The effects of Ammonia on the electrification of freezing and splashing water drops

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ABSTRACT

Experiments were undertaken in which 2 mm diameter water drops contaminated with NaCl and/or $(NH_4)_2CO_3$ were allowed to fall through a cold environment and impinge on an ice target. Charge deposited on the target was measured as a function of environment temperature (0°C to −30°C) and concentration of the solution (10^{-6} M to 10^{-2} M). Maximum negative charge of 2.04 esu/g was produced by 10^{-4} M NaCl at an environment temperature of −20°C. Maximum positive charge of 2.79 esu/g was produced by 10^{-3} M $(NH_4)_2CO_3$ at an environment temperature of −30°C. It was possible to suppress and even reverse the usual negative charge of salt by mixing with ammonia, suggesting the possibility of modifying thunderstorm electricity. All solutions weaker than 10^{-5} M gave complictated waveforms with a net negative charge.

1. Introduction

Many theories have been advanced for the explanation of charge generation in thunderstorms. The most complete physical description is probably provided by the Workman model (Workman, 1967) a comprehensive thunderstorm model which relies on the Workman-Reynolds freezing effect (Workman & Reynolds, 1950) as its charge producer. More recent experiments by Workman (1969) demonstrated that the collision of supercooled water drops with ice is a very strong charge generator. The amount of charge generated was found to be dependent upon the impurities in the water drops, with sodium chloride giving negative ice and ammonia giving positive ice.

The following experiments were designed as a systematic investigation of the impurity and temperature dependence of the charge generation of freezing and splashing water drops as it may occur in a thundercloud. Experiments were performed at environment temperatures ranging from 0°C to −30°C and water drop impurity concentrations of NaCl and $(NH_4)_2CO_3$ from 10^{-2} M to 10^{-6} M.

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2. Experimental apparatus

The experimental apparatus for this work consisted of a closed, refrigerated drop tower 10 ft tall and 6 in in diameter (see Fig. 1). 2 mm diameter drops were formed at the top of the tower by a water dropper arrangement similar to that described by Workman (1969) and allowed to fall and supercool until impact upon a 1.27 cm diameter ice target at the bottom. An electrometer using a 2N3631 field-effect transistor was used to measure the charge deposited on the ice target. The transistor was used in a follower circuit with a gain of 0.8 and the output fed into a Beckman Dynagraph Type K Recorder for a permenent record of each collision (Fig. 2). The input capacitance of the electrometer (including the target) was measured as 10 pf and a leakage resistance of 10^{11} ohms was connected to ground to give a natural instrument time-constant of about 1 sec. This arrangement was easily capable of measuring charges as small as 3×10^{-5} esu. The dropper was constructed to allow drops to fall at the rate of approximately 3 drops per minute. Speed and cooling of the drop were calculated using data for drag coefficients from Gunn & Kinzer (1949) and data for heat transfer due to conduction and evaporation from

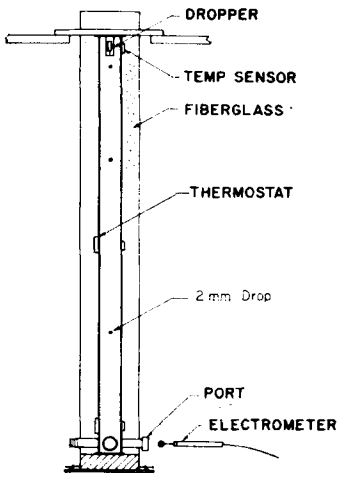


Fig. 1. Drop tower.

Ludlam (1950). Typically, a 2 mm diameter water drop starting from rest at 0°C and falling a distance of 300 cm in a −20°C environment will assume a velocity of about 540 cm/sec and a temperature of about −3°C.

