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THE CHEMICAL WORK OF THE U.S. GEOLOGICAL SURVEY*

THE present Geological Survey of the United States was organized in 1879. In 1880 a chemical laboratory was established at Denver, Colo., in charge of Dr. W. F. Hillebrand, with whom were associated Mr. Antony Guyard and, later, Mr. L. G. In 1882 Dr. W. H. Melville Eakins. opened a second laboratory at San Francisco, and in the autumn of 1883 the central laboratory at Washington began operations with myself as chief chemist. In November, 1885, Dr. Hillebrand was transferred to Washington; early in 1888 he was followed by Mr. Eakins, and the Denver laboratory was discontinued. In the spring of 1890 Dr. Melville also removed to Washington, and the chemical work of the survey was concentrated at headquarters. In recent years a number of other laboratories have been established for special purposes, and the work done in them will be considered in due order later.

The primary purpose for which the chemists of the survey were employed was to assist the geologists in working up their collections. Analyses were needed for the identification of mineral substances, and they were called for in great numbers. Up to January 1, 1909, more than 6,000 analyses have been recorded upon the books of the central laboratory; covering rocks, minerals, ores, coals, waters, sediments, saline incrustations, etc., and their conduct has necessarily occupied a large share of the time of the chemists.¹ But the field of * Prepared for the International Congress of Applied Chemistry in London. Published by per-

Applied Chemistry in London. Published by permission of the Director of the Survey.

¹ Some hundreds of other analyses were made in the Denver and San Francisco laboratories.

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work was not limited to analyses alone; problems for research were frequently suggested; and a variety of interesting investigations have been carried out in the survey laboratories. My aim in this communication is to give a brief summary of the results so far obtained, and to indicate something as to their significance.

In the first place, more than one thousand analyses of igneous rocks have been made, and also many partial analyses for special purposes. This work was called for by the petrographers of the survey, and it has led to some unforeseen consequences. In the beginning, the analyses were made along conventional lines and the minor constituents of the rocks were neglected, a policy which is still followed in many European laboratories. It was soon found, however, that greater refinement of the work was desirable, and that in some cases a rock analysis, to be really satisfactory, needed from fifteen to twenty separate determina-At present the following substances tions. are commonly determined, or at least their absence is proved: silica, alumina, both oxides of iron, magnesia, lime, soda, potash. water at and above 100°, titanic oxide, zirconia, carbonic acid, phosphoric acid, sulphuric acid, sulphur, baryta, strontia, manganese, nickel and chromium: and often also vanadium, chlorine and fluorine. Lithia is sometimes determined, but possible boron and glucina are ignored. Thewater is always determined directly, never by loss on ignition; and recently, because of the researches of Mauzelius, as verified and extended by Hillebrand, the influence of the fineness or coarseness of the rock powder is taken into account. We now know that in fine grinding, part of the ferrous oxide in a rock or mineral becomes oxidized, and also that notable quantities of water are at the same time absorbed from the atmosphere. The errors thus introduced into an analysis are too large to be neglected. As far as possible the analytical operations are performed in platinum dishes, in order to avoid contaminations derived from glass. Furthermore, all reagents are carefully tested as to their purity. Without these precautions accurate work can hardly be done.

The analyses thus made are evidently much more complete than those collected in Roth's well-known tables, and at the same time their summation is better. To be satisfactory a rock analysis should sum up between 99.50 and 100.50 per cent.; the average summation error of the survey analyses being only 0.20 per cent. The determinations of the minor constitutents not only render the analyses more precise, but also aid the petrographer in his discussion of the data. For example, the average proportion of titanic oxide found in 989 analyses is 0.74, and that of phosphoric oxide is 0.26 per cent., or one per cent. together. If these substances are not determined they render the determination of the alumina too high, and when the petrographer attempts to compute the proportion of feldspar in a rock the error is multiplied several times over. The slight value of analyses in which these determinations are neglected is therefore almost self-evident.

