

672. *The Thermal Decomposition of α -Lead Azide.*

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The kinetics of the thermal decomposition *in vacuo* of α -lead azide have been studied by a new technique. With small single crystals of very uniform particle size, initial rapid evolution of gas with an activation energy of 15 kcal. mole⁻¹, due to the decomposition of a surface layer of basic lead carbonate, is followed by the main acceleratory stage of the decomposition characterised by the expression $dV/dt = 10^{86}t^4 \exp(-261,000/RT)$ (cm.³ sec.⁻¹ per unit area of crystal surface). Nuclei are produced on the crystal surface according to the expression $dn/dt = 10^{43.5}t \exp(-110,000/RT)$ (cm.⁻² sec.⁻¹), and grow three-dimensionally with an interface velocity of $10^{14.3} \exp(-50,000/RT)$ (cm. sec.⁻¹). Nuclei are thought to be positions where double pairs of positive holes have decomposed to give nitrogen, and nucleus growth occurs by reaction of pairs of positive holes at the nucleus-crystal interface. The decay stage follows a contracting-sphere mechanism.

IN thermal decomposition *in vacuo* of single crystals of lead azide weighing 2—4 mg., Garner and Gomm¹ found that the surface of the crystals rapidly became coated with lead and that the subsequent decomposition corresponded to an interface-penetration mechanism. Cleavage of partially decomposed crystals of the α -form, showed a well-defined interface. Values between about 30 and 60 kcal. mole⁻¹, with a mean of 47.6, were found for the activation energy of the interface-penetration velocity of the α -form, and between 30 and 50 kcal. mole⁻¹, with a mean of 38.8, for the β -form.

Garner, Gomm, and Hailes² analysed pressure-time curves obtained in the decomposition of smaller crystals of lead azide and deduced that the rate in the accelerating stage of the decomposition was proportional to t^m , where m lies between 1 and 3. Hawkes and Winkler³ in an investigation of the thermal detonation of α -lead azide determined the variation, with temperature, of the time t to reach a fixed degree of decomposition and obtained an activation energy of 37 kcal. mole⁻¹ from a plot of $\log t$ against $1/T$ ($^{\circ}\text{K}$). Duke⁴ showed by X-ray-diffraction experiments that *in vacuo* at 160 $^{\circ}$ c the

¹ Garner and Gomm, *J.*, 1931, 2123.

² Garner, Gomm, and Hailes, *J.*, 1933, 1393.

³ Hawkes and Winkler, *Canad. J. Res.*, 1947, **25**, B, 548.

⁴ Duke, Ministry of Supply, unpublished results.

β -form slowly changes into the α -form and that the α -form does not undergo a phase change at temperatures below those at which decomposition occurs. Todd⁵ by other X-ray-diffraction experiments showed that irradiation in air with visible light or X-rays changes lead azide to basic lead carbonate and, in the absence of carbon dioxide, to basic lead azide. Well-aged crystals of lead azide always have a surface film of basic lead carbonate. Moore⁶ showed that the electrical conductivity of pure α -lead azide in the range 100–140° c is given by the equation $\log \sigma = 0 - 18,500/(4.576T)$ and that the ultraviolet absorption edge occurs at 3980 Å.

The present investigation has been made with an improved technique and a particularly suitable sample of α -lead azide. The kinetics of the acceleratory and decay stages of the decomposition have been determined and reaction mechanisms are suggested.

EXPERIMENTAL

Materials.—Except where stated otherwise, specimens of the same well-aged sample of α -lead azide were used in all the experiments. The azide was made by a special method by Messrs. A. T. Thomas and G. W. C. Taylor of the Explosives Research and Development Establishment, to whom we are indebted. They have measured the density and specific surface of the material, obtaining values of 4.75 g. cm.⁻³ and 600 cm.² g.⁻¹, respectively, and shown that, except for the surface which is chemically changed by ageing processes, the material is of high purity. The sample consisted of single crystals of remarkably uniform particle size and shape. The crystals had a longest dimension of about 45 μ and a section of side 35 μ . By direct count of several 0.1 mg. portions, the sample was found to contain 13,400 crystals per mg.