3. Theory

The classical Workman–Reynolds experiment in which ice is grown at a rapid rate from dilute solutions of some salts has been shown to give large potential differences while freezing is in progress (Workman & Reynolds, 1950). It was found that 10^{-4} M NaCl solutions gave freezing potentials of about 30 V with the ice negative, and that 10^{-5} M ammonium salt solutions gave potentials of the order of 100 V with the ice positive. This freezing effect is explained as the preferential incorporation of ions by the advancing ice surface. In the case of NaCl, the negative chloride ion is preferred by the ice structure. However, in the case of ammonium salts (with the exception of NH_4F) the ammonium ion is preferred. A complete review of the freezing effect has been given by Gross (1968). The freezing effect is used to explain charging during collision of water drops with ice in the following manner: When the supercooled drop strikes the cold ice target, the drop is partially frozen to the target and partially splashed away. At the instant of impact, rapid freezing incorporates chloride ions (in the case of NaCl contamination) into the newly formed ice on the target while sodium ions remain in the splash-off droplets, giving a permanent separation of charge. Since natural atmospheric water contains NaCl at a concentration of 10^{-5} to 10^{-4} M, this collision and freezing process may be extended to the natural thunderstorm process by considering that as the negative ice particles grow they become heavier and fall towards the bottom of the cloud while tiny positive droplets are swept by updrafts to the top of the cloud.

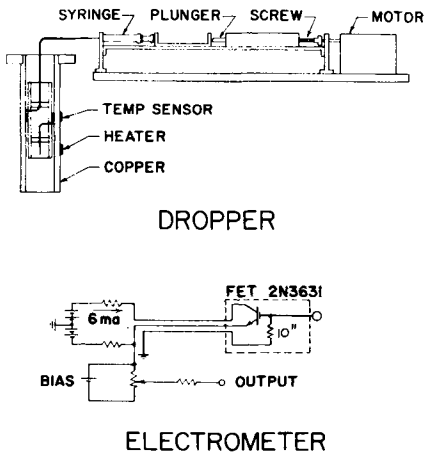


Fig. 2. Motor driven dropper showing details of the thermally isolated needle on which drops are formed. Electrometer is balanced for zero output under quiescent conditions.

4. Experimental results

Sodium chloride

Experiments were performed for a large number of drops, and average charge generation was measured for NaCl concentrations of 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} M at environment temperatures of −30, −25, −20, −15, −10, and −5°C. Solutions were carefully prepared using distilled water with resistivity in excess of 1 megohm-cm and the best available grade of solute. Care was taken to avoid unnecessary exposure of the solution to the air. It was found that strong charge generation occurred for a concentration of 10^{-4} M and an environment temperature of −20°C. See Fig. 3 and Table 1. This concentration corresponds precisely to the ideal NaCl concentration in the classical Workman–Reynolds experiment. It is

Table 1. *NaCl data (esu/g)*

Solution NaCl	Temperature −30°C	−25°C	−20°C	−15°C	−10°C	−5°C	0°C
10^{-3} M	−0.31 esu/g	−0.57	−0.34	−0.11	−0.046	−0.061	*
	16 drops	24	27	24	82	17	
10^{-4} M	−1.88	−2.01	−2.04	−1.61	−1.25	−0.27	*
	14	45	58	64	61	42	
10^{-5} M	−1.35	−1 24	−1.32	−1.26	−0.77	−0.012	*
	23	59	38	66	59	31	
10^{-6} M	−0.33	−0.45	−0.69	−0.87	−0.57	−0.096	*
	21	34	55	79	57	55	
2×10^{-5} M	−0.72	−0.94	−0.97	−0.93	−0.42	−0.08	*
	26	41	18	56	51	61	
4×10^{-5} M	−1.08	−1.82	−1.48	−1.24	−0.48	−0.64	*
	17	38	52	79	91	64	
6×10^{-5} M	−2.22	−1.99	−1.96	−1.61	−0.56	−0.11	*
	42	42	61	41	55	44	

* Less than 0.001.

seen that the temperature dependency is spectacular with maximum charge generation at −20°C and negligible charge generation at temperatures near freeezing. In the −20°C temperature range, charge generation is consistently negative and in excess of 2 esu/g, whereas charge generation is erratic and several magnitudes smaller when freezing does not take place. Average values of charge for 10^{-4} M NaCl in the −20°C temperature range were found by averaging together 58 values of recorded data at temperatures from −17.5°C to −22.5°C. The mean was found to be −2.0 esu/g with a standard deviation of 0.96. Values for other concentrations and temperatures were determined in a similar manner. The small charges observed for warm temperatures must have been due to simple splashing mechanisms not involving the freezing process.