For the work thus done upon the igneous rocks, chief credit must be given to Dr. Hillebrand. He first perceived the importance of more thorough analyses, and did much toward perfecting the analytical methods. His bulletin, "On the Analysis of Silicate and Carbonate Rocks," is already recognized as a classic.²

From a small number of rock analyses only minor conclusions can be drawn. They aid the petrographer in the study of his special group of specimens; but, unless they are correlated with other data, they

² Bulletin 305, U. S. Geological Survey.

do little towards solving any large problems. When, however, such a mass of fairly homogeneous analyses is at hand as that developed in the laboratories of the survey, it becomes possible to study the geochemistry of the igneous rocks in a broad way, and to shed light upon more than one troublesome question. It is seen, for instance, that the minor constituents of the rocks represent a wide diffusion of many chemical elements, whose presence was formerly regarded as insignificant. From an average of the analyses the mean composition of the igneous crust of the earth can be determined, and it then appears that titanium, hitherto unimportant, is really the ninth in point of abundance among all the chemical elements. Oxygen comes first, forming almost one half of all the matter present in the outer ten miles of the earth's crust; then follows silicon, about 25 per cent.; then aluminum, iron and calcium, in the order named. Magnesium. sodium and potassium follow, in about equal proportions, then hydrogen, provided that we include the ocean in our computations, and then titanium, amounting to about four tenths of one per cent. Manganese, phosphorus, sulphur, chlorine, fluorine and carbon are important; barium. strontium and zirconium are found in readily determinable proportions; vanadium, chromium and nickel are by no means negligible. The remaining elements, even including nitrogen, probably amount to less than one per cent., taken all together; a conclusion which is perhaps surprising, but is thoroughly well sustained. The heavy metals, with the sole exception of iron, are, in their total combined amount, statistically less important than titanium alone.

This statistical analysis of the igneous rocks has been verified by other workers, and its details are fully published elsewhere.³ It was first made public in 1889,

and it has since been largely extended and utilized as a basis for other computations. By combining the figures with those representing the known composition and mass of the ocean, it can be shown that a shell of the average igneous rock one third of a mile thick and completely enveloping the globe. would furnish all the sodium of the sea, and Professor Joly has gone even further and used these data as a measure of geological time.⁴ Given values for the rate at which rivers supply salts to the ocean, and assuming that rate to have been constant, the calculation is a matter of simple arithmetic. If the salts of the ocean and the alkalies of the sedimentary rocks were all derived from the decomposition of igneous rocks, then a shell of the latter less than half a mile thick would yield all the sodium required. This estimate is a maximum, and serves to show how slightly the surface of the earth has been eroded during geological time. The greater part of this erosion, of course, was concentrated over the continental areas, being probably insignificant in the depths of the ocean. The land erosion may have been as much as two miles in thickness or four times the average for the entire globe. Going still farther, and using composite analyses of the sedimentary rocks, it can be shown that the half mile of decomposition has yielded determinable proportions of shales, sandstones and limestones. The approximate values for a ten-mile thickness of the earth's crust are, igneous rocks, 95 per cent.; shales, 4 per cent.; sandstones, 0.75 per cent.; limestones, 0.25 per cent.;⁵

³See especially U. S. Geol. Survey Bull. 330, pp. 21-33.

⁴Sci. Trans. Roy. Soc. Dublin, 2d ser., 7, 30, 1899.

⁶ For other estimates, based upon the same fundamental data, see Van Hise, "Treatise on Metamorphism," p. 940; and Mead, *Journ. Geol.*, 15, 238.

figures which can not be very far out of the way. We have here a first approximation to an analysis of the entire crust of the earth, which can be applied to the discussion of various large geological problems.

Upon the basis of the survey analyses, Cross, Iddings, Pirsson and Washington developed their "Quantitative Classification of the Igneous Rocks,"⁶ a classification which became possible only after a large number of complete analyses had been made, and which is applicable only to rocks which have been thoroughly analyzed. In this system, small errors become cumulative; and one effect of its publication has been to encourage better analytical work in several laboratories, and so to increase the accuracy of our knowledge relative to the composition and differentiation of rock It is interesting to note at this magmas. point that the average igneous rock is quite near an andesite in composition, and that it has very close to metasilicate ratios. From the last consideration it may be inferred that in the crust of the earth orthosilicates and trisilicates exist in approximately equivalent molecular proportions.

