SOME QUERIES ON ROCK DIFFERENTIATION.

By GEO. F. BECKER.

ART. III. — *Some Queries on Rock Differentiation;* by
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Hypothesis of differentiation.—As I understand the theory
of what is called the differentiation of rock magmas, now so
generally held by lithologists, its outlines may be expressed in
the following terms: In some extensive districts the massive
rocks are found to possess similarities of composition, and such
rocks have been called consanguineous. This consanguinity
might be accounted for by supposing an originally homogene-
ous magma to have undergone partial segregation into fluid
portions of distinctly different yet allied composition, prior to
eruption, and this is the process called differentiation. It is
also known by observation in the laboratory, that if a more or
less complex, homogeneous solution be exposed to certain
physical conditions, segregation into distinct portions may take
place. It is hence inferred that such is actually the history of
consanguineous rocks.* By a slight extension of this inference
most massive rocks are regarded as resulting by differentiation
from a generalized magma.

The existence of distinct though allied rocks locally asso-
ciated with transitional varieties is undisputed. The validity
of the explanation offered by the modern school for these
occurrences is another matter. The hypothesis of differentia-
tion is extremely attractive and if it were substantiated would
lead to a well organized system of rock investigation. It may
also be correct ; but there are respects in which it appears to
be in need of much explanation, and it does not seem certain
that the fundamental postulate of originally homogeneous
magmas of vast volume is well established.

Possible modes of segregation.—The segregation† of a
homogeneous fluid into distinguishable portions under the
influence of varying temperature or pressure may take place
by different methods. An increase or decrease in the concen-
tration of certain components may occur in the cooler part of
the fluid or in that portion which is under greatest pressure.
There are also cases in which solutions which are homogeneous

* The early literature bearing on this subject. together with fresh contributions,
is given in Mr. Arnold Hague's work on the Geology of the Eureka district, U. S.
Geol. Survey, Mon. 20, 1892, p. 267 et seq. Some of Prof. J. P. Iddings' papers
bearing on the subject are: the Crystallization of Igneous Rocks, 1889; Electric
peak and Sepulchre mountain. 1891 : the Origin of Igneous Rocks. 1892, etc.
The latest of Prof. W. C. Brögger's contributions is: die Eruptionsfolge der triad-
schen Eruptivgesteine bei Predazzo, 1895.

† The term differentiation is ambiguous. In the older, and as it seems to me
the more proper sense. differentiation is the discrimination of existing differences.
One differentiates lime-soda feldspars by their angles of extinction.

at one temperature 'tend to separate at some other temperature into two or more immiscible fluids, or into a fluid portion and a solid one.   There seem to be no other conceivable ways in which segregation or differentiation under purely physical influences can take place, and it is one of the purposes of this paper to examine the mechanism of these processes in the light of the modern conclusions of chemical physics.

It will be most convenient to consider first those cases in which only miscible liquids, or liquids present only in miscible proportions, are concerned, reserving consideration of immiscibility and insolubility for subsequent discussion.

The differentiation of a homogeneous magma, or its segregation into distinct though related miscible fluids, involves relative movement of the particles of the magma.   This movement cannot take place in visible streams or currents, such as would result from convection; for if a tendency to segregation existed, stirring would neutralize or overcome it.   Segregation might, however, be accomplished by what may be called *molecular flow*, this term being understood to mean the progressive translation of portions of a liquid, molecule by molecule, among the similar or dissimilar molecules of the remainder of the liquid.

Instances of molecular flow.—Molecular flow is exhibited in ordinary diffusion, in osmosis, and in some cases of the segregation of fluids.   Although these are seemingly very different manifestations, they are all reducible to the tendency which fluids exhibit to attain a condition of stable equilibrium, through an equalization of the partial pressures of each component in different parts of the fluid.

If two liquids which are miscible in all proportions but are chemically indifferent to one another are placed in a small closed vessel and are maintained at a constant temperature, each diffuses into the other, and the flow of molecules will never cease until the mixture is uniform throughout, so that each liquid occupies the volume formerly occupied by both. If two such liquids are each soluble in a third, each will diffuse into the solvent at its own peculiar rate, and in such cases mere diffusion produces partial separation of the dissolved substances.   At any given time the substance which diffuses more rapidly will be found in greater relative abundance at any point at all distant from the original surface of diffusion. Thus Graham in experimenting on the diffusion in water of a solution which contained 5 per cent of common salt and 5 per cent of sodium sulphate found that the upper layer of water after a certain interval contained ten times as much of the chloride as of the sulphate.

In this case any one layer of the water may be regarded as a kind of septum through which the chloride diffuses at a higher rate than does the sulphate. There are many septa more efficient in separating solutions than is water. Especially familiar is bladder, through which one class of compounds (the crystalloids) passes very readily, while another (the colloids) passes with difficulty. Here indeed the material of the septum perhaps has some molecular action on the solutions, and if so the explanation is thereby complicated. Nevertheless osmosis is regarded by physicists as a case of ordinary diffusion complicated, as some think, by the molecular action of the septum.*

There is another class of septa which seems to be without molecular action and behave as mere "atomic sieves." They are wholly impermeable to some solutions (bladder is not) and easily permeated by others. By means of these "semi-permeable" septa, which are produced by precipitation, it has been found that the molecular flow of a given solution continues until a certain definite pressure exists on one side of the septum, this pressure being characteristic of the substance experimented upon and independent of the nature of the membrane. This is the "osmotic" pressure of the dissolved substance, and Mr. van't Hoff has shown† that it is equal to the pressure which would be exerted by the substance in a gaseous state when occupying the same volume at the same temperature. Evidently then there is a very close analogy between gases and substances in a state of solution, and it is in fact now well recognized that, as van't Hoff pointed out, they obey several of the same fundamental laws when osmotic pressure and simple pressure are considered as interchangeable terms.‡

Mr. W. Nernst§ has discussed the phenomena of simple diffusion in their relation to osmotic pressure and is led to the conclusion that osmotic pressure is the force immediately concerned in the diffusion of liquids, just as the pressure exerted by a gas in confinement is the cause of the diffusion of gases.

