THE CONTACT ELECTRICITY OF SOLID DIELECTRICS

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Abstract

The electric charges produced by wringing optically flat surfaces together were measured in order to determine whether or not there is a possibility of formulating a single contact theory which will include both the metals and the dielectrics. Experiments with flint glass and steel proved that the frictional charge is independent of the amount of friction, provided only that intimate contact be established, and is proportional to the area of contact. *The voltaic nature of the frictional charge.* The charge was in no wise affected by the ionization of the residual air molecules between the surfaces by means of an intense beam of x-rays, and was also found to be independent of the duration of contact for periods varying up to 17 hours. The failure of the double-layer to recombine under these conditions proves that it was sustained by a voltaic field. *The dependence of the effect on the dielectric constant.* The charge per cm^2 Q_{12} of material 1 in contact with material 2, was found for 8 different pairs of the materials, *quartz, fluorite, crown glass, flint glass and steel,* to satisfy, within 14 per cent, the equation $Q_{12}=C(K_1-K_2)$, where K_1 and K_2 are the dielectric constants and C is a positive constant, whose mean value is 4.43 e.s.u., provided the value $K=3.1$ be assigned to steel. This equation is consistent with the results of Coehn's measurements of electric osmosis.

The electric effect of compressing amorphous dielectrics was determined by pressing two kinds of sheet rubber, of dielectric constants 2.94 and 3.96, against seven hard materials, whose dielectric constants ranged from 2.8 to 7.8. The charge on the compressible dielectric was found to be independent of the nature of the material against which it was pressed, proving that this is not a voltaic effect and that amorphous as well as crystalline substances can be electrified by pressure.

The electric effect of collision of a solid insulator and a metal was found, with four pairs of materials, to be consistently opposite in sign to the frictional effect. This result shows that collision must be considered to produce two different effects, one of which is the voltaic charge, while the other is a transfer of electrons from the metal to the dielectric, due in all probability to the inertia of the mobile electrons.

Dielectric constant of steel, as suggested by these results, is not infinity but 3.1.

THE literature of tribo-electricity consists largely of lists in which the various solids are so arranged that any one of them becomes positively electrified when rubbed with a material appearing lower than itself. The singular and disappointing characteristic of these lists is that no two of them are alike.[1] If electrification by friction were

[1] Compare, for example, Shaw, Roy. Soc. Proc. **94**, p. 16, 1917, and Sanford, Phys. Rev. **12**, p. 130, 1918.

an exceedingly small and fugitive effect, the lack of agreement among the data obtained by different experimenters might reasonably be attributed to undetermined contaminations of the surfaces of contact; but the tribo-electric charges are, on the contrary, so large and easily measurable that the inability of one observer to reproduce the results of another, or, indeed, his own, must clearly be referred to other causes. Of the alternative explanations which may be suggested, the most probable and, if found true, the most important, is that the frictional charge results from the superposition, in proportions varying with the manner in which contact is made, of two or more different effects. One of these effects may be expected, if Helmholtz' hypothesis[2] is true, to be exactly similar in nature to the voltaic electrification of two dissimilar metals. Accepting this hypothesis for the moment, and taking account of the fact that the metals are distributed among the dielectrics in most of the available frictional series, we may conclude that a single contact theory can be formulated which will embrace all substances, whether they be good conductors or poor. A unification of theory of such a character is especially desirable because of the fundamental importance of the Volta effect, and the experiments to be described have accordingly been performed with this end in view. The results show that previous discrepancies may be ascribed partly to the impossibility of defining the area over which contact actually occurs in the usual experiment of rubbing a hard solid with a soft buffer;[3] partly to an electric effect of compressing an amorphous material; and partly to the fact that in certain cases the relative velocity of two bodies at the moment of contact determines whether or not an effect due to the inertia of the mobile electrons will be sufficiently large to mask the voltaic electrification. Evidence has been obtained which enables us to speak definitely of the true contact effect of solid insulators; the coefficients of the effect have been measured for several pairs of substances; and these coefficients have been found to depend on the dielectric constants of the materials which are placed in contact.