The chemists of the survey have also analyzed more than four hundred sedimentary rocks; slates, shales, sandstones, limestones, etc. They have also made composite analyses of many commingled samples in each sedimentary group, in order to determine the average composition of each class. The same method was also applied to the analysis of the well-known "red clay," which forms the floor of the ocean at its greatest depths. Fifty-one samples of the clay, kindly furnished by Sir John Murray, and gathered from all of the great oceans, were ground into one uniform sample and then analyzed. Even here the supposedly rarer elements were found in proportions similar to those of the igneous

rocks, and such substances as titanium, barium, strontium, nickel, chromium, vanadium, copper, lead, zinc and arsenic were easily determined.

Next in importance to the rock analyses are the analyses of minerals. Of these over 600 have been analyzed, covering more than 180 species, including eighteen which were described as new. The new species were josephinite, cuprobismutite, warrenite," guitermannite, elpasolite, coronadite, zunyite, ptilolite, hydronephelite, lucasite, morencite, purpurite, antlerite, knoxvillite, redingtonite, plumbojarosite, emmonsite and powellite. Furthermore, the exact composition of many imperfectly described minerals has been well established, as in the cases of tengerite, kleinite, carnotite, roscoelite, patronite, xanthitane, hetærolite, mackintoshite and yttrialite. In Hillebrand's analyses of uraninite its gaseous constituent was first noted; and this gave Ramsay the clue which led to the discovery Molybdic ochre, previously asof helium. sumed to be molybdic oxide, MoO_3 , has been shown by Schaller, by the analysis of samples from five localities, to be a hydrous ferric molybdate. The true composition of dumortierite was also established by Schaller. The twenty complete analyses of tourmaline by R. B. Riggs and also his analyses of the lithia micas are important contributions to chemical mineralogy. The analyses of 29 meteorites can be added to this schedule.

Over 150 analyses of waters have been reported from the central laboratory of the survey. Some of these waters were from springs of commonplace type, but others have been of unusual character. One spring, from southwestern Missouri, according to Hillebrand's analysis, contains zinc sulphate as its principal saline con-

⁶ University of Chicago Press, 1903.

 $^{^{\}tau}$ According to L. J. Spencer warrenite is identical with jamesonite.

stituent, amounting to 233 parts per million out of 540 of total impurity. This water evidently rises from beds of zinc ores, and resembles the mine waters of the same region.

Forty-three waters from the Yellowstone National Park, analyzed by Gooch and Whitfield,⁸ form a group of unusual in-Among them are geyser waters, terest. which deposit siliceous sinter and which contain in nearly all cases appreciable quantities of boric acid, lithia, arsenic and other unusual constituents. One hot spring in this group, the Devil's Inkpot, is Its water is strongly acid, and unique. contains 3.39 grams per kilogram of impurities. Of this impurity ammonium sulphate amounts to 2.82 grams, or more than 83 per cent. In addition to their study of the waters, Gooch and Whitfield analyzed many sinters, tufas, sediments and incrustations deposited by them, finding some substances of peculiar interest. One spring in particular was characterized by a deposit of scorodite, an arsenate of iron.

A second important group of waters is that represented by the saline and alkaline lakes of Nevada and southern California. Some of these waters are highly concentrated, and yield upon fractional evaporation large quantities of sodium carbonate. At Owens Lake, in California, sodium carbonate has been extracted on a commercial scale, and its production was carefully studied by Dr. T. M. Chatard.⁹ The "natural soda" manufactured at Owens Lake was obtained in the form of trona or urao, a compound which Chatard studied thoroughly, and reproduced in the laboratory, thereby establishing its true composition beyond farther doubt. Chatard's memoir

⁸ Bull. 47, U. S. Geol. Survey.

 $^{\circ}$ Bull. 60, U. S. Geological Survey, pp. 27-101. The formula of trona, established by Chatard, is Na₂CO₃.NaHCO₃.2H₂O. upon "natural soda" is a very complete summary of the entire subject.

