeated mastication of food by these animals merely serves to completely comminute the food and thoroughly prepare it for digestion. In this way such animals are able to digest fibrous material to a much greater extent than other animals, like the horse. They can digest more crude fiber and cellulose in this way because these insoluble food constituents are so thoroughly separated and ground up that bacteria and possibly the digestive juices can act on them successfully. In the following discussion of gastric digestion, it will be understood that the processes described apply in the case of ruminants to the fourth stomach only.

After the food reaches the stomach it is mixed with the *gastric juice*, which is secreted by glands in the walls of the stomach and is poured out when the food reaches the stomach. The process of excretion of gastric juice is partly one of response to a mechanical stimulus due to the contact of food with the stomach; partly to psychic impulse caused by the sight or odor of food; and partly in response to nerve impulses when food is masticated. The gastric juice is thoroughly incorporated with the food by to and fro movements of the stomach. Gastric juice is a clear, colorless liquid with a distinctly acid reaction, due to the presence of about 0.2 per cent. hydrochloric acid. It consists largely of water with a little organic matter and mineral salts besides the hydrochloric acid just mentioned. In addition there are present two enzymes: *Pepsin* and *rennin*. When the food first enters the stomach it is alkaline in character due to the admixture of saliva. The action of ptyalin continues as long as the reaction is alkaline. As soon as the food becomes thoroughly mixed with the acid gastric juice the action of ptyalin ceases.

The enzyme pepsin, for which the acid solution is necessary, hydrolyzes proteins to proteoses and peptones which are soluble and diffusible decomposition products of proteins. Not all of the proteins are acted upon in this way, for the food does not remain in the stomach long enough for the complete solution of all proteins to take place. This solvent action of pepsin is also of secondary importance in that it dissolves the protein cell walls of fats, thus disintegrating fatty material and setting free the drops of fat.

Rennin, the other enzyme in the stomach, acts on the caseinogen of milk (Section 244, *c*), which is a soluble compound, changing it or "curdling" it to a solid compound, casein. Just why this is necessary is not apparent. After the change takes place the coagulated casein is dissolved by the pepsin. No other food constituents are acted upon in the stomach. There is no evidence that the hydrochloric acid inverts sucrose, as might be expected (Section 54). The combined action of water, hydrochloric acid, and pepsin, together with the mixing and churning motions of the stomach has now changed the solid elements of food material to a semi-liquid form called *chyme*.

(*c*) INTESTINAL DIGESTION.—The chyme is discharged into the small intestine where the next processes of digestion take place. The food material here is mixed with three different fluids, intestinal juice, pancreatic juice, and bile.

Intestinal juice is secreted by certain glands in the walls of the small intestine and is a watery, light yellow, slightly opalescent, alkaline liquid, containing at least carbonates. Because it is very difficult to obtain it in the pure state, its composition is not accurately known except that it does contain certain enzymes which are active in hydrolyzing some of the carbohydrates. *Invertase* changes sucrose to dextrose and levulose; *maltase* changes maltose to dextrose; and *lactase* changes lactose to dextrose and galactose.

Pancreatic juice is secreted by the pancreas, which is a long flattened gland, and is discharged into the intestine like the intestinal juice when food reaches the stomach. Pancreatic juice is a clear, viscid, decidedly alkaline liquid, containing in addition to water a little organic matter and inorganic salts of which sodium carbonate is the most important and which gives alkalinity to the juice. Pancreatic juice contains the principal digestive enzymes of the alimentary canal.

Amylopsin is the pancreatic amylase which hydrolyzes starch to maltose, being much more energetic in action than ptyalin. An alkaline solution is necessary for it to act.

Steapsin is the pancreatic lipase which hydrolyzes fat to glycerine and fatty acids. The fatty acids thus liberated unite with the alkalies which are present in the juice of the intestine to form soaps. It is not definitely known whether all fats are thus hydrolyzed or whether a part of the fat is so changed and the remainder emulsified in the soap solution. The former is the more probable, however. This enzyme also is only active in an alkaline solution.

Trypsin is the pancreatic protease which hydrolyzes proteins in the alkaline medium and changes them to peptones and possibly to amino-acids. Trypsin is much more energetic in its action than is pepsin in the stomach and the probabilities are that it hydrolyzes the proteins more completely.

Bile is a fluid secreted by the liver and discharged into the small intestine together with intestinal juice and pancreatic juice when food is received into the stomach. It is a thin liquid somewhat viscid, of bitter taste, and very alkaline due to the presence of sodium carbonate and sodium phosphate. It varies in color from greenish yellow to brownish red, depending on the animal. In herbivorous, or plant-eating animals, it is greenish in color; in carnivorous, or meat-eating animals, it is orange or brown. There are present in the bile in addition to the normal secretory compounds some excretory or waste compounds such as cholesterin and lecithin. They are supposed to be decomposition products of the nerve tissue and are eliminated from the blood stream through the liver. The bile has no direct solvent action on any of the food constituents, but its action decidedly increases the power of the pancreatic enzymes and it serves as the principal solvent for the fatty acids in the formation of soaps.

