Some possible chemical contributions towards the formation of the atmospheric electric charge[1]

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ABSTRACT

Laboratory experiments show that some solid particles which occur in the atmosphere can act as strong electron emitters when irradiated with visible light, while other substances, because of their chemical composition, can assume substantial negative electric charges. Implications resulting from these effects are discussed.

1. Introduction

It was recently pointed out (PAPÉE, 1959, 1962) that sodium chloride aerosol particles may, under some circumstances, acquire strong photoelectron emitting properties which are probably associated with formation of lattice defects and consequently of shallow electron traps on the surface of the salt. This has been confirmed by the work of KRAMER (1960) and SEIDL (1960), while a more recent contribution (PAPÉE and PETRICONI, 1962) suggests that formation of surface defects, which may involve electron trapping on halide surfaces (cf. OKHURA, 1961), does not necessarily require high energy radiation or electrical discharges, but may occur in nature by friction on or fragmentation of dry NaCl aerosol particles.

We have recently found that:

(i) strong photoelectric emission of electrons from "strained" sodium chloride particles can easily be detected by illumination of such salts with visible light, which in the presence of an electric field leads to a ready separation of charge;

(ii) some reducing compounds, like soluble ferrous salts, solutions of H_2S, etc., which are known to be present in the atmosphere, readily assume negative electric charges when falling through air under suitable illumination, possibly as a result of a step involving preferential capture of negatively charged oxydizing ions (such as, for example, O^-, O_2^-, NO_2^-, etc.) and consequent oxydative colloid precipitation within a particle.

It is thought that this effect may, under circumstances otherwise suitable, modify local values of the atmospheric electric field.

It is the object of this contribution to present data which illustrate semi-quantitatively the photoelectric effects quoted, as well as to report on the relative orders of magnitude of charges on individual particles or drops of solution containing suitable reducing agents.

2. Experimental procedure and qualitative observations

(*a*) DEFECT SODIUM CHLORIDE

Monodisperse sodium chloride particles of known size were prepared and their dimensions measured using a method recently described (PAPÉE and PETRICONI, 1962). Lattice defects were subsequently induced into the product by means of a procedure previously applied by one of us (PAPÉE, 1959*a*) but with a small modification consisting of the use of an electro magnetic vibrator instead of an electrical motor drive to mix the sample; this improvement enabled the evolved chlorine to be pumped off continuously. A 25 Mc oscillator working at a peak to peak voltage of about 2. kV and with a controlled output of 200 watts, was used to excite the discharge tube. The blue coloration,

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characteristic of sodium chloride which contains Na-colloids, appeared almost immediately; the discharge treatment was continued until a uniform coloration of the particles was achieved, as revealed by microscopic examination. The substance obtained was then introduced into a glass tube, which was provided at the bottom with a narrow orifice made of thick capillary tubing; the tube was suspended centrally above two 20×20 cm vertical aluminium plates. A potential gradient of 625 volts $\times$ cm^{-1} was then formed in the gap between the plates using a stabilized, D.C. high voltage supply with a 200 μF capacitor system in parallel. The voltage applied on the plates was monitored by means of a sensitive electrostatic multirange high voltage measuring instrument (R. Schroeder, Aachen, Germany, Manufacturers). A quartz-lens collimated beam of a Zeiss HBO-200 stabilized high pressure mercury lamp of about 600 W input power, illuminated the gap. The lamp could be fitted with interference band filters (made by Schott Co., Mainz, Germany) which enabled a subdivision of the light into 12 almost "equidistant" monochromatic sectors covering the 300–700 mμ interval. The full, unfiltered light beam of the Zeiss ultraviolet lamp, placed at 1.5 m from the dispenser, was made to envelop the charged plates exactly and to illuminate the gap uniformly by causing the light to pass through a fritted quartz disk homogenizer. The illumination provided was sufficient for photography with a 20 ASA fine grain film. Uniform trickling of the fine powder into the gap between the high voltage plates was achieved by vibrating the salt container electromagnetically. It was observed that the stream of salt particles was abruptly displaced towards the *negative* plate as soon as it fell into the illuminating beam of the mercury lamp. The second part of Fig. 1 shows the effect described; the same phenomenon (although of course less pronounced) was observed when filters, transparent to wavelengths shorter than about 520 mμ, were introduced across the beam of light. No effect could be noticed using light of wavelengths above 550 mμ, the path of the falling particles appearing generally straight, except for a normal symmetrical widening of the "plume".