Another remarkable water, that of Steamboat Springs, Nevada, was studied by Becker and Melville¹⁰ in the San Francisco This water contains notable laboratory. quantities of borates, and it deposits a sinter carrying sulphides of arsenic, antimony, mercury, lead and copper, together with determinable amounts of gold and silver. Two other hot waters, from Sulphur Bank, California, also reported by Becker and Melville, were very rich in borates. At Steamboat Springs such minerals as metastibnite and cinnabar were caught in the very act of their formation. In connection with their study of these waters, Becker and Melville¹¹ made a series of experiments upon the solubility of various substances in solutions of alkaline sulphides and hy-The sulphides of mercury, drosulphides. copper, zinc and iron (both pyrite and marcasite) were found to be, under suitable conditions of temperature and concentration, distinctly soluble; the sulphides of silver and lead were not. Metallic gold also dissolved perceptibly. These experiments shed much light upon the deposition of the metallic ores, and explain the peculiar composition of the sinter mentioned above.

Under the water resources branch of the survey a much larger hydrochemical investigation was undertaken. Under Mr. M. O. Leighton and Mr. R. B. Dole, with the aid of other chemists, the composition of many river and lake waters was determined, partly in a special laboratory in Washington, and partly in laboratories connected with other institutions in various parts of the United States. In all approximately 5,000 analyses were made of waters

¹⁰ See G. F. Becker, U. S. Geological Survey Monograph 13.

¹¹ Amer. Journ. Sci. (3), 33, 199.

from about 180 lakes and rivers, representing the drainage from almost the entire surface of the country. To illustrate the plan of the work one example may be taken, that of the Mississippi just above New Orleans. A sample of water was taken daily, and at the end of each week the seven samples were combined and analyzed. This procedure was followed during a year, and the average of the 52 composite analyses thus made, gave the composition of the saline matter annually contributed from the entire drainage basin of the Mississippi to the Gulf of Mexico. In other cases ten-day composites were taken instead of weekly ones, and in some instances monthly analyses were made. These were combined with careful daily gaugings of the stream flow, so that the contribution of each river system to the ocean could be determined with a considerable degree of accuracy. Α preliminary discussion of the data, which is subject to some small corrections yet to be investigated, leads to the conclusion that thê surface of the United States loses to the ocean annually 87 tons of dissolved solids per square mile and 166 tons of suspended matter. This is equivalent to a lowering of the surface by aqueous denudation, one inch in 760 years. The usefulness of the investigation, however, is not limited to its geologic bearings; it is of direct value for industrial purposes, giving information as to the availability of the several waters for use in steam boilers, or in a variety of manufacturing processes. In its systematic character and its great extent the work is especially notable.

In the prosecution of their analytical work the chemists of the survey have not only been obliged to study existing methods, but also to devise new ones. The work of Hillebrand upon rock analysis has already been mentioned, but it does not stand alone. It was in the survey laboratory that Gooch developed his methods for determining boric acid and titanium, and for separating lithia from the other alkalies. Whitfield studied the indirect determination of chlorine, bromine and iodine; Chatard investigated the separation of titanium. chromium, aluminum, iron, barium and phosphorus; Hillebrand devised methods for the colorimetric estimation of chromium and the volumetric determination of vanadium. A comparison of the wet and crucible methods for the assay of telluride gold ores is due to the joint labors of Hillebrand and Allen;¹² and a process for the estimation of small quantities of fluorine in rock analyses was worked out by Steiger. All of this work, which I can only mention briefly, grew out of the necessities of the chemists in handling the analytical problems submitted to them by the geologists of the survey, and therefore had good reasons for its prosecution.