Since 10^{-4} M and 10^{-5} M concentrations were the most active charge producers, additional experiments were performed for 2×10^{-5}, 4×10^{-5}, and 6×10^{-5}. See Fig 4 and Table 1. It was found that 6×10^{-5} M NaCl gave the maximum charge generation of −2.2 esu/g, sufficient to account for thunderstorm electricity. The intermediate range data were plotted separately because the solutions were mixed using a new batch of distilled water.

Ammonia

Similar experiments were peformed with solutions of $(NH_4)_2CO_3$ at concentrations of

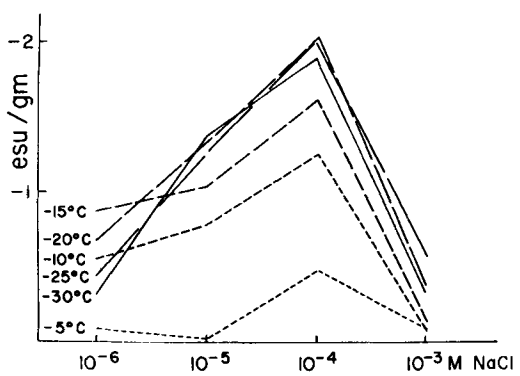


Fig. 3. Charge generated at impact vs. concentration of salt.

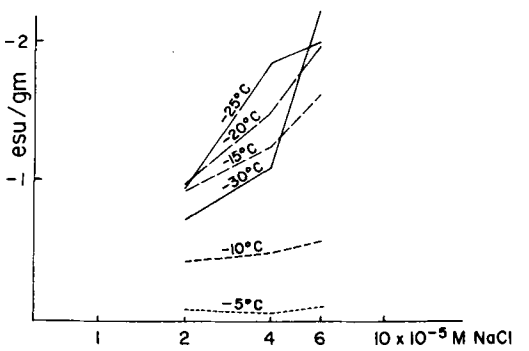


Fig. 4. Charge generated at impact vs. concentration of salt in the most active concentration range.

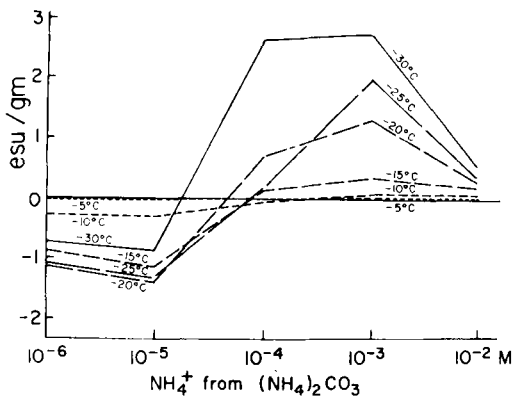


Fig. 5. Charge generated at impact vs. concentration of ammonia.

10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} M. Again, temperature dependency was spectacular with negligible charge generation at temperatures near freezing and pronounced charge generation at temperatures lower than −15°C. See Fig. 5 and Table 2. It is seen that 10^{-3} M gives large, consistently positive charge, 10^{-5} M gives fairly large consistently negative charge, and the transition region gives erratic results and small charge generation. These results are in disagreement with the classical Workman–Reynolds experiment which predicts maximum positive potential at a concentration of 10^{-5} M and maximum charge transfer at 10^{-4} M. It is noteworthy that the negative charges in the dilute concentration region exhibit the same temperature dependency as NaCl, and that whenever positive charging occurs, charging is stronger for lower temperatures.

Average values of charge for 10^{-3} M in the −25°C temperature range were found by averaging 43 values of recorded data at temperatures from −22.5°C to −27.5°C. The mean was found to be 2.01 esu/g with a standard deviation of 1.1. Values for other concentrations and temperatures were determined in a similar manner.

