tion of lithium chloride have been measured at the same temperatures. The decrease in free energy and in heat content accompanying the transfer of one mole of lithium chloride from its solutions in alcohol to an $0.1\ M$ solution in water have been calculated.   Using the values of free energy decrease obtained for these cells, we have calculated the free energy of dilution of lithium chloride in methyl and ethyl alcohol from any concentration c_m to a concentration of $0.01\ M$ in 100 moles of solvent.   The apparent geometric mean activities of the ions of lithium chloride have been calculated for the round concentrations expressed in moles per 100 moles of solvent.

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THE SPONTANEOUS DECOMPOSITION OF AMMONIUM CHLORATE

BY FRED FAIRBROTHER

It has long been known that ammonium chlorate decomposes explosively when heated alone to about $100°$ or on being struck with a hammer if mixed with combustible matter.[1]

The decomposition of ammonium chlorate on keeping has been briefly studied by Groschuff[2] and by Gelhaar.[3]   Groschuff states that ammonium chlorate decomposes easily when kept, evolving oxygen, chlorine, ammonia (nitrogen chloride and chlorine peroxide) and that, heated above $60°$, it explodes, leaving ammonium chloride.   He also states that an aqueous solution saturated in the cold undergoes no marked decomposition on boiling.

Vauquelin[4] states that when ammonium chlorate is gently heated, acid-reacting ammonium chloride is left behind.

Gelhaar observed that a small quantity of dry ammonium chlorate when spread out flat lost in about 7 weeks 80% of its weight as gaseous products, and that the nitrogen became partially oxidized to nitric acid.

The present work shows that a cold saturated solution of ammonium chlorate does not appear to undergo any decomposition when kept indefinitely.   On the other hand, when any solid phase is present, the decomposition becomes apparent in a few days and may become violent if the quantity of solid be considerable.

A quantity of ammonium chlorate (about 30 g.) was submerged for some time in contact with about 100 cc. of the mother liquor.   The salt remained white for longer than 3 weeks, a small quantity of a colorless gas being evolved.   It then became tinged greenish-yellow, and a slow

[1] Mitscherlich, _Pogg. Ann._, **52,** 85 (1841).

[2] Groschuff, _Deut. mechan. Z._, **145,** 153 (1912).

[3] Gelhaar, _Schiess Sprengstoffw._, **11,** 166 (1916).

[4] Vauquelin, Gmelin-Kraut, "Handbuch der anorganischen Chemie," _Bd._ 1, _Abt._ 2, p. 187.

but continuous evolution of gas took place. By the beginning of the
fifth week the liquid had become quite yellow, the amount of solid phase
had decreased and the rate of decomposition appeared to be increasing.
The liquid gradually became darker yellow and considerable quantities
of a gas smelling like "euchlorine" were evolved. The temperature rose
to 30–40° and within a few hours the system exploded violently.

This was the only occasion on which the decomposition became violent.
In the subsequent experiments when quantities of 5 to 10 g. were used,
the decomposition proceeded quietly to its conclusion.

To gain some idea of the rate at which decomposition takes place, the
following experiments were carried out at room temperature.

(1) Ten g. of the dry salt was exposed in a thin layer in a Petrie dish supported on a
stand under a large bell jar. Below the ammonium chlorate was placed a dish of solid
sodium hydroxide. The dish containing the salt was weighed from day to day.

(2) Five g. of the salt was placed in a U-tube fitted with glass stoppers and loosely
plugged with glass wool, and the system weighed each day. Air, dried and purified, was
slowly aspirated over the salt, the water and acid gases being absorbed in tubes contain-
ing calcium chloride and soda lime, respectively.

The percentage losses in weight per day in each case are shown on the
graphs as 1 and 2.

In these experiments the products of decomposition were dissipated
moderately rapidly, although the salt in both cases had a greenish color.

It must be remembered that the loss in weight depends not only on the
velocity of the decomposition but also on the rate at which the volatile
products can diffuse away. The unevenness of the curves, particularly
in the latter portions, may be due to this cause, and also to slight variations
in temperature. The curves, nevertheless, give an indication of the rate
at which the action is proceeding. It will be seen that the decomposition,
which at first is very slow, increases rapidly in speed and then decreases
quickly. It is also very noticeable that the rate of decomposition is much
greater when the salt is confined in a restricted space where the products
can diffuse away only slowly.

Five g. of the dry salt was sealed in a glass bulb ending in a fine capillary; the de-
composition was very rapid and within a week had ceased. The bulb then contained
only a colorless liquid which, on analysis, was found to consist of a solution of ammonium
nitrate with a small amount of unchanged chlorate.