In addition to the normal enzyme secretions of the body which have a solvent action on food constituents, there are ordinarily present in animals large numbers of bacteria, principally in the intestines. Their presence is not necessary for the decomposition and solution of food constituents, but it is probable that their fermentative action is in some cases of benefit in digesting food.

Food material which has been acted upon by the various chemical agents is rendered soluble and ready for absorption. Not all of it, however, can be dissolved. Particularly do crude fiber and cellulose remain unattacked except in the case of some of the domestic animals, more particularly the ruminants, where these food constituents are partly digested, due probably to the activity of bacteria. The undigested portion of the food is discharged into the large intestine for final elimination.

238. **Absorption of Food Constituents.**—The absorption of the various constituents of the food is limited almost wholly to the small intestine, little if any being absorbed from the mouth or stomach into the circulatory system. The interior of the small intestine is covered with minute conical projections called *villi* (Fig. 81), through which all the dissolved material is absorbed. They serve the same purpose in the animal that the root hairs do in the plant, but they differ in that they are not each one a single cell but a large number of cells containing blood capillaries and lymph vessels, which carry the absorbed material into the general circulatory system.

The carbohydrates in the form of dextrose, levulose, and possibly galactose are absorbed through the outer cells of the villi into the capillaries, which finally unite into the portal vein and discharge into the liver. In the liver the carbohydrates are changed into glycogen until such time as dextrose is needed in the blood, when the glycogen is transformed into dextrose. Enzymes in the liver accomplish the dehydration change to glycogen as well as the hydrolytic change to dextrose.

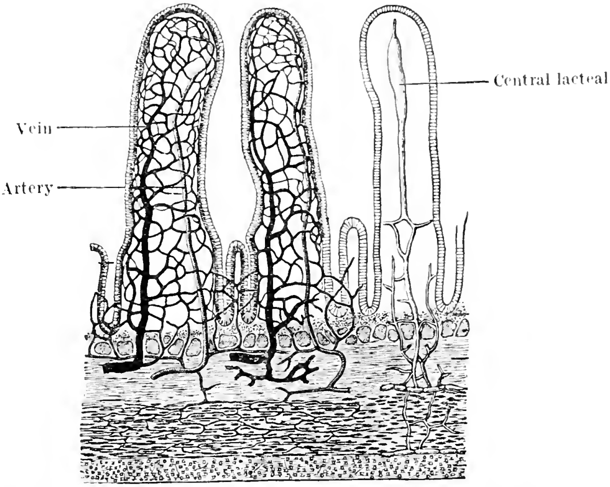

FIG. 81.—Diagrammatic section through villi of small intestine. (From Böhm and Davidoff, after Mall.)

Fats are probably absorbed as glycerine and soaps, although possibly also in the form of emulsified fats, and pass through these outer cells of the villi into the lymph vessels or lacteals. During the process of this absorption the glycerine unites with the fatty acids of the soaps to form fats, so that the lymph as it leaves the villi is charged with liquid globules of fat to such an extent as to give it the appearance of milk. The lymph vessels join the thoracic duct from which the fatty particles are discharged into the veins and thus get into the general circulatory system of the blood.

The proteins in the form of peptones or possibly amino-acids are absorbed into the blood-vessels of the villi, during which process they combine to form the serum-albumin and globulin of the blood. These are the forms of protein which are transported through the body. The proteins pass into the portal vein and through the liver, but are not arrested there as are the carbohydrates.

Water and inorganic salts which have been set free from their organic combination in foods by the various processes of digestion are absorbed through the villi into the capillaries. Under ordinary conditions no water is absorbed by the lymph vessels. The progress of water and inorganic salts is then like that of carbohydrates and proteins, through the portal vein and the liver. Fig. 82 shows the routes of the absorbed material.

239. **Functions of Food Constituents.**—Various constituents of the food after absorption into the body, serve each a more or less distinct function in the activity of the animal and can be discussed separately.

(*a*) Carbohydrate.—The only active form of carbohydrate in the body is dextrose and this material serves primarily as a source of energy. Just as energy is derived in the steam engine from the combustion of fuel so is the energy of the body derived from combustion of fuel. This combustion takes place within the tissues of the body and is caused by enzymes, the final product being carbon dioxide and water. Energy is set free in the form of heat and work. When dextrose is present in larger quantities than is necessary for fuel consumption it is transformed into fat and stored away in the adipose tissue of the body.

(*b*) Fat serves also as fuel for body energy and is the most concentrated source of fuel in the body, yielding more energy per unit of weight than any other form of fuel. Some of the fat absorbed is deposited in adipose tissue, and there is some evidence that dextrose may be formed from fat.