The experiments described above confirmed previous observations (PAPÉE, 1959*a*) concerning the stability of the defect sodium chloride particles, and showed that the same can be said about their photoelectric properties. Thus, a sample of the "blue" NaCl which passed through an A.S.T.M. standard sieve of 270 mesh $\times$ inch^{-1} retained its colour and photoelectric properties for about 4 weeks of exposure to room atmosphere at about 20°C and 60 ± 10 degrees of relative humidity. It was observed, however, that the photoelectric effect seemed to be "poisoned out" by traces of nitrous ($NO_2 + NO$) and H_2S fumes, although no apparent change in the coloration of the product resulted as a consequence of such contamination.

As expected, similar although much smaller electric effects were shown by sodium chloride which was mechanically ground to a fine powder in an atmosphere of dry air (cf. PAPÉE and PETRICONI, 1962).

(*b*) SALTS AND SOLUTIONS CONTAINING H_2S AND POLYSULPHIDES

Oxydative precipitation of sulphur from solutions of hydrogen sulphide (see, for example, REMY, 1960) results in formation of colloids which carry negative electrical charges (WEISER, 1950; ALEXANDER and JOHNSON, 1950). On the other hand, it is well known that elementary sulphur has the property of assuming strong negative electrostatic charges by friction (see REMY, loc. cit. p. 700; and GREEN and LANE, 1957). Although the exact mechanism of this charge formation is still under discussion (ALEXANDER and JOHNSON, 1950), it is not surprising that *negative* electrification of both: (i) sodium chloride particles which were charged with ammonium sulphide; and (ii) drops of solution of sodium sulphide (or polysulphide), ammonium sulphides, or aqueous saturated solutions of hydrogen sulphide, may occur during their free fall through air under suitable illumination.

The sodium chloride particles mentioned above were prepared by mechanical grinding of reagent purity salt under nitrogen with 5% of its weight in sodium sulphide which was dissolved in as little distilled water as possible. The wet, ground paste was desiccated by heating to 160°C in a flow of nitrogen, whereupon it was re-ground until it passed through an A.S.T.M. sieve of 270 mesh $\times$ inch^{-1} and was then separated into monodisperse fractions by centrifuging (PAPÉE and PETRICONI, 1962). The

size of the particles was estimated microscopically. Testing of particles for electrical charge was carried out in the same way as for defect NaCl.

Drops of the saturated aqueous solution of hydrogen sulphide were dispensed from a Pyrex glass tube which was fitted with a stopcock and ended with a narrow orifice made of drawn glass. The shape of the drops, which were made to fall centrally between the plates, was assumed for simplicity to be spherical, and their dimensions were obtained by mechanical counting and subsequent weighing of the collected liquid. The trajectories of the substances falling between the charged plates were evaluated by photography through a cathetometer telescope and examination of negative under an enlarger. An automatic 16 mm Ga-Mi. camera (Officine Galileo, Milan, Manufacturers) was used for photography; eight photographs were taken for each particle fraction of both salts examined and droplet size category; care was taken to reverse the polarities of the condenser plates after every photograph of the series. Deviations of the droplets of water saturated with H_2S from a vertical line of fall are shown in the first part of Fig. 1.

3. Approximate determination of the electric charge on particles and drops

The order of magnitude of the electric charge on a particle or drop which falls under gravity and in a horizontal electric field, can be estimated according to the general principle met in the work of KUNKEL and HANSEN (1950). If the distance of the particle or drop, considered from its point of entry into the electric field, is taken to be the product of their vertical and horizontal terminal velocities with time, then it can be shown that:

$$l_v = \frac{d^2 \mathcal{E} g}{18\mu} t \qquad (1)$$

and

$$l_h = \frac{qE}{3\pi\mu d} t, \qquad (2)$$

where the following symbols and units are used:

l_v: vertical component in centimeters (at time t) of the distance of fall from the orifice of the container; this orifice is situated centrally between the charged plates and level with their upper edge;

l_h: horizontal component at the same position as defined for values of l_v;

d: Stokes diameter of particles or drops falling (cm);

