On the causal relation between nitrogen-oxygen compounds in the troposphere and atmospheric electricity[1]

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ABSTRACT

An atmospheric feedback process is tentatively presented as a possible explanation of the rapid increase of charge densities and field strengths in thunderstorms. This process requires fulfillment of two conditions, viz.: (*a*) Appreciable amounts of nitrous gases are formed inside the cloud by electrical discharges (mainly by silent ones), thereby increasing the NO_3^- ion concentration in precipitation particles; (*b*) When ice crystals break up into pieces, electrical charge separation occurs to an extent depending on the abundance and the distribution of NO_3^- ions inside the crystals.

Field observations: Statistical analysis of NO_3^- concentration data from precipitation sampling simultaneously conducted at 700, 1 800 and 3 000 m a.s.l. throughout a five-year period established a definite increase of NO_3^- abundance with increasing in-cloud turbulence and electrical activity. At 3 000 m, a direct correlation between NO_3^- concentration in precipitation and the time integral of electrical field strength at 3 000 m was found. The NO_3^- ion concentration in precipitation was not affected by the number of lightning discharges. Evidently, the combined effect of all corona discharges on or between precipitation particles or cloud droplets determines the increase of NO_3^- ion concentration in precipitation.

Laboratory measurements. The ion concentration gradient in ice particles prior to fragmentation determines the amount of electrical charge carried by the individual fragments of such particles. The amount of negative charge in a fragment is the greater, the higher its NO_3^- ion concentration is. Where the distribution of NO_3^- ions throughout the crystals is homogeneous, no charge separation occurs. These results may explain both the rapid increase and the subsequent collapse of the electrical activity in individual thunderstorm cells, besides clarifying the processes involved in the formation of the principal space-charge zones of a typical thundercloud. Water drops were dropped onto a rapidly rotating ice sphere, and the droplets thrown off by centrifugal force collected on a surrounding electrode; the charge accumulated on the latter was measured. An investigation of the effect of NO_3^- in the water produced the following result: the charge increases up to a maximum as NO_3^- concentration is increased from below 0.002 to 0.2 γ NO_3^- ions/cm^3, but declines when the latter level is passed. The charge separation caused by collisions of ice particles with raindrops in the lower layers of a thunderstorm or shower cloud are thus seen to be affected by the NO_3^- content of precipitation.

1. Introduction

The last 15 years have seen ever-increasing effort toward clarification of the physical processes involved in the electrification of thunderstorm clouds, and repeated attempts have been made to determine the electricity "budget" of a typical thunderstorm. On reviewing the results of this research as presented at the last three international symposia (Smith, 1959; Coroniti, 1965, 1969), we must conclude that we are, as of now, unable to budget for thunderstorm electricity; moreover, we must concede that we cannot identify the most effective mechanisms of thunderstorm electrification. There will always be several electrifying mechanisms working simultaneously in any given thundercloud, and some of these will play a major part in starting, others in continuing and/or maintaining the space-charge build-up. The processes involved in a given storm, and their succession in time and their relative importance will depend on weather and/or climatic factors.

We still do not know mechanisms that could be invoked to explain the explosive growth of

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cloud charge or the sudden cessation of electrical activity often associated with a thunderstorm cell. This explanation gap exists both for the qualitative and the quantitative aspect of the problem. This situation justifies us in pointing to a mechanism that has gone largely unregarded up to now, although we have taken it into consideration for roughly the last ten years: the process in question does, in fact, fulfill the requirements for a cloud electrification mechanism to a remarkable extent.

2. A re-evaluation of the role of impurities in ice and water with respect to generation of electrical charge

The effect of traces of different inorganic compounds dissolved or enclosed in, or adsorbed on, precipitation particles impinging on one another in or below clouds has been regarded for some years as an important phenomenon in thundercloud electrification. The scope of this Report is too limited to permit discussion of the considerable volume of research done in this field; we may, therefore, restrict ourselves to selected references: (Workman & Reynolds, 1950; Reynolds, 1955; Reynolds, Brook & Gourley, 1955; Workman, 1963, 1967, 1968*a*, *b*). The latest laboratory measurements reported by Workman indicate that ammonium compounds are especially active agents involved in charge separation on physical contact of precipitation particles, especially in the case of supercooled water drops impinging on "cold", i.e. non-melting atmospheric ice.

This thunderstorm electrification mechanism does, however, depend on the amount of inorganic—especially ammonium—compounds stored in the troposphere; the impurities may be present as gases or as adsorbed or enclosed matter in or on particles. In either case, their total amount is subject to appreciable washout (cf. Sect. 6*a*), which in turn is a complex function of intensity, duration and other characteristics (e.g., type, particle-size distribution and time history) of the precipitation concerned (cf. Reiter & Carnuth, 1965; Georgii & Weber, 1964; Georgii & Beilke, 1966; Reiter & Carnuth, 1969). Hence, intense precipitation from thunderclouds—especially of the tropical type with several hours' uninterrupted intense rainfall—must cause very considerable depletion of the stock of anorganic material needed for electrification, and thus must lead to enforced cessation of the electrical activity initiated and maintained by the substances in question.

Early experience gathered at our Institute gave some indications as to the nature of the interrelation between NO_2^- and NO_3^- abundances in precipitation and atmospheric electricity (Reiter & Reiter 1958; Reiter, 1960): the data were consistent with the existence of some "feedback" mechanism that reproduces both N–O compounds and electrical charge in a continuous manner, and sometimes leads to an explosive multiplication of the latter. This hypothesis presupposes catalysis of charge separation by N–O compounds; laboratory tests are necessary to prove that such catalysis exists before the proposed feedback mechanism may be considered as a real electrification factor.