(*c*) Protein.—The primary function of protein is, of course, to supply the principal part of tissue material. It is necessary for cell wall and protoplasmic contents of new cells and also to replace worn out material in old cells. Changes are constantly taking place in the body; old cells wearing out, new cells being formed, in addition to increase in the number of cells when an animal is growing. Protein

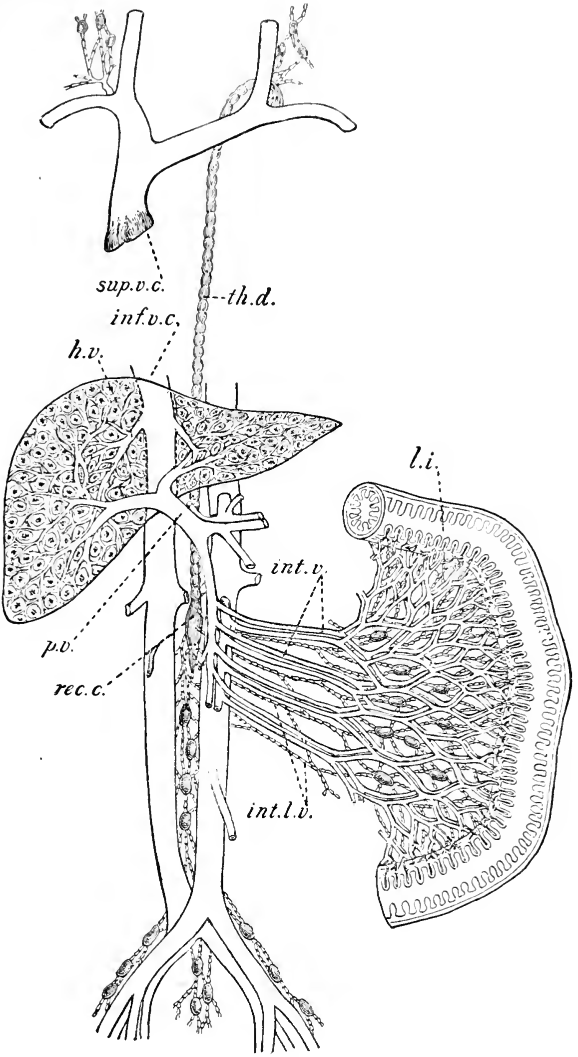

FIG. 82.—Diagram showing the routes by which the absorbed foods reach the blood of the general circulation. (G. Bachman.) *l. i.*, loop of small intestine; *int. v.*, intestinal veins converging to form in part, *p. v.*, the portal vein, which enters the liver and by repeated branchings assists in the formation of the hepatic capillary plexus; *h. v.*, the hepatic veins carrying blood from the liver and discharging it into, *inf. v. c.*, the inferior vena cava; *int. l. v.*, the intestinal lymph vessels converging to discharge their contents, chyle, into, *rec. c.*, the receptaculum chyli, the lower expanded part of the thoracic duct; *th. d.*, the thoracic duct discharging lymph and chyle into the blood at the junction of the internal jugular and subclavian veins; *sup. v. c.*, the superior vena cava.—Brubaker's *Physiology*.

also serves as a source of fuel in the body, particularly when dextrose and fat are not present in sufficient amount. The products of protein oxidation, however, in addition to carbon dioxide and water, are nitrogenous compounds, largely urea. The protein compounds can also be split up in the body into a nitrogenous and a non-nitrogenous residue. From the non-nitrogenous residue carbohydrates can be formed and there is some evidence to show that fat may also be formed. The nitrogenous residue is eliminated as waste material.

(*d*) INORGANIC ELEMENTS.—These constituents in mineral form give rigidity to the skeleton. They serve also as necessary constituents of protoplasm, sulphur and phosphorus, for example, and are combined organically for this purpose. Finally, these elements in the form of inorganic salts are present in the fluids and tissues of the body, having an influence upon the activities of the muscles and nerves, supplying an alkaline or acid reaction as may be necessary, and regulating the osmotic pressure of the cells.

240. **How to Express Food Value.**—As has been stated (Section 237, *c*), not all of the food taken in by the animal is absorbed, and of course, that portion which is not digested is of no use to the animal. It is customary to express the amount of digestible material in each constituent in percentage. These "digestible coefficients," as they are called, are determined by analyzing the original food and also by analyzing all excreted waste products. The difference between the two sets of results gives the percentage of food digested, and hence serves as an indication of the amount of tissue building or energy material in the food eaten. The results, however, are not absolutely correct for several reasons. In the first place the excreted material contains protein and ether soluble material called fat, derived from the intestinal juices and waste cells of the intestines. In the second place, unless there is an analysis of all the gas eliminated from the body there is a waste of some material in this way that is unaccounted for. In the third place, if it is desired to determine the value of the food for the production of work or milk or fat, it is necessary to

take into consideration the food constituents which are consumed by the involuntary activities of the body. An animal absolutely at rest or asleep is constantly using up food constituents. The beating of the heart, expansion and contraction of the lungs, movements of the digestive apparatus are going on constantly. When food is masticated work is done and the oxidation of body fuel is necessary to obtain this energy.

Most of the food taken in by the animal is used up in the production of energy, and since energy can be expressed in terms of heat, it is customary to value food on the basis of heat equivalents. Since the combustion of food material in the body results in the production of exactly as much heat as is derived from the combustion of the same constituents in the air, it is possible to determine the fuel value of foods by well known methods of analysis. And, finally, since an apparatus has been devised for determining the energy value of foods in the animal, and at the same time permitting a complete analysis of all food income and outgo, it is possible to overcome in large measure the defects just mentioned for determining the value of foods.