Apparatus.—The Pyrex-glass apparatus used is illustrated in Fig. 1. It can be evacuated to a pressure of 10⁻⁶ mm. by a pumping system consisting of a solid carbon dioxide-alcohol trap, an oil diffusion pump, and a rotary oil pump. The reaction chamber *A* is surrounded by a movable furnace *B*. The furnace temperature, controlled by a proportional temperature-controller, is maintained constant to better than $\pm 0.05^\circ$ c during a run. The pressure in the reaction chamber is measured by a sensitive Pirani gauge *P*, maintained at constant temperature by immersion in solid carbon-dioxide alcohol.

The azide is decomposed on the surface of the copper block *C* in the reaction chamber, and the design is such that the azide is contained in a radiation enclosure at the same temperature as that of the block. That the latter is necessary is shown by experiments in which lead azide crystals were placed on a heated block *in vacuo* but were free to radiate to a surface above them at room temperature. The reaction rate then corresponded to a temperature more than 10° below that of the block. The edges of the block are raised to prevent azide from spilling. The temperature is measured by means of a copper-constantan thermocouple, the hot junction of which is just beneath the centre of the upper surface of the block. The thermocouple was calibrated against a standard mercury thermometer accurate to 0.1°.

The azide samples are contained initially in four small glass buckets mounted on a glass sledge which is free to move along a ground-glass slide *E* fitted to a B45 cone. The buckets are "top-heavy" and kept upright by fins which are in contact with the slide. The cone fits into the socket *F*. The glass-sheathed iron slug *G*, incorporated in the sledge frame, enables the sledge to be pulled along by a permanent magnet. There is a hole in the slide immediately above the reaction chamber, so that when the sledge is pulled over it, consecutive buckets tip, emptying their contents down the guide tube *H* to spread evenly over the surface of the copper block. The buckets strike the slide on tipping, ensuring that no azide is retained.

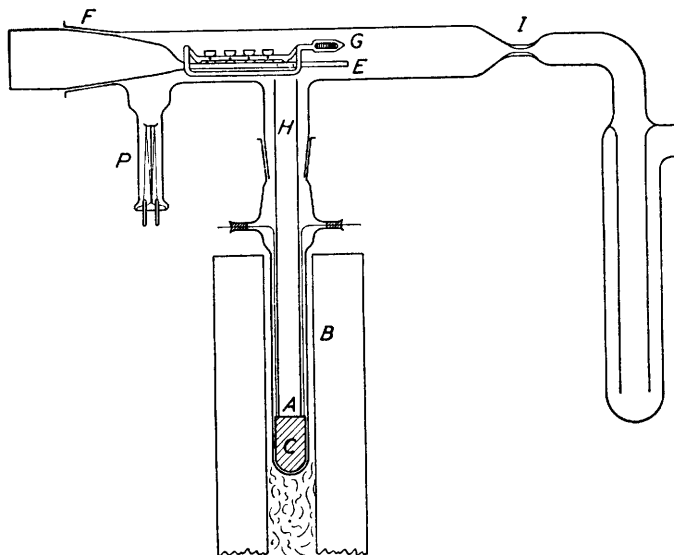
Procedure.—Each set of four runs was subjected to the following routine. Samples (± 0.005 mg.) were loaded into the buckets and the bucket holder was sealed into the apparatus, which was then evacuated to 5×10^{-6} mm. overnight, with the furnace in position and at the desired temperature. Next day, as soon as the reading of the Pirani gauge was steady, the first bucket was tipped and the azide began to decompose with evolution of nitrogen. After the reaction was complete and the apparatus was again in equilibrium, a further run was done. Any samples not used at the end of the day were destroyed, so that all runs were done on samples that had been held in a vacuum of 5×10^{-6} mm. for 19–24 hr.

⁵ Todd, Ministry of Supply, unpublished results.

⁶ Moore, Ministry of Supply, unpublished results.