3. The atmospheric electrical feedback mechanism

In earlier investigations we have shown (Reiter, 1958, 1960, 1964, 1966, 1968*a*, *b*; Reiter & Carnuth, 1965; Reiter & Reiter, 1958) that the NO_3^- ion content of precipitation at altitudes between 700 and 3000 m a.s.l. increases considerably as the meteorological turbulence, the vertical exchange coefficient and the electrical activity in the cloud space increase. From this and other experience we concluded that electric discharges occur on or between precipitation particles in turbulent cloud air (Malan, 1963; Sartor, 1963, 1964, 1967*a*, *b*, 1968 and others) whereby traces of nitrous gases subsequently dissolved in cloud droplets and precipitation particles are produced. A majority of NO_3^- ions (produced by quick oxidation of initially formed NO_2^-) may be finally found as a stable compound (for details see Reiter & Reiter, 1958; Reiter, 1964). Traces of NO_3^- ions in precipitation may (in agreement with investigations of the *Workmann–Reynolds–Brook* team) increase the amounts of charge separated upon fragmentation of solid precipitation particles or upon contact of ice particles with droplets. This increase of separated charges will in turn increase field strength in the space through which the precipitation is falling. This will further increase the concentration of nitrous gases wherever silent or visible electrical discharges occur. The nitrous gases will be absorbed by or incorporated into the precipitation particles,

thus raising the NO_3^- ion concentration. We are thus dealing with a cycle causing a continuous mutual enhancement of the electrical charges of both the cloud and the precipitation particles (Reiter & Reiter, 1958). This concept of a cyclic process seems especially promising as it includes the continual regeneration of the "catalyst", i.e. the nitrous gases and the NO_3^- ions in the precipitation particles.

4. Scope of this paper

The object of this paper is to present a review of the experience gathered on the interrelations between NO_3^- and NH_4^+ abundances in precipitation and meteorological conditions in the lower troposphere, including atmospheric-electrical activity; furthermore, to test the conclusiveness of any results by statistical analysis.

In addition, first results of direct measurements of nitrous trace gases in shower and thunderstorm clouds will be given, and pertinent laboratory experience applied to the problem of recognizing effects (if any) of N–O compounds on charge separation in precipitation particles.

The formulation of a theory of the processes affecting the precipitation particles as a result of N–O incorporation is beyond the scope of this study; the same may be said of deriving an electrical thunderstorm budget and an appropriate model of the feedback mechanism outlined above from the data.

We do intend to clarify beyond reasonable doubt whether the feedback mechanism described in Section 3 may be regarded as an important factor in thunderstorm electrification.

5. Field observations

This Institute comprises three nearby mountain stations, at which simultaneous recordings of all important atmospheric-electrical and meteorological parameters have been made for a considerable number of years. The frequency of precipitation samplings was adjusted to the intensity, type and time history of the precipitation concerned.

In Table 1, name and altitude of each station is listed, and the distance of each site from neighboring stations is given in km. The concentration of NH_4^+ and NO_3^- in precipitation is measured by means of a spectral photometer; Nessler's reagent is used for the former and a process devised by Pötzl & Reiter, 1960 employed for the latter. A superior degree of sensitivity and accuracy is thereby attained.

Table 1. *The stations*

Name	NO_3^- and NH_4^+ measurements since	Altitude m. a.s.l.	Horizontal distance from Station *G*, km
Garmisch-Partenkirchen, *G*	1956	740	0
Wank, *W*	1958	1780	3.5
Zugspitze, *Z*	1963	2964	12

6. Results of field studies

(a) Effect of rainfall quantity on NO_3^- and NH_4^+ concentration in precipitation

If an inorganic compound is to maintain the feedback mechanism, it may not be severely depleted by wash-out due to heavy rainfall from shower or thunderstorm clouds. Substances undergoing severe washout depletion and lacking sources in the free atmosphere must become less and less concentrated with increasing rainfall amount. This well-known relationship thus becomes a criterion for the effectiveness of a compound as a catalyst for cloud electrification. We have therefore scrutinized the correlation obtaining between the NH_4^+ or NO_3^- concentration on the one hand and the amount of rainfall on the other. The results are summarized in Tables 2 to 3.

It is readily seen from Table 2 that there is no significant correlation between rainfall amount and NO_3^- concentration as against altitude and type of precipitation. However, if all of the NO_3^- data for each station are combined without differentiating types of rainfall, a surprisingly significant *positive* correlation is found at all levels (example: Station G, NO_3^- see Fig. 6*a*). NH_4^+ ions are markedly different in this regard. Even when precipitation events are separated as to types, a *negative* correlation is invariably obtained (Table 3). If all types are combined, a significant *negative* correlation between concentration and rainfall amount is found, holding good at all levels. The regression lines evidencing this are shown in Fig. 6*a*.

Table 2. *Correlation of NO_3'-content in precipitation with precipitation amount*

Explanation of symbols: *G, W, Z* = Name of stations (cf. Table 1); r = correlation coefficient, r_z confidence limit of r (for $3 \times \sigma$); N = number of cases

Station	Precipitation type	r	r_z	N
W	●	−0.09	0.48	35
G	●	+0.12	0.35	71
Z	✳	+0.06	0.29	99
W	✳	−0.04	0.35	71
G	✳	+0.28	0.55	25
Z	▲ ●	−0.18	0.61	20
W	▲ ●	−0.09	0.30	95
G	▲ ●	+0.03	0.24	150
Z	✳ ▽	−0.04	0.23	184
W	✳ ▽	+1.10	0.29	109
G	✳ ▽	−0.09	0.39	55
Z	⊼	+0.28	0.30	95
W	⊼	−0.02	0.30	95
G	⊼	+0.09	0.30	96

Obviously, there is a marked contrast between NO_3' and NH_4' with regard to concentration as affected by the amount of precipitation per given event. NH_4' concentration declines as rainfall increases: this must be attributed to marked washout in the absence of regeneration. Hence, no ammonium source of any consequence can exist in an unpolluted atmosphere. Therefore, ammonium compounds need hardly be considered as possible factors in cloud electrification. Most of the ammonium compounds in precipitation is formed at ground sources by compustion and decomposition. Some of the N–O compounds must certainly be also washed out, but there must be an in-cloud source overcompensating such losses, as mean NO_3' concentration is seen to increase significantly with the quantity of precipitation. It must be borne in mind that an increase in mean the rainfall amount is a reflection of transition from steady to shower to thunderstorm precipitation. As will be shown below, reproduction of NO_3' is primarily a function of atmospheric instability.