Apart from the routine analytical work of the laboratory, a variety of researches upon mineralogical and geochemical problems have been carried out. Some of the mineral analyses were made with direct reference to purely abstract investigations. such as the series of researches upon the constitution of the natural silicates: a problem which was commonly assumed to be hopelessly complex. The silicates, however, are not remarkably complicated substances, their complications being more apparent than real. The conditions under which they are formed, by deposition from molten magmas, or by alteration of such primary compounds, would seem to preclude any great complexity. Only relatively stable and therefore presumably simple compounds could exist; a conclusion which is borne out by their comparatively The apparent complicasmall number. tions are due to impurities, to alterations

12 Bull. 253, U. S. Geol. Survey.

and to isomorphous mixtures; when these sources of doubt are eliminated, simple empirical formulæ can in most cases be deduced. To obtain such formulæ is obviously the first step in the general investigation; a task which, fortunately, had already been largely performed by others.

Empirical formulæ, however, do not solve That has to the problem of constitution. be attacked along other lines. The natural associations of the silicates, their isomorphous relations and their alterations all supply evidence, which can be supplemented by experiments in the laboratory. How does a mineral come into existence? How does it decompose? What characteristic reactions are possible with it? To each of these questions answers have been sought in the laboratories of the survey, and important data have been obtained. The synthetic work of Day and Allen on the feldspars was done in the Geological Survey, and similar researches are now being undertaken in the Carnegie Institution of Washington, to which that class of investigations has been transferred. The geophysical laboratory of the Carnegie Institution is a direct outgrowth from the survey, in which its work began.

The decomposition and alteration of silicates can be studied both in their natural occurrences and in the laboratory. When one mineral alters into another, a direct relation is established between the two, which the constitutional formulæ ought to In the laboratory, such alterasymbolize. tions may be often brought about artificially, as was done long ago by Lemberg The decomposiand other investigators. tion of minerals by heating is even more easily studied, and two or three reactions of this kind have been established in the For example, talc, H₂Mg₃Si₄O₁₂, survey. was commonly interpreted as an acid metasilicate, but Groth regarded it as a basic

salt of metadisilicic acid. H.Si.O. In the latter case heating should of course eliminate water, but there could be no further breaking down. Clarke and Schneider. however, have shown that when talc is sharply ignited, one fourth of the silica is split off in the free state: a reaction which is intelligible only on the basis of a meta-A similar reaction is silicate formula. furnished by pectolite, HNaCa₂Si₃O₉, which, as G. Steiger found, gives up one sixth of its silica upon ignition. In this instance. as in the case of talc, the liberated silica is proportional to the acid hydrogen in the initial substance. How far such reactions can be trusted in discriminating between metasilicates and the salts of other silicic acids is vet undetermined.

Similar experiments with serpentine gave even more important results. Daubrée had shown, qualitatively, that when serpentine is fused the residue is a mixture of enstatite and olivine. Olivine is easily soluble in dilute acids, enstatite is insoluble and it was therefore easy to ignite serpentine, to dissolve out the olivine, and so to prove that the reaction is quantitative. Now for its application. Tschermak had proposed a theory of the chloritic minerals, in which they were treated as mixtures of two end products, serpentine and amesite, the latter being an extremely basic salt to which the formula H₄Mg₂Al₂SiO₉ was assigned. If this were true, a chlorite like clinochlore should vield on ignition an insoluble residue containing the enstatite end of the serpentinous decomposition. In fact, a clinochlore which ought to have given 18 per cent. of enstatite gave none at all, but a residue consisting of spinel, MgAl₂O₄. That is, it failed to give the decomposition products of serpentine, therefore serpentine was absent, and the Tschermak theory fell to the ground. Other allied minerals furnished a similar spinel reaction, and in

each case the amount of spinel formed was quantitatively proportional to the excess of oxygen in the original silicate over the orthosilicate ratio. These reactions are, furthermore, applicable to the analysis of mixtures of talc and serpentine. It is only necessary to ignite the mixture, and then, with sodium carbonate to dissolve out the liberated silica of the talc, and with dilute hydrochloric acid the soluble olivine from the serpentine. Such an analysis is of course only approximate, but it is better than none at all.