Measurement of Rates.—During a run the rate of decomposition of lead azide is given directly by the rate at which nitrogen is evolved. Because of the constriction *I* in the vacuum line pressure increases in the reaction chamber, being measured by the Pirani gauge and continuously recorded on a photographic trace. For gas pressures at which the mean free path of the molecules is appreciably greater than the minimum diameter of the constriction, the mass flow of gas through the constriction is directly proportional to the pressure difference across it.⁷ If, in addition, the pumping rate is such that the pressure on the pump side of the constriction is negligible compared with that on the reaction chamber side, the pressure in the reaction chamber will be directly proportional to the rate of decomposition of the azide for constant rates. Changes in rate cannot be recorded instantaneously because of lags in the pressure gauge and recording equipment and also because of the finite capacity of the reaction chamber. A linear change of rate with time is recorded with a delay equal to the product of the resistance of the orifice (sec. cm.⁻³) multiplied by the volume of the reaction chamber. These lags were not significant for the relatively slow changes of rate of these experiments.

FIG. 1.



The apparatus was calibrated by admitting air into the apparatus at a constant rate and measuring the resulting deflection of the Pirani gauge. If the air is drawn from a small reservoir initially containing a volume V_1 (ml.) at pressure P_1 (atm.), and t seconds later the volume has been reduced to V_2 and the pressure to P_2 (as indicated by an oil manometer), the rate of admission of air is $(P_1V_1 - P_2V_2)/t$ ml. atm. sec.⁻¹. If the temperature of the reservoir is known, $(P_1V_1 - P_2V_2)$ can readily be converted into the equivalent weight of lead azide. The gas flow into the apparatus was controlled by a precision needle-valve and for a particular setting the rate of admission remained constant. By varying the needle-valve setting, Pirani gauge deflections corresponding to several different azide decomposition rates were obtained. From these the rate was found to be directly proportional to the deflection, 1 cm. on the Pirani gauge being equivalent to a rate of decomposition of lead azide of $(4.1 \pm 0.08) \times 10^{-4}$ mg. sec.⁻¹. This value includes the small correction required because air rather than nitrogen was used for the calibration.

RESULTS

The thermal decomposition at constant temperature (Fig. 2) commences with an initial rapid evolution of gas, after which the rate falls swiftly. It then increases to a maximum and finally falls off to zero. Measurements of the area beneath the rate-time curve show that complete decomposition has then occurred. Values of log rate were plotted against log time

⁷ See, e.g., Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, New York, 1949, p. 90.

for the early parts of the decomposition and gave a linear relation for the second acceleratory stage. Typical plots are shown in Fig. 3. At *A* (Fig. 3) the effect of the first acceleratory stage is present, *B* is the linear region, and at *C* the final maximum is being approached. For 23 decompositions in the range 285–294° c the slope of the linear regions of these plots showed no systematic variation with temperature. A mean value of $3.94 \pm 11\%$ was found.

Values of $\log (\frac{d\alpha}{dt})_\tau$ (taken from the log rate–log time graphs), $\log A$, $\log t_m$, and $\log (\frac{d\alpha}{dt})_m$ (taken from the rate–time traces), and $\log \alpha_m$ (obtained by measurement of the area under the rate–time traces) gave straight-line plots against $1/T$ (°K). Here $(\frac{d\alpha}{dt})_\tau$ = rate of decomposition at constant time τ , A = the maximum value of the rate of the initial evolution of gas, t_m = time to reach the final maximum rate, $(\frac{d\alpha}{dt})_m$ = final maximum rate, and α_m = fractional decomposition at maximum rate.

For the decay period of the decomposition, values of both $\log (\frac{d\alpha}{dt})$ and $(\frac{d\alpha}{dt})^{\frac{1}{2}}$ were plotted against t . The curvature of the rate–time traces for this region is not great and at low rates errors produced by drift of the Pirani gauge become significant. It is not unexpected

FIG. 2. Variation of rate of decomposition (cm. deflection) with time. *A* = 567.1° K; *B* = 564.4° K; *C* = 559.3° K.