Table 3. *Correlation of NH_4'-content of precipitation with precipitation amount*

Explanation of symbols: cf. Table 2. Regression line, cf. Fig. 6*a*

Station	Precipitation	r	r_z	N
W	●	−0.17	0.56	24
G	●	−0.25	0.42	47
Z	✳	−0.29	0.38	61
W	✳	−0.24	0.43	45
G	✳	−0.40	0.61	20
Z	✳ ▽	−0.65	0.74	12
W	✳ ▽	−0.33	0.36	65
G	✳ ▽	−0.33	0.29	107
Z	✳ ▽	−0.13	0.24	140
W	✳ ▽	−0.17	0.33	81
G	✳ ▽	−0.21	0.43	40
Z	⊼	−0.44	0.36	65
W	⊼	−0.33	0.37	62
G	⊼	−0.23	0.36	65

(b) *The correlation between NO_3' and NH_4' content in precipitation collected simultaneously at different altitudes*

If an intracloud source of the N–O compounds found in precipitation exists, there must be a strong intercorrelation of the amounts of such compounds found at different levels after ecah precipitation event. Fig. 6*b* proves that this proposition is well founded in fact: the said correlation is actually a strongly significant positive one. A similar study of NH_4' content also furnishes a statistically significant positive correlation (Table 4), but this is less marked than the NO_3' correlation. It may be surprising that a significant positive correlation can be found at all for NH_4', as washout studies indicate that no significant in-cloud ammonium sources exist; only the well-known ground sources of NH_4' can possibly be involved. The correlation as found must therefore be ascribed to vertical mixing; we will discuss this in Sect. 6*e*.

Table 4. *Correlation coefficients for NH_4'-contents in precipitation collected simultaneously at 2 stations*

Explanation of symbols: cf. Table 2

Stations	r	r_z	N
G/W	+0.34	0.17	280
G/Z	+0.29	0.17	279

(c) *Variation of NO_3' and NH_4' concentration in precipitates with height, as influenced by the type of precipitation*

As the source of nitrous compounds found in precipitation is located inside clouds, there can be no marked variation of NO_3' in precipitation

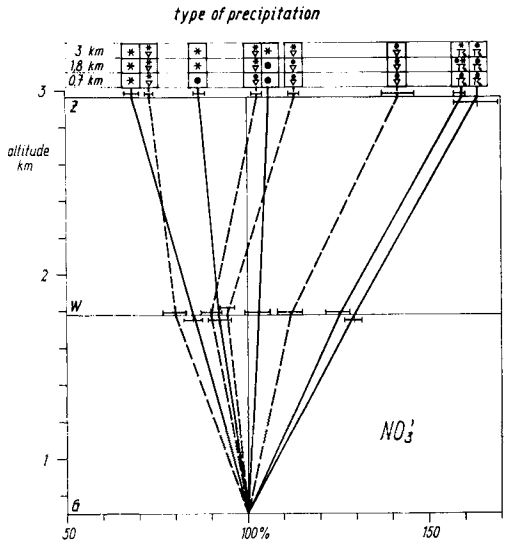

Fig. 1. Variation of NO_3' concentration in precipitation with height, as found from simultaneous measurements at three stations (Zugspitze *Z*, Wank *W*, Garmisch *G*), for different types of precipitation; statistical scatter of the averaged percentages H; (NO_3' conc. at $G = 100$ %).

with height, except for intracloud variations near active NO_3' source centers; such centers are probably very limited in extent, but may make themselves felt by producing exceptionally high NO_3' readings at mountain stations.

In Fig. 1, the variation of NO_3' concentration in precipitation is plotted in terms of valley station readings, the latter being equated to 100 %. The relative deviation of NO_3' concentration versus height was determined for each individual "event". Precipitation of the same type (cf. top of Fig. 1) was averaged as to NO_3' to obtain reliable data on the extent of relative variation with height. The scatter of the averaged NO_3' percentages is shown by the horizontal bars in Figs. 1 and 2. We can draw the following conclusions from Fig. 1: in steady precipitation, NO_3' concentration increases downward, especially where snow is concerned. In rain, concentration increases the less, the thicker the layer of rain involved. No increase in concentration shows up from a rain-layer thickness of 2 km on. This is readily understood, as the wash-out effect is greater in snow than in rain. However, there must be an increase of nitrous gas abundance downward, or an even distribution of such gases with height, if the thickness effect is to exist as observed. This condition would be fulfilled if primary sources of NO_3' are located near the ground.

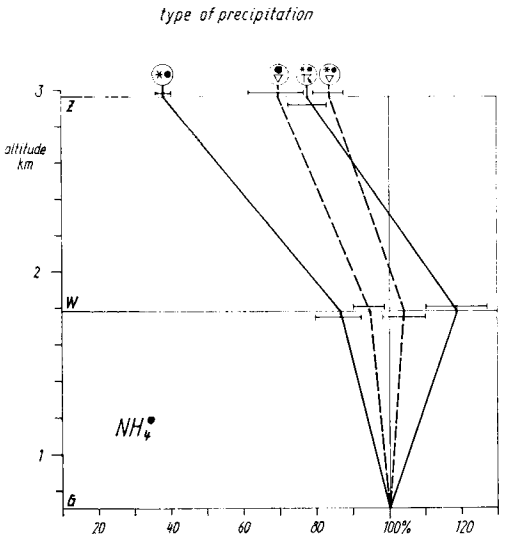

Fig. 2. As in Fig. 1, with NH_4' substituted for NO_3'.

Increases in NO_3' concentration downward are found in snow shower conditions. In showers with increasingly thick rain layers, the NO_3' concentration increases steadily with altitude, and showers with rain at 3000 m a.s.l. are marked by a uniform increase of NO_3' from the lowest to the highest level. This phenomenon is strikingly enhanced in thunderstorms. We explain these results by assuming that nitrous gases are generated in quantity by shower and thunderstorm processes in the immediate or more remote neighborhood of the mountain stations, and that less nitrous gas is formed above the valleys than near mountain peaks.

We now may safely state that considerable amounts of nitrous gases are incorporated in shower and thunderstorm clouds, and that these gases are produced within the clouds by updrafts and turbulent mixing associated with electrical processes, as will be shown later.

Much may be learned by comparing the NH_4' and the NO_3' content of precipitation in their different variation with height. NH_4' concentration always declines (Fig. 2) markedly with height between 1800 and 3000 m a.s.l., without specific differences due to the type of precipitation. There is sometimes a slight upward increase in NH_4' between 700 and 1800 m. This is likely to be due to local mixing entailing

Table 5. *Average NO_3'- and NH_4'-concentrations in (γ/cm³) different types of precipitation at the stations Zugspitze (Z), Wank (W) and Garmisch (G)*

Chemical compound	Station	Type of precipitation				
		●	✳	⁘	⁂	⁋
NO_3'	Z	0.41 ± 0.10	0.54 ± 0.03	1.44 ± 0.14	1.78 ± 0.07	1.83 ± 0.04
	W	0.72 ± 0.08	0.79 ± 0.10	1.28 ± 0.07	1.91 ± 0.09	1.68 ± 0.07
	G	0.79 ± 0.07	1.12 ± 0.18	1.29 ± 0.07	1.67 ± 0.10	1.39 ± 0.08
NH_4'	Z	0.54 ± 0.20	0.30 ± 0.05	0.47 ± 0.14	0.57 ± 0.05	0.62 ± 0.08
	W	0.48 ± 0.18	0.38 ± 0.08	0.52 ± 0.08	0.41 ± 0.05	0.55 ± 0.09
	G	0.43 ± 0.12	0.24 ± 0.09	0.68 ± 0.06	0.62 ± 0.12	0.51 ± 0.08

