

**150.** *The Thermal Decomposition of Sodium and Potassium Azides.*

By W. E. GARNER and D. J. B. MARKE.

THE alkaline-earth azides possess activation energies in the neighbourhood of 20 kg.-cals., whereas for lead azide, this energy is 38 kg.-cals. for the  $\alpha$ -form, and 37 kg.-cals. for the  $\beta$ -form (see later). The alkali azides have not been investigated from this point of view, and one of the objects of the present investigation is to fill this gap in our knowledge.

According to earlier investigations, the decomposition of the alkali azides begins to be appreciable at temperatures 30–40° below the melting points of the salts, *i.e.*, at 260–320°, whereas the more sensitive azides of the alkaline-earth metals decompose at temperatures in the neighbourhood of 100° (Tiede, *Ber.*, 1916, **49**, 1742; Andreew, *Physikal. Z. Sowjet-Union*, 1934, **6**, 121; Harvey, *Trans. Faraday Soc.*, 1933, **29**, 653). Lead azide, on the other hand, which is much more sensitive than the azides of the alkaline earths, decomposes at appreciable rates only at temperatures above 220° (Garner and Gomm, *J.*, 1931, 2129). Since the activation energy is usually greater the higher the temperatures at which the reactions take place, it appeared likely that the activation energies of the alkali azides would be higher than those of any of the azides hitherto studied; this has not been found to be the case, although the values, 36.1 and 34.4 kg.-cals. for the potassium and the sodium salt respectively, are much higher than those of the azides of the alkaline earths. The cause of the discrepancy is shown to lie in the high volatility of the metallic products of the alkali azides, which reduces the area of the interface at which the reaction can proceed, and thereby increases the temperature at which reaction can first be observed.

A further point of interest in the study of the alkali azides concerns the nature of the nuclei from which the reaction spreads. The decomposition of solids normally commences at nuclei which increase in number and size as the reaction proceeds. In the majority of solid reactions there is an induction period followed by a reaction at an accelerating rate. The induction period, certainly in the case of hydrates and probably also in the case of other solids, is mainly due to the very slow rate of growth of the nuclei when first formed (Bright and Garner, *J.*, 1934, 1872; Garner, Gomm, and Hailes, *J.*, 1933, 1393; Garner and Southon, *J.*, 1935, 1705). The causes of the slow rate of growth of small nuclei are still obscure, but one of the authors, on the basis of the fact that rate of evolution of gas in many cases is given by  $dp/dt = \text{const. } e^{kt}$ , has concluded that the nuclei grow by means of a branching-chain mechanism. For potassium azide, experimental evidence is brought forward which shows that in the neighbourhood of 330° the reaction spreads into the mass of the crystal at an accelerating rate and possesses the characteristics of a chain reaction.

EXPERIMENTAL.

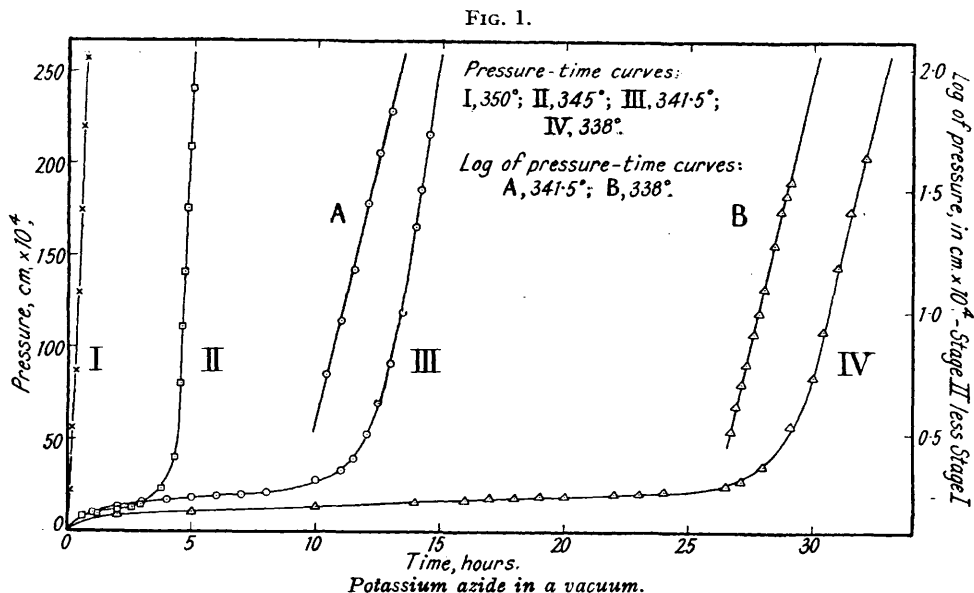
*Preparation of Sodium and Potassium Azide Crystals.*—Two specimens of sodium azide, from Schuchardt's and from British Drug Houses, were employed. Schuchardt's potassium