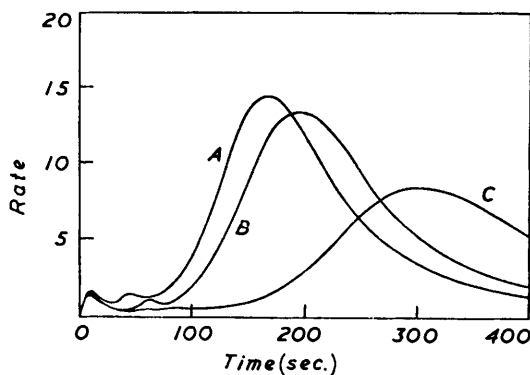
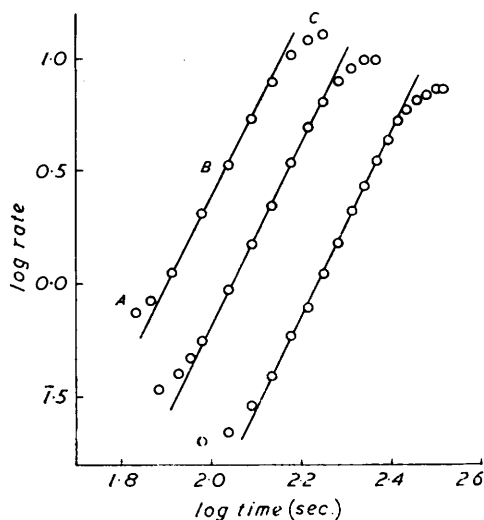


FIG. 3. Plot of log rate (cm. deflection) against log time at (from left to right) 566.2° K, 562.4° K, and 558.7° K.



therefore that within the experimental error both plots gave fair straight lines. For different runs $\log P$ and $\log Q$, where P is the slope of the $(\frac{d\alpha}{dt})^{\frac{1}{2}}-t$ plot and Q is the slope of the $\log (\frac{d\alpha}{dt})-t$ plot, were plotted against $1/T$ (°K). In all cases values of slopes and intercepts, together with their standard deviations, were calculated by the method of least squares on the A.R.D.E. AMOS digital computer. These values, adjusted so that slopes are in the units of activation energy (kcal. mole⁻¹), and intercepts are calculated from rate values in units of sec.⁻¹, are given in Table 1. For temperatures below 280° c it was only possible to obtain values of t_m , these being independent of weighing errors and errors due to drift of the Pirani gauge. For t_m the values of the constants obtained from results in the range 262–295° c are little different from those in the range 280–295°, suggesting that the reaction mechanism is essentially the same throughout the wider range. In subsequent calculations the constants from the 280–295° range are used to correspond with the other experimental results.

Other α -Lead Azide Types.—Several other types of α -lead azide were investigated in a more conventional apparatus, in which the azide, contained in a platinum bucket, was lowered into the heated reaction chamber. Activation energies were obtained from values of the maximum rate and these are given in Table 2.

The shape of the decomposition curve in all cases was roughly as described above. For the pure α -lead azide, which had been recrystallised from ammonium acetate, samples of different crystal size were investigated. The maximum rate, for the same temperature and the same

sample weight, was found to be directly proportional to the surface area of the crystals. For crystals of 240—300 B.S.S. mesh, $(d\alpha/dt)_m$ was 2.5 times that of 60—100 mesh crystals. With this apparatus and with these azide types the experimental reproducibility was not good, and no further quantitative analysis of the decomposition curves was possible.

In other experiments, the surfaces of single crystals of lead azide, thermally decomposing *in vacuo*, were watched through a microscope. The surface darkened and rapidly became black as the decomposition proceeded, but discrete nuclei could not be resolved. The resolving

TABLE 1.

Plot (T in $^{\circ}\text{K}$)	Slope (kcal. mole $^{-1}$)	Intercept	No. of decompns.	Temp. range ($^{\circ}\text{C}$)
(a) Log t_m against $1/T$	50.4 ± 0.9	-17.1 ± 0.3	41	262—295
(b) Log t_m against $1/T$	52.6 ± 1.0	-18.0 ± 0.4	30	280—295
(c) Log $(d\alpha/dt)_r$ against $1/T$	-262 ± 11	89.7 ± 4.4	26	280—295
(d) Log $(d\alpha/dt)_m$ against $1/T$	-46.6 ± 1.1	15.5 ± 0.4	30	280—295
(e) Log α_m against $1/T$	3.3 ± 0.3	-0.89 ± 0.13	16	280—295
(f) Log Q against $1/T$	-33.0 ± 4.4	10.4 ± 1.7	16	286—297
(g) Log P against $1/T$	-55.3 ± 3.4	19.4 ± 1.3	16	286—297

TABLE 2.