In another group of experiments Clarke and Steiger¹³ attacked the silicate problem by a different method. It was found that certain silicates when heated with dry ammonium chloride to its temperature of dissociation reacted with it, forming derivatives of unexpected stability. Analcite, $NaAlSi_2O_6 \cdot H_2O$, heated with the reagent in a sealed tube, yielded sodium chloride, and the silicate NH₄AlSi₂O₆, which was stable Leucite, KAlSi₂O₆, similarly at 300°. treated, gave the same derivative, thus establishing a structural relationship between the two species. By means of this reaction it became possible to determine, quantitatively, the proportion of either mineral in an igneous rock. The rock powder was heated with ammonium chloride, and then leached with water. The amount of ammonium fixed in the residue gave a good estimate of the amount of analcite or leucite in the rock. Natrolite gave with ammonium chloride another silicate, $(NH_4)_2Al_2Si_3O_{10}$, also quite stable, and other zeolites were capable of partial transformations. Going further, Mr. Steiger, by fusing the same minerals with silver nitrate or thallium nitrate, succeeded in substituting the alkaline bases by the two heavy metals, producing silver aluminum and thallium aluminum silicates identical in type with the original compounds and with the ammonium salts. These reactions are effected with great ease and open up a new line of attack upon the general problem of silicate constitution. In short, the silicates have been found to be chemically more plastic, that is, more open to measurable transformations than they were formerly supposed to be; a conclusion which is evidently of considerable theoretic importance. A new field of research has been opened, but its full extent is yet unknown.

From data such as these, and from the natural occurrences, associations and alterations of minerals, some progress has been made toward a theory of the silicates. At least, some relationships are now established, which can be rationally expressed by constitutional formulæ. Formulæ of that kind are easily written when one does not go beyond simple empirical composition, but unfortunately they can be written in several different ways. Each substance must be studied in its relations to other substances before a formula of real significance can be devised. When that is done a system of formulæ develops which becomes a useful tool in later investigations.

I can not, in a paper of this scope, enter into details. I can only give a brief indication of the theory which has grown out from the observed facts. First, the natural silicates are considered as definite salts, normal, acid or basic, of relatively simple silicic acids. Second, many silicates are easily interpreted as substitution derivatives of normal salts. For example, the normal orthosilicate of aluminum is represented by the formula $Al_4(SiO_4)_3$. This compound is not known to exist by itself in nature, but many minerals are easily interpreted, at least stoichiometrically, as derivatives of it. Thus we have

¹³ Bull. 207, U. S. Geological Survey.

Nephelite,	$Al_{3}(SiO_{4})_{3}Na_{3}.$
Eucryptite,	$Al_3(SiO_4)_3Li_3.$
Kaliophilite,	$Al_3(SiO_4)_3K_3$.
Andalusite,	$Al_3(SiO_4)_3(AlO)_3$.
Topaz,	$Al_{3}(SiO_{4})_{3}(AlF_{2})_{3}.$

All of these formulæ are equivalent to the simplest empirical formulæ tripled; a multiplication which is suggested by the fact that all of the minerals named alter into muscovite, $Al_3(SiO_4)_3KH_2$. This species in turn is correlated with the other normal micas, as follows:

Muscovite,	$\mathrm{Al}_{3}(\mathrm{SiO}_{4})_{3}\mathrm{KH}_{2}.$
Biotite,	$\mathrm{Al}_2(\mathrm{SiO}_4)_3\mathrm{Mg}_2\mathrm{KH}.$
Phlogopite,	$\mathrm{Al}(\mathrm{SiO}_4)_3\mathrm{Mg}_8\mathrm{KH}_2.$

Between these micas there are intermediate mixtures, and sometimes admixtures of molecules derived in precisely the same way from trisilicic acid, $H_4Si_3O_8$. That is, the radicles SiO_4 and Si_3O_8 replace each other isomorphously, a relation which is also indicated in the feldspar group. Albite is a trisilicate, anorthite is an orthosilicate; the other soda lime feldspars are mixtures of these two.

This formulation of the micas has had considerable acceptance, and it brings the allied compounds under one general set of expressions. These again connect with the vermiculites and chlorites, and with a number of other species such as the garnets, prehnite, some zeolites, etc. In short, a system of formulæ has developed from work done in the survey laboratory which expresses in symbolic form known relations, and is therefore legitimate so far as it goes.¹⁴ It is probably not final, but its usefulness is apparent and has been tested for many years. When a better system offers, one which correlates a larger number of facts, it will be time to abandon this and to accept the new.