It seemed perfectly evident from the first that consistent results could be obtained only by carefully defining the area of actual contact. For this reason the first experiments consisted simply in wringing two optically flat disks together, removing one of them, and measuring the electric charge retained by the other. The metal disks were surfaced for this work by the Pratt and Whitney Company, and the dielectric specimens were obtained from various sources. Tests made by the

[2] Helmholtz, Wissenschaftliche Abhandlungen, Erster Band, p. 860.

[3] Cardani, N. Cimento **23**, p. 199, 1922.

method of interference showed that the surfaces were flat to within half a wave-length of sodium light. The apparatus was so arranged that after one of the disks had been removed, the other remained firmly mounted on a brass plate which formed the bottom of a closed, cylindrical brass vessel. When a metal was used as the fixed disk, its charge was shared directly by conduction with the measuring system; and the charge of an insulator could readily be determined by measuring the potential which it induced on the metal vessel surrounding it. This vessel was supported by an ebonite pedestal, and during a measurement was entirely enclosed by an earthed metal shield. Both disks were discharged before they were wrung together, metals by earthing, and insulators by x-raying in air; and the movable specimen was held in a metal socket which remained earthed throughout the experiment. Capacities were determined by comparison with condensers which had recently been calibrated in the Bureau of Standards, and the potentials produced by the frictional charges were measured with a Dolezalek electrometer. There was no trouble on the score of sensitivity, for the charges were so great that capacities as large as 8000 centimeters were required to reduce the potentials to values within the range of an ordinary electrometer having a phosphor-bronze suspension. This instrument was calibrated with a potentiometer and a Weston standard cell.

The Characteristic Coefficient

The dependence of the frictional charge on the area of contact was determined by using, with the same specimen of steel, three glass disks of different sizes, which had all been cut from the same block of flint glass. Typical values of the charge are given in Table I. In the course

Table I

Flint Glass on Steel

Area of contact (cm^2)	Total charge (extremes) (e. s. u.)	Max. variation from mean (percent)	Charge per unit area (mean of 10 tests) (e. s. u./cm^2)
4.99	93–109	9	20.0
3.53	69–80	7	21.1
2.22	46–51	6	21.7

of many experiments it has been found that these results can be duplicated, within the limits of variation shown in the table, at any time; all that is necessary is to clean the flat surfaces with ethyl alcohol and cotton and then allow them to dry completely before a test is made. The usual method of producing intimate contact was to slide the glass disk across the steel surface and then twist it through a quarter-turn under the pressure of the hand. No effort was made to wring the surfaces together with the same amount of friction at every trial, for many tests showed that after contact had once been established the charge remained independent of the amount of friction. The steel was consistently negative with respect to the glass. So far as the magnitude of the charge is concerned, the figures in the third and fourth columns show that the consistency was not as good with the larger disks as with the smallest one, and the average charge less. The discrepancies are slight, however, and may be referred to the fact that the difficulty of establishing intimate contact over the entire surface increases with the size of the disk. The results show clearly that the charge per unit area is the characteristic coefficient of the tribo-electric effect.

Nature of the Effect

Additional experiments were performed with the flint glass and steel in order to determine whether this effect depends primarily on friction, or on contact. The smallest of the glass disks which had been used in the preceding experiments was wrung upon a flat steel disk, and then the contact interface was irradiated with an intense beam of x-rays. Certainly a good many molecules remain imprisoned between the two surfaces, even when these are optically plane; and it seems evident that the double-layer of electricity could not withstand the discharging effect of the x-rays unless it were maintained by an intrinsic difference of potential arising from the dissimilar natures of the two materials. A Coolidge tube of medium focus was used, mounted at a distance of 33 cm from the contact interface and carrying a current of 30 m-amp at 80 kv; and the long runs were made without melting the target, by operating the tube intermittently. The electrostatic shields surrounding the apparatus were provided with windows of metal gauze to give the x-rays free passage to the specimens, and the beam was so directed as to strike the interface at a small angle after passing through the glass disk. Tests with a fluoroscope showed that the beam was properly directed and amply penetrating. Examples of the results are given in Table II, together with measurements which were made after contacts of long durations. The tests under varying conditions were alternated with others in which the charge was measured after the usual contact of 40 sec., and the results are recorded for comparison. No significance is to be assigned to the particular interval of 40 sec.; this was merely the time ordinarily required to wring the specimens together, close the apparatus, and insulate the measuring system.