The most important case of molecular flow for the purposes of this discussion arises when a homogeneous solution is heated at the top. Molecular flow then takes place from the top

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* Tait: Prop. of Matter, 2d ed , p. 275. It is probable that the osmotic action of animal membranes is exactly the same in principle as that of precipitated ones. They are both "atom sieves," only the "meshes" are of a different size, perhaps. If any "molecular action" (whatever that may be) exists in one case, it probably does in the other also. The evidence of such action is not distinct.

† Zeitschr. phys. Chem., vol. i, 1887, p. 481.

‡ The osmotic pressure is inversely proportional to the volume of the fluid in a given space. The osmotic pressure at constant volume is proportional to the absolute temperature. Solutions of equal volume of different substances which contain equal numbers of molecules at equal temperatures exert equal osmotic pressure. These laws correspond to those of Boyle, Gay-Lussac and Avogadro.

§ Zeitschr. phys. Chem., vol. ii, 1888, p. 613.

towards the bottom, so that a concentration of the substance in solution occurs in the lower portion.   This fact appears to have been observed first by Mr. C. Ludwig in 1856[*] and was subsequently studied by Mr. Ch. Soret.[†]   The phenomenon has been explained by Mr. van't Hoff.[‡]   The osmotic pressure of a substance in solution is proportional to the absolute temperature.   Hence there is a resultant pressure in an unequally heated fluid which is directed towards the cooler portion, and this will not be equilibrated until the osmotic pressure in the cooler portion is appropriately increased.   Now the osmotic pressure is proportional to the concentration as well as to the temperature ; and the condition of equilibrium is therefore that the concentrations should be inversely as the absolute temperatures.   Thus if a magma were heated to $T = 1500°$ at the top while the bottom of the mass were kept at $T = 1400°$, the concentration of the substances dissolved in the magma would increase until that at the bottom were $15/14 = 1·07$ of that at the top.   Mr. van't Hoff's theory of this case agrees somewhat roughly but substantially with Mr. Soret's experiments.

The solution of any substance in a fluid is attended by a change in the total volume.   When this change is a decrease in volume, solubility increases with increasing pressure ; and vice versa.   Hence in a deep mass of solution of constant temperature there is believed to be a tendency to concentration through pressure at the bottom or the top of the mass.   The change of concentration, however, would be so small that physicists are not hopeful of demonstrating it experimentally. The thermodynamical discussion of Messrs. Gouy and Chaperon[§] seems to show that even in vessels 100 meters in depth the effect of gravity on sodium chloride solution would influence concentration only to the extent of a fraction of 1 per cent, the concentration being greater at the bottom.   It is evident that the process by which concentration is effected is molecular flow.   Further remarks on the variability of solubility with pressure will be made in discussing the properties of immiscible fluids.

There is no question that molecular flow does play a part in lithogenesis.   One may often see blebs or smears of matter in either granular or porphyritic rocks which have manifestly undergone at least superficial solution, the rock around the bleb showing an aureole of diffusion.   So, too, crystallization in many cases is explicable only by the molecular flow of a cer-

[*] Wien Sitz. Ber., vol. xx, 1856, p. 539.
[†] Comptes Rendus, Paris, vol. xci, 1880, p. 289.
[‡] Zeitschr. phys. Chem , vol. i, 1887, p. 487.
[§] Ann. de ch. phys. (VI), vol. xii, 1887, p. 384.

tain ingredient to one spot from the adjacent mass. There is absolutely no theoretical reason why such processes should not occur, for at very short distances molecular flow is a very rapid process, as will be explained presently. On the other hand, it is questionable whether masses of rock of hundreds of meters in thickness could be thus separated, even if the time allowed for completion of the process were equal to an entire geological period.

Character of diffusion.—It has been explained above that all the processes of molecular flow are reducible to the same elementary action, viz: movements due to differences of osmotic pressnre. This kind of flow is most simply manifested in ordinary diffusion, and it is also in the ordinary diffusion of concentrated solutions that molecular flow takes place most rapidly. It is possible to bring an indefinitely large mass of an absolutely and permanently concentrated liquid in contact with another liquid in which the first is thoroughly soluble. Under these conditions, the resultant osmotic pressure being proportional to concentration, must have its highest value, and molecular flow (measured by the amount of substance passing through a given area in a given time) must be greater than it otherwise can be. Think, for example, of a tall vessel at the bottom of which is a layer of solid sulphate of copper, the rest of the vessel being full of pure water. Then a concentrated solution of the sulphate will form in contact with the solid sulphate and this layer will continue concentrated until solution is complete. Diffusion will then proceed as rapidly as it can do at the temperature of the experiment. Under such conditions the amount of a dissolved substance which diffuses through an area of one square centimeter in one second, when the gradient of concentration (perpendicular to the area) is one gram of substance per cubic centimeter of fluid per centimeter of distance, is a constant called the " diffusivity " of the substance in water.[*] In the case of gases Maxwell showed that a simple numerical relation exists between the diffusivity of substance, the diffusivity of energy or heat, and the diffusivity of momentum which gives rise to viscosity.[†] In the case of fluids the *a priori* determination of these constants is not yet possible and they must be found by experiment.