$\mathcal{E}$: density of salt or solution, which is taken to be here 2.16 and 1.00 g × cm^{-3} respectively;

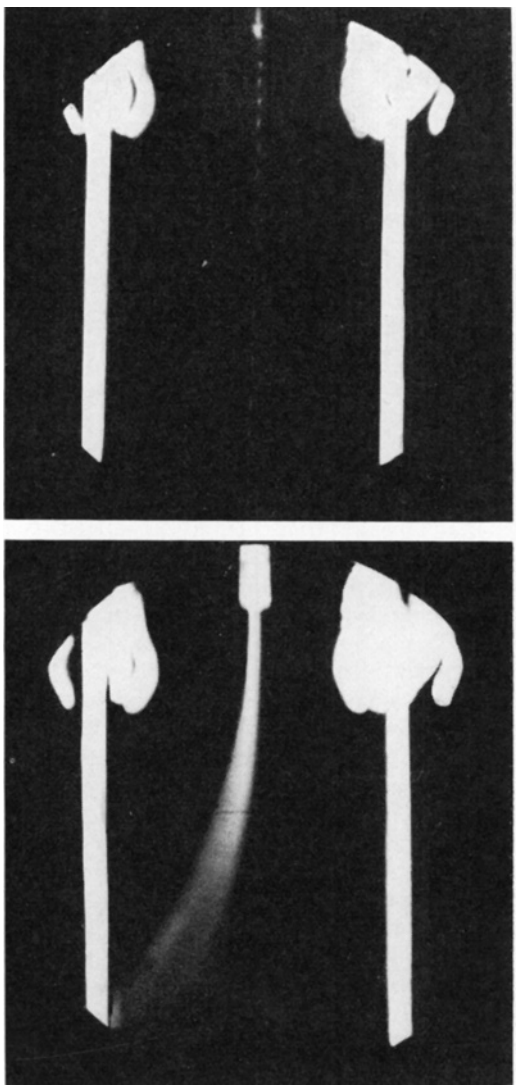

FIG. 1. Paths of fall of particles between charged plates: (*a*) drops of saturated aqueous solution of hydrogen sulphide; (*b*) monodisperse sodium chloride defect particles. Photographs were made through cathetometer telescope.

g: acceleration due to gravity, taken as 980 cm × sec^{-2};
μ: viscosity of the air, taken as 185×10^{-6} poise;
t: time, seconds;
E: electrical field, CGS units; this parameter was kept constant throughout the experiments at 2.08 volts × cm^{-1};
q: charge on particle, CGS units.

(a) Drops of saturated aqueous solution of hydrogen sulphide

A marked displacement of the particles towards the *positive* plate, indicating development of a *negative* charge on the falling drops, is observed when the solution is made to fall between the electrodes, and although careful examination of the path followed by these drops indicates a slightly parabolic curvature suggesting increase of the average charge per drop during fall, this deviation from a straight line of fall appears here to be within the limits of error. Since the evaluation of only an approximate measure of the total charge on the drops is sought in this preliminary investigation, the trajectory of fall recorded photographically will be taken here as a straight line between the upper and the lower extreme of the visual field. This is equivalent to considering the charge on the drops as being approximately constant, so that eq. (1) and (2) hence become after elimination of t:

$$l_v = \frac{\mathcal{E} g \pi d^3}{6qE} l_h. \tag{3}$$

The charge q can therefore be calculated from the gradient of a plot of l_v vs. l_h; the results obtained, allowing for a possible error of 10% in the diameter of the drops, are shown in Table 1.

Table 1.

