SENSITIVITY OF CUPROUS AZIDES TOWARDS HEAT AND IMPACT

by

Kartar Singh

Institute of Armament Studies, Kirkee

ABSTRACT

Rates of thermal decomposition of cuprous azide at six different temperatures have been measured. The sigmoid shapes of the curves representing increase in pressure with time suggest that at a given temperature a fixed number of nuclei are formed at the end of the induction period. The nuclei increase in size in three dimensions. The radius of any nucleus at any instant (t) is directly proportional to $(t - t_0)$ where t_0 is the induction period. The activation energy involved in thermal decomposition has been found to be 26·5 K calories. It is suggested that this activation energy corresponds to the energy required for thermal transition of an electron from 3 d band to the Fermi level of the metallic copper nuclei.

The impact sensitivity and induction period necessary for explosion at various temperatures for crystalline and precipitated samples of cuprous azide have been measured. The results indicate that cuprous azide is more sensitive towards heat and impact than lead azide. The impact sensitivity of cuprous azide is found to increase with increase in crystal size.

Introduction

Cuprous azide possess high sensitivity both towards heat and impact. This is an increasing combination of explosive properties. A detailed study of its behaviour on thermal decomposition and its sensitivity towards heat and impact is likely to yield valuable information regarding the mechanism of explosive reactions.

In a large variety of detonators, lead azide is often put in brass containers. On storage under hot and humid conditions cuprous azide is formed on the surface of the containers. A slight friction on such surfaces often leads to serious accidents. An investigation of explosive behaviour of this compound is likely to be useful in safe handling of ammunition in which cuprous azide has formed.

Preparation and properties of cuprous azide were first studied by Wohler and Krupko[1] Straumanis and Circulis[2] extended their work. In the present investigations it was necessary to obtain large single crystals. For this purpose Wohler and Krupko's method with some modifications was found to give good results.

EXPERIMENTAL

(i) *Preparation*

Cuprous chloride weighing about 5 grams was washed successively with dilute acetic acid and distilled water. It was suspended in saturated solution of sodium chloride. To this suspension 2 c.c. of 2·3 per cent solution of potassium bisulphate were added when cuprous chloride went into solution. The solution was acidified with acetic acid and to this 10 per cent solution of sodium azide was slowly added. During this addition slow agitation was maintained. A fine precipitate of cuprous azide was obtained. It was filtered and washed successively with distilled water, alcohol and ether. It was dried in vacuum. The specific gravity was found to be 3·31.

For the purpose of crystallization, a saturated solution of potassium chloride containing about 0·1 per cent potassium bisulphate was saturated with dry cuprous azide at 65°C. The clear solution was filtered while hot and allowed to cool slowly. A crop of tetragonal crystals of cuprous azide was thus obtained. A photograph of a single crystal is shown in Fig. 1.

(ii) *Thermal Decomposition*

Thermal decomposition of single crystals was studied in an apparatus similar in design to one described by Yoffe[3] A crystal weighing about 2 mgms was dropped from a spoon fitted within the evacuated apparatus into decomposition tube. The latter was maintained at fixed temperature with the help of an electric furnace whose temperature was controlled by Sunvic RT_2 controller. The accuracy of the control was $\pm$ 0·15°C. The rise of pressure with time was studied.

(iii) *Thermal Sensitivity*

The temperature of explosion was measured in an apparatus similar in design to one employed by Copp et al[4] About 5 mgms of the material was enclosed in a copper cap having a diameter of 0·2″ and depth of 0·2″. The cap was dropped in a Wood's metal bath maintained at fixed temperature. The induction period to explosion was recorded at various temperatures. At each temperature 15 readings were taken.

(iv) *Impact Sensitivity*

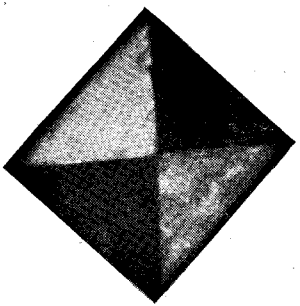
The heights of the steel ball which bring about 50 per cent explosions on impact in samples of cuprous azide were determined on a machine similar in design to one used by Taylor and Weale[5] The base of the machine was a steel disc having a diameter of 8″ and a height of 3″. It was face hardened to about 650 Vickers hardness number and polished. The sample was placed between a disc and a pin fitted in a collar. The ball was allowed to fall on pin. At each height 15 trials were carried and numbers of explosions were recorded.