Type of α -lead azide	Activation energy (kcal. mole $^{-1}$)
Service	36
Pptd. in the presence of carboxymethylcellulose	38
Pure (fine particles)	40
Pure (large particles)	52

power of the optical system was better than 10 microns, surface diffraction effects preventing the use of higher resolution. Cleavage of partially decomposed crystals, about 1 mm. in linear dimensions, showed that parts of the crystal remained white and gave some indication of the presence of a lead-lead azide interface, confirming Garner and Gomm's result.¹

DISCUSSION

The experimental method of tipping the azide alone into the reaction chamber gives a very rapid heat-up time. Calculations assuming heat transfer by radiation only, with black-body conditions, show that the reaction rate will be within 1% of its correct value in about 0.5 second. In addition, heat conduction from the copper block will occur and the gas present will also transfer heat. The more conventional method of lowering a metal bucket into the reaction chamber gives a heat-up time of a few minutes and could not have been used for most of these experiments in which the maximum rate was reached in less than 10 min. During decomposition, heat is produced in the azide by the strongly exothermal reaction and the escape of this heat requires that the temperature of the azide must always be higher by ΔT than that of the reaction vessel. However, if the heat-transfer conditions are good and the reaction rate is not too high, ΔT will be small and the reaction rate will be negligibly different from that corresponding to the measured temperature. In these experiments only about 1 part in 50 of the surface of the copper block was covered with the small crystals and no acceleration of reaction rate attributable to self-heating was observed. In other experiments, at higher temperatures, which will be reported later, self-heating had a significant effect and high reaction rates and detonations were observed. The method of measuring the rate of reaction, apart from its convenience, had the further advantage that the entire decomposition could be followed with the gas pressure always less than 5×10^{-3} mm.

The First Acceleratory Stage.—The azide samples used were "well-aged" and the initial sharp evolution of gas is considered to be due to the decomposition of the surface layer of basic lead carbonate. The slope of the log A against $1/T$ plot gave an activation energy of 15 kcal. mole $^{-1}$ and this value is probably approximately correct, even though the apparatus was not designed for use with carbon dioxide, because the slope of the plot is independent of the absolute values of A .

in terms of a positive-hole mechanism, whereas Thomas and Tompkins¹¹ found that the photolysis rate of barium azide was proportional to the square of the intensity of irradiation and used an exciton mechanism to explain this. It is therefore probable that the mechanism of the thermal decomposition of lead azide depends upon the production of positive holes rather than excitons. Lead azide has a very much higher enthalpy of formation than the alkaline-earth azides,¹² and it absorbs light at much longer wavelength, implying that the necessary energy for electronic transitions is lower. These factors should make lead azide less stable than the alkaline-earth azides, but in fact lead azide does not decompose appreciably at temperatures below 250° whereas the alkaline-earth azides decompose in the range 100–120°. The stability of lead azide may arise from dependence of its decomposition on reaction between positive holes, this requiring a high activation energy because of the electrostatic repulsion forces to be overcome. A mechanism of nucleus formation which depends upon reaction of positive holes and gives good agreement with the experimental results will therefore be described.

On the surface an equilibrium between positive holes and azide ions will rapidly be attained, *i.e.*, in the reaction $N_3^- \xrightleftharpoons[k_2]{k_1} N_3 + e$, when $k_1(N_3^-) = k_2(N_3)(e)$. If $(N_3) \ll (N_3^-)$, $(N_3) = (k_1 N / k_2)^{\frac{1}{2}}$, and this condition will be satisfied if $(k_1 / k_2 N)^{\frac{1}{2}} \ll 1$. Here N is the total number of azide ions per unit area of crystal surface ($\sim 10^{15}$). The positive holes will be mobile and it is suggested that reaction to give three molecules of nitrogen will occur whenever collision takes place between two positive holes with the necessary activation energy, *i.e.*, $dp/dt = k_3(N_3)^2$, where p is the concentration per unit area of positions where this decomposition has taken place. If this concentration is zero at the time heating commences, $p = k_3(N_3)^2 t$. The rate of production of nuclei, *i.e.*, places where this decomposition has occurred in neighbouring positions, will be given by $dn/dt = (2bp/N) dp/dt$, where b is the number of positions adjacent to a decomposition position, in which decomposition will result in nucleus formation. The rate of nucleus formation is now given by $dn/dt = 2b(k_1 k_3 / k_2)^2 N t$ ($\text{cm.}^{-2} \text{sec.}^{-1}$), which is of the form of the experimental equation (ii).