	Diam. of drop, mm	q, esu
	3.6 ± 0.4	-0.37 ± 0.1
	4.1 ± 0.4	-0.57 ± 0.2
	4.2 ± 0.4	-0.75 ± 0.2
Average of values obtained and mean square error	4.0 ± 0.4	-0.56 ± 0.2

(b) Sodium chloride particles containing sodium sulphide

The trajectory of the particle stream is found to deviate substantially here from a straight line, suggesting increase of (negative) electric charge on the solid during its fall through the air. It can be expected that if adsorption of water on the surface of the solid followed by preferential capture of negative ions, oxidative hydrolysis and consequent precipitation of colloids is the cause of charge formation, the extent of electrification of a particle will be approximately proportional under our experimental conditions both to its surface and time of flight as indicated by the equation below:

$$q_t = q_0 + \alpha \pi d^2 t. \tag{4}$$

Combination of eqs. (1), (2) and (4) yields:

$$l_v = \frac{\mathcal{E}^2 g^2}{108 E \mu \alpha} d^3 \frac{l_h}{l_v} - \frac{q_0 \mathcal{E} g}{18 \pi \mu \alpha}. \tag{5}$$

Eq. (5) enables an estimation of both α and q_0 to be carried out by calculation of regression parameters of the plot of l_v against l_h/l_v. The results obtained for the four fractions considered, and computed on the basis of an average of eight median trajectories per fraction, are summarized in Fig. 2, where gradients according to the regression quoted above are plotted against the cube of the diameter. The constant α, the rate of formation of the electric charge per unit surface, can be obtained from the slope of the plot in Fig. 2 and is found to be:

$$\alpha = 0.09_4 \pm 0.003 \text{ esu} \times \text{sec}^{-1} \times \text{cm}^{-2}$$

for the system studied here.

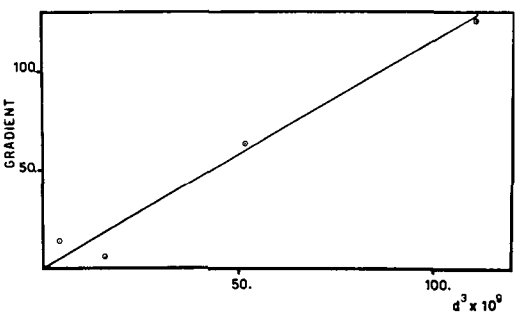

Fig. 2. NaCl–$(NH_4)_2S$ particles. Plot of gradients of the relation l_v vs. l_h/l_v, against the cube of the particle diameter (in centimeters). Least squares line is made to pass through origin.

It is clear that a substantial error may arise here from the fact that diameters of particles, which are estimated microscopically, will differ from the Stokes' diameter in eq. (5). Therefore, only a rather approximate calculation of the order of magnitude of the electrical charge which a particle has attained at the level of the lower edge of the charged plates, can be made. The particle diameters of the four monodisperse fractions examined, and the constants q_0 obtained from intercepts of a plot according to eq. (5), are given in Table 2.

TABLE 2.

	Diameter of particles, μ	$q_0 \times 10^6$ esu
	$1_{6.2} \pm 2$	$+0.43 \pm 0.13$
	$2_{5.1} \pm 2$	-0.11 ± 0.15
	$3_{7.2} \pm 4$	-0.20 ± 0.20
	$4_{8.0} \pm 5$	$+0.59 \pm 0.52$
Average and mean square error	$3_{1.6} \pm 3.5$	$+0.18 \pm 0.30$

Thus, for example, according to eq. (1), a particle of 32 μ in diameter will require 3.0 sec to fall 20 cm along the vertical component, and its charge generated at the end of its trajectory between the condenser plates and measured under the experimental conditions described will be given according to eq. (4) by

$$q \approx -8.7 \times 10^{-6} \text{ esu.}$$

As previously stated, this result gives a very approximate and tentative order of magnitude of the phenomenon studied; it is therefore proposed to carry out in the future a closer systematic investigation of this problem, under more controlled chemical conditions.

(c) Sodium chloride containing lattice defects and surface colloids

The deviation from a vertical line of fall is, under the conditions described, rather abrupt in the case of particles of NaCl which were treated in electric discharges, suggesting relatively large emission of photoelectrons. It may be thought here, that the rate of electrical charging of a particle illuminated with constant intensity, will be approximately proportional to the area of a circle of diameter corresponding to that of the particle; it can furthermore be thought that this initial rate of charging will be reduced as the charge increases, by a term directly proportional to the charge itself, and inversely to the radius of the particle.