When this constant called diffusivity of substance is determined, the process of diffusion can be accurately predicted under uniform conditions of temperature and pressure at least for weak solutions. In 1855 Prof. A. Fick[‡] advanced the hypothesis that the time rate at which a salt diffuses through a

[*] Tait: Prop. of Matter, 2d ed., 1890, p. 271.
[†] Theory of Heat, 1894, p. 332, and Nature, vol. viii.
[‡] Pogg. Ann., vol. xciv, 1855, p. 59.

stated area is proportional to the difference between the concentrations of two areas infinitely near one another. This is, *mutatis mutandis*, the same law which underlies Fourier's treatment of heat conduction.* Very extended researches by many physicists have confirmed Fick's law, excepting for very strong solutions, and therefore also the applicability of Fourier's mathematical developments concerning conduction to the elucidation of diffusion. It can be shown that Fick's hypothesis would be strictly applicable to solutions of any concentration if Pfeffer's law, that osmotic pressure and concentration are proportional, were exact. But this law corresponds to Boyle's law that gaseous pressure and volume are inversely proportional, and this, as every one knows, is exact only when the number of molecules per unit volume is not too great. At least two influences tend to render Pfeffer's law and Fick's hypothesis inexact for high concentration. There is a tendency to change of molecular weight with increasing concentration, a species of polymerization, and this would be attended by decreased diffusibility. When there is no such aggregation there is an increase of diffusibility, due, it is thought, to the attraction between the solvent and the dissolved substance.

While it is proper to point out the deviation of very strong solutions undergoing diffusion from the law of Fick, this deviation is of importance only near the contact from which diffusion takes place, and not always then. For if a solvent dissolves a salt only to a limited extent, even a saturated solution may be a weak one, and dissolved molecules will not be so crowded as to show irregular behavior. Thus in the case of magmas undergoing molecular flow, Fick's law will be valid at least to within a short distance from contacts and may hold absolutely up to the contact. In the differentiation of a homogeneous magma into consanguineous portions it is hardly supposable that the molecules undergoing transfer are densely crowded. Consanguineous rocks do not differ very greatly in composition, so that no extensive transfer of material is called for. Furthermore, magmas must be regarded as solutions of a series of very similar substances, and it is known that in such cases the solubility of each is diminished by the presence of the others. This was first pointed out by Mr. Nernst and has been confirmed on experimental and theoretical grounds by Dr.

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* If v is the quantity of substance in solution per unit volume in Fick's case (or the temperature in Fourier's), if x is the distance measured in the single direction in which diffusion is supposed to take place, and if κ is the diffusivity regarded as constant, then in either problem

$$\frac{dv}{dt} = \kappa \frac{d^2v}{dx^2}.$$

A. A. Noyes.* Thus the solubility of lead chloride is reduced by the presence of other chlorides to something like one-half of its separate solubility. It appears substantially certain therefore that a series of silicates in solution must restrict the solubility of each. Consequently conclusions drawn from the assumption that Fick's hypothesis is exact will be applicable to the process of differentiation.

It is interesting and extremely important to observe that the problem of determining the distribution of a diffusing lava is formally the same as that of finding the distribution of temperature in a cooling globe of large radius. This last is a subject which has become familiar to geologists through Lord Kelvin's application of the results in estimating the age of the earth.

The diffusivity of a substance is inversely proportional to the molecular friction which the molecules or the ions experience. Thus if r_1 and r_2 are the frictional resistances of the ions of an electrolyte, O the osmotic pressure and D the diffusivity, then, as was shown by Nernst:

$$D = \frac{O}{r_1 + r_2}$$

This internal friction is usually known in English as viscosity. The viscosity of liquids so far as is known increases with the pressure to which they are subjected, with the exception of water, which at ordinary temperatures becomes less viscous with increasing pressure. Of course water at temperatures approaching its freezing point is an anomalous liquid. According to Amagat, the anomalous expansion of water ceases at 50° C. and Tammann suggests that the exceptional relation between viscosity and pressure is probably confined to the same limit.

Rate of diffusion.—If two miscible solutions are brought in contact and a time t, measured in seconds, is allowed to elapse, the fluid at a distance of x centimeters from the contact will contain a certain amount of the diffusing fluid per cubic centimeter, which may be called s. One of the fluids may be supposed kept at constant composition, as in the case of a solid dissolving in a solvent. Then this same concentration s will be found at nx centimeters after the lapse of n^2t seconds. For example, if common salt is brought in contact with water, the water in immediate contact with the salt will soon become saturated. At the distance of 1^{cm} the solution will be half saturated in about one day ; at 2^{cm} it will be semi-saturated in four days and at 100^{cm} in $100^2 = 10,000$ days ; at 100 meters the

* Zeitsch. phys. Chemie, vol. ix, 1892, p. 623.

water would contain half as much salt as it could dissolve after 10,000×10,000 days, some 270,000 years.

It is because of these relations that stirring is so efficaceous in assisting solution. If a mass of fluid consisting of equal but separate parts of concentrated brine and water were so stirred that the streaks of each were not more than a couple of centimeters in thickness, a day would complete by diffusion a homogeneity which unassisted diffusion could accomplish only after hundreds of thousands of years.