On the other hand, 5 g. of ammonium chlorate was allowed to decompose in a vac-
uum, the water vapor, of which a considerable quantity was evolved, and the acid gases
being removed by absorbents and the residual gas frequently pumped off. The de-
composition proceeded very slowly, taking altogether many months.

The residual gas was found to consist principally of nitrogen with a
small and varying admixture of oxygen. The absorption tubes contained
at the end of the decomposition much chloride and chlorate, but no nitrite
or nitrate.

The dry solid residues in the different experiments consisted of almost

pure ammonium nitrate, to the amount of about 30% of the original weight of ammonium chlorate, with no trace of chloride or perchlorate.

This entire absence of chloride from the solid residue when the decomposition had been allowed to proceed in the proximity of drying or acid absorbing reagents, or in a vacuum, points to the fact that hydrochloric acid is not produced as a primary product of the decomposition. On the other hand, when the salt had decomposed under the mother liquor, the latter was found to contain considerable chloride, probably from interaction between the chlorine and the water.
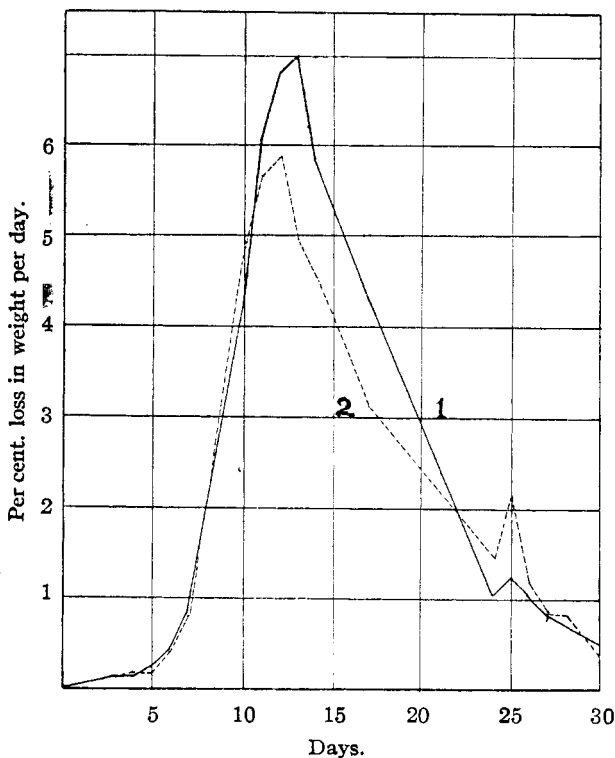

Fig. 1.

It would appear that the course of the spontaneous decomposition of ammonium chlorate probably is as follows.

The first stage is a very slow autoxidation of the molecule with the production of nitric acid, nitrogen, chlorine and water. The nitric acid reacts with more chlorate with the production of chloric acid and chlorine peroxide. These then oxidize more of the ammonium radical with the formation of more nitric acid and the liberation of chlorine. This takes place more rapidly than the initial phase, and consequently the decomposition tends to increase in speed unless the acid gases are removed quickly.

The more stable perchlorate does not appear to be formed. The relative amounts of the products vary with the conditions under which the decomposition takes place.

A mixture of ammonium chloride and potassium chlorate, unless perfectly dry, decomposes in a similar manner.

Summary

1. The rate of the spontaneous decomposition of ammonium chlorate is autocatalytically accelerated when the products of decomposition are not quickly removed.

2. The solid residue from the decomposition is ammonium nitrate with no chloride.

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THE CALIBRATION OF CELLS FOR CONDUCTANCE MEASUREMENTS

BY CHARLES A. KRAUS AND HENRY C. PARKER

In carrying out an investigation on the electrical conductance of dil. aqueous solutions of iodic acid, the constants of the cells used were determined by comparison with an auxiliary cell whose constant was obtained by means of a solution of $0.1 N$ potassium chloride made up according to the weight method, following directions given in Kohlrausch and Holborn.[1] In order to secure a check on the value obtained, the auxiliary cell was also standardized with reference to a $0.01 N$ potassium chloride solution which was similarly made up according to the directions of Kohlrausch and Holborn. The determination with respect to the $0.1 N$ solution gave a value 3.42316 and that with respect to the $0.01 N$ solution 3.40693, the difference amounting to 0.48%. Since no sources of error of this order of magnitude were apparent in connection with the calibration procedure, the directions given in Kohlrausch and Holborn were examined and found to be in error. This led to a somewhat more extended investigation of the data underlying the methods of calibrating cells for conductance measurements according to the weight method. In view of the desirability of having the results of various investigators expressed in terms of comparable units, the results are given below in some detail.

The standard solutions for the purpose of calibrating conductance

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[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Teubner, Leipzig, **1898**, p. 76. See also Kohlrausch, Holborn and Diesselhorst, *Ann. Physik*, **64**, 440 (1898).