The increase in G for potassium nitrate above room temperature can be well correlated with the increase in 'free space' resulting from thermal expansion (see graph). However, G for sodium nitrate increases with temperature out of all proportion to the increase in 'free space': we do not know why.

A full account of this work, and of many other results from the irradiation of nitrates, is being prepared for publication.

The idea that the 'free space' difference might explain the difference between the rates of decomposition of potassium and sodium in a nuclear reactor was first put forward by Hennig, Lees and Matheson².

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Esterification by the Nitronium Ion in Aqueous Perchloric Acid

THE nitronium ion, NO_2^+ , has been shown to be the active nitrating entity in the O-nitration of certain alcohols in organic solvents¹ in which nitric acid is present in large excess. Kinetic studies in progress on the esterification of *iso*amyl alcohol with nitric acid in 55–62 per cent aqueous perchloric acid have now indicated that here also O-nitration proceeds through the nitronium ion, although only a very small fraction of the nitric acid can be present in this cationic form in media of such high water-content. Rate measurements at 25° C. made by ultra-violet spectrometric analysis of the unchanged nitric acid after dilution of aliquots with water and extraction of the *iso*amyl nitrate product show that the rate equation (1) is obeyed:

$$d[\text{iso-AmNO}_3]/dt = k[\text{iso-AmOH}][\text{HNO}_3] - k'[\text{iso-AmNO}_3] \quad (1)$$

In the range of media studied, about 30–55 per cent conversion to the nitrate ester occurs. Interaction of the medium with *iso*amyl alcohol is negligible. The identification of the nitronium ion as the esterifying agent follows from the demonstration of parallelism over a range of media of $\log k$ and $\log R$ where R is the ionization ratio $[R^+]/[ROH]$ for a base ROH which ionizes to form R^+ by the same process as that which converts nitric acid to the nitronium ion². The relationship between $\log k$ and $\log R$ has been tested in the form of equation (2):

$$d \log k / d \text{ percentage HClO}_4 = d \log R / d \text{ percentage HClO}_4 \quad (2)$$

in which R is the ratio $[\text{NO}^+]/[\text{HNO}_2]$ for the ionization of nitrous acid to the nitrosonium ion, NO^+ , in aqueous perchloric acid³, and as shown in Fig. 1, the rate of change of $\log k$ and of $\log [\text{NO}^+]/[\text{HNO}_2]$ with the medium are the same. The lack of parallelism of $\log k$ with the Hammett acidity function⁴ H_0 indicates that the esterifying agent is unlikely to be the nitracidium ion H_2NO_3^+ .

Fig. 1

Equation 2 in its appropriate form was first used for aqueous sulphuric acid media⁵ to verify that nitration of aromatic compounds proceeds through the nitronium ion over a wide range of media; R values used were those for the ionization ratio for a triphenylcarbinol indicator, and appreciable deviations were found from equation 2 in certain ranges. We have found that $\log R$ for 4-trimethylammonium triphenylcarbinyl methyl ether perchlorate plotted over the range 50–60 per cent perchloric acid gives a straight line of slope of 3.04, which is 10 per cent higher than those for the esterification rate and the $[\text{NO}^+]/[\text{HNO}_2]$ ratio given in Fig. 1. This suggests that correlations between rate and ionization ratio are dependent on the size of the molecules and ions concerned.

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A Photon Counter of High Sensitivity for the Vacuum Ultra-violet Region

PHOTO-EMISSIVE receivers for the region of the spectrum below 2000 Å. have generally been used for the sensitive surface pure metals (platinum, tungsten, copper) or alloys (beryllium-copper¹, chrome-iron²) the photo-thresholds of which lie near 2000 Å., thus rendering them insensitive to stray light in the near ultra-violet. Such materials, while lending themselves to reproducibility of surface, have not shown high quantum efficiencies except at the very short wavelengths³—below 1000 Å. In the measurement of low light-levels, for which purpose counting of photo-electrons, whether by electron multiplier or gas amplification, is best suited, quantum efficiency may best be defined as the fraction of incident quanta detected, that is, which cause emission of one or more electrons detectable as a group. Values of the efficiency defined in terms of the average number of electrons per incident quantum, which may be rather