azide was used. Purification was effected by dissolving the crystals in water to give saturated solutions. After filtration, an equal volume of alcohol was added and the precipitated azide was washed with alcohol and dried in a vacuum desiccator (cf. Briner and Winkler, *J. Chim. physique*, 1923, 20, 206). The azides were then redissolved in water, and crystals obtained by slow evaporation at room temperature. The solutions were rejected after they had stood for 5 or 6 days, as it was considered probable that hydrolysis of the azide and the evaporation of hydrazoic acid would interfere with the quality of the crystals.

*Potassium azide.* The crystals were well-formed tetrahedra except for one face, the under side of the crystals, where a deep crater occurred. These crystals were free from chloride, and analysis by conversion into silver azide and weighing the silver as chloride gave their purity as 99.5, 100.1%.

*Sodium azide.* This salt could not be obtained as single crystals but as star-shaped aggregates 1—2 mm. in length. It was analysed by the above method and shown to contain the theoretical quantity of azide (99.8, 100.9%).

*Decomposition of Crystals of Potassium Azide in a Vacuum.*—Measurements of the rates of decomposition were carried out in an apparatus of the type described previously (Garner and



Hailes, *Proc. Roy. Soc.*, 1933, A, 139, 576). A single crystal, 1—3 mg., was employed, and this was lowered into the evacuated reaction vessel in a small platinum bucket. The course of the reaction was followed on a McLeod gauge by measurements of the nitrogen liberated. The m. p. of potassium azide is about 350° and it was not found possible to study the rate of decomposition below 330°. The typical pressure-time curves in Fig. 1 show that when the azide is solid, there is an initial evolution of gas, the rate of which slowly decreases to an approximately constant value. After a period of time which increases as the temperature is lowered, the reaction commences to accelerate, the acceleration obeying the same relationship as found previously for mercury fulminate, lead azide, barium azide, and lead styphnate, viz.,  $dp/dt = \text{const. } e^{kt}$  (Fig. 1, A and B). The rate of this reaction varies as the 10th to the 30th power of the time. The solid reaction thus takes place in two stages, and in this respect potassium azide resembles mercury fulminate, although for the latter the initial surface reaction is less prominent. Above the m. p., the rate of reaction is very rapid and resembles in character the second stage of the solid reaction (Fig. 1).

Microscopical examination of the crystals after various periods of heating has thrown light on the two stages of the reaction. During stage I, the crystals become rounded at the edges, and the surface becomes eroded along lines which may have been originally cracks. The crystals remain colourless, and since the potassium produced by the decomposition volatilises away, no nuclei can be observed on the surface. The reaction is obviously occurring mainly along the

edges of the crystal and may be due to incipient melting or loosening of the lattice along these edges. The rate of this stage of the reaction is not much affected by temperature.

Stage II is accompanied by marked changes in the appearance of the crystal: it becomes divided into rounded blocks some of which are blue and others colourless. Holes of the approximate size of a block appear in the crystal, which soon has the appearance of a honey-comb. This stage of the reaction is apparently a process which is disseminated throughout isolated portions of the crystal lattice, and is accompanied by the liberation of potassium metal in a finely divided state. The process must start from nuclei, since it is limited to individual blocks of the crystal. The reaction being of the accelerating type, the infected blocks decompose rapidly, giving rise to the honey-comb structure.

The degree of reproducibility of the rate of reaction from one crystal to another is poor, and also irregularities occur which make it impossible to determine the temperature coefficients for

FIG. 2.