RESULTS

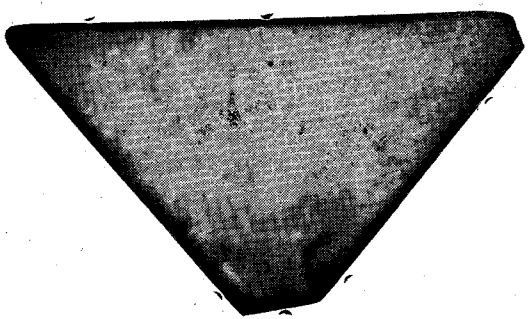
Thermal Decomposition

On thermal decomposition the rise of pressure with time was studied at temperatures of 170, 175, 180, 185 190 and 195° C. The pressure versus time curved are sigmoid in shape. For first four temperatures these curves are shown in Fig. II. For these temperatures the plots of $(p)^{\frac{1}{3}}$ versus $(t—t_o)$ are shown in Fig. III. It is seen from these figures that the data fit well into the following expression:—

$$\sqrt[3]{p} = k\,(t - t_o)$$

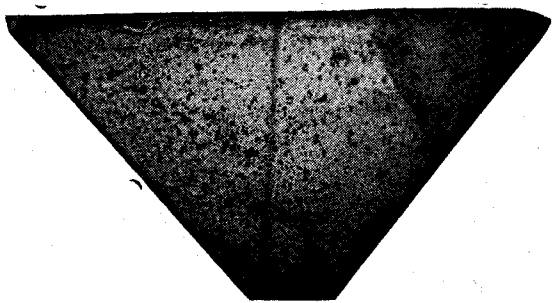


×65
Crystal of cuprous azide.



×310
One face of the crystal of cuprous azide.

N



×310
The same face after heating at 65°C for 10 minutes at 0·5 mm pressure.

