ART. XXXII.—*Note on the change of electric conductivity observed in rock magmas of different composition on passing from liquid to solid;* by CARL BARUS and JOSEPH P. IDDINGS.

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§ 1. *Introduction.*—The chemical composition of rock magmas and the process and results of their crystallization and solidification have been studied with more or less thoroughness; but direct investigation of their physical properties has not been systematically undertaken until recently.

Conceptions of the physical nature of molten rock magmas, however, have been obtained by observing the phenomena of their crystallization, and by pointing out analogies between the latter and the behavior of aqueous solutions, and of metallic alloys.

Evidences that a chemico-physical differentiation of molten magmas was the cause of chemical differences in igneous rocks, which evidences have been reviewed by one of us in a paper on the origin of such rocks,* have led to the further analogy between this process of differentiation and the concentration and partial dissociation of salts in aqueous solution. They also suggested the possibility of testing the fact of dissociation by electrolytic investigation.

The method employed was the determination of the electric resistance encountered by a current in passing through fused rock magma, whose temperature was gradually lowered. The investigation, though of a preliminary character has been productive of such definite results that we have embodied them in the present paper in order that they may become known as early as possible.

§ 2. *Observations.*—The following table contains typical ex-

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*J. P. Iddings. The origin of igneous rocks, Bull. Phil. Soc. Washington, 8°. Washington, 1892, vol. xii, pp. 89–214.

amples of sixteen series of electric measurements made with three kinds of rock magmas, which cooled slowly in a furnace from the molten state. Temperatures* and resistances were noted simultaneously every two minutes during each series. The resistances were measured by Kohlrausch's method of intermittent currents. The data for mean temperatures are closely accordant, but at very high temperatures and at low temperature sharpness is lost, owing to polarization and to the immense range of electrolytic resistances encountered. These difficulties are largely unavoidable, although our method is capable of much improvement. Reductions to absolute values are approximate.

TABLE I.

Table 1. The specific electrolytic resistances of rock magmas, varying with temperature and composition.

1. Acid magma. 75·50 per cent SiO_2.			2. Intermediate magma. 61·5 per cent SiO_2.			3. Basic magma. 48·5 per cent SiO_2.		
Series.	Temperature.	Resistance.	Series.	Temperature.	Resistance.	Series.	Temperature.	Resistance.
xiv	°C	ohms × 10^6	xiii	°C	ohms × 10^6	viii	°C	ohms × 10^6
	1640	1·8		1430	1·8		1400	2·9
	1320	2·2		1260	2·5		1230	4·4
	1164	2·9		1114	4·2		1124	5·4
	1086	3·1		1034	6·3		1050	14·7
	1011	3·8		956	8·8		995	27·8
	948	4·7		894	13·4		939	54·7
	890	6·5		843	20·0		883	94·0
	827	8·0		754	46·4		834	152
	787	11·6		715	70·2		792	227
	746	15·3		680	105		754	321
	705	21·6		643	158		723	432
	665	29·5		608	239		692	602
	626	41·3		580	344		645	1000
	598	53·8		552	497		612	1400
	582	64·2		496	1140			
	560	82·2						
	533	114						
	504	166						
	467	281						
	444	417						
	425	584						
	395	1060						
	355	2540						
	320	5700						

The results of these observations have been plotted as in the diagram, fig. 1, the ordinates being specific resistances in

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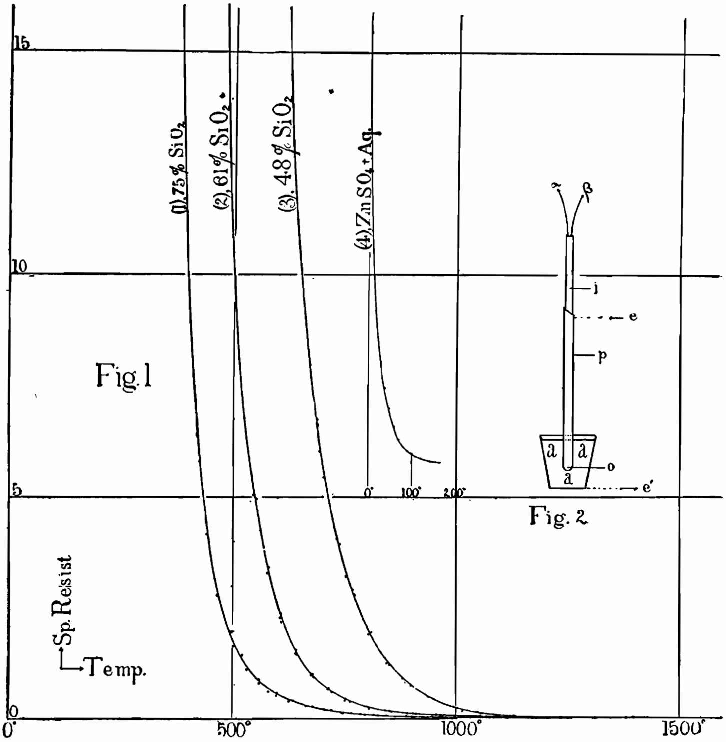
* Regarding temperature measurements see Phil. Mag., July, p. 1, 1892.

megohms, the abscissæ temperatures in °C. The curves (which, as shown, contain *all* our observations) are numbered (1), (2), (3), as in Table I, relatively to the magmas. Between 1000° and 1500° the points lie so near the axis, that a discrimination is no longer possible. This can be done, however, by expressing the variations of conductivity with temperature for the interval. It is here omitted because it leads to no novelties. The corresponding curve for a concentrated solution of



Legends.