¹⁴ See U. S. Geol. Survey Bulletin 125 for a complete statement of the silicate theory. Some of the conclusions reached in that memoir need to be revised in the light of more recent knowledge.

Another group of researches, now under way in the survey laboratory, relates to the theory of ore deposition. It had been observed by geologists connected with the survey that ore deposits often exhibit the phenomenon of secondary enrichment; that is, the heavier metals are more or less dissolved from the upper part of a lode, to be reprecipitated at lower levels. The chemical processes governing this leaching and redeposition are among the subjects under investigation in the laboratory. This problem, obviously, interlaces with other related problems, and some interesting results have already been obtained. Dr. H. N. Stokes has studied the relations between pyrite and marcasite,¹⁵ and in another investigation¹⁶ he has determined some of the conditions governing the solution, transportation and deposition of silver, copper and gold. The details of these experiments do not admit of any brief summary here. Dr. E. C. Sullivan¹⁷ has shown that many secondary precipitations of the heavy metals are of the nature of double decompositions; a copper solution, for example, reacting with silicates such as the feldspars to give up its copper and to receive some other base in return. He has also found¹⁸ that the wall rock of a vein may act like a semi-permeable membrane and so effect the separation of certain bases from their salts. A solution of ferric sulphate, for instance, hydrolyzes, and then contains ferric hydroxide in the colloidal condition. When this operation takes place in a Pasteur filter tube the colloidal substance is retained, while the liberated acid passes through. In short, dialysis seems to be one of the processes by which mineral solutions are separated into fractions of different composi-

¹⁵ Bull. 186, U. S. Geol. Survey; and *Economic* Geology, 2, 15.

¹⁶ Economic Geology, 1, 644.

¹⁷Bull. 312, U. S. Geol. Survey.

¹⁸ Economic Geology, 3, 750.

tion; a process which has an important influence in the filling of metalliferous veins. Researches of this class are being continued, and should lead in time to useful conclusions.

One research, outside of the normal work of the survey, was carried out by Dr. H. N. Stokes in the survey laboratory. I refer to his remarkable investigation of nitrogen chlorophosphide.¹⁹ From this supposedly well-known compound, $P_3N_3Cl_6$, Dr. Stokes developed a series of polymeric bodies, $P_4N_4Cl_8$, $P_5N_5Cl_{10}$, $P_6N_6Cl_{12}$ and $P_7N_7Cl_{14}$. Each of these yielded its own characteristic phosphimic acids, and other derivatives, and thus a new field of study in inorganic chemistry has been opened, which deserves to be carefully cultivated in the future.

From what has been said so far it is clear that the chemical work of the Geological Survey is not limited by utilitarian considerations, but is also distinctly scientific in its aims. It was felt that the investigations of the geologists could be aided fully as much by chemical researches as by mere routine analyses, and the results obtained seem to justify this supposition. As a further help to geology, the more important data of geochemistry have recently been brought together in the form of a large bulletin,²⁰ in which the carefully verified bibliographic references are quite as useful as the text. Furthermore, the chemical work has been carried on in close relations with various physical researches, among which the studies by Carl Barus of the iron carburets, the thermoelectric measurement of high temperatures, and the behavior of fused rocks as electrolytes are conspicuous. At present, under G. F. Becker, the subject of elasticity is being investigated, with reference to some of the larger problems of Physics and chemistry are in geophysics.

¹⁹ Bull. 167, U. S. Geol. Survey, p. 77.

²⁰ "The Data of Geochemistry," by F. W. Clarke. Bull. 330 of the U. S. Geological Survey, 1908. contact at so many points that applications of the one inevitably compel consideration of the other.

