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by

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ABSTRACT

New equipment for measuring the rate of decomposition of perchlorate ion in fused NaOH is described. Evidence is presented to show that as the $NaClO_4$ starting concentration was increased the rate decreased. In the case of $KClO_4$, as the concentration is increased the rate increases. The results of preliminary experiments may indicate that the rate decreases with decreasing NaOH concentration. A large increase in the solubility of $BaSO_4$ in fused $NaNO_3$ is produced by the addition of NaOH.

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Fused Sodium Hydroxide

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I. Decomposition of Perchlorate Ion in Fused Sodium Hydroxide

New equipment for measuring the rate of decomposition of perchlorate ion in fused sodium hydroxide has been designed and built. A need for new equipment was indicated as a result of some of the experiments mentioned earlier in Report NYO-7580 (June, 1959). First, the results of experiments in which the NaOH melt was not preheated to 450° to expell water indicated that the rate of reaction may be accelerated to a small extent by the presence of a small amount of water. Secondly, when NaOH pellets are slowly dropped into an aluminum container which has been preheated to 450°C., creep of the melt is virtually eliminated. However, when NaOH pellets in an aluminum container are slowly heated to 450°C., considerable creep is observed. It would appear that the creep of the melt may somehow be dependent on the presence of water in the melt. Therefore, the efficiency with which water is eliminated from the melt seems to be dependent on the procedure used. Thirdly, it seemed desirable to be able to conduct two experiments simultaneously under the same experimental conditions. Only one experiment could be conducted at one time with the old apparatus. And finally, temperature control up to this time was only 1° in the 300-400° range using a thermister controller. It seemed desirable to improve the temperature control to 0.1°C.

Metal Block Thermostat:

Basically the apparatus is the same as that described earlier in Report NYO-7578 (June, 1957). However, in addition to the holes drilled into a large aluminum block to accomodate a Fenwal Thermoswitch and a chromel-alumel thermocouple, two receptacles were drilled for two reaction cups. The reaction cups were machined to a wall thickness of about 2 mm. and a diameter such that they would fit into the receptacles in the metal block thermostat with a maximum clearance of 0.05 inches.

A thermocouple was used to probe the reaction cups in the metal block thermostat for temperature gradients. No gradients larger than 0.01° exist either between or inside of the two reaction cups.

Furnace:

The furnace is equipped with a main resistance heater (about 200 watts at 300-400°C.) and an auxiliary resistance heater (15-30 watts) operated through Variacs powered by a constant voltage source (Sola Constant Voltage Transformer). The auxiliary heater was controlled either automatically by the Fenwal Thermoswitch or manually. The metal block thermostat is completely enclosed in the furnace with only two small access holes to extract samples. The access holes are fitted with two small aluminum tubes whose inside diameter is somewhat smaller than the inside diameter of the reaction cell. These tubes serve as a guide so that all of the perchlorate sample will drop into the melt.

Method of Operation and Temperature Control:

The main heater is adjusted to about 10° below the desired operating temperature. Then the Fenwal Thermoswitch is adjusted to the desired temperature, and the apparatus is allowed to come to equilibrium overnight. The aluminum reaction cups are heated in another furnace to about 470-490°C. NaOH pellets are slowly dropped into the hot cups. After allowing about 30 minutes for the water to be expelled, the cups are allowed to cool to about 350° and transferred to the receptacles in the metal block thermostat. About one hour is required for the apparatus to come to equilibrium again. The Fenwal Thermoswitch is then shunted and the auxiliary heater controlled manually with a Variac. While the temperature was previously controlled to 1°, with a little practice control of 0.5° is possible.

Dependence of Rate of Decomposition on Initial Perchlorate Concentration:

A number of additional experiments have been carried out to re-examine the dependence of the rate of decomposition of perchlorate on the initial perchlorate ion concentration. As mentioned earlier in Report NYO-7580, a reaction rate dependency on the starting concentration of $KClO_4$ has been observed. Subsequent calculations indicated that a simple relationship between rate of decomposition and initial $KClO_4$ concentration does not exist. Facts were also presented to indicate that the rate might be dependent on the potassium ion concentration.