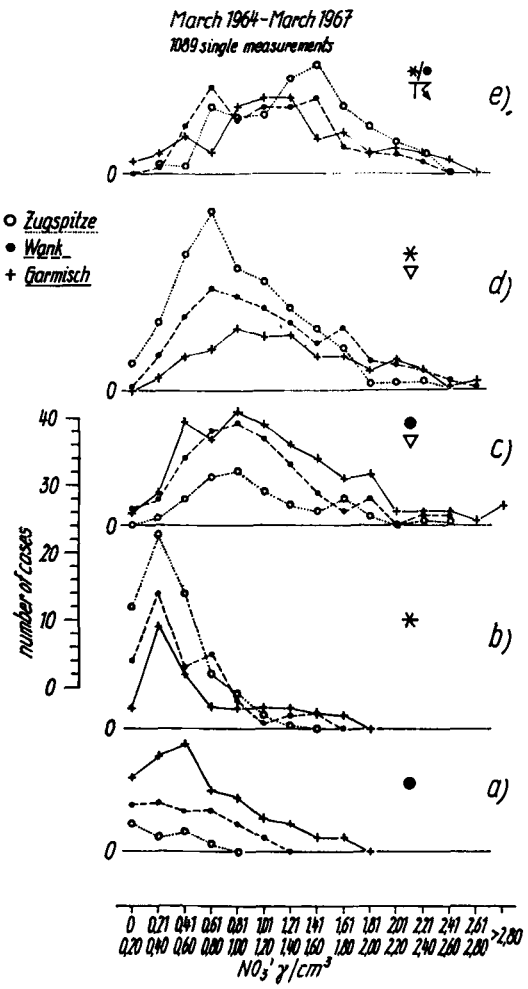

Fig. 3. Frequency distribution of NO_3' ion concentration values for different types of precipitation, based on 1089 samples collected between March 1964 and March 1967.

lifting of pollutants from the valley floor to the 2 km level. As NH_4' concentration in precipitates diminishes upward above this level, we may conclude that there are no ammonium sources of any consequence in the free atmosphere, as against the important sources of NO_3' existing at high levels.

(d) *Concentration of NO_3' and NH_4' in precipitation as affected by the type of precipitation at each of the three station levels*

The results stated in Sect. 6c are proof of an effect of precipitation type on the concentration of NO_3'. This "type effect", however, is not only observed at mountain locations, but also—cf. Table 5—at the valley station. Centers of generation of nitrous gases cannot be exclusively confined to the neighborhood of mountain-tops, but must exist in any shower or thunderstorm cloud. As our averages do not furnish a sufficient degree of reliability, we have plotted a frequency graph for NO_3' concentration "classes" (each of which is defined by an upper and a lower limit) for each type and station level involved (Fig. 3). The shifts in the curves on transition between steady to shower and shower to thunderstorm rainfall are very marked indeed, and can by no means be construed as effects of mere chance, as the shift is seen in each station diagram. On the other hand, no such effect was seen to exist with respect to NH_4' concentration.

(e) *Relationship between NO_3' concentration and vertical mixing activity*

The findings described up to now indicate that production of nitrous gases in clouds is some function of turbulence or mixing activity

in and around formation centers. This proposition may be checked by reference to vertical-mass-exchange coefficients computed from RaB data; the latter originate from simultaneous measurements of RaB abundance in ambient air (for details, cf Reiter, 1964, 1968*b*, 1967, 1969). We have two sets of mass-exchange data at our disposal:

Mean vertical-mass-exchange coefficient A_1 for layer 700–1800 m. Mean vertical-mass-exchange coefficient A_2 for layer 1800–3000 m, the units of A being [$g\ cm^{-1}\ sec^{-1}$].

Fig. 6*c* shows the correlation of A_2 with NO_3' concentration in precipitates collected at the three sites. Correlation of A_1 with NO_3' concentration in precipitate at W and G:

$W{:}r = +0.05 r_z = 0.17\text{N} = 276$
$G{:}r = +0.11 r_z = 0.17\text{N} = 278.$

Table 6 comprises similar data for NH_4'.

We draw the following conclusions from the tables and the regression diagrams:

A significant positive correlation exists between the NO_3' concentrations observed at all three levels and the value of vertical mixing activity between 1800 and 3000 m. The strength of the correlation increases upward (Garmisch→Wank→Zugspitze) and is quite impressive at the Zugspitze Station (3000 m). There is, however, no significant relationship between NO_3' abundance and vertical mixing between 700 and 1800 m a.s.l. We conclude that turbulence in the "free" upper layers only is a factor in NO_3' generation. This is in agreement with our conception of production centers existing inside clouds while precipitation is falling. Such centers would be expected to be located wherever there is a maximum of physical activity, i.e., a peak number of particle collisions (ice–ice and ice–water), particle fragmentations and electrical discharges.

If the sources of nitrous gases were located exclusively, or even predominantly, near the ground[1], the NO_3' concentration would certainly be affected by variations of the mixing activity near the ground; this is not borne out by our observations, as these show no such relationship to exist. There is, for instance, no increase in NO_3' at 1800 m after the onset of active mixing between 700 and 1800 m. However, just this is found for NH_4', as can be gathered from Table 6: there is a statistically significant positive correlation between NH_4' concentration at W and the vertical-mass-exchange coefficient A_1. All other correlations compiled in Table 6 are insignificant, with the possible exception of a marked effect of mixing activity between 1800 and 3000 m on NH_4' concentration, which can be explained as outlined above. The crucial fact is that NH_4' concentration, in contradistinction to NO_3' concentration, is *not affected by instability prevailing above the level at which the precipitate is collected.*

Table 6. *Correlation of A_1, resp. A_2 with NH_4' content in precipitation*

A_1: Vertical mass-exchange coefficient for the layer between G and W (800–1800 m); A_2: for the layer between W and Z (1800–3000 m); for the other symbols, see Table 2. 1 Regression line cf. Fig. 6*d*