Ammonia Mixed with Sodium Chloride

Finally, experiments were performed with solutions of $(NH_4)_2CO_3$ and NaCl mixed to the concentrations shown in Fig. 6 and Table 2. 10^{-3} M ammonia (the most active concentration for ammonia) with NaCl gave strong positive charge in both cases with the most active concentration of ammonia prevailing over the most active concentration of salt. Charging in the −20°C region is less than with ammonia alone because salt is most active at warmer temperatures than is ammonia. 10^{-4} M ammonia is active enough to prevail over the fairly active 10^{-5} M NaCl. As usual, charging drops

Table 2. *Ammonia and mixture data (esu/g)*

Solution NH_4^+	Temperature −30°C	−25°C	−20°C	−15°C	−10°C	−5°C	0°C
10^{-2} M	+0.54 esu/g	+0.39	+0.31	+0.22	+0.035	*	*
	62 drops	66	65	75	70		
10^{-3} M	+2.79	+2.01	+1.37	+0.36	+0.076	+0.04	*
	33	43	62	75	90	23	
10^{-4} M	+2.66	+0.22	+0.72	+0.16	+0.042	+0.03	*
	41	28	50	94	107	82	
10^{-5} M	−0.89	−1.31	−1.34	−1.16	−0.34	−0.006	*
	56	55	59	85	104	78	
10^{-6} M	−0.73	−1.09	−1.11	−0.9	−0.34	−0.03	*
	38	50	63	85	92	58	
Mixtures							
10^{-3} NH_4^+, 10^{-4} NaCl	+2.54	+2.5	+1.71	+0.43	+0.046	*	*
	33	21	24	41	74		
10^{-3} NH_4^+, 10^{-5} NaCl	+1.36	+1.12	+0.94	+0.19	+0.03	*	*
	33	36	28	29	47		
10^{-4} NH_4^+, 10^{-4} NaCl	−0.032	−0.004	−0.043	−0.059	−0.012	*	*
	25	42	46	59	98		
10^{-4} NH_4^+, 10^{-5} NaCl	+3.82	+3.01	+0.89	+0.24	+0.061	+0.001	*

* Less than 0.001.

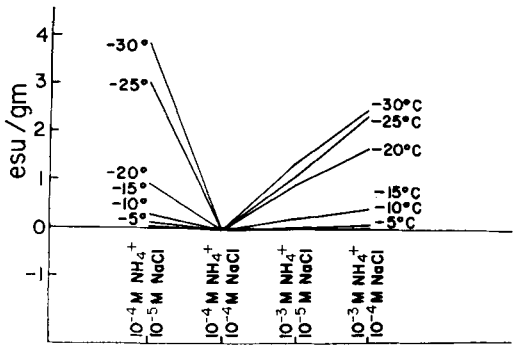


Fig. 6. Charge generated at impact for various mixtures of salt and ammonia.

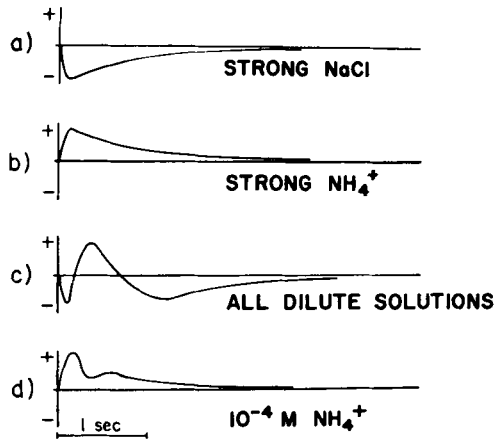


Fig. 7. Typical waveforms of recorded data.

off sharply in all cases for temperatures near freezing.

10^{-4} M ammonia with 10^{-4} M salt is the most interesting case since the effects of the two tend to cancel giving a very small net negative charge. The concentration of the ammonia is is not quite strong enough to reverse the effect of the very active 10^{-4} M NaCl. Interference phenomena of this type have been investigated in the classical experiment by Gross (1970).