A number of experiments have been made in which the starting concentration of $NaClO_4$ in fused NaOH is varied. The results of these experiments are reported in the following table:

Rate Dependence on $NaClO_4$ Concentration*

$NaClO_4$ Starting Concentration (Molons#)	$t_{1/2}$ (min.)
1.22	100
1.15	84
0.55	70
0.40	46

* reaction temperature 382°C.
\# moles of solute per 1000 grams of solution

On the basis of this evidence it is concluded that a reaction rate dependency on the initial perchlorate ion concentration does exist. It is interesting to note that whereas the rate of decomposition increased with increasing $KClO_4$ concentration (Report NYO-7580), in the case of $NaClO_4$ the rate decreases with increasing concentration. However, since these experiments were carried out before the new apparatus was completed, additional experiments are planned to study concentration effects. A complete mathematical analysis will then be made for the reactions.

Stirring Effects:

Several experiments have been carried out to determine whether a stirring mechanism is really necessary. A mechanical stirrer and N_2-gas bubbling stirrer, and a N_2-gas bubbling stirrer and no stirrer comparison was made using the new apparatus described earlier in this report. The results of this study are presented in the following table:

Stirring Effects*

Stirrer	$NaClO_4$ Starting Concentration (Molons#)	$t_{1/2}$ (min.)	Temperature (°C)
N_2-gas	0.109	68	390°
Mechanical	0.110	84	
N_2-gas	0.087	137	389
Mechanical	0.086	122	
N_2-gas	0.031	95	388
Mechanical	0.031	87	
N_2-gas	0.498	139	389
Mechanical	0.615	114	
None	0.674	109	388
N_2-gas	0.609	150	
None	0.674	112	388
N_2-gas	0.574	165	

*$NaClO_4$ samples used for decomposition in these experiments
\#moles of solute per 1000 grams of solution

Unfortunately because of the nature of the system it was impossible to make up exactly the same $NaClO_4$ starting concentration for each pair of experiments. However, it is possible to get an idea of the magnitude of the starting concentration effect on the half-life of the reaction from the table on page 4. Thus it is concluded that within experimental error, it is immaterial whether or not one of the three different stirrers referred to above is used.

II. Perchlorate Ion Decomposition in NaOH - $NaNO_3$ Mixtures

A preliminary investigation was made of the effect in diluting the NaOH concentration by adding fused $NaNO_3$ on the rate of decomposition. As mentioned in Report-7580, the very slow decomposition of perchlorate in fused KNO_3 indicates the hydroxyl ion to be important. The results indicate that the reaction is dependent on hydroxyl ion concentration. Furthermore, the rate decreases with decreasing hydroxyl ion concentration. However, since the experiments were all conducted in approximately 50% (by weight) NaOH solutions, the effects were quite small. It is planned to further study these effects in solutions very dilute in NaOH.

III. The Effect of Sodium Hydroxide on the Solubility of Barium Sulfate in Fused Sodium Nitrate

The solubility of barium sulfate in fused sodium nitrate at 330° has been measured and found to be roughly ten times its solubility in water at room temperature. The effect of an added salt with an ion in common to the barium sulfate has been investigated. On addition of either barium nitrate or sodium sulfate, a decrease in barium sulfate solubility was observed; within the limit of experimental uncertainty, corresponding to the existance of a constant solubility product. Due to difficulties of filtration which were not overcome in the short time put on this investigation, the results were quantitatively not very satisfactory. However, it was observed that addition of sodium hydroxide caused a great increase in the solubility of barium hydroxide in sodium nitrate. No explanation of this effect has been found. It is the sort of thing which deserves further investigation.