FIG. 1. Chart showing the relation of the specific electrolytic resistance (megohms, *cc*) to Temperature (°C), in case of

(1) An acid magma,
(2) An intermediate magma,
(3) A basic magma.
(4) Zinc sulphate, concentrated aqueous solution. Resistance relative.

FIG. 2. Crucible and appurtenances with the furnace withdrawn:

aaa, rock magma in platinum crucible;
p, tubular platinum electrode;
i, insulator (fire clay) of the thermocouple;
αβ, thermocouple with its junction at *o*;
ee′, electrolytic current (intermittent).

zinc sulphate in water has been added for comparison. Here the ordinates are ratios in terms of the resistance of the solution at 100°. Points above 100° were obtained under pressure. Fig. 2 explains itself.

A series of observations with another basic magma gave corroborative evidence. The only electrical indication of fusion was found in the case of the basalt (3). It was somewhat above 1100°, but is not certain. The rhyolitic or acid magma (1) changes character suddenly below 500°, for reasons probably accidental which must be further examined. In this rock, which is very viscous even at 1600°, it is almost impossible to free the magma of gas bubbles. We have not been able to make allowance for volume expansion of the magma, and the residual errors are in keeping with this omission. Finally, without sacrificing accuracy of temperature measurement, it is difficult to make the electrodes sufficiently large in area to exclude polarization.

§ 3. *The magmas.*—The magmas investigated represent three phases of igneous rocks from the same region. The first is a rhyolite; the second, a crystalline andesite or porphyrite; and the third, a basalt. The chemical composition of the rocks is shown by the following analyses made by Mr. J. E. Whitfield.

	I.	II.	III.
SiO_2	75.50	61·50	48·49
TiO_2	none	none	2·19
Al_2O_3	13·25	17·42	18.35
Fe_2O_3	1·02	4·66	7·63
FeO	·91	1·09	1·21
MnO	none	tr.	none
CaO	·90	5·33	10·40
MgO	·07	1·26	6·72
Li_2O	·06	·03	·02
Na_2O	4·76	3·99	3·02
K_2O	2·85	1·29	·57
P_2O_5	none	·60	·20
SO_3	·32	·35	·52
H_2O	·41	2·44	·67
	100·05	99.96	99·99

The three magmas clearly form the middle and extremes of a chemical series.

When heated in a platinum crucible, the basalt melts at about 1250° to a fluid which at slightly higher temperatures becomes quite liquid, and upon solidification forms a black glass that is brown in the thinnest edges and is without gas bubbles.

The porphyrite when heated decrepitates, and afterward fuses in the neighborhood of 1400°, but does not become as liquid as the basalt for like temperatures. It solidifies as a dark brown glass with some gas bubbles.

The rhyolite melts at about 1500°, but remains quite viscid at 1700°, and solidifies as a gray glass filled with minute gas bubbles.

The amount of gas bubbles serves as an indication of the relative viscosity of the different magmas at the temperatures to which they were subjected.

§ 4. *Relation to temperature.*—In making the present deductions the outspoken parts of the data of Table I can alone be taken, viz: in case of the magma (1) between 900° and 500°; in case of (2) below 1034°, and in case of (3) between 1124° and 692°. Careful scrutiny of the relation of resistance to temperature then shows, that the ratio, dr/dt, of corresponding decrements of specific resistance, $-dr$, and of temperature, dt, is proportional to the corresponding resistance at the given temperature. In other words we have $-r' = a + bt$, whence

$$ln(a + br) = c - bt \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where a, b, c, are constants. Relative to Table I these values are approximately (r in megohms)

	(1)	(2)	(3)
a	—·10	—·05	+·05
b	·0134	·0125	·0091
c	7·59	8·78	7·96

It is probable that a merely reflects the errors of observation and that its real value is zero. The constant b, which is an index of the composition will be discussed in §§ 5, 6. The quantity c/b, which is a temperature, has no apparent meaning. These results are exceedingly interesting since a relation similar to equation (1) was found* for the thermal variation of the viscosity of a highly viscous body like pitch. Again the acid magmas at least, betray no evidences of circumflexure, or anything that would be an electrical index of polymerism or melting point. An aqueous solution of zinc sulphate carried under pressure through a large interval of temperature, shows changes of resistance† quite akin to the present. In both cases, therefore, we have similar solution phenomena, exhibiting a thoroughly regular change of the electrical character with temperature.

Moreover the nature of the law embodied in equation (1), for silicates, the enormous range of temperatures to which they

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* Proc. Am. Acad., xxvii, p. 13, 1892.