FIG. I

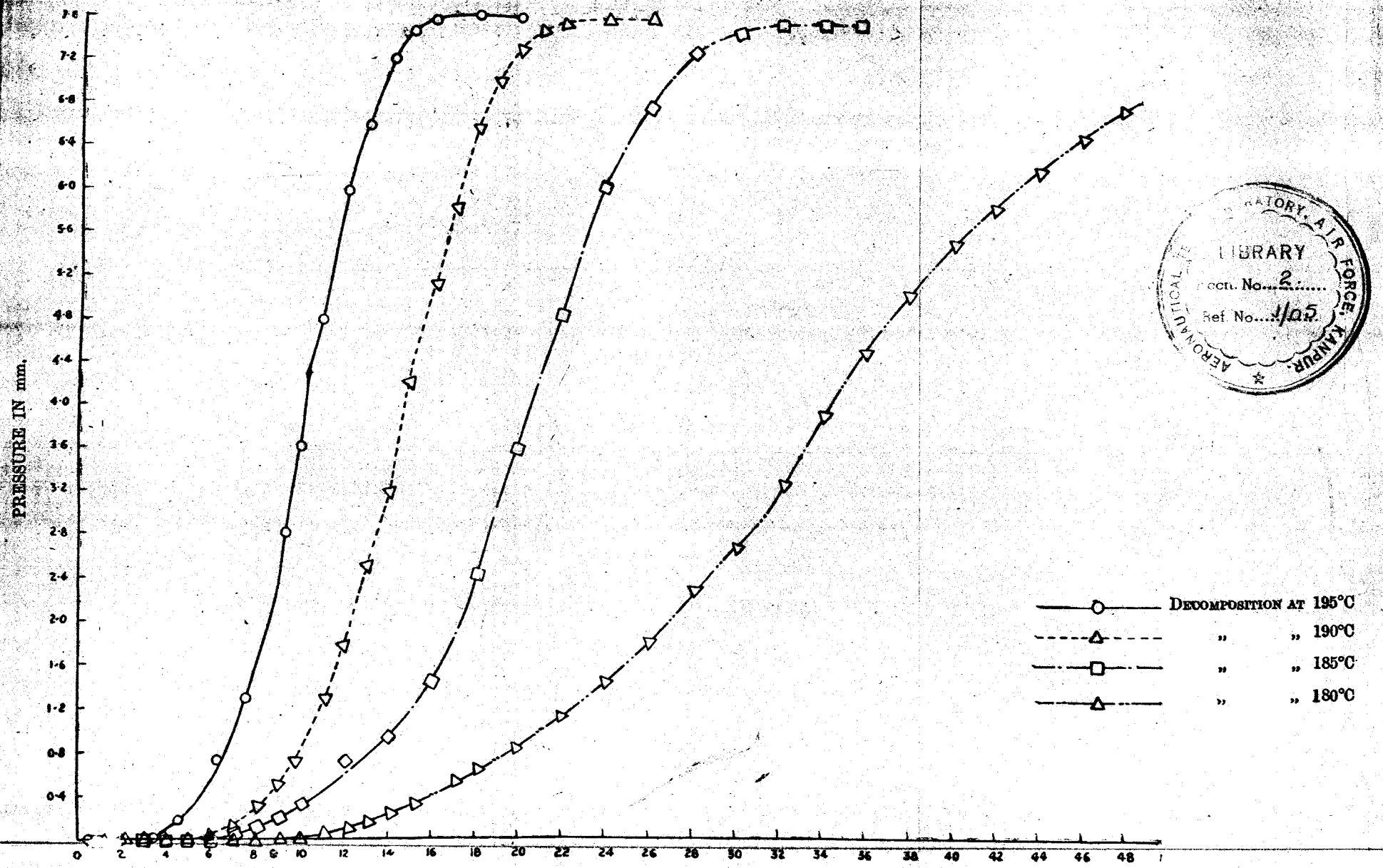


FIG. II:—THERMAL DECOMPOSITION OF CUPROUS AZIDE

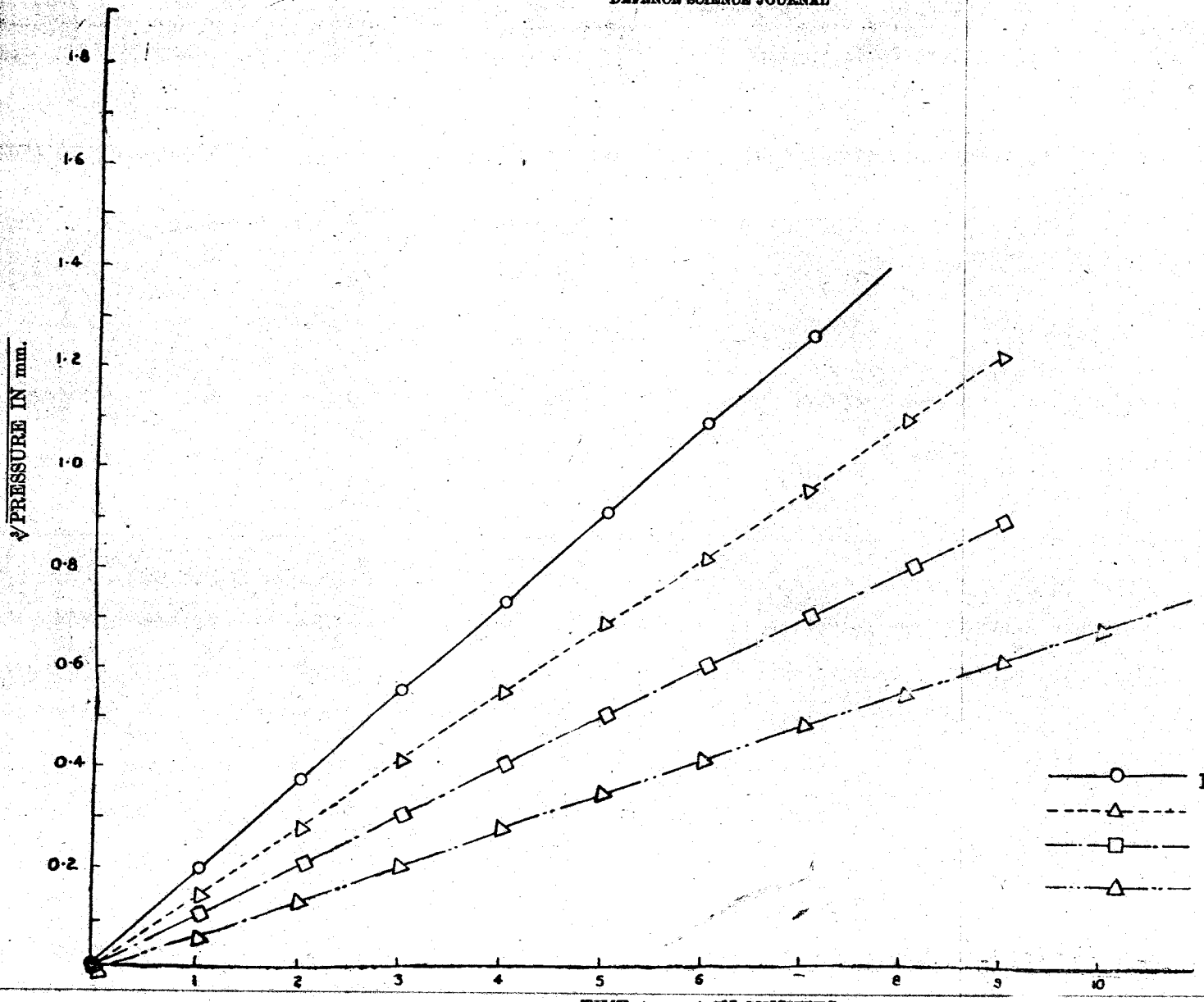


FIG. III:—VARIATION OF CUBE ROOT OF PRESSURE IN mm. WITH TIME AFTER INDUCTION PERIOD IN MINUTES.

where p, k, t and t_o are the pressure (mm of H_g), rate constant of reaction, time (minutes) and induction period respectively. The values of k and t_o at various temperatures are given in Table I.

TABLE I

Induction periods and reaction rate constants at various temperatures for crystalline cuprous azides.

Temp °C	Reaction rate constant k (Relative values)	Induction period to minutes
170	0·184	7·0
175	0·259	6·0
180	0·357	5·0
185	0·493	4·0
190	0·675	3·0
195	0·916	1·5

A plot of log k against 1/T where T is the absolute temperature is shown in Fig. IV. The slope of the curve gives the value of activation energy equal to 26·5 K calories.

Thermal Sensitivity

