Thermal Decomposition of Perchlorates

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The thermal decomposition of a series of seven perchlorates has been studied by means of a thermobalance, the construction and operation of which are illustrated. The data obtained are presented in the form of plots of weight loss versus temperature. The thermal decomposition of a perchlorate may proceed by one of two mechanisms: (1) by dehydration followed by decomposition to yield oxygen and a chloride, and (2) by gradual hydrolysis of hydrated compounds to yield perchloric acid and an oxide.

IT HAS been known for a number of years that when a perchlorate is heated to a sufficiently high temperature, oxygen is evolved and a chloride is left—for instance, the following reaction takes place readily at a dull red heat:

$$KClO_4 = KCl + 2O_2$$

However, no reliable data have been published on the temperatures required to bring about reactions of this type. Some scattered figures are given in the literature, but the agreement among investigators is not all that could be desired. For example, Scobai (*8*) gives the melting point of sodium perchlorate as 482° C. and states that decomposition takes place at this temperature. Carnelly and O'Shea (*1*) make the same claim but give the melting point as 432° C. Richards and Willard (*6*) give the fusion point of lithium perchlorate as 236° C. and state that it loses no oxygen at 300° C. Richards and Cox (*5*) state that pure lithium perchlorate decomposes very slowly from 410° to 430° C. and rapidly at 450° C., and that dust particles tend to lower the decomposition temperature. Inasmuch as a more accurate knowledge of the thermal decomposition of some of the commoner perchlorates was required, it became necessary to collect these data experimentally.

The choice of a suitable experimental technique for determining the decomposition temperatures of the perchlorates is complicated by the nature of the reaction. Decompositions of this type have a reputation of sometimes proceeding with explosive violence. However, even if the reaction goes smoothly, 485 ml. of oxygen are released from 100 mg. of potassium perchlorate over a short space of time, assuming 500° C. as an approximate decomposition point. Obviously, any closed-type apparatus would be inapplicable and perhaps dangerous. Glass is excluded as a material of construction but is suitable as a container for the sample. Of the remaining methods available, the thermobalance offered the best choice considering the factors involved—sensitivity, accuracy, ease of manipulation, simplicity of construction, and safety.

The literature contains considerable information concerning the construction and operation of a thermobalance. The most notable work was done by Orosco (*4*) who applied this technique to the dehydration of such materials as $BaCl_2.2H_2O$, $CuSO_4.5H_2O$, and $3MgCO_3.Mg[OH]_23H_2O$. For this work a recording-type instrument with a torsion balance was used. Practically all the other published work has been done by the Japanese (*2, 3, 7, 9, 10*), who studied the application of the thermobalance to quantitative analysis.

APPARATUS

The thermobalance used for this investigation is shown in detail in Figure 1. One significant detail in the construction of this apparatus is the use of a large billet of Duralumin to furnish a chamber which will resist the action of evolved oxygen gas at reasonable temperatures.

EXPERIMENTAL

A series of seven perchlorates was prepared, ground to a powder, and stored over phosphorus pentoxide. A convenient size sample for decomposition was found to be 100 mg. Each of the seven perchlorates—lithium, sodium, potassium, magnesium, calcium, ferric, and aluminum—was investigated by a series of three runs in the thermobalance. In the first run, which gave only an approximation of the decomposition point, the current supplied to the furnace was adjusted to give a fairly rapid rise in temperature. The second run was made at a much slower rate and gave the decomposition point within a few degrees. In the third run the current supplied to the furnace was regulated so that, at the decomposition point, the increase in temperature per minute was practically zero. By this means any lag of decomposition behind temperature was reduced to a minimum. The data of the final runs are presented in Figures 2, 3, and 4. These data were collected in conjunction with John Peterson.

Table I. Decomposition of Perchlorates

Sample	Weight of Anhydrous Material	Weight of Residue	Theoretical Weight of Chloride	Theoretical Weight of Oxide	Residue
$LiClO_4$	0.5522	0.2129	0.2200	0.0775	LiCl
$NaClO_4$	0.3394	0.1608	0.1602	0.0859	NaCl
$KClO_4$	0.5892	0.3139	0.3170	0.2003	KCl
$Ca(ClO_4)_2$	0.2025	0.0927	0.0940	0.0474	Basic $CaCl_2$
$Mg(ClO_4)_2$	0.1725	0.0224	0.0552	0.0234	MgO
$Fe(ClO_4)_3$	0.1930	0.0328	0.0722	0.0349	Fe_2O_3
$Al(ClO_4)_3$	0.1877	0.0291	0.0767	0.0294	Al_2O_3

Quantitative Decomposition of Perchlorates. Samples of each of the seven perchlorates studied were decomposed by heat in such a manner that the residue could be weighed. In all cases except potassium, a sample of the perchlorate was weighed into a small quartz dish and cautiously ignited. The dish was cooled in a desiccator and weighed.