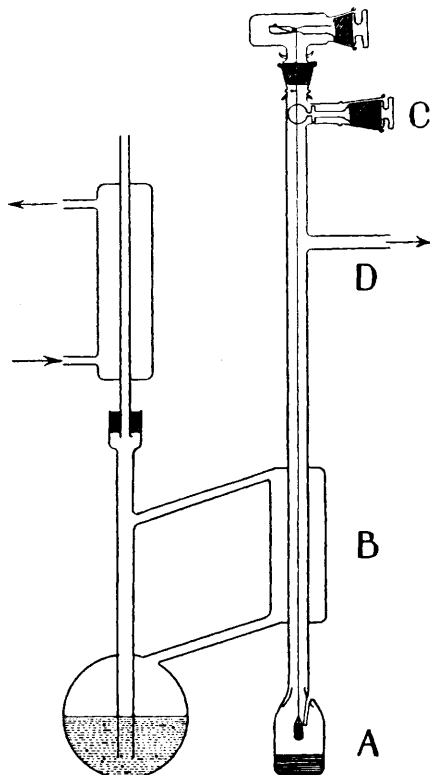
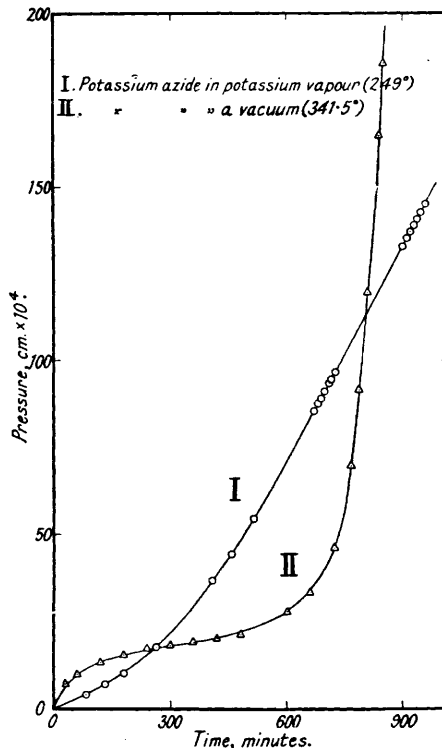


FIG. 3.



either stage I or stage II. In the case of solid reactions, there is always found some variation in the rate of reaction from crystal to crystal due to minute differences in crystal structure, but potassium azide shows much greater irregularities than usual. These it was thought might be due to variations in the rate at which potassium metal evaporated from the surface, so it was decided to study the decomposition in the presence of a constant vapour pressure of potassium.

*Decomposition of Potassium Azide in Potassium Vapour.*—After many attempts a suitable type of apparatus was designed (Fig. 2). The reaction vessel consists of a cylindrical Pyrex bulb *A*, into which is fused a glass tube to take the thermocouple junction. After a thorough baking-out of the apparatus, potassium, carefully freed from paraffin, is distilled into *A*. This metal can be vaporised by surrounding the reaction vessel with an electric furnace at the required temperature, and condensed by means of the condenser *B*, which is attached to a boiler containing a non-inflammable liquid of which the b.p. is above the m. p. of the metal. Glass flanges at the top of the reaction vessel direct the condensed potassium away from the centre of the reaction vessel where the crystal is suspended. The inner tube of the condenser is extended up to a circular glass stop at *C* which can be rotated by a ground joint. This extension serves

as an air condenser, and the glass stop prevents any potassium atoms not condensed below from reaching the ground joints at the top of the apparatus. The crystal was lowered into the reaction vessel in a heavy platinum bucket by means of a thin platinum wire attached to the spindle device previously described. The wire is corroded by the potassium vapour and has to be frequently renewed. The pumps were connected at *D* through a liquid-air trap.

The potassium interacts with the water in the glass at 200–300° and gas is given off in considerable quantities, so it was necessary to bake out for 1–3 weeks before introducing a crystal. After being baked out, the apparatus is filled with dry nitrogen, and the crystal introduced at the top of the apparatus. After re-evacuation, the crystal is lowered into the potassium vapour in the reaction vessel, and measurements of the pressure started immediately.

In potassium vapour, the decomposition could be followed down to 220°, which is 100° lower than the lowest temperatures at which observations could be made in a vacuum. The form of the pressure–time curve is radically different from that obtained in a vacuum : those obtained

FIG. 4.