Therefore

$$\frac{dq}{dt} = \alpha\pi \frac{d^2}{2} - 2\frac{\beta}{d} q. \tag{6}$$

Since monodisperse powders of uniform sodium content per unit surface are used in each experiment, eq. (6) can be integrated and becomes, under the conditions such that:

$$t = 0 \quad \text{when} \quad q = q_0,$$

$$t = \frac{d}{2\beta} \log_e \left\{ \frac{\frac{\alpha\pi}{4\beta} d^3 - q}{\frac{\alpha\pi}{4\beta} d^3 - q_0} \right\}. \tag{7}$$

Resolution of eq. (3) with respect to q, and substitution into eq. (7), followed by substitution of the function of the parameter t thus obtained into eq. (1) and rearrangement, yields:

$$l_v = \frac{d^3 \mathcal{E} g}{36 \mu \beta} \log_e \left\{ \frac{1 - \frac{4\beta \mathcal{E} g}{\alpha 6 E} \frac{l_h}{l_v}}{1 - \frac{4\beta q_0}{\alpha\pi d^3}} \right\}. \tag{8}$$

The highest value permitted by the corona limit, of an electrostatic charge on a spherical particle of about 10^{-3} cm in diameter, is of the order of 5×10^{-5} esu. If the second term of eq. (6) is to have any bearing on our measurements, then it should not be substantially smaller than about 10% of the first term. Hence the order of magnitude of β/α can be obtained; and if q_0 is taken to be of the order of 1% of the corona limit, it is found that the quantity

$$\frac{4\beta q_0}{\alpha\pi d^3}$$

is negligible with respect to unity. For the same reason the expression

$$\frac{4\beta \mathcal{E} g}{\alpha 6 E} \frac{l_h}{l_v}$$

is found to be but a small fraction of unity; this permits a series expansion of the logarithm in

eq. (8) to be carried out to two terms. Eq. (8) thus becomes:

$$\frac{l_v^2}{l_h}\frac{1}{d^3} = \frac{1}{162}\frac{g^3\mathcal{E}^3\beta^3}{\mu E^2\alpha^2}\frac{l_h}{l_v} + \frac{\mathcal{E}^2 g^2}{54\mu E\alpha}. \qquad (8')$$

Analysis of the experimental data according to a plot of:

$$\frac{l_v^2}{l_h}\frac{1}{d^3} \quad \text{vs.} \quad \frac{l_h}{l_v}$$

indicates in our case a fairly constant distribution of values suggesting that the constant β is small and that the term of eq. (8') in which β appears may be neglected. This allows the equation to be put in its final form:

$$l_v = \frac{\mathcal{E}^2 g^2}{53\mu E}\frac{1}{\alpha}d^3\frac{l_h}{l_v}, \qquad (9)$$

which is substantially very similar to eq. (5), with the difference that the constant term is omitted here. The constant α can thus be evaluated according to the method previously outlined; Fig. 3 shows calculated regression gradients of l_v vs. l_h/l_v which are plotted against the cube of the diameter of particles of the four monodisperse fractions studied. α is hence obtained from the slope; for our particular conditions of illumination (about $10^{15} - 10^{16}$ quanta $\times$ cm^{-2} $\times$ min^{-1}) which are of the order of magnitude of the intensity of sunlight on a clear day, the value obtained is:

$$\alpha = 1.1_4 \pm 0.01 \text{ esu.} \times \text{sec}^{-1} \times \text{cm}^{-2}.$$

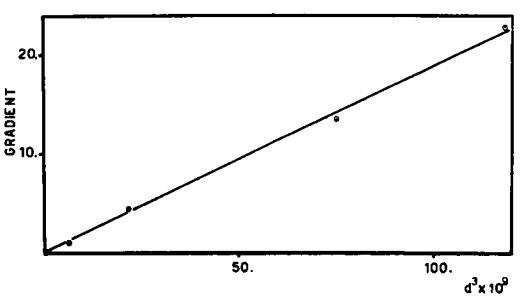

FIG. 3. "Blue" NaCl particles. Plot of gradients of the relation l_v vs. l_h/l_v, against the cube of the particle diameter (in cm). Least squares line is made to pass through origin.