Plots of induction period (t_o) versus temperature of explosion in degrees absolute (T) are given in Fig. V for precipitated and crystalline samples of cuprous azide. The curves representing the relationship $\log t_o = E/4{\cdot}57T + B$ where E is the activation energy and B is a constant are shown in figure VI. From the slopes of these curves which are almost rectilinear values of activation energy have been estimated and are given in Table II.

TABLE II

Values of E and B for samples of cuprous azide

Samples	Temperature of explosion for induction period of 5 seconds	Activation energy E K calories	Constant B
Crystalline	216·7°C	20·5	—8·33
Precipitated	217·8°C	31·2	—13·39

It is not possible to associate any physico-chemical process with these energies of activation. It is significant, however, that these values are roughly equal to the activation energy involved in thermal decomposition. The data show that cuprous azide is more sensitive towards heat than lead azide[4].

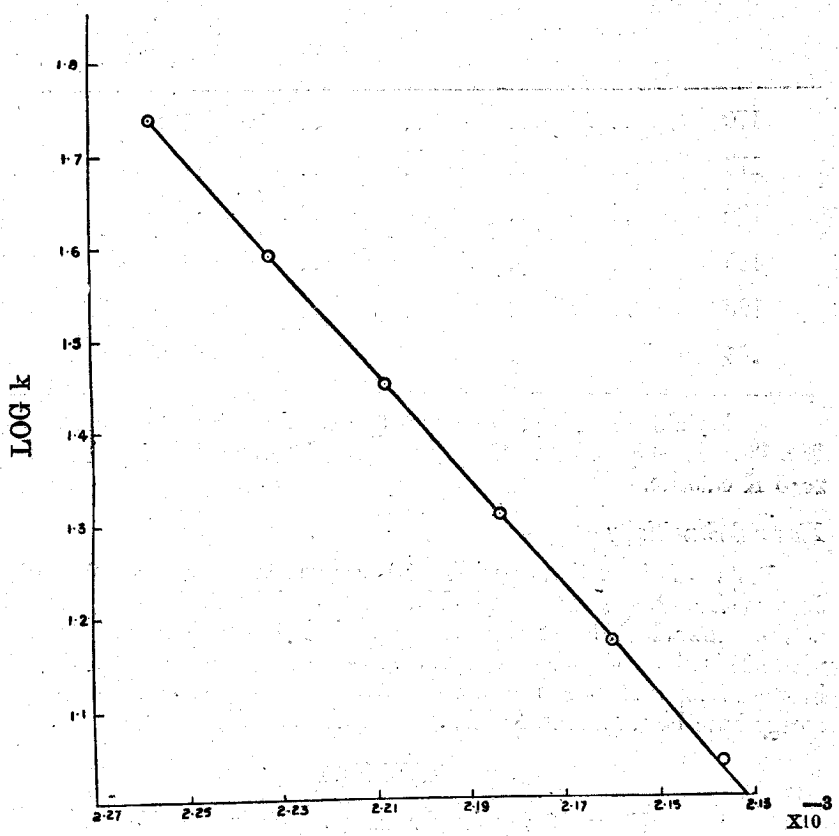


FIG. IV:—VARIATION OF LOG K WITH RECIPROCAL OF ABSOLUTE TEMPERATURE OF REACTION.