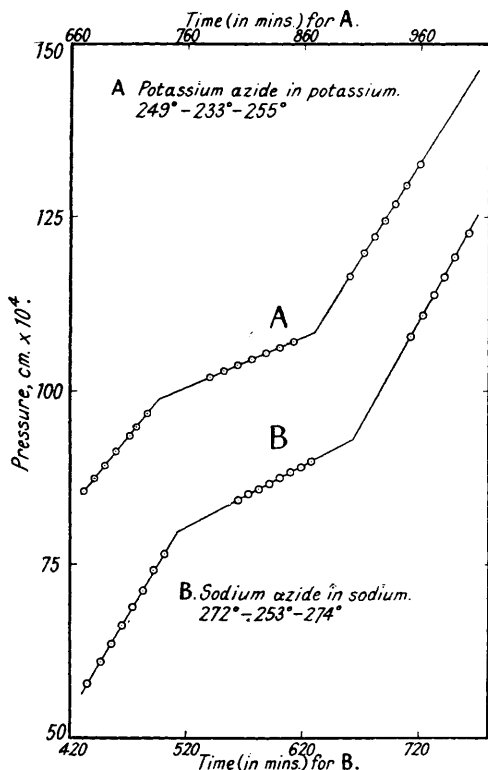
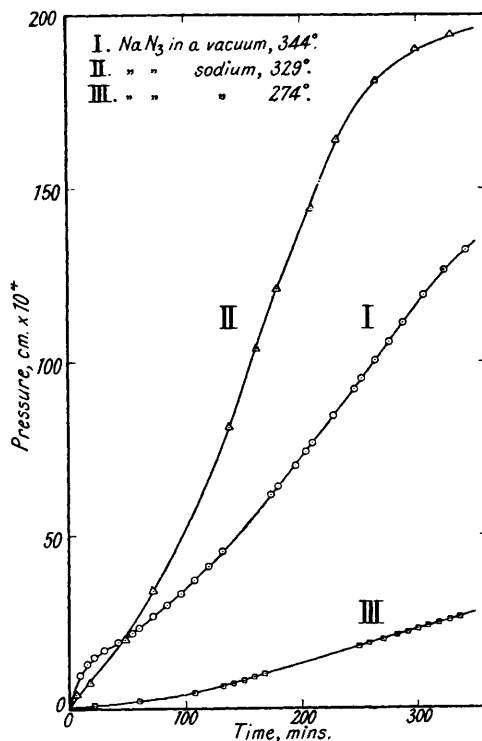


FIG. 5.



in a vacuum at 341.5° and in potassium vapour at 249° are given in Fig. 3. In potassium vapour, the initial stage of the solid reaction mentioned above is not observed, and after a very short period of acceleration, the rate of reaction soon becomes linear. The reproducibility from crystal to crystal was still unsatisfactory, however, but the linear rate of reaction made it possible to determine the activation energy with one crystal (see later). Examination of a partly decomposed crystal showed that the reaction was occurring mainly on the external surface, and that the honey-comb structure was not formed to any appreciable extent. Observation of the surface is, however, difficult on account of the presence of the metal, which rapidly oxidises in the air.

*The Activation Energy of Potassium Azide.*—A crystal of the azide was heated until it gave a constant rate of evolution of gas, and then the temperature of the furnace was lowered by about 20° and further readings taken. The temperature was then raised to its original value and the rate again measured (Fig. 4, A). If the rate of evolution of gas was unaffected by the double change of temperature and remained linear throughout, the experiment was considered satis-

factory. It is important that the crystals be not subjected to too great or too sudden a change in temperature, otherwise the rate of reaction on return to the original temperature may be increased, probably owing to an increase of the surface due to cracking. It is rare that more than one experiment can be carried out with one filling of potassium, on account of the breaking of the suspension wire on attempts to remove the crystal. The results are summarised in Table I, where  $E$  represents the activation energy. The rates in col. 4 are given as the number of molecules of nitrogen evolved for unit area of the crystal in one second. The areas of a number of crystals were measured and found on an average to give an external area of  $0.141 \text{ cm.}^2$  for  $4.5 \text{ mg.}$

TABLE I.