In several of the earlier experimens with x-rays, consecutive observations were more consistent than those which had been obtained without irradiating the interface, and so for a time it was thought that the x-rays helped to establish the contact charge. An extended series of observations failed to confirm this conclusion, however, and proved that neither the magnitude of the charge nor the consistency of repeated observations was appreciably affected by the ionizing action of the x-rays. If we assume that a single layer of air molecules remained between the flat surfaces after they had been wrung together, a simple calculation shows that in the absence of a sustaining field the expulsion of one electron from every fifteenth molecule would have reduced the electrification to zero. Since the charge was in no wise diminished we must conclude that the sustaining field was supplied by the steel and the glass. This conclusion is confirmed by the results of contact of long duration; although after the surfaces had remained in contact for many hours the results were not as consistent as those obtained after shorter intervals, and the average charge was 10 per cent less than the maximum. This discrepancy, however, was easily proved to be entirely too small to account for the recombination which would occur if there were no intrinsic difference of potential. Two disks of the same kind of glass were selected, each having an optically flat surface; and the two surfaces were then electrified with charges of opposite sign but approximately the same magnitude. With fur and silk as buffers the desired electrification could usually be obtained after several trials. The two electrified disks were then pressed into contact, without friction; and measurements made after different periods of contact showed that from 90 to 95 per cent of the charge disappeared during the first five minutes.

TABLE II

Flint Glass on Steel
Area of contact interface = 2.22 cm^2

Time of x-raying (min.):	1	2	3	8	0	0	
Time of contact (min.):	2	4	8	40	720	1020	
Charge (e. s. u.):	49	51	46	42	40	47	Mean = 45.8
Charge (40 sec. contact without x-rays):	48	50	46	47	48	50	Mean = 48.2

Thus the charge is independent of the duration of contact; it is not diminished when the residual air between the surfaces is ionized; and within wide limits it has been found to be independent of the amount of friction. These results show the fallacy of the view[4] that electrification

[4] Jones, Phil. Mag. **29**, p. 272, 1915.

by friction depends primarily on the work done, and we may conclude on this evidence that the only fundamental difference between tribo-electricity and the Volta effect lies in the greater number of points at which contact must take place to produce the characteristic electrification of an insulator. In a recent paper[5] the same conclusion was reached after experiments had shown that the collision of a solid dielectric and a metal produces a quantity of electric energy which does not depend in any direct way on the mechanical energy lost during the impact. It is now known, however, that the conclusion was not valid on that ground; and later on in this article evidence will be given to show that an intrinsic difference of potential is only one of two factors in producing electrification by collision. Other writers have concluded that tribo-electricity is essentially voltaic, because one substance remains positive with respect to another in the frictional series; and Owen, working with surfaces which were not optically flat, furnished additional ground for this view by proving that the work required to produce the maximum frictional charge may be reduced by increasing the pressure of the rubbing surfaces.[6] Recently, important evidence[7] of a different nature has been obtained. Two disks, one of brass and one of glass, were placed in contact with the same surface of mercury, and simultaneous measurements were made of the brass-mercury difference of potential and the glass-mercury contact charge. As the surface of the mercury changed under the influence of the atmosphere, the two effects varied; and when successive measurements of the Volta effect were plotted against the corresponding values of the tribo-electric excitability, the curve was found to be approximately a straight line. This result is entirely consistent with the evidence of the present experiments.

Dependence on the Dielectric Constant

In spite of the essential similarity of the two effects, however, there is good reason for believing that the contact electricity of dielectrics cannot be explained by the accepted theory of the Volta effect. Richardson has pointed out[8] that since at the same temperature two metals emit electrons at different rates, useful work could be gained in violation of the second law of thermodynamics if the metals should come to the same potential when placed in contact; and it is found that if the Peltier heat be neglected, the contact effect of two metals is equal to the differ-

[5] H. F. Richards, Phys. Rev. **16**, p. 290, 1920.
[6] Owen, Phil. Mag. **17**, p. 457, 1909.
[7] E. Perucca, N. Cimento **22**, p. 56, 1921.
[8] Richardson, Electron Theory, p. 455; Nature **108**, p. 374, 1921.