Now salt (in common with other haloids) is a highly diffusive substance. The oxygen salts, such as the sulphates of zinc, copper and magnesium, are more analogous to the silicates which compose magmas. Of these the magnesian salt diffuses fastest and the zinc salt the slowest. As an illustration, the copper salt may be taken. Its diffusivity has been determined by Mr. T. Schuhmeister at 0·00000243 in square centimeters per second. With this datum it is easy to compute the distribution of the diffusing salt at any time.* The following table is computed for one year and for 1000 years from the commencement of diffusion. The distances are measured in centimeters from the contact, and under "saturation" the quantity of sulphate of copper per unit volume of the substance at corresponding distance is given, the strength of the original undiffused sulphate solution being taken as unity :

Saturation.	Distance in centimeters; time 1 year.	Distance in meters; time 1000 years.
1·000	0·	0.
·750	3·96^{cm}	1·25^m
·500	8·36	2·77
·250	14·24	4·50
·100	20·37	6·44
·050	24·45	7·73
·025	27·76	8·78
·010	31·91	10·19
·005	35·04	11·08

Diffusion of $CuSO_4$ at the end of 1 year and of 1000 years [or of hypothetical lava at the end of 50 times these periods; or of heat in underground strata after 2^h 8^m and of 89 days].

The last number in this table shows only half of 1 per cent of the original solution and this may be taken as the limit of sensible diffusion. It is easy to derive from this table the figures for any other time. Thus after a hundred years the distances answering to the given saturations will be ten times as great; sensible diffusion will cease at 350^{cm} and semi-saturation

* For the necessary information on this computation see Kelvin's Math. and Phys. Papers, vol. iii, p. 432, or Brit. Assoc. Rep., 1888.

will occur at 84^{cm} from the original contact. After 10,000 years the distances just stated will each be multiplied by 10. At the expiration of a million years the water would be just sensibly discolored by bluestone at 350^m and semi-saturation would have reached to a distance of some 84^m.

Viscosity of lavas.—Lavas are assuredly far less diffusible and far more viscous substances than sulphate of copper solution.[*] There is no means of determining with any approach to accuracy what the diffusivity of lava really is, but there is some reason to think that the viscosity of even the most fluid lavas is more than 50 times as great as that of water.[†] If one

[*] It is of course needless to call attention to the difference between fusibility and fluidity. A mass may be easily fusible but very viscous when fused, or it may fuse with great difficulty and when fused be very fluid. That a lava is very fluid does not indicate that it is considerably superheated. Water at 0° C. is sensibly as mobile as at 100°, though refined experiments reveal a difference.

[†] The viscosity of lavas is evinced by the slowness with which lava streams advance. Thus in the Kilauea eruption of 1840 the lava flowed eleven miles down a declivity of 1244 feet in two days, yet according to Wilkes and Dana (Characteristics of Volcanoes, 1890, p. 63) in this case the stream was fed from several fissures along its whole course instead of being an overflow from a single opening. The heat of the stream must have been pretty well maintained by such accessions. The average rate of flow of this lava down a 2 per cent slope was about ¼ mile per hour or 22 feet per minute. Now water in a stream of such a cross section on such a grade would flow at about 6 miles per hour or about 24 times as fast. Since lava is about 2·5 times as dense as water, these data roughly indicate for the kinetic viscosity 2·5 × 24 or 60 times the viscosity of water.

In the case of gases Maxwell shows that the diffusivity of mass is 1·5435 the kinetic viscosity (Theory of Heat, chapter 22) and that the ratio of diffusivity to viscosity in the case of liquids is much smaller than in gases. Hence it seems safe to assume the diffusivity of lava as not more than $\frac{1}{80}$ of that of a solution like that of bluestone.

In the more recent literature I have not met with investigations which throw light on the relations between diffusivity and viscosity. The resistance which molecules, atoms or ions meet when undergoing diffusion Ostwald illustrates by the slow subsidence of pulverized solids in air (Lehrbuch der Allgem. Chemie. vol. i. 189:, p. 698). This slowness is due, at least in part, to the viscosity of the air, and Stokes in 1851 showed that the resistance of spherical particles is proportional to the radius. As has been mentioned, viscosity is a resistance due to the diffusion of momentum. That viscosity impedes diffusion of matter appears evident, for example, from the behavior of sealing wax, which is an ultra-viscous fluid. Sticks of wax of different colors which have become adherent during hot weather do not diffuse into one another sensibly even after months of contact. On the other hand diffusion of crystalloids takes place in quasi-solid gelatine jelly at the same rate as in a fluid (Graham). This, however. I take to be not comparable to the action of a viscous fluid, but to the behavior of a colloid septum such as bladder, but of great thickness. The jelly seems to me to have a structure similar to a sponge of very fine grain preventing convection but not the diffusion of crystalloids. Colloids do not diffuse in such a jelly.

In discussing lavas it should not be forgotten that high temperature accelerates diffusion, which adds to the difficulty of making any estimate of the diffusivity of rock magmas.

In choosing as an illustration of diffusion an hypothetical magma with $\frac{1}{80}$ of the diffusivity of bluestone, I have been guided in part by observation on lavas. Lavas with this diffusivity mingled in thin layers; like banded rhyolite, would diffuse into approximate uniformity in a few hours. No one can doubt that the rhyolitic bands have been in contact for at least a few hours in the fluid state and that they must, therefore, be less diffusible than my hypothetical lava. Similar banding is not infrequent in andesites though it is less common than in rhyolite.

supposes the diffusivity of such a lava to be $\frac{1}{50}$ that of sulphate of copper solution, then the time needful to give a certain saturation at a certain point will be 50 times as great. It would take 50 years instead of 1 to establish the. conditions given in the second column of the table. A million years is $20,000 \times$ 50 or $141^2 \times 50$ and consequently in this vast period sensible impregnation of the lava would have extended to only about 49^m from contact (i. e. 141×35^{cm}) and semi-saturation to some 12^m.