	Station	r	r_z	N
A_2 (W/Z)	Z	+0.32	0.22	176
	W	+0.18	0.22	175
	G	+0.15	0.22	175
A_1 (G/W)	W	+0.36	0.21	202
	G	−0.03	0.21	200

The contrasting findings for NO_3' and NH_4' lead us to the following conclusions:

The NH_4' readings typify impurities in pre-

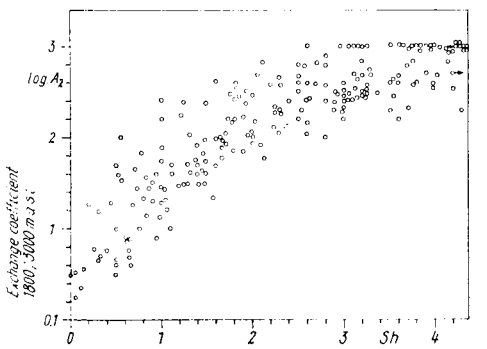

Fig. 4. Relationship between log A_2 and Sh; A_2 denotes the vertical-mass-exchange coefficient averaged for the layer Wank–Zugspitze (1800–3000 m), and Sh number of sign reversals per hour of the field strength during precipitations.

[1] The total intracloud production of N–O compounds (which takes place only during precipitation events and in active atmospheric turbulence) is, of course, negligible as compared with amounts of such components produced by combustion and industrial processes; this, however, is irrelevant for the feedback process. Details on O-N-compounds in the atmosphere in general and their respective sources are given by D. R. Bates and P. B. Hays (Planetary and Space Science, *15*, 189 (1967)).

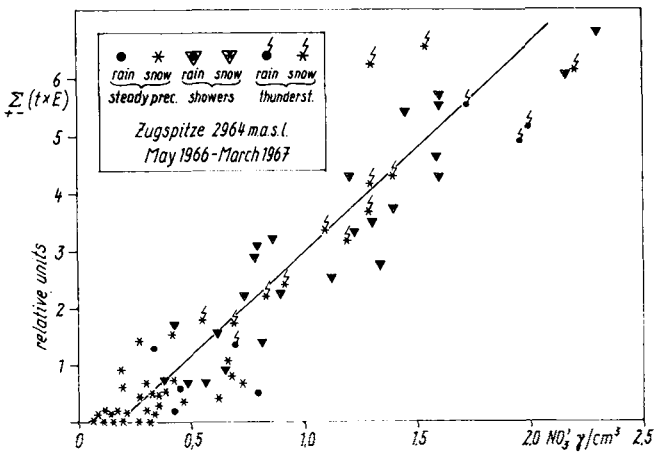

Fig. 5. Relation between the time-field strength ($t \times E$) product area recorded at Zugspitze station (3000 m) during precipitation and the NO_3' concentration in samples of same precipitation.

Table 7. *Correlation of NH_4'-content in precipitation with Sh*

Sh = frequency of sign reversal of field strength per hour; for other symbols see Tab. 2

Station	r	r_z	N
Z	+0.17	0.21	196
W	+0.16	0.21	192
G	+0.10	0.21	192

cipitation originating from low-level sources and incorporated in precipitation by the washout process. Such impurities may well be man-made. Unlike such pollutants, nitrous gases originate at higher levels inside clouds, and their abundance at any observation site depends on the mixing activity at and around the centers of generation (i.e., the intracloud sources).

(f) *The relationship between the concentration of NO_3' and NH_4' in precipitation and atmospheric electricity*

Some years ago, we were able to show that the hourly frequency of sign reversal of field strength during precipitation events depends on the degree of instability inside the clouds (Reiter, 1958, 1960, 1964). This relationship is presented in Fig. 4, using updated observational data; the logarithm of the mean vertical-mass-exchange coefficient 1800–3000 m (i.e., log A_2) is plotted as a function of the number of sign reversals of field strength per hour (Sh). The latter quantity, which may be interpreted as being indicative of "atmospheric-electrical turbulence", is set in correlation to the NO_3' and NH_4' content of precipitation. The result is expressed in Fig. 6*e* and Table 7. The correlation between Sh and NO_3' concentration is strong and shows some improvement with altitude. There is, however, no such relationship between Sh and NH_4'. This proves beyond reasonable doubt that variations of NO_3' concentration in precipitation are determined by corresponding variations of atmospheric-electrical activity. This conclusion holds good for any non-polluted atmospheric environment. However, we have succeeded in furnishing additional, independent evidence: observations made at the Zugspitze station resulted in a very good positive correlation between NO_3' in precipitates and the product of electrical field strength[1] (irrespective of sign) and the duration of the precipitation event in question. The results are given in Fig. 6*f*. No significant relationship can be found for NH_4'. This result demonstrates clearly that the concentration of NO_3' in intracloud precipitation is directly controlled by atmospheric-electrical processes, as far as local air pollution is not involved. The interrelationship between NO_3' concentration in precipitation, and the product of electrical field strength (with sign disregarded) and duration of precipitation, is represented as a point graph in

[1] Field strengths were measured with a field mill.