ence of their thermionic work functions. Millikan has recently expressed essentially the same law in terms of Planck's constant and the threshold frequency of the photoelectric emission.[9] Clearly this law cannot be considered adequate to account for the large contact effects of dielectrics, unless the latter can be shown to possess characteristic constants which are analogous to the thermionic work functions of the metals. The dielectric constant suggests itself as the coefficient which is most similar to the thermionic work function, since it is proportional to the ease with which an electron can be displaced within an insulator, whereas the thermionic work function is inversely proportional to the facility with which an electron escapes from the surface of a metal. No experiments of rubbing two solid insulators together have hitherto yielded consistent results which might furnish a test of the similarity of these two constants; but Coehn has succeeded in an admirable series of researches[10] in proving that when a poorly conducting liquid is placed in contact with a solid insulator, the material of greater dielectric constant becomes positive with respect to the other, the difference of potential being proportional to the difference of the two dielectric constants. Coehn established this law by measuring the vertical displacement of current-carrying liquids and combining the results with a relation[11] which Helmholtz had deduced from the theory of the double-layer. The law was verified for twenty poorly conducting liquids in contact with glass, quartz, paraffin, and diamond, and was also found to give the sign of the charge which a gas acquires when it is bubbled through a liquid. Additional confirmation of the law has been furnished by Ulrey's measurements[12] of the metal-liquid contact effect. Nernst's theory of this effect has been attacked by several writers because of the enormous solution-pressures which it assigns to certain of the metals, the pressure of magnesium being so great that it need act through a molecular distance, only, in order to project a magnesium ion into water with a velocity much greater than that of light; and Ulrey has shown that when two similar metals are immersed in different poorly conducting liquids, their difference of potential is proportional to the difference of the dielectric constants of the liquids. Thus there is ample evidence to show that Coehn's law applies not only to the contact of a solid dielectric and a liquid, but to the contact of two liquids as well; and whether or not it describes

[9] Millikan, Phys. Rev. **18**, p. 236, 1921.

[10] Coehn, Wied. Ann. **64**, p. 217, 1898; Ann. der Phys. **30**, p. 777, 1909; **43**, p. 1048, 1914.

[11] Winkelmann's Handb. **3**, p. 499.

[12] Ulrey, Phys. Rev. **12**, p. 47, 1918.

the contact effect of two solids has been tested by measuring the characteristic coefficient of the effect for several pairs of materials.

The results of these measurements are given in Table III. Each value of Q_{12}, the charge per unit area of specimen No. 1 in contact with specimen No. 2, is the mean result of a series of ten or more tests, which were made in the manner previously described. Wringing was used regularly as the method of producing contact; for it was found by

TABLE III

Specimen No. 1	Specimen No. 2	K_1	K_2	Q_{12} (e. s. u./cm.^{2})	C
crown	steel	6.7	3.1	+15.8	4.39
flint	steel	7.8	3.1	+20.9	4.45
quartz	steel	4.6	3.1	+ 7.1	4.73
fluorite	steel	6.9	3.1	+16.0	4.21
fluorite	quartz	6.9	4.6	+ 9.3	4.04
crown	flint	6.7	7.8	− 5.1	4.64
crown	quartz	6.7	4.6	+ 8.2	3.90
quartz	flint	4.6	7.8	−16.2	5.06
flint	flint	7.8	7.8	± 1.5	—
ebonite	steel	2.8	3.1	−18.6	(62.0)

experiment that although easily measurable charges of the usual sign could be obtained by pressing the two surfaces together, without sliding friction, the amount of the electrification produced in this manner, with pressures estimated at 75 kg per cm^2, was only 15 per cent of the maximum. With the exception of ebonite, all the specimens were provided with optically flat surfaces. The ebonite disks, however, became polished when wrung upon a flat surface of steel, so that after an experiment it was easy to estimate the area of actual contact by observing the reflection of light from the surface. The results of several experiments with ebonite disks of different sizes were consistent in such a degree that the value of the ebonite-steel coefficient may be considered quite as reliable as any of the other results. The dielectric constants of fluorite[13] and quartz[14] were taken from published tables, values corresponding to a field in the direction of the optic axis being selected because the flat face of each disk was perpendicular to the axis; and the dielectric constants of flint glass, crown glass, and ebonite were determined directly by measuring larger blocks from which the disks were cut. The constant C is given by the equation

$$Q_{12} = C(K_1 - K_2),$$

where K_1 and K_2 are the dielectric constants of specimens No. 1 and No. 2, respectively. This equation is an expression of Coehn's law, and

[13] Curtis, Phys. Rev. **34**, p. 155, 1912.
[14] Constantes Physiques, Soc. Franc. de Phys., p. 561, 1913.

the agreement among the different values of C is a measure of the extent to which the law has been verified for the materials examined. The dielectric constant 3.1 is assigned to steel as the value giving the most concordant results for C.