*Activation Energy of Potassium Azide in Potassium Vapour.*

Expt.	Wt., mg.	Temp.	Rate $\times 10^{-15}$ .	$E$ , kg.-cals.	Expt.	Wt., mg.	Temp.	Rate $\times 10^{-15}$ .	$E$ , kg.-cals.
7	2.8	243.6°	1.02	} 33.1	10	5.45	250.8°	1.74	} 36.2
		224.6	0.30				230.4	0.43	
8	5.2	247.9	4.55	} 35.6	11	4.45	249.0	1.23	} 36.4
		221.7	0.75				233.1	0.41	
		238.3	2.76				255.0	1.57	

In Expts. 7 and 10, the second stage of the experiment was unsatisfactory since the reaction was no longer linear. The greatest weight is placed on the first values of Expts. 8, 10, and 11, and these give a mean of  $36.1 \text{ kg.-cals.}$  The calculated rate of condensation of potassium on the surface of the azide is more than 1000 times greater than the rate of reaction, being  $7.2 \times 10^{18}$  atoms/cm.<sup>2</sup>/sec. at  $222^\circ$ .

*The Decomposition of Sodium Azide.*—The m. p. lies above  $365^\circ$  according to our measurements, and it was possible to follow the solid reaction from this temperature down to  $257^\circ$ . In a vacuum, the pressure-time curves are similar to those of the potassium salt in potassium vapour, except that an initial surface reaction is present to a very slight extent. The acceleration of the rate commences very soon after the insertion of the crystal, but it soon disappears in a practically linear rate of reaction. A partly decomposed crystal shows a block structure, but the honey-comb is only slightly developed. Some of the blocks are coloured pink instead of blue, as observed with potassium azide. A typical curve for sodium azide in a vacuum at  $344^\circ$  is shown in Fig. 5, together with curves for the azide in sodium vapour at  $329^\circ$  and  $274^\circ$ . The catalytic effect of sodium vapour is much smaller than that of potassium on potassium azide.

*Activation Energy of Sodium Azide.*—This was obtained by measurements in sodium vapour as previously described for potassium. Special care has to be taken in purifying the sodium, otherwise faulty results may be obtained. This, we consider, is due to the coating of the surface of the azide with the impurities present. The results are collected together in Table II, and a typical pressure-time curve is given in Fig. 4, B. The rates of decomposition are calculated and expressed as before. The crystals of sodium azide were much more irregular in shape than those for the potassium salt, and hence the rates in col. 4 will be maximum values.

TABLE II.

*Activation Energy of Sodium Azide in Sodium Vapour.*

Expt.	Wt., mg.	Temp.	Rate $\times 10^{-15}$ .	$E$ , kg.-cals.	Expt.	Wt., mg.	Temp.	Rate $\times 10^{-15}$ .	$E$ , kg.-cals.	
6	4.45	271.9°	1.71	} 35.0	9	4.8	273.9°	(3.69)	} (27.9)	
		252.6	0.525				241.6	0.75		33.6
		273.6	1.81				260.8	2.42		32.4
7	4.75	268.3	0.99	} 35.8			240.6	0.73	} 33.2	
		247.6	0.265				260.6	2.46		
		264.3	0.77							

The rate of collision of sodium atoms per second with  $1 \text{ cm.}^2$  of surface is  $1.31 \times 10^{18}$  at  $272^\circ$  and  $0.58 \times 10^{18}$  at  $253^\circ$ , and these rates are approximately 1000 times greater than the rates of reaction. Thus the surface of the crystals is probably completely covered with sodium during the reaction. The average activation energy for the range  $240\text{--}275^\circ$  is  $34.4 \text{ kg.-cals.}$

*Residue after Decomposition.*—With both azides, particularly the sodium salt, it was difficult to carry the decomposition through to the end, and with sodium azide in a vacuum at  $348^\circ$ , the reaction almost reached a standstill when only 85% of the gas had been given off. Analysis of

the white amorphous residue with silver nitrate showed that it was not hydroxide but possessed the properties of an azide, giving a white precipitate soluble in nitric acid. On heating to 361° in vacuum, sodium azide was decomposed to the extent of 92%, but it was only when the azide was heated in the metallic vapour at 329° that complete decomposition could be brought about. Even in this case, the final stages of the reaction were always slow. Since the analyses showed that there could be only a small amount of impurity present, it is concluded that the retardation of the rate of evolution of gas which occurs at the end of the experiment is due to the coating of the crystal blocks with a layer of non-volatile impurity. A very small amount of impurity would be sufficient to account for the results. This effect of impurity is very marked in the case of the alkali-metal azides, since the whole of the products are volatile.