Analysis of the data shows a variety of recorded wave-forms but the net effect is small. The average value of charge in the −20°C temperature range was found by averaging 46 values of recorded data at temperatures from −17.5°C to −22.5°C. The mean was found to be −0.04 esu/g with a standard deviation of 0.2. Values for other mixtures and temperatures were determined in a similar manner.

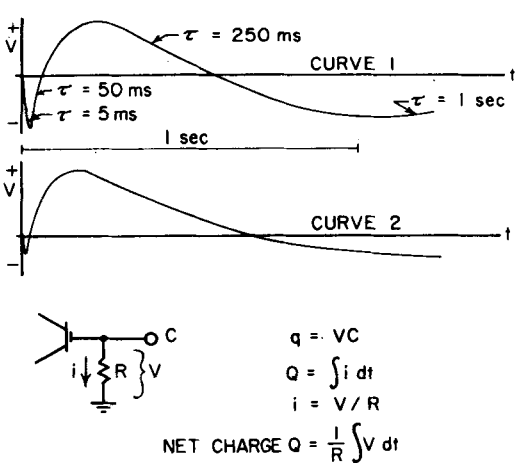
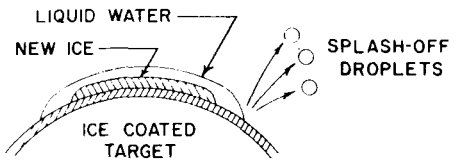


Fig. 8. Charge analysis of typical complicated waveforms. In both curves 1 and 2, net charge is given by the height of the initial peak.

5. Interpretation of recorded data

Experimental data may be divided into two general classes: 1) data for solutions stronger than about 10^{-4} M (see Fig. 7*a*, *b*), and 2) data for solutions weaker than about 10^{-5} M (see Fig. 7*c*, *d*). The initial peak is a measure of charge transferred during the initial freezing and splashing and the final decay back to zero is the natural leakage of the instrument. For solutions weaker than 10^{-5} M, a typical recording is shown in Fig. 8 with time constants given for the various portions of the curve. Since this curve is a time plot of the voltage at the gate of the transistor it is also a time plot of the current through the leakage resistance. A graphical integration of this curve shows that the initial peak is a measure of the net charge transferred during the initial freezing and splashing. The complicated waveform is generated as liquid water remaining on the target completes its freezing (see Fig. 9). As freezing is completed, charge separated by the Workman–Reynolds freezing effect spreads according to the Maxwellian relaxation time-constant of ice. Maxwellian relaxation is the tendency of charge to spread from the interior to the surface of a conductor and the Maxwellian time-constant of a substance is $\tau = \varepsilon/\sigma$ where ε is the dielectric constant and σ is the conductivity of the sub-



$$\rho = \rho_0 e^{-\frac{\sigma}{\epsilon} t}$$

$\sigma_s = 10^{-9}$ mho/cm $\quad \tau_s =$ milliseconds

$\sigma_b = 10^{-11}$ mho/cm $\quad \tau_b \square$ 100's of milliseconds

Fig. 9. Maxwellian relaxation. ϱ_0 is initial charge in the interior of a body. Subscripts s and b refer to surface and bulk properties respectively.

stance (Stratton, 1941). In all but the poorest conductors, τ is very small. For matters of comparison, τ for sea water is about 10^{-10} sec, τ for distilled water is about 10^{-6} sec, and τ for fused quartz is about 10^{6} sec. The relaxation time depends primarily on σ, since ε is about the same for ice and water. Since the conductivity of ice ranges from 10^{-9} mho/cm surface conductivity to 10^{-11} mho/cm bulk conductivity (Gross, 1968), and the time constant of 10^{-6} mho/cm water is about 10^{-6} sec, it is seen that τ for ice varies from milliseconds (surface) to hundreds of milliseconds (bulk).

Referring again to Figs. 8 and 9, it is seen that the initial risetime is rapid, of the order of milliseconds as the initial charge generated at impact is induced at the gate of the transistor. As freezing of the liquid water remaining on the target is completed, charge actively being separated in the liquid decays immediately to the edges and through the surface ice with a time-constant of about 50 ms. The negative charge being generated at the interface in the ice layer is exposed to the full bulk conductivity of the ice and has a time-constant of about 250 ms. Since the target is essentially a closed system after the initial impact, there can be no net charge transferred by the subsequent freezing process. This is verified by the integration of the curve.