It may seem to some readers that I have exaggerated the viscosity of lava. Certainly literature contains some accounts of lavas said to "run like water," but I have been able to find no approximately precise data indicating such fluidity. That most lava streams, those of Vesuvius, for example, advance even on steep declivities at a small fraction of a mile an hour is certain. It will be seen, however, that the arguments of this paper would not be essentially changed if lava were supposed no more viscous than a bluestone solution. But it may also be asked why even greater fluidity may not be assumed in lavas prior to eruption, a fluidity sufficient to allow of segregation in a moderate time. There seem to me abundant grounds for refusing assent to such an assumption. Hypogeal magmas must be under great pressure and they must be close to their melting points; for if they were considerably superheated the surrounding rock masses would melt and the temperature would fall to the melting point. To bring about considerable superheating would be almost as difficult as to boil water in a vessel of ice. The less viscous the magma the more difficult would superheating be. Now liquids which, like lava, condense in solidifying are most viscous at the melting point, and pressure increases their viscosity. Hence hypogeal lavas must be more viscous than they are when they reach the surface. The relief of pressure is equivalent to superheating. It is, therefore, irrational to assume that lavas prior to eruption are at all more fluid than they are at eruption. All indications point to the opposite conclusion.

These illustrations show that diffusion of fluids, particularly viscous ones, is an excessively slow process. It is instructive to compare its rate with that of the diffusion of heat. According to Lord Kelvin, the time required for the diffusion of common salt in water to be represented by a given curve is more than 870 times as long as that needful to diffuse heat through underground strata in such a way as to be represented by the same curve.* Copper sulphate requires five times as much time

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* The diffusivity of heat in underground strata has an average value of 0·01. In Lord Kelvin's article on heat, Enc. Brit , 9th ed., vol. XI, p. 582, Table B (autograph issue), the time required for the diffusion of heat in underground strata should be given as 3,170,000 years instead of as $\frac{1}{10}$ of this period.

as salt and the hypothetical lava 50 times as much as the sulphate. Diffusion of matter in the lava, therefore, takes over 200,000 times as long as the diffusion of heat in solid rock at ordinary temperatures. Even if melted lava conducts heat many thousand times worse than solid rock, so that the conductivity of the fluid might be neglected, the temperature in an unequally heated mass of melted lava would be sensibly equalized by the conduction of the solid walls of the reservoir before any tendency to molecular flow which difference of temperature might have induced would have had time to produce sensible effects.

Now in any case of the segregation of homogeneous, miscible, fluid magmas by molecular flow, the available osmotic force is only the difference between two osmotic forces, and the transfer of a given quantity of matter to a given distance will be much slower than in simple diffusion. Hence, so far as I can see, a mass of lava of volume, say 1 cubic kilometer, would not have had time to segregate into distinctly different rocks by molecular flow if it had been kept melted since the close of the Archæan, even if the temperature of the top could have been kept sensibly above the temperature of the bottom. But it is very difficult to imagine how a mass of lava could be more highly heated at the top than at the bottom, since in general temperature increases with depth. If the bottom were more highly heated than the top, of course convection currents would be set up and those would effectually prevent any segregation on Soret's method. I do not think this method should be invoked in explanation of rock differences unless it can be shown how heating from the top can occur.

No such difficulties present themselves in such cases as that of the growth of a crystal. A supersaturated solution of a given substance cannot exist in immediate contact with the solid form of the same substance, but a solution may be supersaturated at a very short distance from the solid mass. In cases of crystallization there is thus an osmotic pressure-difference directed toward the growing crystal, and molecular flow results. The molecular flow attending the formation of phenocrysts is usually confined to distances of a few millimeters, or at most a few centimeters, and is clearly a process involving no unreasonable amount of time. Similarly the formation of aureoles of diffusion around blebs to distances of a few centimeters is not a very lengthened process. Thus if such a bleb had the properties of the hypothetical lava discussed above, an aureole 5^{cm} in depth might form around it in about a year, and sensible diffusion would extend to a distance of 1^{mm} in the comparatively short period of $3\frac{1}{2}$ hours.

Convection unavoidable.—It has been shown above that

segregation of magmas by the method of Ludwig and Soret would occupy a stupendous time even if a mass of melted lava could be kept free from convection currents. This freedom, however, could only be secured by permanent, regular decrease of temperature from the upper surface of the magma downwards. In any fluid of only moderate viscosity even a very small rise of temperature at the bottom would cause convection currents which in a day would undo the segregation it had taken thousands of years to accomplish by Soret's method. Lavas of very great viscosity would also mingle by convection far more rapidly than the most diffusible solutions could segregate through differences of temperature. Mingling again might occur in the absence of bottom-heating by any mechanical disturbance of surrounding rock masses.

That in general the temperature of the globe increases with depth is perhaps the best established generalization of geology. Hence even if it be granted for the sake of argument that in some particular locality the temperature decreases with depth, it is clear that such a thermal distribution is a case of unstable equilibrium. It can, therefore, only be temporary and it would surely be a strange exception were such an abnormal distribution of temperature to last for 1000 years. Yet in that time no segregation worth mentioning as an origin of rock differences could occur. The normal condition of a hypogeal molten magma must be that in which temperature increases with depth and in which convection effectually precludes any process of segregation by molecular flow.

Immiscible fluids.—Another method of segregation, which is quite distinct from that discussed above, depends upon changes in the mutual solubility of fluids. Some fluids which at certain temperatures mingle in all proportions dissolve one another only in certain proportions at other temperatures. Thus benzol and acetic acid mix without limit at 15°, but below this temperature separate out into two layers, one of which contains nearly twice as much acetic acid as the other. So, too, phenol and water mingle freely above 69°, but not below this temperature ; and there are many similar instances. The phenomena were studied by Mr. Alexejew, who concluded that in all cases where the solutions do not react chemically upon one another they become miscible above a certain temperature.[*]

Though Mr. Alexejew studied some of the physical relations of solutions of fluids in fluids, he did not determine whether the passage from complete to partial miscibility is accompanied by expansion or contraction. This step, however, has been taken by Mr. Herman Pfeiffer in Prof. Ostwald's laboratory. He finds that this change is accompanied by a sudden sharp

* Wied. Ann., vol. xxviii, 1886, p. 327.

contraction of volume.* It appears to follow of necessity that at the temperature of complete miscibility under a given pressure an increase of pressure would resolve the homogeneous fluid into immiscible portions.