The direction of the effect is seen to be consistent with the view that the larger values of K are associated with substances in which the electrons can the more readily be displaced, for C was positive in every case; and the numerical agreement among the different values of C, while not excellent, is sufficiently good to show that the dielectric constant is the important factor in determining the contact effect. Ebonite is an exception, showing no agreement with Coehn's law except so far as the sign is concerned. In all probability the effect depends on $K-1$ rather than K, since $K-1$ measures the difference which may in general be produced by substituting a dielectric medium for free space, and this quantity, of course, satisfies the equation equally as well as K. For the present no attempt is made to interpret the significance of the fact that steel enters the contact series exactly as if it were an insulator having a dielectric constant of 3.1; for an interpretation of this phenomenon should be based upon concordant results for a series of metals, whereas the present type of experiment did not yield sufficiently consistent results to show a definite difference when a nickel disk was substituted for steel. There are other grounds, however, for believing that the dielectric constants of the metals are not infinite, notably the fact[15] that induction takes place freely through very thin metallic films; and Sanford has found,[16] furthermore, that the tribo-electric series contains the insulators in the order of their dielectric constants, the metals being distributed among them in places for which the dielectric constants should be of the order of 4. It is well known that the dielectric constants of many inferior conductors can be measured with rapidly alternating fields, although the conductivity may be so great that static or low-frequency methods are of no avail; and the most recent determination[17] of the dielectric constant of mercury vapor shows that a uniform distribution of fine metallic particles does not greatly increase the dielectric constant of a non-conducting medium. Indeed, the fact that a metallic shield of sufficient thickness furnishes electrostatic protection need not be interpreted to mean that the metal suffers a complete polarization in the Maxwellian sense; for we may consider that the motion of the free electrons masks whatever displacement of

[15] Miss Hyatt, Phys. Rev. **35**, p. 337, 1912.
[16] Sanford, Phys. Rev. **12**, p. 130, 1918.
[17] Bedeau, Comptes Rendus, **175**, p. 147, 1922.

the bound electrons there may be. The results of the present experiments furnish ample ground for the belief that determinations of the characteristic coefficients of a greater variety of materials than those here studied, including substances which are incapable of retaining optically plane surfaces, may be expected to bear significantly on the magnitude of the dielectric constants of the metals.

Effect of Compressing Amorphous Dielectrics

It is well known that compressible dielectrics can be strongly electrified by pressing them against hard substances. This effect, in common with others which have been classified as tribo-electric, has quite generally been regarded as one of the voltaic phenomena. The results which have already been described in this paper, while in no wise proving the truth of this assumption, suggest at once the importance of putting it to the test of experiment. This has been done; and the coefficients of the effect, for a variety of different materials, are recorded in Table IV. The two compressible materials, para rubber and a rubber compound known commercially as pure sheet, were selected because of the large difference of their dielectric constants. These were found to be 2.94 and 3.96, in the order named. Circular sheets of the rubber, 1.6 mm thick, were mounted on flat steel disks, thoroughly cleaned with sandpaper and alcohol, and then placed in contact with various surfaces under pressures ranging from 0.5 to 5 kg per cm^2. As the pressure was

Table IV

Charge on rubber in contact with	Charge (e. s. u./$cm.^2$)	
	On pure sheet	On para
steel	−21.7	−17.2
shellac	−21.1	−15.5
flint glass	−19.4	−16.1
ebonite	−20.3	−18.6
mica	−18.9	−15.3
crown glass	−19.2	−16.7
lead	−19.7	−17.0
para rubber	± 8.	± 5.