6. Discussion

Perhaps the most striking result of this experiment is the spectacular temperature dependency. In all cases, charging of the ice target was negligible at temperatures near freezing, increasing to at least 2 esu/g for temperatures in the -15°C to -20°C range. It is interesting that the -15°C to -20°C temperature range is believed by most investigators to be the charge production region in a thundercloud. Another striking result of this experiment is the concentration dependency with maximum charging occurring in the 10^{-5} to 10^{-4} M range. Again, this is the usual concentration of salts in natural atmospheric water. These results point very strongly to a thunderstorm charge generation mechanism involving the rapid freezing of supercooled liquid water such as Workman (1967) has described.

It should be pointed out that the water drops were not in temperature equilibrium with their environment and therefore the experiment is not entirely representative of conditions occurring inside natural clouds. It is possible that heat transfer, freezing, and charging characteristics may be quite different from those occurring in clouds. However, further experiments have shown that smaller drops experiencing stronger supercooling show even stronger charge generation. This suggests that as actual cloud conditions are approached, charge generation will be enhanced. The applicability of this mechanism to conditions occurring within natural clouds has been discussed in some detail by several investigators (e.g. Reynolds, et al., 1957; Latham & Mason, 1961; Latham, 1965; Latham & Miller, 1965; and Workman, 1967).

Objections have been raised by various workers that there is insufficient liquid water in a thunderstorm and that ice in the cloud is in the spongy form, not suitable for the mechanism described. We await more precise measurements of the liquid water content of thunderclouds, probably by doppler and polarizing radar techniques. However, it must be remembered that a 1° beam width gives a width of 560 m at 20 miles, not sufficient to resolve the narrow convection filaments most certainly present in an active thunderstorm cell. Workman (1967) has replied to objections involving spongy ice, and Pruppacher (1968) has given support to the Workman model through his experiments with spongy ice.

Perhaps the most puzzling result of these experiments is the behavior of ammonium carbonate (Fig. 5) since it gives strong positive

charge for strong concentrations and crosses to strong negative charge for weak concentrations. This may be explained by referring to the classical Workman–Reynolds experiment. At the instant freezing begins in the classical experiment, typical salt solutions show fast risetimes of potential and ammonium salts show much slower rises of potential. This is explained by a dipole orientation at the freezing interface which prefers to incorporate negative ions. However, the structure of the ammonium ion is better suited to the ice structure and is preferentially incorporated as the interface slowly rearranges itself for accommodation. This idea is supported by experiments described by Gross (1968) in which ice is grown from a typical salt solution and the solution is poured off and replaced by an ammonium salt solution. When growth resumes, polarity is at first the same as that of the salt solution and then slowly reverses. However, if ice is first grown from an ammonium salt solution which is replaced by a typical salt solution, an instantaneous reversal of polarity occurs. In addition, for an ammonium salt solution, the classical experiment occassionally gives a negative potential at the beginning of freezing and slowly reverts to the usual positive potential. Evidently, it takes time for the ice to begin accommodation of the ammonium ion even though it is eventually preferred. In the limited time available for freezing in this impacting drop experiment, ammonium ions are not preferentially incorporated unless their concentration is fairly high. The classical experiment does not show a high potential in this case because of the higher conductivity of the ice being formed.

Experiments with mixtures of NaCl and $(NH_4)_2CO_3$ show that the addition of ammonia to a salt solution will suppress charge generation and even reverse it for sufficiently strong concentrations. Assuming that the Workman–Reynolds effect is the charge producer in a thunderstorm, it is seen that an ammonium ion concentration of 10^{-4} M in thunderstorm water will suppress or possibly even reverse the electrification of the thunderstorm. Since a typical young thunderstorm cell is thought to contain approximately 10^{11} gm of water, 170 kg NH_3 would be required in solution in the cloud water to give the correct concentration. Experimental verification of this suggestion has been crudely attempted by Workman & Reynolds (unpublished) with inconclusive results. It is not clear how quickly ammonia would go into solution in atmospheric water; however, it is not unusual to measure concentrations of ammonia as high as 10^{-4} M in natural rainwater at the ground (Junge, 1958). If Workman's speculations are correct, this is theoretically high enough to suppress thunderstorm electrification and it would be interesting to discover coincident abnormally low thunderstorm activity. It must be remembered, however, that observed concentration at the ground does not necessarily imply the same values in charge generation centers because of the scrubbing action of rain.