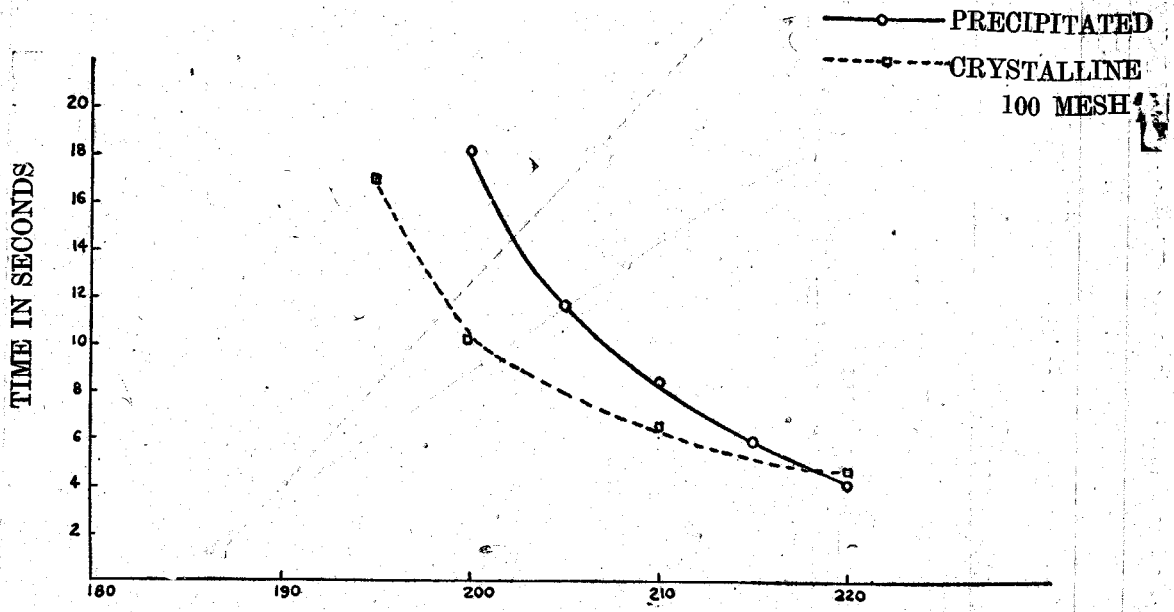


FIG. V:—VARIATION OF INDUCTION PERIOD WITH TEMPERATURE.

Impact Sensitivity

Curves showing percentage of explosions out of 15 trials at various heights are shown in Fig. VII. The critical heights which bring about 50 per cent. explosions in crystalline and precipitated samples are given in Table III.

TABLE III

Heights for 50 per cent explosions. Diameter of steel Ball 7·8″

Sample		Height in inches
Crystalline	240 mesh	22·5
	150 mesh	15·0
Precipitated		20·0