increased to 2 kg/cm^2, the charge rose to a maximum, and then remained constant for pressures up to 5 kg/cm^2. The quantities recorded in the table are the mean values of this maximum charge. Except when the two kinds of rubber were pressed against each other, the charge of the rubber was negative in every case. The results show that although the dielectric constants of the hard substances ranged from 2.8 for ebonite to 7.8 for flint glass, the charge of the compressible material remained approximately independent, both in sign and in magnitude, of the nature of the material against which it was pressed. Since an electrification of this sort cannot be entirely a Volta effect, we may conclude that the greater portion of it is due either to the distortion of the surface of the compressible dielectric or to an internal distortion like that which produces the phenomenon of piezo-electricity. The second hypothesis does not seem probable; for, although the pure sheet contained a certain amount of crystalline sulphur, the para contained very little, if any; and inasmuch as the electrification is approximately 2000 times as large as that which is always associated with the formation of a new surface of a liquid,[18] the distortion of the surface does not seem adequate to account for the whole of the effect. There is nothing in the results, however, to preclude the possibility that a hitherto undescribed effect of compressing an amorphous material occurs in a degree large enough to mask both the surface and the Volta effects.

Effect of Collision

In a recent paper[5] it has been shown that a solid dielectric acquires a perfectly definite charge whenever it collides with a metal, provided the relative velocity of the two bodies exceeds a certain minimum value at the moment of contact. The quantity of electric energy produced in this manner was found to be independent of the amount of mechanical energy lost during the collision, and the conclusion was therefore drawn that electrification by impact is the true Volta effect of the colliding materials. The results of the present experiments, however, considered together with the data of electrification by collision, show that the latter can be due only in part to an intrinsic difference of potential. In particular, quartz, flint glass, crown glass, fluorite, calcite, ivory, and ebonite are all *negatively* charged by collision with steel, brass, or zinc; whereas the results given in Table III prove that the first four of these materials are consistently *positive* to steel in the true contact series. Here are four pairs of substances for which the effects of contact and collision, respectively, are oppositely directed. The difference of sign cannot be considered to prove that impact does not give rise to the Volta effect; for the results given in the earlier portions of this article show clearly that the collision of a polished glass sphere and a metal, at a relative velocity of 200 to 250 cm per sec., may be expected to produce a sufficiently intimate contact to establish the characteristic voltaic charge. We must therefore conclude that collision gives rise to two different effects, one of which is the contact electrification, while

[18] Nolan and Enright, Roy. Dublin Soc., Proc. **17**, p. 1, 1922.

the other is a transfer of electrons from the metal to the dielectric, due to the inertia of the mobile electrons. In the cases referred to here, the second of these effects was not only greater than the characteristic contact charge, but also approximately 200 times as large as the well known inertia effect discovered by Tolman and Stewart.[19] There is no conflict, however, with their results, for the rate of change of momentum occurring at the instant when an elastic sphere collides with a massive metal body, after having been projected vertically upwards with a moderately large velocity, is much greater than that which Tolman was able to produce in bringing his moving conductor to rest; and furthermore, the rate of change of momentum in the latter case was not important so long as the velocity was reduced to zero in a time sufficiently small to satisfy the requirement that the galvanometer used to detect the inertial effect should operate ballistically.

The discovery of the importance of the relative velocity of two bodies in determining the contact electrification shows that the e.m.f. of a voltaic cell may be expected to vary with the acceleration of the electrodes, as Professor Kleeman has recently suggested,[20] although his theory of the transition layer does not seem necessary to account for such an effect. The so-called anomalous behavior of mercury,[1] which becomes positively charged when struck with glass but negatively when rubbed with the same material, is also easily seen to be in accord with the present results; and numerous other discrepancies, usually attributed to the contamination of the surfaces of contact, may now be referred to the failure of experimenters to distinguish among the different electrifications which are due, respectively, to collision, to compression, and to the voltaic difference of potential. More accurate determinations of the constants of these effects, for a larger variety of materials, may be expected not only to furnish a single contact theory which will include both the metals and the dielectrics, but also to shed a good deal of light on the structural differences of these two kinds of matter.

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[19] Tolman and Stewart, Phys. Rev. **8**, p. 97, 1916; also **9**, p. 164, 1917.
[20] Kleeman, Phys. Rev. **20**, p. 174, 1922.