In order to establish a basis for calculation a sample of each perchlorate (except sodium, potassium, and lithium) was analyzed for its metallic constituent. This step was necessary because the amount of hydration of the samples was not known. In the case of sodium, a sample of sodium chloride was weighed into the quartz dish and converted to the perchlorate by evaporation with perchloric acid. This material was then ignited and the weight of the residue compared with the original weight of sodium chloride. A pure sample of lithium perchlorate trihydrate was used as a source of lithium perchlorate. This material is stable in air and has a definite amount of hydration when crystallized from water solution.

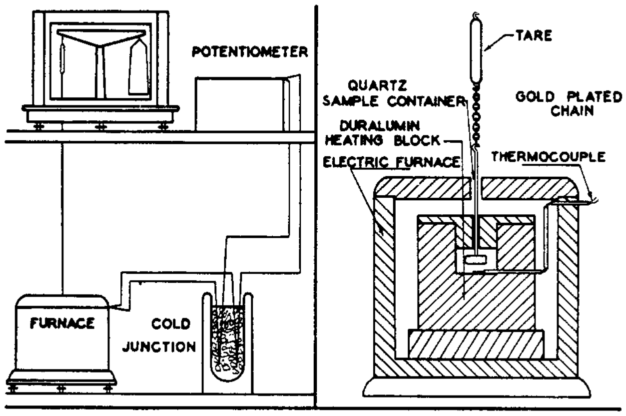

Figure 1. Thermobalance

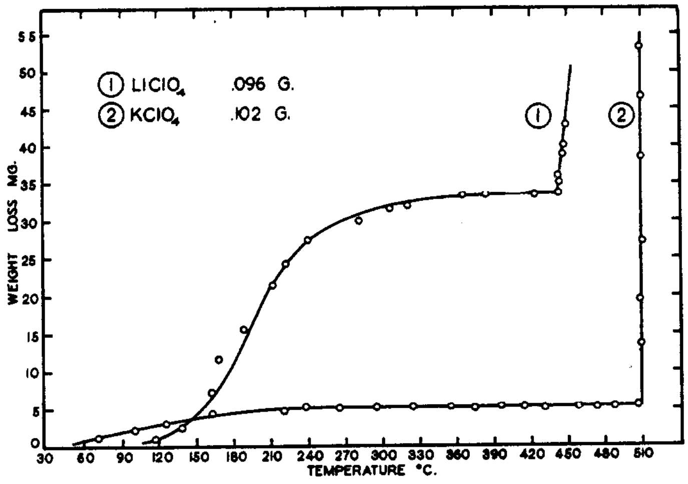

Figure 2

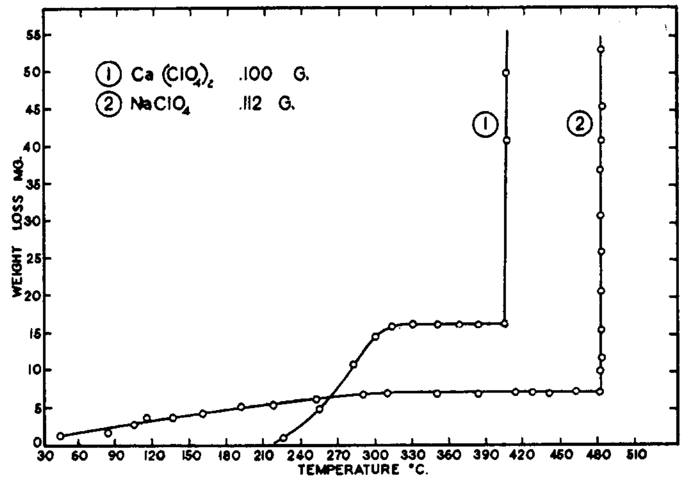

Figure 3

When a sample of potassium perchlorate was weighed into the quartz dish and ignited as above, consistently low results were obtained. Although potassium perchlorate forms no hydrates, the natural assumption was that there was some moisture still in the sample. However, an analysis conducted on a sample of salt which had been heated for 30 minutes at 500° C. was still low. The best analysis was obtained by mixing the sample in a platinum crucible with sodium carbonate, igniting, and determining chloride on the cooled melt. The result in this case corresponded to a purity of 98.98% calculated as potassium perchlorate. It is believed that the low results were due to the loss of solid material in the form of a smoke suspended in the oxygen evolved.