#### DISCUSSION.

Potassium and sodium azide crystals undergo appreciable decomposition at temperatures above 330° and 270° respectively, to give the metal and nitrogen. On account of the volatility of the metal, there is no permanent interface between the salt and its products; and the reaction occurs partly on the external surface of the crystal and partly in the interior. The surface reaction is rapid at first and then falls off to a steady rate. The internal process possesses an induction period which is very marked in the case of potassium azide and decreases with increase in temperature. The internal reaction proceeds stepwise from one fragment of the crystal to another, and the blocks become penetrated by the metal, and the disappearance of some of them gives rise to the honey-comb structure. The phenomena are of such a coarse texture that 'bumps' sometimes appear on the pressure-time curves. The relation  $dp/dt = \text{const. } e^{kt}$  is, however, obeyed within the experimental error. The process occurring within the solid is so complex that it is difficult to decide whether the rate-determining process is the spread of reaction chains throughout the individual grains or is due to a chain-like propagation of the reaction throughout the blocks. Either process would account for the acceleration of the reaction.

The rate of decomposition of the alkali azides in the presence of the saturated vapour of the metal is greater than in a vacuum: for the potassium salt the rate of reaction at 240° in the metal vapour is approximately the same as that in a vacuum at 340°. In the presence of the saturated metallic vapour, the azide surface will be covered with a metallic film possibly many atoms thick, and since the rate of condensation of potassium from the vapour phase is 1000 times greater than the rate of liberation of potassium by the chemical reaction, this film of potassium atoms will be maintained practically intact throughout the reaction. The reaction at the lower temperatures occurs mainly in the neighbourhood of the interface between the azide and the metal, and the reaction in the interface is thus the most rapid process occurring, as is usually observed with solid reactions. The only exception so far known is the decomposition of "nitrogen iodide" ( $\text{NI}_3, \text{NH}_3$ ), where the reaction is retarded by the products (Garner and Latchem, *Trans. Faraday Soc.*, 1936, **32**, 567). Sodium vapour accelerates the decomposition of sodium azide, but since the volatility of sodium is less than that of potassium, the interface in a vacuum possesses greater stability, and the acceleration is not so marked.

*The Activation Energies of the Azides.*—Since the activation energies found for sodium and potassium azide are derived from the temperature coefficient of the surface reaction occurring at the interface between the azide and the metal, they can be directly compared with the energies derived for lead, calcium, and barium azides, where the metal is practically non-volatile at the temperature of the experiment. The experimental values for the  $\alpha$ - and  $\beta$ -lead azides have been re-examined in order to decide upon the accuracy of the results previously quoted for the activation energies.

*$\alpha$ -Lead Azide.*—There are three values for each range of temperature and these have been averaged and the activation energies calculated for each range.

Temp. ....	220—230°	230—240°	240—250°	250—260°	260—270°	270—280°
<i>E</i> , kg.-cals. ....	37.9	38.1	39.3	37.8	54.4	70.3

It is evident that *E* is rapidly rising above 260°, and only below this temperature is it approximately constant. The average value between 220° and 260° is 38 kg.-cals.

$\beta$ -Lead Azide.—Only four experiments were made :

Temp. ....	200—210°	210—220°	250—260°	260—270°
<i>E</i> , kg.-cals. ....	29.1	34.0	49.7	36.2

The average is 37 kg.-cals. and is very approximate since individual values are so discrepant.

*Calcium Azide*.—Andreew (*loc. cit.*) showed that this substance gave a strongly accelerating reaction and that the activation energy increased with temperature.

Temp. ....	60—80°	80—100°	93—105°	120—130°
<i>E</i> , kg.-cals. ....	21	22	27	30

*Barium Azide*.—Harvey (*loc. cit.*) found that *E*, calculated from the acceleration constant of the reaction, showed no signs of increase between 100° and 130°, remaining constant at 21 kg.-cals.