† This Journal, xlii, p. 135, 1891.

can be exposed, the extreme sensitiveness of the electrical indications, and the simplicity of the necessary apparatus, suggest a method of pyrometry specially available for temperature approaching the melting point of platinum. One would obviously select an exceedingly acid magma, both because of its relatively great infusibility, and because of the occurrence of the maximum of uniform electrical conduction, in such a case, as will be shown in the next paragraphs.

§ 5. *Relations to chemical composition.* — Endeavoring to interpret these results with reference to their chemical bearing by means of Kohlrausch's* law we are handicapped at the outset because the rates of procession of ions (Hittorf's "Überführungszahlen") in silicate solutions are not known. In other words the quantities expressing the velocity of either ion relative to the combined velocities of both are unknown. We cannot even state what the structure of the electrochemical equivalents may be. It makes a difference whether the cations travel singly or in groups, or whether the anions be $\frac{1}{2}SiO_3$, $\frac{1}{4}SiO_4$, etc., singly or combined. We could not therefore express more than a mere opinion relative to the velocities of the ions, even if the specific molecular conductivities were computed. Nevertheless, in the face of these difficulties we are able to deduce certain striking results insomuch as the method of this paper is one in which the cation is brought gradually, and as nearly as possible to vanish in amount. An index of acidity, independent of temperature, is given by the constant b of equation (1). We regard the anions, whatever their specific structure may be, as identical in the three magmas examined; and the cations, from the large number of elements contained in the magmas, as possessed of a common or average property.

Several general deductions, however, may be drawn from the work, incomplete as it is at present. In the first place, Table I shows strikingly that electric conduction increases with the degree of the acidity of the magma, that is, with the degree of dilution of the cation. And since fusibility decreases in a marked way as the composition of the magma approaches pure silica, it follows that *in a series of different magmas electric conduction at any given temperature increases in proportion as the viscosity increases.*

Thus the most acid of the rocks investigated, (1), is a stiff paste above 1500,° whereas the basalt, (3), can be poured at a temperature much below 1300° ; and yet the rhyolite, in virtue of its acidity is a better conductor than basalt at any given temperature.

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* Kohlrausch, Wied. Ann., vi, pp. 145 et seq., 1879.

The table also shows that the conductivity of rock magmas at high temperatures is considerable even when they have passed from a liquid to a solid state, that is, when they exist as highly heated glasses.

In general, therefore, a thorough change of chemical structure through ionic diffusion, whether directed by an electrical field or otherwise, must be an easy possibility in a sufficiently temperatured but otherwise solid magma.

§ 6. The second point gained is more specific. Kohlrausch* has shown that the contribution of a single ion in promoting electrical conductivity decreases with the number of ions present. In other words in concentrated solutions the ions are stopped *en route* by what may be termed friction, but what is probably temporary intercombination with each other. Hence their mean velocity, and consequently the specific molecular conductivity of the solution falls short of the proportionate quantity. Moreover, it is perfectly well known† that many solutions (H_2SO_4, HCl, $ZnSO_4$ etc.) show maxima of electric conductivity for gradual changes of concentration. The case of an aqueous electrolyte decreasing in electric conductivity with increasing concentration is therefore given by many examples, and doubtless their number could be indefinitely increased by employing aqueous solutions at high temperatures under pressure.

Now this is exactly what we observe in our series of three silicate solutions. Conduction increases markedly from (3) to (1), that is, from basic to acid, and it seems altogether probable that the anticipative maximum will correspond to a degree of silicic dilution greater than 75 per cent of silica.

Tracing this inference further we come to the conclusion that pure silica is probably an insulator, or that it occupies a position in siliceous electrolysis very closely analogous to that of water in aqueous electrolysis. It is to be remarked that we here refer to the electrolytic solvent and leave the question of chemical solvent temporarily out of consideration. This is in accord with the observations of Warburg,‡ who has elaborately investigated the insulation of a film of pure silica at about 300,° the film having been produced by the electrolysis of glass. The insulator was found to be so perfect that the capacity of the condenser was measureable. The insulation of quartz relative to glass has to some extent (as far as 224°) been tested by Warburg and Tegetmeier,§ though the conditions were complicated in this instance both by crystalline structure and the impurity of the mineral.

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* Kohlrausch, l. c. p. 183. † l. c. p. 43.

‡ Warburg, Wied. Ann., xxi, p. 622, 1884.

§ Warburg and Tegetmeier, Wied. Ann., xxxv, p. 463, 466, 1888.

§ 7. *Conclusion.*—Looking at our results as a whole we find them trenching in a novel way on the solution theories of Arrhenius, Ostwald and vant' Hoff. It is difficult to withhold one's assent from the proposition, that the ions of a molten magma are largely present in the dissociated state, and more especially so as we approach very acid magmas. Terms like *colloid* applied to these magmas are absolutely without relevancy so far as we can make out. To the extent of our enquiry, the behavior of molten rock magmas is in its nature quite identical with that of any aqueous or other solution, the difference being one of solvent.

The above paragraphs give a mere draft of a series of experiments which we propose to carry out with greater vigor. We desire, however, to express our conviction that electrolytic resistance is not only a valuable aid to petrological research, but that the definition of molecular structure is possibly within the reach of the method.