For the determination of the heat value of substances, an instrument called a calorimeter is used, which consists essentially of a closed chamber in which organic material can be burned in an atmosphere of oxygen and the resulting heat accurately measured by the rise in temperature of a surrounding body of water after making certain necessary corrections. Modern scientific ingenuity has gone one step further and devised calorimeters which will contain a living animal and in this way the amount of heat developed by the combustion of food in the body can be accurately measured. In addition these animal calorimeters are equipped with elaborate apparatus for measuring the intake of oxygen and the output of carbon dioxide and other gases. These factors, together with the weighing and analyzing of all foods consumed and all solid and liquid material excreted, make it possible by a series of calculations to arrive very accurately at the proper value of any food for any particular animal. The respiration calorimeter devised by Armsby of the Pennsylvania Station is the most complete apparatus of this kind in existence. Fig. 83 shows the apparatus from the outside.

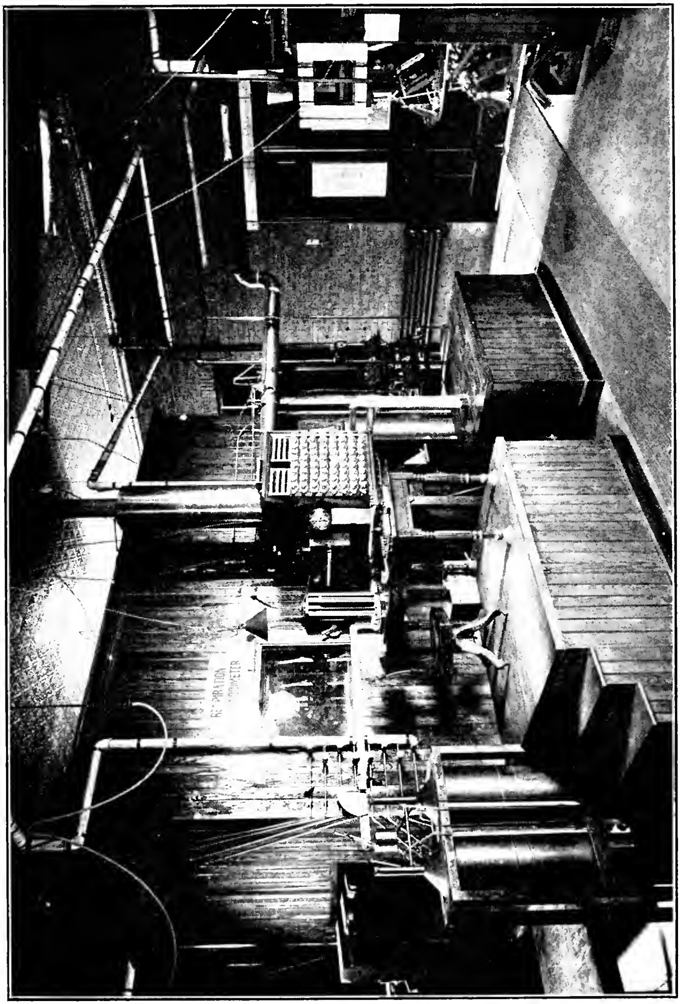

Fig. 83.—Armsby's respiration calorimeter at the Institute of Animal Nutrition, Pennsylvania Station.

The unit for expressing food values in terms of heat is the large *Calorie* which is the amount of heat necessary to raise the temperature of 1000 grams of water 1° C. For many purposes, however, this unit is not large enough for convenience and as a result the unit *therm* is now in use by Armsby. A therm is the quantity of heat necessary to raise the temperature of 1000 kilograms of water 1° C., and it is customary in expressing the value of food to do so as therms per 100 pounds.

241. **Feeding Standards.**—Ever since the functions of the various food constituents in animal metabolism have been known there has been a desire to determine scientifically the amount of these constituents necessary for various classes of animals and for various purposes. As a result we have the so-called "feeding standards," which are based on analytical and experimental data. The accurate observations of Armsby with his respiration calorimeter now make it possible to establish standards which are reasonably correct. Although even so, our knowledge is not by any means perfect. The question of the proper feeding of stock, and what should be more important the proper feeding of man, is too large a one to be considered here. For further information along this line the reader is directed to the references given at the end of the chapter.

242. **Summary.**—Food is defined as substances which supply the body with material for its tissue, or with energy for its activities. It is composed of various constituents, each of which serves special functions and which requires separate treatment in the animal body before being absorbed. This process of solution of food constituents is called digestion and takes place in the mouth, stomach, and small intestine.

Salivary digestion is that which takes place in the mouth where food is first ground up by the process of mastication. Alkaline saliva is mixed with the food and the enzyme ptyalin hydrolyzes starch to maltose. In the stomach where gastric digestion takes place the food is mixed with the acid gastric juice containing two enzymes: Pepsin, which dissolves proteins to proteoses and peptones; and rennin, which coagulates the caseinogen of milk, preparing it for solution by pepsin. Food material in a semi-liquid form called chyme passes into the small intestine where intestinal digestion takes place. The intestinal juice, alkaline in character, supplies the enzyme maltase for changing maltose to dextrose, lactase for changing lactose to dextrose and galactose, and invertase for changing sucrose to dextrose and levulose. Pancreatic juice is also an alkaline liquid, and is secreted by the pancreas. It contains amylopsin which hydrolyzes starch to maltose; steapsin which hydrolyzes fat to glycerine and fatty acids, the latter uniting with alkalies to form soaps; and trypsin which changes proteins to peptones and possibly to amino-acids. These enzymes are all more active than the corresponding enzymes in the mouth and stomach. The bile is a fluid secreted by the liver and its function is to assist the enzymes in their activities.