There is, however, a natural call for data of immediate economic significance; and to meet this demand some special laboratories have been recently organized. In 1904, at the St. Louis Exposition, the Geological Survey established a coal-testing plant, in which a great number of coals were studied from various technical points of view. From this enterprise the technologic branch of the survey was developed and in it a variety of chemical investigations are now being conducted. Coals, including lignites and also peat, are collected and sampled in large lots, and analyzed both proximately and ultimately. Their calorific value is directly measured, their availability for briquetting or for the manufacture of producer gas is studied, and certain problems which arise in mining operations are also taken into account. For instance, the gases evolved from coal within the mine are carefully examined, and the explosives used by the miners are investigated also. At present the prevention of mine explosions is receiving special attention; and one laboratory is devoted to that subject alone. In another laboratory the proximate constituents of coal are being isolated, with a view to ascertaining their true character. Work of this kind is evidently capable of indefinite extension, and how far it may ultimately go it is impossible to foretell.

Another group of investigations, which is partly chemical, relates to the manufacture and properties of cement, and its use as a structural material. Clays, limestones and finished cements are subjected to analysis, and the question of their durability under special conditions is also studied. The government of the United States is engaged in the reclamation of great areas of arid lands, and is constructing large

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reservoirs and dams to impound water for purposes of irrigation. These waters are often strongly alkaline, and affect the concrete of the dams most injuriously. To avoid this evil is one of the important problems now in hand.

One laboratory of the technologic branch is in Washington, and its particular function is to examine the coal purchased for the use of the government, and also to pass upon the quality of the structural materials used in public works. This latter heading covers not only substances like cement, plaster, clay, brick and terra cotta, but also iron and steel, mineral paints, and roofing materials, whether of metal or of asphalt. In short, this laboratory is entirely technologic in character, and its chemists find their time fully occupied with routine affairs.

Although petroleum is studied by the technologic branch with reference to its efficiency as fuel; still other investigations upon it are carried on in a distinct laboratory under Dr. David T. Day. Dr. Day is engaged upon a systematic study of all the petroleum fields of the United States, determining the physical properties of the oils and examining their distillation products. In each oil he determines sulphur, asphaltum, paraffin, water and the unsaturated hydrocarbons, and when this preliminary investigation is finished the work will be further developed with regard to special details. It is proposed also to reexamine the oils from time to time, in order to ascertain whether the wells have undergone any change in character. In this work Dr. Day cooperates with a committee of the International Congress on Petroleum. for the purpose of establishing uniform and trustworthy methods of research. Dr. Day has also, for several years, been studying the filtration of petroleum through clavs and shales, in which he finds that a fractionation is effected similar to that produced by distillation. This work is being continued, and is yielding interesting results.

F. W. CLARKE

U. S. GEOLOGICAL SURVEY

THE POPULATION OF FRANCE

IN view of the interest in the thirteenth census of the United States for 1910, of which the law governing the enumeration has just been passed, the readers of SCIENCE may be interested in the report of the chief of general statistics of the movement of population in France, during the year 1908, as given in the Journal Official. This is all the more interesting because of the views entertained in some quarters that France should be numbered among the so-called decadent peoples. The figures for 1908, however, show that the excess of births over deaths, based upon an enumeration of 315,928 marriages, amounts to 46,441. The corresponding figure for the ten years ending with 1907 was 40,550. The following table gives the comparative returns for the decade, with which 1908 is compared:

	1	 			<u></u>
	Mar-		Deaths	Excess of	
	riages		s Direns Deuten		Births
1898	287,179	\$43,933	810,073	23,860	
1899	295,752	\$47,627	\$16,233	31,394	
1900	299,084	827,297	\$53,285		25,988
1901	303,469	857,274	784.876	72,398	
1902	294,786			83,944	
1903	295,996			73,106	
1904	2:15,721	\$15,229	761,200	57,026	
1905	302,623			37,120	
1906	306,487			26,651	
1907	314,756		793, 537		19,892
Av.1898-1907	299,885	825,423	788,461	40,550	4,588
1908	315,928	791,712	745,271	46,441	••••

It is noteworthy that for 1908 the number of deaths was the smallest in eleven years and considerably smaller, of course, than the average for ten preceding years. In births there is a recovery from the minimum of 1907, and marriages are the largest in eleven years, being five per cent. greater than the