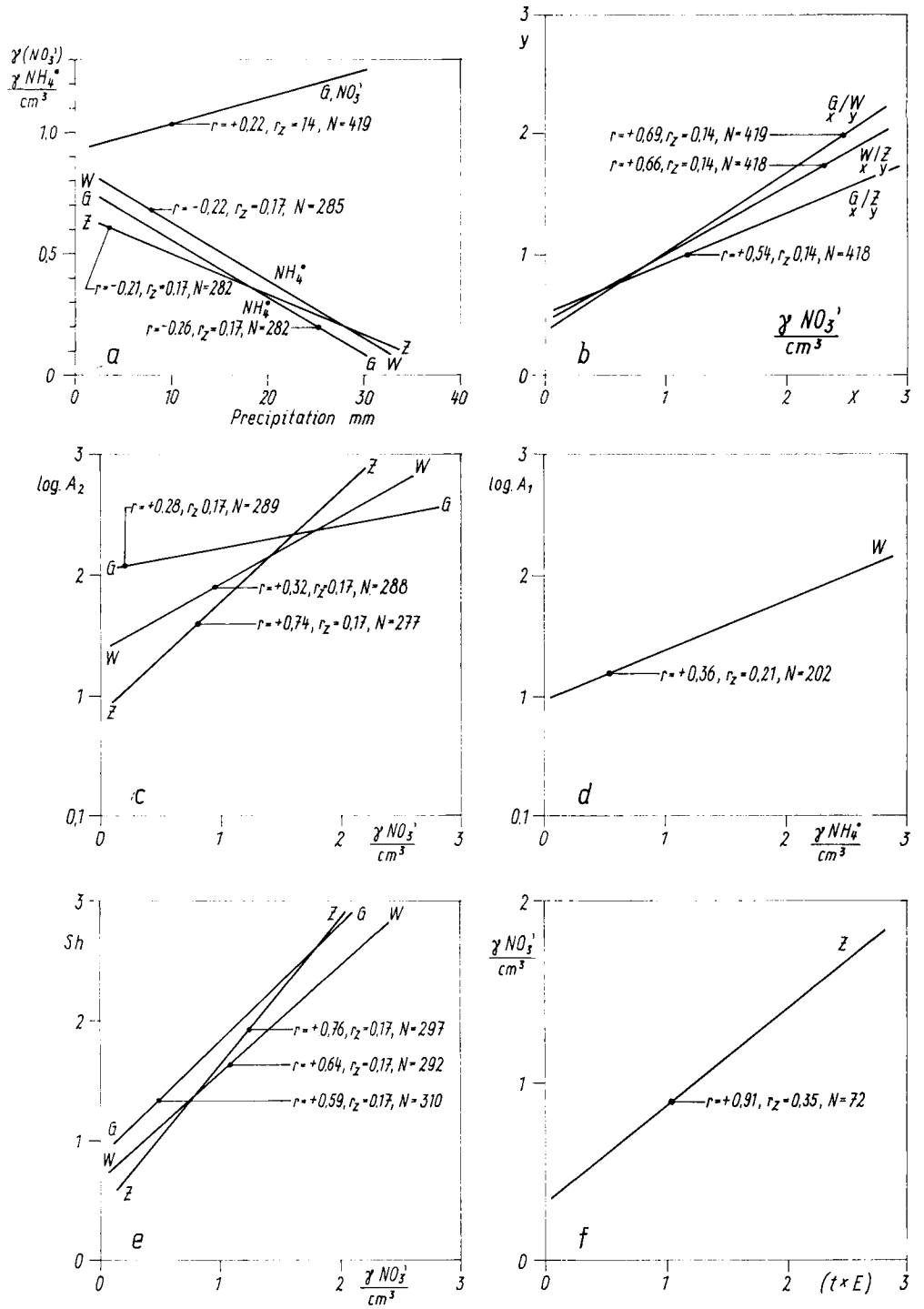

Fig. 6. Results of statistical tests of the data; regression lines, r = correlation coefficient, r_z = confidence limit of r (for $3 \times \sigma$).

Fig. 5, with due reference to the effects of different types of precipitation. It is readily seen from the graph that there is a good correlation *for all types* of precipitation, and that both the above-specified "product" and the NO_3^- concentration are affected by the type of precipitation involved.

Occasionally the possibility of the NO_3^- content of precipitation being influenced by atmospheric electrical processes has been examined by checking concentration data merely against thunderstorm and lightning frequency (Viemeister, 1960; Gambell & Fisher, 1964). Already on a previous occasion (Reiter & Reiter, 1958), we stated that lightning alone could hardly be considered as a sufficiently abundant source of nitrous gases. In order to examine this question once again, we used the field-mill curves recorded during thunderstorms to count the number of lightning flashes occurring within a maximum distance of 0.5 km.

We have studied the correlation between NO_3^- in precipitates and the number of lightning flashes during the precipitation events in question. The result is: $r = 0.02$, i.e. the two quantities are unrelated. We must therefore consider the silent electric discharges inside the cloud, especially at the surface of precipitation particles and between such particles.

Reference should be made to papers by Sartor who has shown that microdischarges of this type occur in convective clouds in very large numbers per unit space.

(g) *Measurements of nitrous trace gases in ambient air during showers and thunderstorms.*

Recordings of NO_2 gas traces were made by means of a special instrument developed by the German corporation Hartmann & Braun. This novel device works on the basis of a chemical reaction between NO_2 gas and a diluted KJ solution. NO_2 oxidizes potassium iodide ions to iodine; subsequent adsorption of J on KJ creates J_3^- ions, which enter the measuring cell by diffusion. The current thus generated is proportional to the concentration of NO_2, and is automatically recorded. The lowest detectable concentration is 0.002 mg NO_2/m^3.

The results hitherto obtained by this method must be regarded as necessarily tentative. Some problems were encountered as the instrument was used at the Wank mountain site and not all of these could be eliminated during the period covered by this study.

The results hitherto obtained may be summarized as follows: The basic ("background") level of NO_2 concentration is so extremely low in the clean air of a mountain site that it cannot be measured with the instrument referred to above. No detectable NO_2 occurred during showers in the absence of thunderstorm activity. However, measurable NO_2 traces were encountered during 17 thunderstorms located at or very near the Wank station. Peak readings were mostly around 0.005 mg NO_2/m^3, i.e., slightly above the threshold of detectability. There were only four cases in which peak concentrations ranging from 0.01 to 0.08 mg NO_2/m^3 were attained.

Although the above results must be regarded as tentative, they indicate that traces of nitrous gases exist in thunderclouds; these gases cannot originate from any other source than the electrical processes peculiar to thunderstorms.

7. Results of laboratory measurement

During a first period of our work, only the charge separation occuring upon fragmentation of needle-shaped ice crystals was taken into consideration (Reiter, 1963, 1966, 1968; Reiter & Carnuth, 1965). In an atmospheric-electric cloud chamber needle-shaped ice crystals were formed under certain experimental conditions on a cap-shaped copper plate. This "breederplate" was grounded. We produced NO_3^- ion concentration gradients along the growing ice needles by adding traces of nitrous gases to the air within the chamber. Another method we employed was the following: ice needles were grown in an electric field between the breederplate and a positively charged insulated water surface located below the horizontally mounted breederplate. Weak glow discharges at the growing crystal-points formed traces of nitrous gases, and NO_3^- ions were incorporated in the ice crystals during the growing phase. Thus, well-defined NO_3^- concentrations were produced in the ice crystals. After the voltage applied between the water surface and the breederplate was cut off, sufficient time was allowed to make sure that the crystal charges induced by the electric field had been equalized before fragmentation of the crystal points was effected by mechanical shock. The temperature gradient along the crystals was measured and kept as low

as possible. The crystal points broken off by the shocks were collected in a gold bowl connected with a vibrating-reed electrometer. The crystal fragments were weighed immediately after charge measurement and removed by rinsing with a few ml of extra pure distilled water. The NO_3' ion concentration was determined by a special micro-chemical method (Pötzl & Reiter, 1960). All NO_3' ion data and all measured amounts of charge were related to 1 g of ice splinters.