Carbohydrates in the form of dextrose, levulose, and possibly galactose, are absorbed through the outer cells of the villi, which are conical projections in the walls of the small intestine. Practically no absorption takes place from the mouth and stomach. The carbohydrates pass through the capillaries into the portal vein and thence to the liver where they are dehydrated and stored as glycogen until needed by the blood, when glycogen is transformed into dextrose. Fats in the form of glycerine and soaps are absorbed through the walls of the villi, changed into fats again and pass through the lymph vessels into the thoracic duct and thence into the veins. The proteins in the form of peptones and amino-acids during their absorption through the walls of the villi are changed to serum-albumin and globulin, passing through the blood capillaries to the liver and thence into the circulatory system. Inorganic salts follow the same route as do the carbohydrates and proteins.

The carbohydrates in the form of dextrose are utilized by the body tissues as a source of energy by combustion with oxygen. Carbon dioxide and water are the final products. Excess of dextrose is converted into fat and deposited in the adipose tissue. Fats also serve as a source of energy, being the most concentrated form in the body. There is also some evidence to suppose that dextrose is formed from fat. Proteins are the source of cell material in the body and are useful in building up new cells and repairing old cells. They also serve as a source of fuel when dextrose and fats are not present in sufficient quantities. From the non-nitrogenous residue of proteins carbohydrates are formed. The inorganic elements serve as necessary constituents of protoplasm and give rigidity to the skeleton in their mineral form. They are also present in the tissues and fluids of the body, regulating the tone of the muscles and nerves, and the osmotic pressure of the cells.

The value of food may be expressed in terms of percentage digestibility, called coefficients of digestion, which are determined by a chemical analysis and represent the amount of material actually absorbed by the body. Further advances in the expression of food values have resulted in the use of a respiration calorimeter whereby all income and outgo of the animal can be measured in addition to the heat production. Since the value of foods to the animal can be expressed in terms of heat units this form of expression is now used very largely in calculating animal rations.

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CHAPTER XIX

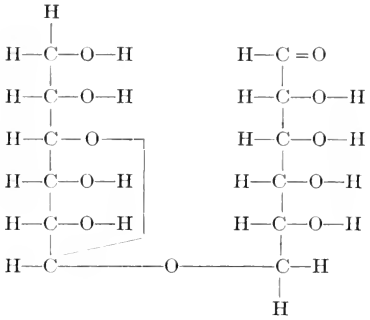
MILK AND DAIRY PRODUCTS

THE most valuable products of the animal are milk and its derivatives. Most of these materials are used as food for man. Milk in particular, as Hawk says, is the most satisfactory individual food material elaborated by nature, in that it contains protein, fat, and carbohydrate in addition to mineral matter, all combined in such form and proportion as to make it palatable, nourishing, and easily digested. The following discussion applies solely to milk from cows, since that has been most studied and since milk from other animals differs from it only in the proportion of the various constituents.

243. **Physical Appearance.**—Milk is a white, opaque liquid, the specific gravity of which is about 1.03, with a slightly sweet, pleasing taste, and a freezing point of −0.56° C. Its color is due to minute particles of fat in suspension and also to the presence of a protein, caseinogen, in pseudo-solution.

244. **Chemical Composition.**—Milk is composed of a clear, aqueous solution of carbohydrate, inorganic salts, and protein, in which are suspended fat globules, calcium phosphate, and a protein in semi-suspension. The average composition is as follows: Water, 87.75 per cent.; fat, 3.4 per cent.; protein, 3.5 per cent.; carbohydrate, 4.6 per cent.; and inorganic salts, 0.75 per cent.

(*a*) CARBOHYDRATE.—Lactose is the only carbohydrate present in milk sugar. It is an aldose sugar whose formula is $C_{12}H_{22}O_{11}$, graphically:



It is dextrorotatory and reduces Fehling's solution, although to a less extent than dextrose. It is hydrolyzed by enzymes and acids to dextrose and galactose. It does not undergo ordinary alcoholic fermentation except under the influence of certain yeasts. The principal change in lactose is due to the so-called lactic bacteria which hydrolyze it to lactic acid, thus:

$$C_{12}H_{22}O_{11} + H_2O = 4C_3H_6O_3.$$

It is this lactic acid to which is due the taste of sour milk, and it is produced so quickly that ordinary milk contains about 0.2 per cent. of lactic acid. The taste is apparent when the proportion rises to 0.4 per cent., and at 0.7 per cent. milk "curdles." Curdling is due to the coagulation of caseinogen (see below). The percentage of lactic acid rarely rises above 2 because in that amount the action of the lactic acid bacteria is inhibited. Lactose is only one-tenth as sweet as sucrose.