In this equation, k_1 may reasonably be given by $k_1 = \gamma \exp(-E_1/RT)$, where γ is the lattice vibration frequency ($\sim 10^{13} \text{sec.}^{-1}$) and E_1 is the activation energy for positive-hole formation. k_2 is likely to have a very low activation energy and it may be assumed that a conduction-band electron will be trapped if it passes within one or two ionic radii of a hole, say, within 10^{-7}cm . If the electrons have thermal energy their velocity will be about $10^7 \text{cm. sec.}^{-1}$ at 550° K, so that $k_2 \sim 1$. k_3 will depend upon a similar interaction between two positive holes, and because of the lower mobility of these compared with conduction-band electrons will probably have a velocity about an order less. In this case an activation energy E_3 will be required for reaction, so that $k_3 \approx 0.1 \exp(-E_3/RT)$. The rate of production of nuclei is now given by: $dn/dt \approx (10^{40}/t) \exp[-2(E_1 + E_3)/RT]$ ($\text{cm.}^{-2} \text{sec.}^{-1}$). In view of the approximations made, the pre-exponential term is in reasonable agreement with the experimental value for k_i of 10^{43-5} . From the exponential term $E_1 + E_3 = 55 \text{kcal. mole}^{-1}$. For barium azide Thomas and Tompkins¹³ assume that absorption of light at 2600 Å gives rise to the electron transition from the full to the conduction band and calculate that the corresponding thermal activation energy should be 35–48 kcal. mole^{-1} . The same calculation applied to α -lead azide gives the value $E_1 = 22\text{--}30$, and from this $E_3 = 25\text{--}33 \text{kcal. mole}^{-1}$.

The validity of some of the assumptions made in this derivation can now be considered. The expression $(N_3) = (k_1 N / k_2)^{\frac{1}{2}}$ is true if $(k_1 / k_2 N)^{\frac{1}{2}} \ll 1$, and from the calculated values it can be shown that $(k_1 / k_2 N)^{\frac{1}{2}} < 10^{-6}$. The concentration of positive holes will be lower than is given by the equilibrium reaction because positive holes are being destroyed continually

¹¹ Thomas and Tompkins, *Proc. Roy. Soc.*, 1951, A, **209**, 550.

¹² Gray and Waddington, *ibid.*, 1956, A, **235**, 106.

¹³ Thomas and Tompkins, *J. Chem. Phys.*, 1952, **20**, 662.

by decomposition. However, from the values calculated above, it can be shown that for the reaction $N_3^- \xrightleftharpoons[k_2]{k_1} N_3 + e$ starting with $(N_3) = 0$, (N_3) is within 99% of its equilibrium value of 10^9 cm.⁻² in 3×10^{-9} sec., whereas the overall process is slow, the whole acceleratory stage of the decomposition taking many seconds. Therefore, in any region in which a decomposition centre is formed the equilibrium concentration of positive holes will be restored extremely rapidly.