In close relation to this separation of a homogeneous fluid into different layers is the precipitation of a solid from a fluid. The process of solution of a solid is one involving the absorption of heat, and in general the solubility of solids increases with the temperature. Anomalous cases appear to be referable to changes in molecular aggregation, the formation of hydrates and like causes. The influence of pressure on the solubility of solids was first carefully investigated by Dr. Sorby†, and Mr. F. Braun‡ has more recently made a very thorough study of the subject. Experiments have naturally dealt almost exclusively with aqueous solutions at ordinary temperatures, and it must be borne in mind that as water is a fluid of very exceptional properties the direct results of experiments on solutions in water are not immediately applicable to other fluids such as lavas. Most substances dissolve in water under contraction of volume and only about half a dozen compounds are known which undergo dilatation during solution. Now when contraction takes place increase of pressure will and does assist solution. If contraction were a universal concomitant of solution the interior of the earth would be fluid. But Mr. Braun gives apparently sound reasons for believing that even in aqueous solutions under high pressure and temperature, dilatation and not contraction would attend solution. The investigations of Prof. Carl Barus§ and others and some observations of mine on dikes‖ show that lavas contract in solidifying. The frequent corrosion of phenocrysts is seemingly due to increase of solubility attending relief of pressure. Thus for magmas it appears that increase of pressure promotes precipitation of solids as well as segregation into distinct fluids.

Segregation by immiscibility.—In fluids which, though originally homogeneous, tend to break up into two or more immiscible parts, two distinguishable modes of separation may be followed. As the temperature of separation is approached, the walls of the vessel being cooler than the fluid, any component about to separate out will separate to some extent on the containing walls much as frost or dew forms on good conductors. It does not appear that any large part of a large mass of even a moderately viscous fluid could be segregated in this way, for the process involves molecular flow from the interior of the fluid.

* Zeitschr. phys. Chemie, vol. ix, 1892, p. 469.
† Proc. R. S., vol. xii, 1863, p. 538.
‡ Wied. Ann., vol. xxx, 1887, p. 250.
§ This Journal, vol. xliii, 1892, p. 56; vol. xlv, 1893, p. 1.
‖ North Amer. Rev., April, 1893.

Thus in a spherical mass of 100^m radius, if half of a compo-nent were thus to be deposited on the walls, a portion of this deposit would have traversed a distance of nearly 21^m by molecular flow, which would take thousands of years even in the case of a solution of bluestone in water.

If the separating fluid does not condense on the sides of the enclosing cavity, it must condense somewhat like fog in the mass of the fluid. Now in a very fluid mass, like water, the larger drops of such a fluid will rise or sink more rapidly than the smaller ones, coalescence will occur and the lighter fluid may separate out in a layer. Bnt even in the case of a foreign material suspended in air viscosity greatly delays such separa-tion. The clonds are substantially aggregates of small water drops which, because of the viscosity of the air, fall so slowly that the slightest current sweeps them along. So, too, dust remains snspended in the atmosphere because air is viscous.* In fluids snch as lava it scarcely seems credible that any exten-sive separation of a precipitated immiscible liquid should occnr. It may be that spherulites and perhaps some phenocrysts are crystallized from drops of such liquids. However this may be, it is certain that many of the phenocrysts form before eruption and remain suspended in the magma in spite of densi-ties differing considerably from that of the medium.† Thus even in the process of the separation of fluids into immiscible òr partially miscible fractions I can see no adequate explana-tion of rock segregation. Furthermore, if, as seems to follow from the law of fusion, magmas are not heated much above the melting point, there is bnt a small range of temperature within which such separations could occur and they wonld be correspondingly rare.

Heterogeneity of the earth.—If the physical theory of solu-tion fails to account for rock segregation, two alternatives are left. Either segregation takes place in accordance with some principle of physics as yet undiscovered (*ignotum per ignotius*), or the facts which have led to the hypothesis of segregation are capable of a different interpretation not at variance with the known properties of matter and compatible with reason-able limits to geological time.

So far as I know, all geologists and astronomers are in unison

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* The viscosity of media is probably only one of the influences affecting the sub-sidence of disseminated fluid or solid particles.

† It is well known that phenocrysts in fresh surface-flows are often bent and even broken. Sometimes black borders have formed about hornblendes thus frac-tured. Such fractures must have happened during eruption. The lithologist will not require to be reminded that phenocrysts of augite and of amphibole with a density of say 3·25 are often of about the same size as those of feldspar with a density of say 2·65, yet there is as a rule no tendency to the separation of the lighter and heavier phenocrysts into distinct layers.