(*b*) Fat in milk is, of course, like other fixed oils in that it is composed of glycerides of fatty acids. Milk fat differs from other animal fat in that it is composed of a number of lower fatty acids, there having been found the following:

Butyric,	C_3H_7COOH
Caproic,	$C_5H_{11}COOH$
Caprylic,	$C_7H_{15}COOH$
Capric,	$C_9H_{19}COOH$
Lauric,	$C_{11}H_{23}COOH$
Myristic,	$C_{13}H_{27}COOH$
Palmitic,	$C_{15}H_{31}COOH$
Stearic,	$C_{17}H_{35}COOH$
Oleic,	$C_{17}H_{33}COOH$

In general, oleic and palmitic acids are present to the greatest extent. The fats from butyric, caproic, caprylic, and oleic acids are liquid. The fats from the other acids are solid. The first three mentioned fatty acids are soluble in water and volatile in steam. All the acids are saturated with the exception of oleic. Milk fat is soluble in the usual solvents: Ether, carbon disulphide, acetone, and liquid hydrocarbons.

Milk fat occurs in small globules from 1.6 to 10 microns in diameter (0.0016 to 0.01 mm.). They are liquid in the animal, but solid at ordinary temperatures, the melting point varying from 29.5° to 33° C. The fat globules in milk are in the form of a true emulsion—minute, oily particles suspended in a slightly viscous medium (Section 216, II, *b*), the viscosity of the milk plasma being due to the soluble proteins. Referring to the specific gravity of milk, it may be noted that an increase in the amount of fat causes a lowering of the specific gravity.

(*c*) PROTEINS consist of caseinogen, lactalbumin, and one or two others not of sufficient importance to deserve mention. Caseinogen helps to give the opaque color to milk, being present in a condition of pseudosolution. It contains sulphur and phosphorus in addition to the ordinary protein elements, carbon, hydrogen, nitrogen, and oxygen, and is probably combined with calcium or with calcium phosphate. Acids precipitate the casein by removing the calcium, thus setting free the protein proper. The action of rennin in precipitating casein is somewhat different. It splits the caseinogen into two different soluble proteins, at the same time liberating the calcium phosphate. One of the proteins unites with the liberated calcium phosphate to form the insoluble curd. Casein is insoluble in water, alcohol, ether, and dilute acids, but soluble in strong acids and in alkalies.

Lactalbumin is coagulated by heat and precipitated by tannin and saturated solutions of sodium and magnesium sulphates. It contains carbon, hydrogen, oxygen, nitrogen, and sulphur, but no phosphorus.

(*d*) INORGANIC SALTS are present in the form of chlorides of sodium and potassium, mono- and dipotassium phosphates, dimagnesium phosphate, di- and tricalcium phosphates, calcium and magnesium citrates. All the salts are present in solution except tricalcium phosphate, which is suspended in finely divided form. It is to be noted that some of the inorganic elements are combined with citric acid. It may be noted that an increase in the amount of inorganic salts raises the specific gravity.

(*e*) OTHER CONSTITUENTS.—In addition to those substances already mentioned, milk contains lecithin, cholesterol, proteolytic enzymes, carbon dioxide, oxygen and other gases, especially when the milk is fresh drawn, not to mention various kinds of foreign matter including bacteria. The amount of dirt and bacteria depends on the care with which milk is handled.

245. **Secretion.**—Milk is secreted in certain glands especially adapted for the purpose, and evidence points to the fact that the various components of this fluid are elaborated in these gland cells only and not merely filtered from the blood plasma. Lactose, for example, is not found in the blood stream, but must be manufactured, probably from dextrose, in the milk glands. Milk fat and casein are not found in any other part of the body.

The influence of breed of cow on the quality of milk secretion is of much greater importance than that of food. The Jersey, for example, produces large globules of milk fat, which causes cream to rise rapidly and in considerable quantities. The Holstein produces small globules of milk fat and not so great a total quantity. Modifying the food has very little influence on the composition of milk. The same food, for example, fed to different breeds produces different kinds of milk, but changing the food for one particular breed does not change the kind of milk produced by that breed. There are some exceptions to this statement, but they are not of sufficient importance to be discussed here.

246. **Adulteration and Preservation.**—Since milk has become such a very valuable food product, the temptation to adulterate it is very great. The addition of water is the commonest method of adulteration, detection of which is not particularly easy. For example, the specific gravity of milk might be used as a test for purity, but by removing fat and adding water, the specific gravity can be made to remain the same. It is, however, a requirement in some states that milk shall not be sold under a certain content of butter fat. This serves as a protection to the consumer, but in some instances it works a hardship against the producer for it is quite possible that perfectly pure milk may contain less than the stated legal minimum amount of fat.

Milk is not only a perfect nutrient for man, but it is also a perfect nutrient for bacteria, and exposure to the air for any length of time permits the entrance of large numbers of bacteria, many of them dangerous to health. No bacteria are present in the milk within the animal, but as soon as it is drawn bacteria begin to accumulate. Since bacteria thrive best in warm milk, immediate cooling is of help in preventing their activity to some extent.