The results of the experiments are given in Table I. The figures in column 2 represent not the actual weight of sample taken, but the calculated weight of anhydrous salt corresponding to the amount of hydrated material. In this way all samples can be placed on a common basis. Column 4 gives a theoretical weight for the residue that would be obtained by the ignition of that weight of anhydrous salt given in column 2 if the residue is a chloride. These figures were obtained by calculating the weight of material given in column 2 to the weight of the corresponding chloride. A theoretical weight for the residue, if it were an oxide, was obtained in a similar fashion and is tabulated in column 5. By comparing the experimental weight of the residue (column 3) with columns 4 and 5, it was possible to decide whether the residue was a chloride, oxide, or mixture. These results are given in column 6.

DISCUSSION

Examination of Figures 2, 3, and 4 shows that there are two general types of curves. The first has a point where a sharp change in the slope takes place. The second has no such point, but instead, the slope changes over the full length of the curve. Lithium, sodium, potassium, and calcium perchlorates are of the first type, while magnesium, ferric, and aluminum perchlorates are of the second.

All the perchlorates, except potassium, are highly hydrated when crystallized from water solution. Two possible reactions can take place when a hydrated perchlorate is heated. First, the salt may be dehydrated to leave an anhydrous material which decomposes on further heating to yield a chloride and oxygen:

$$LiClO_4.3H_2O = LiClO_4 + 3H_2O \quad (1)$$

$$LiClO_4 = LiCl + 2O_2 \quad (2)$$

Secondly, the water contained in the crystal may actually hydrolyze the salt portion of the crystal:

$$Mg(ClO_4)_2.6H_2O = Mg(OH)_2 + 2HClO_4 + 4H_2O \quad (3)$$

In this case perchloric acid and water escape from the system and a hydroxide or oxide is left. For the most part, the extent to which Reaction 3 proceeds depends upon the temperature. Thus, as the temperature is raised, the salt is gradually hydrolyzed and no sharp break is obtained in a curve of weight loss versus temperature. This reasoning also applies to the dehydration portion of the curve for the first type of decomposition (see Figure 2). However, there is a temperature above which the anhydrous salt is unstable. When this temperature is reached, reaction takes place, evolving oxygen, and becomes evident by a sharp loss in weight.

The question as to whether complete decomposition accompanied by the evolution of oxygen takes place at a definite temperature or over a range of temperature is beyond the scope of this paper. It is certain, however, that decomposition actually begins at a definite temperature and will continue, faster and faster, over an indefinite range upwards. Since it is very easy to extend the decomposition over a considerable range of temperature by rapid heating, a very slow rise in temperature is required to fix the temperature at which measurable decomposition occurs.

The following facts are submitted in justification of the above explanation for the two types of weight loss versus temperature curves obtained. Of the perchlorates investigated sodium, lithium, potassium, and calcium decomposed to give a sharp break in the curve, while magnesium, iron, and aluminum did not. Of the seven metals listed, the first four are generally considered strong bases. On the other hand, iron and aluminum are

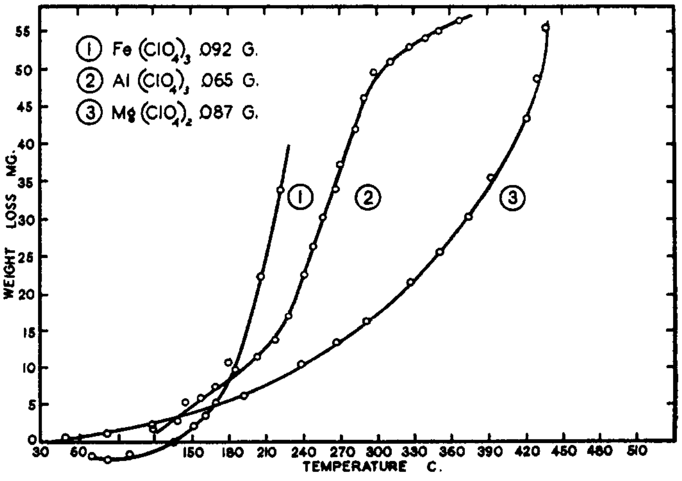

Figure 4

very weakly basic and magnesium is on the border line. It is a well-known fact that the salts of the weaker bases are more easily hydrolyzed than those of the strong bases. Thus, even though lithium, sodium, and calcium perchlorates are hydrated, they are sufficiently strong bases to withstand the action of the water. The basic strength of magnesium, iron, and aluminum, however, is not sufficient to prevent hydrolysis.