Mechanism of Nucleus Growth.—In the preceding sub-section the nuclei for decomposition were characterised as positions where decomposition of four azide ions had occurred. The residue of two lead atoms or lead ions and associated F -centres is thought to function as a decomposition nucleus because the activation energy for positive-hole formation will be reduced in its vicinity, electrons being excited from the full band of the azide lattice to the metal nucleus rather than to the conduction band, and the reverse reaction will be inhibited. In the interface decomposition is thought to proceed, as in nucleus formation, by the bimolecular reaction of positive holes, the reaction mechanism being $N_3^- \xrightleftharpoons[k_2^1]{k_1^1} N_3 + e$ and $2N_3 \xrightarrow{k_3^1} 3N_2$. The decomposition exposes another layer of azide ions to the interface and therefore for unit area of interface $(N_3^-) + (N_3) = N$ (a constant). The velocity of progression of the interface is constant, so that the attainment of equilibrium can be assumed, *i.e.*, $d(N_3)/dt = k_1^1(N_3^-) - k_2^1(N_3)(e) - k_3^1(N_3)^2 = 0$, $(N_3) = (e)$, and $(N_3) \ll (N_3^-)$, so that $(N_3)^2 = k_1^1 N / (k_2^1 + k_3^1)$ and the reaction rate = $k_3^1(N_3)^2 = k_1^1 k_3^1 N / (k_2^1 + k_3^1)$. The velocity of penetration of the interface is then $v = \sigma k_1^1 k_3^1 / (k_2^1 + k_3^1)$, where σ is the thickness of an ionic layer (4×10^{-8} cm.). Now $k_1^1 = \gamma \exp(-E_1^1/RT)$, where E_1^1 is the activation energy for excitation of an electron from an azide ion to the metal nucleus, and $k_3^1 \approx k_3 = 0.1 \exp(-E_3/RT)$. It is to be expected that $k_2^1 < k_2$, say $k_2 = xk_2^1$, and it is likely that $k_2^1 \gg k_3$, so that

$$v \sim 4 \times 10^4 x \exp[-(E_1^1 + E_3)/RT] \text{ (cm. sec.}^{-1}\text{)}.$$

Experimentally $E_1^1 + E_3 = 50.2$ kcal. mole⁻¹, whereas $E_1 + E_3 = 55$ kcal. mole⁻¹, and $E_1^1 < E_1$, as is expected. The value of x may be sufficiently high for the pre-exponential term to approach the value of 4×10^5 cm. sec.⁻¹ given by simple application of the Polanyi-Wigner equation. It is, however, very much below the experimental value and this suggests that in the reaction $2N_3 \xrightarrow{k_3^1} 3N_2$ the activated complex has a very disordered structure so that a big increase in entropy results.

The Decay Stage.—As the early stages of the decomposition proceed by a mechanism of nucleus formation and growth on the crystal surface it is to be expected that after coalescence of the nuclei the decomposition will be controlled by the rate of penetration of the lead-lead azide interface into the crystal. At nucleus coalescence the particles used in this work can be considered to be identical spheres of undecomposed azide surrounded by a metallic layer. If the interface moves at a constant velocity, *i.e.*, $dr/dt = -k$, where r is the radius of each sphere at time t , the rate of decomposition is $d\alpha/dt = 4\pi r^2(dr/dt)c\rho$, where c is the number of particles in unit weight of the sample and ρ is the density of lead azide. If the radius of the particles is a at time τ it can readily be shown that $(d\alpha/dt)^{\frac{1}{2}} = (4\pi c\rho k)^{\frac{1}{2}}(a + k\tau) - (4\pi c\rho)^{\frac{1}{2}}k^{\frac{1}{2}}t$, and a plot of $(d\alpha/dt)^{\frac{1}{2}}$ against t should give a straight line, as found experimentally. The slope of this line, $P = -(4\pi c\rho)^{\frac{1}{2}}k^{\frac{1}{2}}$, is independent of a and τ and is therefore unaffected by the acceleratory stage variation of V_0 with temperature. k is given by $k = k_i \exp(-E_i/RT)$, so that a plot of $\log P$ against $1/T$ will give an activation energy of $\frac{3}{2}E_i$ and a pre-exponential term of $(4\pi c\rho)^{\frac{1}{2}}k_i^{\frac{1}{2}}$. From the experimental values given in plot (g) (Table 1), $k_i = 10^{10}$ cm. sec.⁻¹ and $E_i = 37$ kcal. mole⁻¹. These values are not in very good agreement with the corresponding terms k_g and E_g for the nucleus-growth stage, but the values resulting from the assumption of a unimolecular process for the decay stage (plot f, Table 1) are slightly worse and the standard deviation

is twice as large. These facts and the supporting evidence, *e.g.*, the microscopic evidence for a lead-lead azide interface, indicate that the contracting-interface mechanism is probably correct, although the simple treatment used here in which the particles are assumed to be spheres of uniform size, may not be strictly applicable.

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