The azides are arranged below in the order of increasing sensitivity :

Substance .....	NaN <sub>3</sub>	KN <sub>3</sub>	BaN <sub>3</sub>	CaN <sub>3</sub>	$\alpha$ -PbN <sub>3</sub>	$\beta$ -PbN <sub>3</sub>
Range of temp. ....	240—275°	222—255°	100—130°	60—130°	220—260°	200—270°
<i>E</i> , kg.-cals. ....	34.4	36.1	21	20—30	38	(37)

It will be observed that the activation energies are of the same order as those of gaseous reactions at similar temperatures, and that the activation energy is the greater the higher the temperature at which the solid reaction first becomes measurable. There is no direct relationship between sensitivity and activation energy, the sensitive lead azide decomposing over the same temperature range as and with a similar activation energy to those found for the inert alkali azides. The azides of the alkaline earths, with an intermediate sensitivity, possess much smaller activation energies. Andreew has shown that nitrides are produced as intermediate compounds from calcium and barium azides, so it is possible that the mechanism of the reaction in these cases is not the same as for the lead and the alkali azides, where the metal and nitrogen are produced directly. It may be that in the azides of the alkaline earths only one N<sub>3</sub> ion is activated at a time, whereas in the other azides the ions are activated in pairs.

For the experiments on lead and potassium azides, the area of the interface is known approximately, and hence it is possible to calculate the rate of reaction by means of the Polanyi-Wigner equation. Topley (*Proc. Roy. Soc.*, 1932, *A*, **136**, 413), who discovered this relationship independently, has applied it in various forms to the endothermic changes  $\text{Ag}_2\text{CO}_3 \rightarrow \text{Ag}_2\text{O} + \text{CO}_2$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$ , and obtains as good an agreement between the calculated and experimental rates as could be expected in view of uncertainties in the area of the interface. For lead and potassium azides, from the equation  $dN/dt = N\nu e^{-E/RT}$ , where  $N = 6 \times 10^{14}$  N<sub>3</sub> ions/cm.<sup>2</sup>, and  $\nu$  = the frequency of vibration of the N<sub>3</sub> ion found experimentally, *viz.*,  $2 \times 10^{13}$ , the following values of the calculated and the experimental rates are obtained :

	Temp.	Rate, mols./cm. <sup>2</sup> /sec.	
		Calc.	Exptl.
Lead azide .....	270°	$1.2 \times 10^{13}$	$5.3 \times 10^{15}$
Potassium azide .....	251	$2.0 \times 10^{13}$	$1.7 \times 10^{15}$

The discrepancies between the experimental and calculated values are no greater than those found by Topley for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . They can be explained by assuming that the interface between the salt and its product is diffuse, for which assumption there is ample evidence in the case of potassium azide at higher temperatures. Although no very great accuracy can be ascribed to the above calculations, they are of interest in showing that there are no marked differences between the behaviour of lead and potassium azides, such as might have been expected from the sensitivity of the former and inertness of the latter.

Much higher rates of reaction per cm.<sup>2</sup> of interface can be observed for potassium and sodium than for lead azide. The latter detonates in a vacuum at 290°, consequent upon the attainment of a rate of reaction much smaller than can be observed for the alkali azides without detonation occurring. This inertness of the alkali azides is probably related to the volatilisation of the metal atoms, which process will absorb energy. In the case of lead

azide, the production of a stable interface will prevent the evaporation of the metal, even momentarily, and hence there will be available in this case a greater fraction of the total energy of the reaction for the activation of adjacent molecules.

SUMMARY.

The thermal decomposition of potassium and sodium azides has been studied in a vacuum and in the presence of the alkali-metal vapour. The decomposition of the former in potassium vapour is very much more rapid than in a vacuum, but the catalytic effect of sodium vapour on the decomposition of the sodium salt is small. From the appearance of the partially decomposed solids, it is concluded that the reaction penetrates into the interior of the crystals at the higher temperatures. This process obeys the equation for chain reactions.

The activation energies of the processes occurring in metallic vapour have been measured, and the values compared with those for other azides. The bearing of these values on the sensitivity of the azides is discussed.

The authors wish to express their indebtedness to the Department of Scientific and Industrial Research and to Imperial Chemical Industries Limited for grants which have enabled them to carry out this work.

THE UNIVERSITY, BRISTOL.

[Received, March 19th, 1936.]

---