Acknowledgments

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REFERENCES

Gross, G. W. 1968. Some effects of trace inorganics on the ice/water system. *Adv. Chem. Ser. 73*, 27–97.

Gross, G. W. 1970. *Electrical properties of ice.* Final Report, New Mexico Institute of Mining and Technology, Socorro, New Mexico.

Gunn, R. & Kinzer, G. D. 1949. The terminal velocity of fall for water droplets in stagnant air. *J. Meteor. 6*, 243–248.

Junge, C. E. 1958. The distribution of ammonia and nitrate in rain water over the United States. *Trans. Amer. Geophys. U. 39*, 241–248.

Latham, J. 1965. Electrification produced by the growth of soft hail in thunderclouds. *Tellus 17*, 204.

Latham, J. & Mason, B. J. 1961. Generation of electric charge associated with the formation of soft hail in thunderclouds. *Proc. Roy. Soc. London, A, 260*, 537.

Latham, J. & Miller, H. A. 1965. The role of ice specimen geometry and impact velocities in the Reynolds-Brook theory of thunder electrification. *J. Atmos. Sci. 22*, 505.

Ludlam, F. H. 1950. The composition of coagulation elements in cumulonimbus. *Quart. J. Royal Met. Soc. 76*, 52–58.

Pruppacher, H. R., Steinberger, E. H. & Wang, T. L. 1968. On the electrical effects that accompany the spontaneous growth of ice in super-

cooled aqueous Solutions. *J. Geophys. Res. 73*, 571–584.
Reynolds, S. E., Brook, M. & Gourley, M. F. 1957. Thunderstorm charge separation. *J. Meteor. 14*, 426–436.
Stratton, J. A. 1941. *Electromagnetic theory*, pp. 15–16. New York. McGraw-Hill,
Workman, E. J. 1967. The production of thunderstorm electricity. *J. Frank. Inst. 283*, 540–557.
Workman, E. J. 1969. Atmospheric electrical effects resulting from the collision of supercooled water drops and hail. *Physics of ice*, pp. 594–602. Plenum Press, New York.
Workman, E. J. & Reynolds, S. E. 1950. Electrical phenomena occurring during the freezing of dilute aqueous solutions and their possible relationship to thunderstorm electricity. *Phys. Rev. 78*, 254–259.

ВЛИЯНИЕ АММИАКА НА ЭЛЕКТРИЗАЦИЮ ЗАМЕРЗАЮЩИХ И РАЗБИВАЮЩИХСЯ КАПЕЛЬ ВОДЫ

Производились эксперименты, в которых капли воды диаметром 2 *мм* с примесью NaCl и/или $(NH_4)_2CO_3$ падали в холодном воздухе и разбивались об лед. Заряд, собиравшийся на льду, измерялся как функция температуры окружающей среды (от 0 до $-30°C$) и концентрации раствора (от 10^{-6} М до 10^{-2} М). Максимальный отрицательный заряд в 2,04 эсе/*г* получался при температуре $-20°C$ и концентрации NaCl, равной 10^{-4} М. Максимальный положительный заряд 2,79 эсе/*г* получался при концентрации $(NH^4)_2CO_3$, равной 10^{-3} М и температуре среды $-30°C$. Оказывалось возможным уменьшить и даже обратить знак обычно отрицательного электрического заряда соли добавлением аммиака, что предполагает возможность модификации грозового электричества. Все растворы с концентрациями, слабее 10^{-5} М, дают сложные волнообразные зависимости с суммарным отрицательным зарядом.