There are two ways of freeing milk from bacteria, which are legitimate. One is by pasteurization which consists in heating the milk to a temperature of 60° to 80° C. for twenty minutes, and then cooling it. This treatment kills practically all of the bacteria, and if carried out in sealed containers no more bacteria can enter. Pasteurization does not alter the taste or smell of the milk, and is practised quite largely by the best dairies.

The other way of treating milk is by sterilization which consists in heating the milk to 115° C., accomplished by steam under pressure. This absolutely kills all bacteria, but it alters the taste and smell of the milk. Albumin is precipitated, calcium citrate is deposited, and other changes also take place which affect the quality of the milk.

It is unfortunately easier to stop the action of bacteria by the addition of chemical preservatives, and the ones which are most effective in killing bacteria are also the ones which harm the consumer. Formaldehyde, boric acid, salicylic acid, and benzoic acid, are compounds which have been used, but the law in most states prevents their use at all, so that at the present time the consumer is safe from such a dangerous practice.

247. **Cream.**—Cream consists merely of the greater part of the milk fat separated from the remainder of the milk, and is obtained by allowing the milk to stand quietly when the fat globules, being lighter than the rest of the milk, rise to the surface and can be skimmed off. Another way to obtain cream is by use of the separator, which is a machine where the fresh drawn milk can be subjected to centrifugal force, the heavier part being thrown to the outside and the lighter part rising in the centre. By appropriate devices the two parts of the milk can be drawn off in separate streams and by regulating the cream discharge pipe, cream of different fat content can be obtained. The fat can be withdrawn more completely from milk in this way than it can by the old-fashioned skimming process, the former removing from 97 to 98 per cent. of the butter fat under the best conditions, and the latter not more than 90 to 95 per cent.

248. **Butter.**—Both butter and cream consist of milk fat, but cream is mixed with more or less of the other constituents of milk, whereas butter consists practically of milk fat only. It is made by agitating cream in a churn whereby the globules of milk fat coalesce into a mass. This is removed and worked over to remove the last trace of *buttermilk,* which consists of milk minus butter. Buttermilk usually contains about 4 per cent. of lactic acid, giving it a sour taste. This is because the best quality of butter is obtained from cream which has been properly "ripened," or, to put it plainly, which is somewhat sour. The souring, however, is not permitted to take place spontaneously, because of the danger of introducing harmful bacteria, but is accomplished

by adding artificial lactic acid bacteria cultures. Butter contains about 84 per cent. of fat, 13 per cent. of water, and about 3 per cent. of lactose, albumin, and sodium chloride, the latter having been added to improve the flavor and also to serve as a preservative. Since it is possible to produce butter which contains considerable water and thus sell an adulterated product, it is not permitted in the United States for butter to contain more than 16 per cent. of water.

Butter frequently becomes rancid, a condition which is due probably to the action of bacteria, molds, light, and oxygen. This combination of factors results in the hydrolysis of fat, which sets free some of the fatty acids, one of them at least, butyric, being volatile, and some of them oxidizing to aldehydes.

Oleomargarine.—At this point it may be well to mention one of the principal butter substitutes, which is a perfectly nutritious article of food, but which not being butter should not be sold as such. It is manufactured from beef fat by rendering the latter and allowing the resultant product to stand at a low temperature for some time, when part of the solid fats crystallize. The soft mass is now subjected to pressure, and a liquid oil consisting of olein and palmitin principally are pressed out. This "oleo oil" is worked up by itself or with lard, cottonseed oil, cocoanut and other oils. It is then churned with milk, sometimes with a little butter, after which it is worked and salted.

249. **Cheese.**—This is one of the oldest articles of food, being used 1000 years B. C., and still retaining its popularity as a nutritious article of diet. It consists essentially of the casein from milk with considerable fat entangled with it and some water, lactose, and inorganic salts. The solid product is submitted to seasoning and ripening processes which favorably affect its composition and flavor. Ordinary American cheese contains about 34.4 per cent. water, 26.4 per cent. protein, 32.7 per cent. fat, 2.9 per cent. lactose, and 3.6 per cent. ash.

Cheddar, or *American cheese,* is the commonest form of this food. It is made by first ripening the milk with an artificial starter until it contains a small amount of lactic acid. Then rennet is added. This is a preparation made from calves' stomachs and contains the enzyme rennin which coagulates the casein in the milk. The temperature is maintained at about 30° C. until a curd settles, when it is raised somewhat higher and maintained for one or two hours. After separating the curd from the "whey," as the residual liquid is called, the solid mass is ground, salted, and pressed into cakes, after which it is placed in a curing room where it is kept for some time at a temperature of 13° C. There should be present also about 65 to 75 per cent. of moisture in the curing room. If the temperature is too high fat exudes from the cheese, and too much moisture is lost. The changes which take place during ripening are not purely bacterial but are largely due to enzymes. Some water is lost by vaporization; lactose is converted to lactic acid; and proteins are hydrolyzed, many of them to soluble products. Odor and flavor are developed which impart quality to the cheese. The result of the various changes is a decided improvement in the palatability and digestibility of the material.

Cheshire cheese is made in England from fresh milk. The method and care of cutting the curd and removal of the whey is important.

Stilton cheese is made between March and September, from the milk of cows fed only on natural pasture, and the rennet is obtained from lambs' stomachs and not from calves.