Since the diameters of particles forming the four monodisperse fractions studied as are shown in Table 3 it follows that at the end of a 20 cm vertical trajectory a defect particle of the type investigated and having a diameter of 34 μ, will bear a charge of

$$q \approx +6 \times 10^{-5} \text{ esu.}$$

TABLE 3.

	Diameter of particles, μ
	18.6 ± 2
	27.9 ± 3
	42.2 ± 4
	49.0 ± 5
Average and mean square error	34.4 ± 4

In fact, eq. (7) rearranges to:

$$q = \frac{\alpha\pi d^3}{4\beta}\left(1 - \exp\left[\frac{-2\beta}{d}t\right]\right) + q_0 \exp\left[\frac{-2\beta}{d}t\right]. \qquad (7')$$

Since q_0 is very small with respect to q, and since β is small, the second term of eq. (7') can be neglected and the exponential in the first term expanded in series to two terms; hence

$$q = \tfrac{1}{2}\alpha\pi d^2 t, \qquad (10)$$

and the evaluation of the charge at time t is carried out in the same way as in the case of particles contaminated with sulphidic material.

In dry air and on a spherical particle, this value would be close to the corona limit (cf. TWOMEY, 1956); since, however, during the process of grinding large amounts of imperfections in the shape of particles will be formed, it can be safely assumed that the substance studied becomes photoelectrically charged to that limit almost instantaneously under the present experimental conditions.

A small modification of eq. (6) and following expressions, permits a correction for the number of defects per unit surface to be introduced into the general pattern of computations. An evaluation of this type, which was based on corrections for surface nonstoichiometry, as obtained by means of pH measurements, led, however, to non-systematic dispersions of experimental values. It was hence tentatively concluded that the outer crystalline strata of the particles had in all cases a structure saturated towards their electron-emitting power, and that exces-

sive treatment in the discharge tube has provoked changes in deeper strata of the crystalline lattice, from which photoelectrons could not as readily be emitted.

4. Discussion and concluding remarks

The experiments reported here strongly indicate that a generation and separation of electric charge may readily occur in the atmosphere due to chemical phenomena such as described above and be dependent on the type of particles involved.

(*a*) Dry particles of sodium chloride aerosol of *low mobility*, and carrying surface defects induced by electrical discharges and/or short wave radiation, will readily become positively charged when illuminated with shorter components of the visible spectrum, because of the photoelectric effect on colloids in the salt (PAPÉE and SMITH, 1959), or on lattice vacancies contained on the surface (SZAYNOK, 1960). It is clear that the exo-electrons emitted will promptly be captured by the *highly mobile* gas molecules surrounding the particle of aerosol, and that under suitable conditions this may contribute to the separation of atmospheric electric charge.

(*b*) Sparsely mobile aerosols containing mixtures of other compounds which commonly occur in the atmosphere (H_2S, sulphides, thiosulphates, etc.) may develop during their fall through air negative charges, probably due to preferential capture of negative oxidizing ions and consequent oxidative precipitation of colloids on the surface of the particles (or drops); this may again lead to a separation of charge, in line with the behaviour quoted under point (*a*).

(*c*) Changes in illumination, oxidation, photo-oxidation, and surface sintering due to humidity, as well as mixing of air masses which carry "electrically active" NaCl particles with masses containing promoters (ETZEL and PATTERSON, 1958) or inhibitors of the electrical activity (oxides of nitrogen, H_2S, etc.) of the aerosol, may again lead to detectable changes in the charge of an aerosol-containing air cell.

The data presented appear to compare in an interesting way with some recent work of MUHLEISEN (1959) which points towards large differences observed during measurements of the atmospheric electric field, according to whether an air mass moves from the sea or land, or according to illumination (cf. MUHLEISEN, 1961). This paper shows, in fact, that apart from a possible role of electrical atmospheric charges which could arise, for example, from spray effects (BLANCHARD, 1958), icing, etc., simple *chemical processes* can act on aerosol particles, and may result in measurable fluctuations of atmospheric electricity, according to the composition and properties of the many types of airborne particles and the physico-chemical conditions acting upon them.

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