The results obtained in the quantitative decomposition of the perchlorates bear out even more conclusively the two types of decomposition. If the above explanation is valid, one would expect chlorides in the case of lithium, sodium, potassium, and calcium, and oxides from magnesium, iron, and aluminum. As the results indicate, this is a fact, except in the case of calcium. However, the weight of residue obtained from the ignition of $Ca(ClO_4)_2.XH_2O$ corresponds very nearly to the empirical formula $CaO.20CaCl_2$, which has no particular significance. Obviously, calcium is just on the border line between the two types of decomposition but is still predominantly of the first type.

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Ring and Ball Softening Points of Resins

A Constant-Temperature Air-Bath Method

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A method of determining softening points of resins is described, in which the sample is heated in an air bath immersed in a liquid bath held at a constant temperature. A scheme and tentative formula are presented for correlating the varying observed softening points of a resin obtained when different liquid bath temperatures are used, together with a basis for selection of the bath temperature suitable for making the test.

THE suitability of many resinous products for particular uses is often related to the softening point—that is, the temperature at which the material reaches some specified degree of fluidity. The temperature range within which such fluidity is to be maintained—that is, the softening point limits—is frequently incorporated in specifications. However, this softness or fluidity (softening point), as determined by the usual test methods, is a function not only of temperature but also of the duration of the exposure of the resin to the heat. It is also affected by the medium by or through which the heat energy is conducted to the resin. Therefore, all numerical values depend entirely on the purely arbitrary and empirical procedure used in their determination, and must be identified with the name or description of the method.

Perhaps the best known method for determining softening points is the A.S.T.M. ring and ball method, first adopted as a tentative method in 1916 for use with bituminous materials, and now designated as A.S.T.M. D36–26 (*1*). In order to adapt the method to resinous materials, Walker (*6*) proposed certain modifications, principally a change in the design of the ring in which the sample is molded. On recommendation of Committee D-17 on Naval Stores of the American Society for Testing Materials, this method was adopted as a new tentative standard in 1936, and is now known as A.S.T.M. E28–42T (*2*).

Although this method has proved satisfactory and is often specified as the test method when the softening point is incorporated in specifications for rosins and related resins, several features have limited its usefulness. One is the time required to run a large number of samples, as must be done in some plant control laboratories. Another is the provision that, for softening points up to 80° C., water shall be used as the bath medium, while for softening points above that temperature glycerol shall be used. For resins softening at or near 80°, the bath medium must be stated, since these softening points may differ according to the bath liquid used. Finally, in some cases the hot glycerol has a softening or plasticizing effect on certain synthetic resins that soften in the higher temperature ranges.

One of the projects of A.S.T.M. Committee D-17, through its Subcommittee I on Softening Point of Rosin, is the survey or development of new methods and modifications of present methods for determining the softening point, with the view of developing, if possible, a method that will be better adapted to the needs of the industry. Five requirements have been set (*4*):

1. Apparatus to be of simple design and low cost
2. Procedure to be more rapid than the present one
3. Results to have good reproducibility within ±1.0° C.
4. Method to be applicable to a wide range of softening points
5. Results to have close correlation with present ring and ball softening point values

This paper describes a method of test, in which the sample is heated in an air bath immersed in a liquid bath held at a constant temperature. The method is believed to meet the above requirements and also to overcome the objections to the present method, E28–42T. A scheme for determining the proper bath temperature at which any resin is to be tested is also presented, together with the experimental data and theory upon which the temperature selection is based.

Several air-bath methods are already in use. A method developed by the Bakelite Company has been included in Navy Department Specification 52R 10b for *p*-phenylphenol-formaldehyde resins (*5*). In addition to employing a different size ball and ring, it retains the feature of a rising temperature for the heating bath. Both the General Electric Company and Hercules Powder Company have methods for bituminous materials and rosins, using the so-called "thermometer drop" principle. These methods employ a specified weight of sample that is molded onto the bulb of a thermometer, and placed in a preheated air bath until it forms a tear drop which falls slowly from the thermometer bulb. These two methods, although satisfactory when used by experienced plant control chemists, have not been considered suitable for collaborative study and standardization for adoption as A.S.T.M. methods.

Another constant-temperature method is that of Hershberger