Camembert and *Brie* are soft cheeses made in France by somewhat similar processes, except that during the curing mold develops on the outside and the enzyme changes are more pronounced within. Proteins are broken down to a greater extent.

Roquefort is made from sheeps' milk and during ripening a green mold grows throughout the mass of cheese, breaking down the protein compounds so as to give it the characteristic taste and odor.

Limburger was made in Belgium originally, but is now considered strictly a German cheese. The curd is formed at a high temperature, and it is ripened at a somewhat higher temperature than usual, and in a very moist atmosphere. Under these conditions bacterial changes take place to such an extent that putrefactive fermentation sets in, giving it the high odor for which it is noted.

250. **Koumiss.**—Koumiss is a drink made properly from mares' milk by the nomadic tribes of Asia Minor. Mares' milk is richer in lactose than is cows' milk and on the addition of old or dried koumiss part of the lactose ferments to alcohol and carbon dioxide, some of it changing also to lactic acid.

Kephir is a somewhat similar drink prepared from cows' milk by the inhabitants of the Caucasus. Fermentation is caused by the addition of the so-called kephir grains, the origin of which is not known, but which contain certain microörganisms capable of causing the production of lactic acid, alcohol, and carbon dioxide from lactose. Both of these slightly alcoholic drinks are easily digested by invalids and have assumed some importance as drinks for medicinal purposes.

251. **Condensed and Desiccated Milk.**—For the purpose of keeping milk, it is condensed by evaporation in a partial vacuum, with or without the addition of sugar, to a thick consistency of one-third to one-fourth its original volume. This substance can be sealed up in air-tight cans and kept for a long time, being mixed with water in various proportions just before use. Desiccated milk can be made by various processes, one of which is to spray the milk against a rapidly revolving hot plate which instantly drives off the water and permits the collection of the dry milk powder. This resumes its original condition when it is stirred up with water.

252. **Summary.**—Milk, the most valuable product of the animal, is a white, opaque liquid, the color of which is due to particles of fat in suspension and particles of protein in semi-solution. It is composed of a carbohydrate and inorganic salts in solution, with fat globules and proteins in suspension or partial suspension. Lactose is the only carbohydrate. It is a sugar of slightly sweet taste, the formula of which is $C_{12}H_{22}O_{11}$. It is dextrorotatory, reduces Fehling's solution, and hydrolyzes to dextrose and galactose. The principal change, however, is to lactic acid, which is brought about by bacteria.

Milk fat consists of the glycerides of nine fatty acids, three of which are soluble in water and volatile in steam. It is liquid at the animal temperature, but solid at ordinary temperature. The minute fat globules occur in milk in the form of a true emulsion. Milk protein consists principally of caseinogen, which contains sulphur and phosphorus in addition to the usual protein elements. Caseinogen exists in milk combined with a calcium compound, probably calcium phosphate. It is precipitated by rennin, an enzyme of the gastric juice, by being split into two different soluble proteins, one of which unites with calcium phosphate to form the insoluble curd. Acids coagulate casein by removing the calcium compound and precipitating the protein. The other protein is lactalbumin which contains sulphur but no phosphorus. It is coagulated by heat. Inorganic salts are present in milk, principally chlorides and phosphates, with some citrates. Milk is secreted in certain glands of the animal especially adapted for the purpose, and some of its constituents such as lactose and caseinogen are not found elsewhere in the animal body.

Milk is subject to some adulteration, principally with water, but since this reduces the percentage of fat in milk the consumer is protected by law, which in most States specifies the minimum amount of fat allowable. Since milk is an excellent nutrient for bacteria, great care must be taken in keeping and handling the product. Immediate cooling and keeping cold serves to a considerable extent to prevent the action of bacteria, but still further protection is assured by pasteurization which consists in heating the milk to 60° or 80° C., for twenty minutes and cooling. This destroys most of the bacteria and does not interfere with the taste and flavor of milk. Sterilization consists in heating the milk to 115° C., a process which kills all bacteria, but which interferes with the taste and flavor of the milk. Various chemicals, such as formaldehyde and boric acid, which kill bacteria, are unfit for use because of their harmful effect on man.

Of the various milk products, cream is an important one, consisting principally of fat which has been allowed to rise and is skimmed off, or separated by centrifugal force. It is mixed with several other milk compounds, whereas butter is practically nothing but fat with some water and salt added to flavor it. Oleomargarine, a butter substitute, is obtained from beef fat and other oils.

Cheese is prepared from slightly sour milk by adding rennet to coagulate the casein. The precipitated casein, containing also the fat of the milk, is pressed into cakes and ripened in various ways by which the flavor and digestibility are improved through the action of bacteria and enzymes on the protein compounds. By using different kinds of milk and maintaining different temperatures during the setting of the curd and the curing, different kinds of cheese may be obtained.

Koumiss and kephir are two alcoholic drinks made from milk by fermentation of the lactose to alcohol and carbon dioxide in addition to lactic acid.

Condensed and desiccated milk are two results of attempts to preserve milk. The former consists of milk evaporated to a thick consistency in a partial vacuum, and the latter of milk completely dried to a powder which later will take up water and resume its original consistency.

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