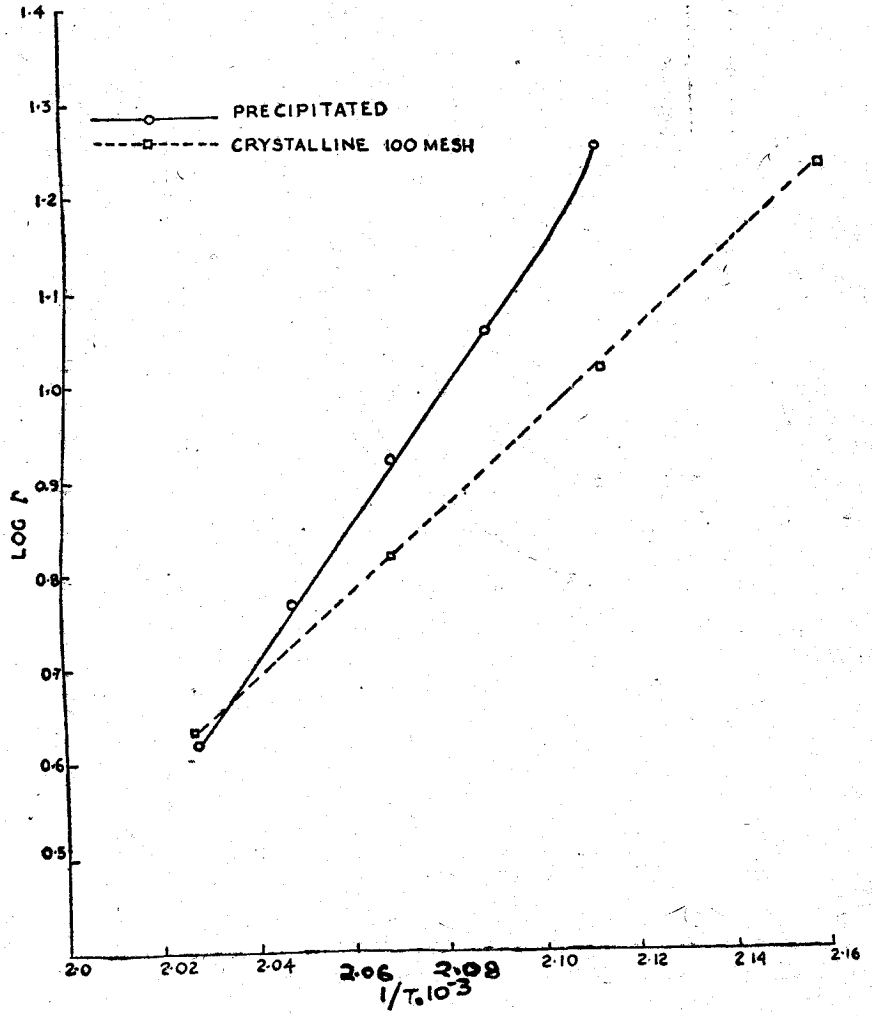


FIG. VI:—VARIATION OF LOG t_0 WITH RECIPROCAL OF ABSOLUTE TEMPERATURE.