in the belief that the earth has been fluid, not indeed at any one time from center to its present surface, but at least to a great depth from the temporary surface of the growing globe. Yet the earth is clearly not a homogeneous mass, nor is it a system of concentric shells, each homogeneous. The mere fact that one hemisphere is almost entirely covered by water shows that the globe is of greater density below this great ocean than beneath the opposite continental surface. Were the shells homogeneous no continents could protrude above the sea. Were the earth of uniform composition no mountain ranges could stand above the plains. Were the material below the plains uniformly distribnted there could be no anomalies of gravity such as occur near Moscow, in Kansas, and elsewhere. The distribution of feldspars in the western part of this continent shows lack of homogeneity, for on the Pacific slope potash feldspars are marvelously rare. No trachyte and extremely little typical granite is known from the Wahsatch range to the Pacific ocean. The distribution of metallic ores shows heterogeneity. Much more than 90 per cent of the known tin ores of the world lie in a belt stretching from the straits of Malacca to Tasmania. There has been deposition of mercurial ores in this belt also; but their quantity is insignificant. A belt of quicksilver deposits extends from British Columbia to Chili. In this belt there is tinstone at many points, but the total product of tin on this belt is scarcely worth mentioning. I can only infer from these facts that quicksilver is an extremely subordinate component of the earth in the Australasian region and that the globe contains little tin along the Cordilleran belt. It is needless to observe that in almost any small area the rocks show marked variations or that two hand specimens from the same locality are rarely indistinguishable. Deserving of special mention, however, are the striped rhyolites, the banded gabbros studied by Sir Archibald Geikie aud Mr. Teall, and the ribbon gneisses so abundant, for example, in the southern Appalachians. The rhyolite at least has been fluid, and most geologists consider gabbroitic and granitic magmas as fluids. The diffusion exhibited in these cases is slight and sometimes hardly perceptible to the naked eye, yet it is scarcely supposable that these bands were not in contact for days at least in their mobile state. Now my hypothetical lava would diffuse to the depth of a millimeter in three or four hours. Hence these sharply banded rocks must be much less diffusible than my assnmed lava and the diffusivity of the granular rocks and their fluidity would scarcely exceed zero.* Thus from the surface of the globe to its minutest

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* Banding such as is found in gueiss and rhyolite could not result directly from segregation on Soret's methods or by difference of pressure, for these processes

portions there are clear indications of heterogeneity, notwithstanding that similar rocks and similar series of rocks occur in widely dispersed localities.

Is there any valid indication that uniformity ever reigned? It used to be thought that the Archæan rocks were uniform, but it is well known now that they are not so. The early eruptions and intrusions seem quite as diverse as the modern ones, excepting so far as original differences are masked by metamorphism. The theory of the permanence of continental areas has many very strong supporters, and that land areas have existed since the Cambrian seems certain. The mountain system of the world in its larger features appears to have been outlined during the Archæan, and there are observations indicating a highly accentuated topography even in those days. Were the indications of heterogeneous composition confined to the immediate neighborhood of the earth's surface, it might be maintained that these inequalities had been brought about since consolidation, but everything tends to show that only the shell of the earth next to the surface and a few miles in depth partake sensibly in orogenic movements, while several of the evidences of heterogeneity point to inequalities at great depth.

Uniformity unattainable.—If the earth condensed from a nebulous ring, it is fairly inconceivable that the successive shells of the growing mass should each have been uniform in composition; and if the origin of the earth is a ring thrown off from the sun, the coalescence of this ring to a globe cannot have resulted immediately in uniform distribution of matter. The sun spots show that the sun is not even yet an aggregate of shells each uniform in composition. The exterior layer of the globe must have retained such fluidity as it possessed for a very long time, and must have passed by insensible gradations through every temperature between the initial one and that of consolidation. Had the various .component portions of this layer been of large size, of low viscosity, and not miscible with one another, they would have arranged themselves in the order of density quite irrespective of chemical composition. If the masses were viscous, however, nothing like a perfect separation according to density could occur in

can lead only to very gradual transitions. Banding might conceivably result from such a segregation followed by active stirring. but only on condition that stirring was immediately followed by solidification, for otherwise diffusion would restore homogeneity. Separation of a magma into immiscible portions followed by active stirring might also produce banding, but again only on condition of immediate consolidation. since otherwise separation into two layers would again take place and much more rapidly than at first.

Miscible substances in contact which do not diffuse at a finite rate can have no sensible vapor tension and must be solids or ultra viscous fluids. Immiscible fluids must have a perfectly sharp contact like that between a lead button in an assayer's crucible and the enveloping slag.

this way and only a rude approximation to regularity would be attained.

If the melted masses were partially or wholly miscible, much the same arrangement would take place at first because diffusion on any large scale is at best a relatively slow process. Then diffusion and convection would come in play, tending to equalize the composition.

On the other hand, unless the originally heterogeneous masses had very different properties from those of remelted rocks, whether of Algonkian or modern time, they cannot have diffused on any large scale, and uniformity along equipotential surfaces cannot have been attained even if fifty million years were allowed for the process, unless the convection currents were so powerful and universal as to break up the original masses into streaks of a few meters in width. I see no cause for convection so active as this. In the nebulous state the material of the earth must have assumed some approach to convective equilibrium of temperature, and though here and there the solidifying globe may have been affected by disturbances of frightful intensity, analogous to sun spots, a general diversity of temperature sufficient to stir the whole or most of the melted layer into uniformity seems utterly improbable.

What is known of the properties of matter seems to me to point to the hypothesis that the material of the earth is rudely arranged by density irrespective of chemical composition, the different masses mingling for a few meters or scores of meters along their common boundaries, this structure being due to original heterogeneity. If segregation took place at all, prior to the consolidation of such a globe, this process would be limited to particular masses and would tend to still greater heterogeneity.