The results obtained by this method are represented in Fig. 7, where the amount of liberated specific charge (C/g, ordinates) has been plotted vs. the quotient Q_K (logarithmic scale):

$$Q_K = \frac{\text{NO}_3' \text{ ion concentration in the crystal points}}{\text{NO}_3' \text{ ion concentration in the truncated crystals.}}$$

In this manner, an approximately linear relation of the two parameters was discovered.

From the practically linear curve in Fig. 7, we may conclude: charge separation upon ice crystal fragmentation is hardly ever effected by the NO_3' ion concentration, but strongly dependent on the NO_3' ion concentration gradient inside the crystals. If the gradient is zero, the amount of liberated charge is likewise zero; if the gradient differs from zero, the crystal part having the higher NO_3' ion concentration will be found to be charged negatively with respect to the other, and vice versa. Moreover, we are very well justified in assuming that these effects occur only if the absolute NO_3' ion concentration inside the crystals exceeds a certain threshold value (0.6 to 1.8 γ NO_3'/cm^3 approx). Otherwise, other impurities incorporated into the ice crystals during their growth in the free atmosphere will give rise to similar effects. (Mention should be made of the results reported by the Workman–Reynolds–Brook team, New Mexico, which we have discussed in our previous work, and of the findings of Parreira & Eydt, 1965). Thermal effects (Mason *et al.*) may obscure the phenomenon.

In view of the relation represented in Fig. 7, it may appear surprising that it was possible at all to find any relations between NO_3' ion concentration and atmospheric electrical activity and/or atmospheric turbulence, as explained in detail in the sections above. If nitrous gases are formed in zones of turbulence and

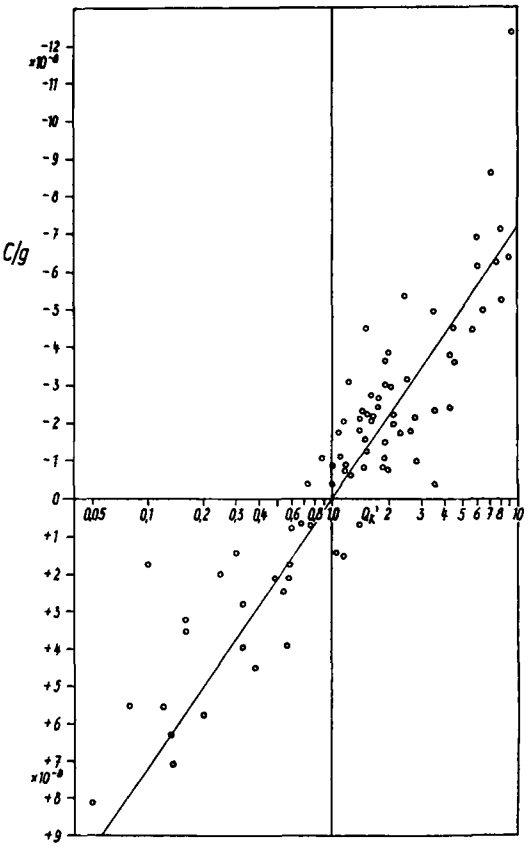

Fig. 7. Relationship between the electrical charge created by fragmentation of ice crystals and the NO_3' ion concentration quotient Q_K.

bring about an increased NO_3' ion concentration in precipitation particles, the NO_3' ions cannot be supplied to the ice crystals at a constant rate or be homogeneously distributed in them. It will be readily understood that the inhomogeneity will tend to be the greater, the higher the total concentration becomes. For, if an ice particle with a low initial NO_3' ion concentration falls through a cloud cell where a higher concentration of nitrous gases obtains, both its final NO_3' ion concentration and the inhomogeneity will be enhanced accordingly.

An attempt was made to explain the charge separation accompanying crystal fragmentation by a diffusion process. It can be assumed that NO_3' ions are non-incorporable extraneous matter in the microstructure of ice crystals, and hence are immovably located at lattice faults, as against the free diffusion of hydrogen ions

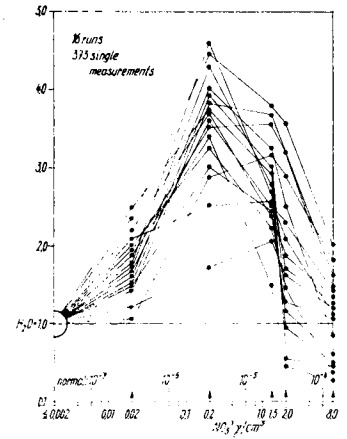

Fig. 8. Charge separation efficacy factor as a function of NO_3' ion concentration of dilute nitrate solutions. Points represent averages of several measurements; lines connecting points represent sets of measurements.

(i.e., protons). If a gradient of NO_3' exists under such circumstances, *the protons will tend to move down any such gradient*, thus creating space charges and a resultant electrical field. The latter, in turn, resist the diffusion process; the final outcome is a state of equilibrium. By introducing some simplifications of this system, a theoretical estimate of the maximum diffusion-generated space-charge density for a given NO_3' concentration gradient may be made. These model estimates, however, furnish charges of only about 1% of the experimentally observed amount. However, the calculated electrical polarity of the charged ice crystal agrees with our experimental findings. (For details, see Reiter & Carnuth, 1965; Carnuth, 1968.) It is clear from the foregoing that a refinement of the theory is needed.

Experiments of a different type have been carried out recently (Reiter, 1968). Water drops were dropped onto a rapidly rotating ice sphere, the droplets thrown off by centrifugal force collected on a surrounding electrode, and the electrical charge accumulated on the electrode was measured. An investigation as to whether the amount of charge was influenced by the NO_3' ion concentration in the water used led to the following result (Fig. 8): with NO_3' ion concentration increasing from less than 0.002 to 0.2 γ NO_3' ions per cm^3, the charge increases to a maximum (amount of charge approx. 3.5 times as much as in pure water); a further increase in concentration however, leads to a decrease in charge (Parreira & Eydt, 1965). The charge-separation processes occurring in the lower layers of a thunderstorm or shower cloud as ice particles collide with raindrops have thus been shown to be influenced by the NO_3' content of precipitation.