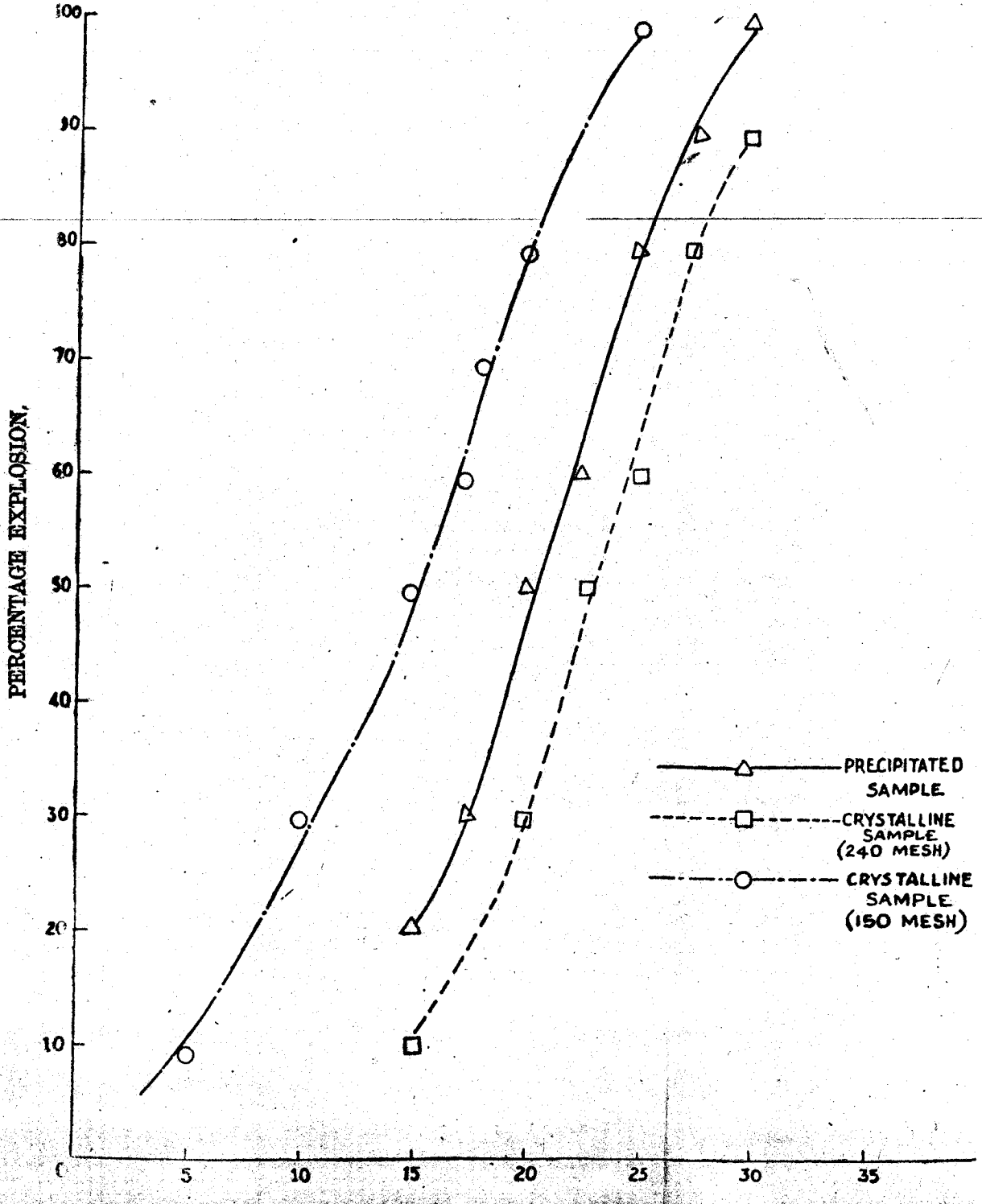


FIG. VII.—IMPACT SENSITIVITY OF CUPROUS-AZIDE

These results show that cuprous azide is more sensitive towards impact than lead azide. Again it is observed that the sensitivity of a crystalline sample of cuprous azide increases with increase in crystal size.

Discussions

The sigmoid shape of the thermal decomposition curves suggest that the chemical reaction is catalysed by the interface between the nuclei that are formed at the end of the induction period and the crystal. The Kinetics of interfacial reactions may be represented with the help of the following equations:—

$$(\bar{N}_3/\square A) \overset{k_1}{\geqslant} (N_3/\square A) + e \quad \ldots\ldots(1)$$

The electron tunnels to the metallic nucleus

$$2(N_3/\square A) \overset{k_2}{\geqslant} 2\square A + 3N_2 \quad \ldots\ldots(2)$$

$$(N_3/\square A) + e \overset{k_3}{\geqslant} (\bar{N}_3/\square A) \quad \ldots\ldots(3)$$

$$T + e \overset{k_4}{\geqslant} cu \quad \ldots\ldots(4)$$

In these equations $(N_3/\square A)$, e, $(N_3/\square A)$, T, $A\square$ denote anion in lattice site, electron, hole, trap and vacant anion sites respectively. If the value of k_3 be negligible in comparison with k_1, it can be shown as has been done by Gray and Waddington[6] that

$$\frac{d}{dt}(N_2) = k\,(\bar{N}_3/\square A) \quad \ldots\ldots(5)$$

According to this equation the rate of chemical reaction at the end of induction period is proportional to the number of anions at the interface. If the radius (r) of the nucleus at any time t is assumed to be proportional to $(t—t_o)$ where t_o is the induction period and it is assumed that fixed number of nuclei appear at the end of induction period which grow later in size it can be shown that the pressure (p) at any instant t is given by the expression

$$\sqrt[3]{P} = k(t—t_o) \quad \ldots\ldots(6)$$

The fact that experimental results on thermal decomposition obey the relationship (6) suggests that the assumptions made above are reasonably correct.

It is likely that the activation energies involved in steps (2), (3) and (4) of the chain reactions are very small and that mainly step (1) determines the activation energy involved in thermal decomposition. In this step an electron tunnels from the azide band to the metallic nucleus. The energy required for this purpose can be estimated on the basis of considerations given below.

The energy levels in metallic copper and cuprous azide are shown in Fig. VIII. The energy levels in cuprous azide have been assumed to be those in cuprous bromide. Lukrisky, Gudris and Kulikowa[7,8] have measured the energy required to remove an electron from cuprous bromide crystallites and have found a value of 6·2 e.v. The energy gap between conduction and empty bands in cuprous bromide has been estimated to be 5 e. v. by Marton[9]. The electron affinity of the crystal is therefore 1·2 e.v. The energy levels in metallic copper have been evaluated by Howarth[10]. Some of his results are given in Fig. VIII.