Hypogeal refusion.—Consider now the effect of the refusion of any portion of the earth's mass. Unless the temperature of the magma were raised essentially above the initial temperature of the molten globe, or unless it were melted at a very different pressure, the magma would simply be restored to the condition in which it existed before the primal consolidation. There is no indication that lavas prior to eruption are really raised to temperatures greatly above that of fusion, for almost all of them bring solid phenocrysts to the surface, nor is it easy to see how they could be heated much above the melting point, for so long as there was unfused material of a similar character in the neighborhood of the subterranean mass undergoing fusion, any heat increment would of course melt more rock instead of raising the temperature of that already fused. Thus it is substantially certain that in the molten globe

a given magma passed very gradually through the temperature at which it has more recently been remelted. As for the pressure, it seems possible that under continental areas a given fusing subterranean mass may exist under a somewhat smaller load than that to which it was subjected at primal consolidation, for the general tendency of continents is to upheaval and degradation by erosion. If this change of pressure is of any consequence at all, it will tend to make the refusing mass more fusible and more miscible.

If now the mass were both homogeneous and in molecular equilibrium before the primal consolidation, it may be in equilibrium after refusion. If the pressure is smaller than the original one, this difference would have no tendency to promote segregation. If by some almost inconceivable coincidence, the upper portion of the refused mass were heated to a higher temperature than the lower part, this temperature would be equalized by conduction through the walls, if not through the liquid, before any sensible segregation could occur.

If the mass were heterogeneous in consequence of primal segregation, fusion would again tend to restore molecular equilibrium and the only chance of a new segregation would lie in the possible difference between primitive and ultimate pressure, which, if positive, would tend to mixture rather than to separation.

If the mass were heterogeneous because the primal fusion had not continued long enough to bring about homogeneity, refusion would be accompanied by a tendency to continue the process of molecular flow and to decrease the heterogeneity of the mass; but even if the refused mass were kept molten for a million years, this tendency would probably have only insignificant results.

Mixture by eruption.—Little or nothing is known of the process of refusion of subterranean masses to eruptive magmas. Supposing a mass which is fused and near its melting point to remain in its subterranean reservoir, it must in general receive or lose heat. In the latter case it will reconsolidate, in the former the mass of melted material will increase. In the case of rocks, fusion is accompanied by expansion and the magma must have more space than it occupied in a solid condition. Any elastic strains in surrounding masses will also tend to expel it and it would seem to me most probable that magmas are expelled as soon as the mass of melted material had increased to a certain limit dependent upon local conditions. If so, there must be little time for the fulfillment on a large scale of a process so slow as molecular flow. Doubtless fusion may be confined to a nearly homogeneous portion of the earth's lithoid shell. If the hypothesis explained above of

primitive, unmingled, unsegregated masses is correct, a good many of these must have the composition of augite-andesite; for this as well as several other simple rock types has issued at most distant points with almost constant characteristics. Fusion may, however, also affect two or more diverse masses and then eruption tends to mingle them. Ejection through pipes or fissures must indeed be a most efficient stirring process, and since relief of pressure is accompanied by depression of the melting point, different magmas thus ejected are superheated and may mingle to an observable extent by diffusion before they finally consolidate. In such cases one would probably find two (or more) rock types accompanied by mixtures of variable composition. Again, a fissure through which different types were extruded successively or in mixture might at the close of the eruption be filled with a single type or with a mixture. If such a mixture were at all intimate, diffusion would mask the original differences and the case would be one of apparent transition.*

Possibly some of the observed occurrences which have led to the hypothesis of differentiation are really of this character, for I think it has been shown in the foregoing pages both that transitions can be explained on the hypothesis of primitive heterogeneity and that the explanation of differentiation itself presents formidable difficulties. I do not see why it should be necessary or desirable to assume that in the early history of the globe the vast shell from which eruptions issue was reduced to substantial uniformity. Experience affords no analogy in support of such an assumption nor has any theory been propounded which will account for it.

If primitive heterogeneity is still an important feature in the earth's structure, and if unmingled magmas represent primitive differences, the labors of lithologists would naturally be directed to detecting these original types. These would probably be recognizable by their wide distribution and constant character. Then areas of rapid variation would be regarded as representing mere mixtures and it might be possible to reduce instead of increasing the number of rock species.

Abstract.—All known processes by which the segregation or differentiation of a fluid magma could take place involve

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* The order of mixture and extrusion would seem to depend on many circumstances, among others on the shape of the subterranean reservoirs. If this were a cone with its vertex nearest the surface, the disposition of the ejecta would be very different from that which would be observed if the reservoir were a flattened lens with its edge horizontal and a vent on one surface. If each eruption represents a separate melting, still other dispositions will result. It appears to me anything but remarkable that different observers find eruptions in different areas taking different orders. Gradual solidification from fissure walls of dike magmas circulating by convection may lead to preponderance of less fusible ingredients near the edges of a solid dike.

molecular flow.   This is demonstrably an excessively slow process excepting for distances not exceeding a few centimeters. Soret's method of segregation, even if it were not too slow, seems inapplicable because it involves a temperature unaccountably decreasing with depth.   The normal variation of temperature, an increase with distance from the surface, would be fatal to such segregation.   The least objectionable method of segregation would be the separation of a magma into immiscible fractions; but this seems to involve a superheated, very fluid magma, while the law of fusion and the distribution of phenocrysts in rocks indicate that magmas prior to eruption are not superheated to any considerable extent and are very viscous.

The homogeneity of vast subterranean masses called for by the hypothesis of differentiation is unproved and improbable. The differences between well-defined rock types are more probably due to original and persistent heterogeneity in the composition of the globe.   Hypogeal fusion and eruption tend rather to mingling than to segregation, and transitional rock varieties are not improbably mere fortuitous mixtures of the diverse primitive, relatively small masses of which the lithoid shell of the earth was built up.*

Washington, D. C., October, 1896.

* I owe thanks to Dr. Arthur A. Noyes of the Mass. Institute of Technology for kindly examining the manuscript of this paper.   Dr. Noyes's reputation as an investigator in osmotic questions gives his approval of my argument great value.