8. Conclusions

The field observations as described in Sect. 6 prove that nitrous gases are produced by atmospheric-electrical processes inside clouds: the gases are formed by electrical activity, as indicated by the data pertaining to space and time. The nitrous gases are incorporated in precipitation particles and dissolved in cloud droplets; the former process causes the increase observed in NO_3' concentration in precipitates.[1] NO_3' concentration depends both on atmospheric mixing and electrical activity; these two combine to ensure both the onset and the maintenance of the feedback mechanism described in Section 3. This conclusion is further corroborated by the results of our laboratory studies.

However, it is as yet not feasible to draw far-reaching conclusions from the results so far obtained. Being well substantiated by experiments, the conception of the NO_3' ion concentration gradient inside ice crystals is of considerable importance for the atmospheric electrical feedback process. The assumption that such a mechanism does actually exist agrees well with the conception of the cellular structure of thunderstorms. If the NO_3' gradient in a given cell increases and the conditions for break-up of ice crystal points and for transport of fragments of different sizes away from each other are fulfilled, the consequence may be either an avalanche-like increase of charge in the cloud cell due to the feedback process or neutralization of existing space charges and stoppage of the feedback process. The former will occur if the NO_3' ion concentration gradient causes the particles to carry charges of the same polarity as that of the space charge into which they are being transported by wind or gravitational forces; the latter, if polarities are opposite, whereupon the

[1] As demonstrated in detail in Section 6, NH_4' ion content in precipitates differs greatly from NO_3' content. The washout depletion of NH_4' is construed as evidence that it is not involved in an electrification process.

production of nitrous gases will cease and the atmospheric-electrical activity of the cell concerned will rapidly decline. Both cases, the avalanche-like increase as well as the collapse of the electrical activity in shower or thunderstorm clouds, have actually and regularly been observed. The fact that high space charge densities of either polarity originate in closely limited zones of thunderclouds agrees well with the conception outlined above concerning the importance of the amount and sign of the NO_3^- ion concentration gradient inside ice crystals and of its changes with time and place. The predominantly positive charge found in the upper regions of thunderstorm clouds may be explained as follows: In the center or base of the cloud where isolated spaces with charges of opposite polarity exist, ice particles will first capture relatively large amounts of NO_3^- ions. In funnel-shaped up-draughts, ice particles with high NO_3^- content will be carried upward into spaces where the electric field strength is lower. They will continue to grow there, but will incorporate less or no nitrous gases. Due to the sign of the NO_3^- ion concentration gradient thereby determined, small ice splinters breaking away from the surface will now carry positive charges. Updrafts carry them to higher levels of the cloud.

As our results indicate that the magnitude of the electrical charge created by collision and/or breakup of water drops and ice particles depends on the concentration of NO_3^- in such drops, we conclude that both the formation and the destruction of small-scale pockets of charge in the base layer of thunderstorms are controlled, or at least materially affected, by the feedback mechanism described above. It is, however, not yet possible to set up a thunderstorm model based on this feedback process and the assumption of a balanced budget of electrical charge, as any such theory would necessarily have to include arbitrary hypotheses concerning the mechanical separation of ice fragments of various sizes by wind (turbulence), gravity and collision-related forces.[1] The same reservations must be made for our laboratory studies on water-ice collisions at different NO_3^- concentration levels: further experience must be gained before the relevance of these laboratory results to thunderstorm conditions may be properly assessed.

We definitely do not feel that the feedback mechanism is a full "explanation" of thunderstorm activity. This is readily seen from the fact that a different mechanism is needed to get the electification started in the first place. We accept the proposition that several processes operate in an average thundercloud and that the interconnection of these mechanisms has yet to be clarified; however, we do believe to have proved that the feedback mechanism described in this paper is a substantive factor in the electrical build-up and the general electrical economy of thunderstorms.

[1] Theoretical "thunderstorm electricity budgets" in the literature are, strictly speaking, based on more or less arbitrary assumptions and/or simplifications; these hypothetical elements have not, as yet, been verified satisfactorily with respect to the general nature and phenomenonology of thunderstorms.

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О СЛУЧАЙНОЙ СВЯЗИ МЕЖДУ АЗОТНО-КИСЛОРОДНЫМИ КОМПОНЕНТАМИ В ТРОПОСФЕРЕ И АТМОСФЕРНЫМ ЭЛЕКТРИЧЕСТВОМ

Для предварительного объяснения быстрого увеличения плотности заряда и напряжения электрического поля во время гроз предложен механизм обратной связи в атмосфере. Этот процесс требует выполнения двух условий, именно: а) формирование заметных количеств азотных соединений внутри облака при электрических разрядах (главным образом, при тихих), что увеличивает концентрацию ионов NO_3' в частицах осадков; в) когда ледяные кристаллы распадаются на части, то разделение электрического заряда должно происходить в отношении, зависящем от содержания и распределения ионов NO_3' внутри осколков.

Полевые наблюдения. Статистический анализ данных по концентрации ионов NO_3' в пробах осадков, проведенных одновременно на высотах 700, 1800 і 3000 *м* над уровнем моря в течение пятилетнего периода, установил определенное увеличение содержания NO_3', с увеличением внутриоблачной турбулентности и электрической активности. На уровне 3000 *м* была найдена прямая корреляция между концентрацией NO_3' в осадках и интегралом по времени от напряженности электрического поля. Концентрация ионов NO_3' в осадках не зависит от числа разрядов молний. Очевидно, что комбинированный эф-

фект всех коронных разрядов на или между частицами осадков или облачными каплями определяет увеличение концентрации ионов NO_3' в осадках.

Лабораторные измерения. Градиент концентрации ионов в частицах льда до их распада определяет величину электрического заряда, уносимого отдельными осколками этих частиц. Величина отрицательного заряда в осколке тем больше, чем выше в нем содержание ионов NO_3'. Там, где распределение этих ионов в кристалле однородно, разделение заряда не происходит. Эти результаты могут объяснить как быстрое увеличение, так и последующее прекращение электрической активности в индивидуальных грозовых ячейках, проясняя кроме того процессы, ответственные за формирование основных зон пространственного заряда и типичном грозовом облаке.

На быстро вращающуюся ледяную сферу наносились капли воды; капельки, отброшенные центробежной силой, собирались окружающим электродом, измерялся заряд, собранный на электроде. Исследование влияния ионов NO_3' в воде дало следующий результат: заряд растет до максимума по мере увеличения концентрации ионов NO_3' от 0,002 до 0,2 γ *ион/см*^{3}, но затем уменьшается с дальнейшим ростом концентрации. Таким образом, видно, что разделение зарядов, вызываемое соударениями частиц льда с каплями дождя в нижних слоях грозовых или дождевых облаков, испытывает влияние величины концентрации ионов в осадках.