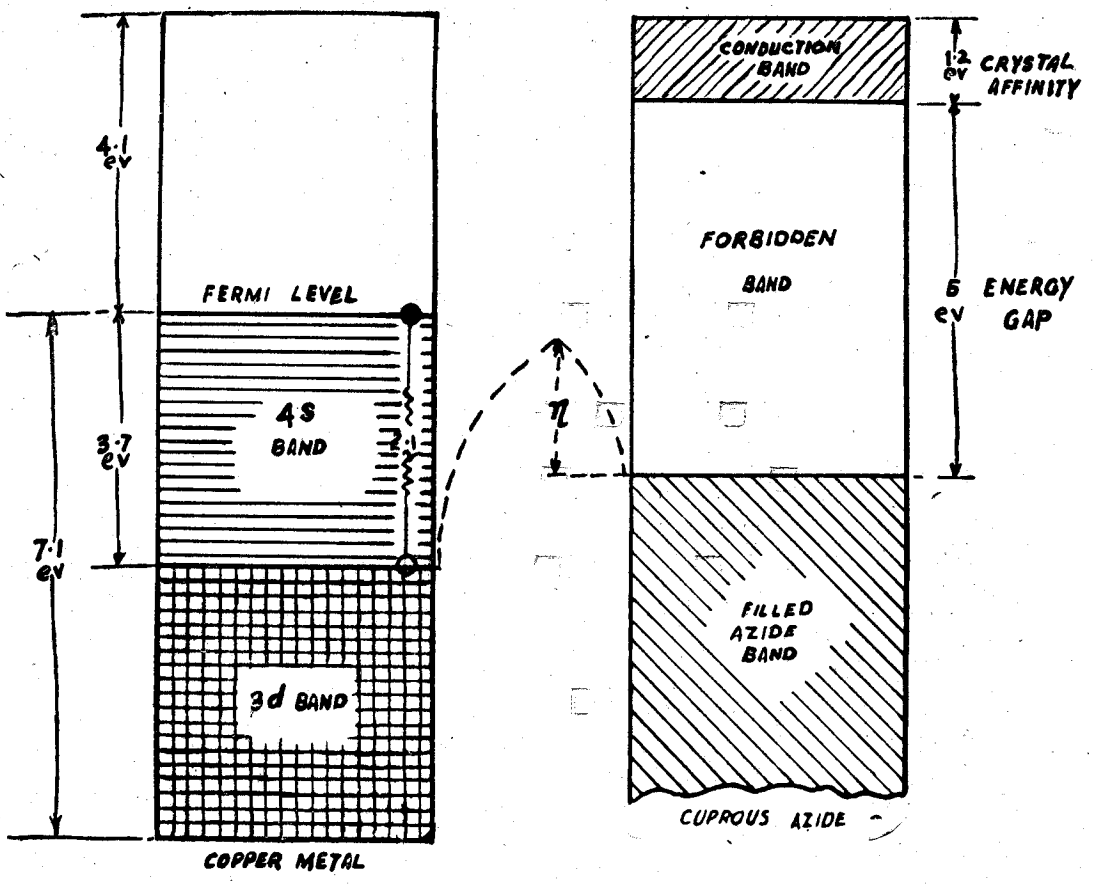


FIG. VIII:—ENERGY LEVELS IN METALLIC COPPER AND CRYSTAL OF CUPROUS AZIDE

As mentioned earlier the initial and rate determining step is the transfer of an electron from the azide band to the Fermi level of the metallic nuclei. There are two possible routes for this step viz. (*i*) direct transfer of an electron from the azide band to the Fermi level of the metallic nuclei, and (*ii*) indirect transfer involving thermal excitation of an electron from the top of 3 d band to the Fermi level of metallic nuclei followed by jumping of an electron from the azide band into the hole in 3 d band of copper nuclei formed on the surface of the crystal. The energy required for direct transfer of an electron (ζ) can be calculated with the help of the following expression[11].

$$\zeta = \psi + \eta - I - \frac{\pi^2 k^3 T^2}{6} (d \log g/d\epsilon)$$

where ψ is the energy required to remove an electron from the azide ion at the interface, I is the work function of the metallic nuclei, k is Boltzmann's constant, T is the absolute temperature, g is the density of electronic levels of energy (ϵ), η is the extra activation energy as shown in Fig. IX. The value of (ζ) works out to be high. On the other hand indirect transfer requires less energy. Metallic copper shows strong absorption at 5750 A. It has been suggested

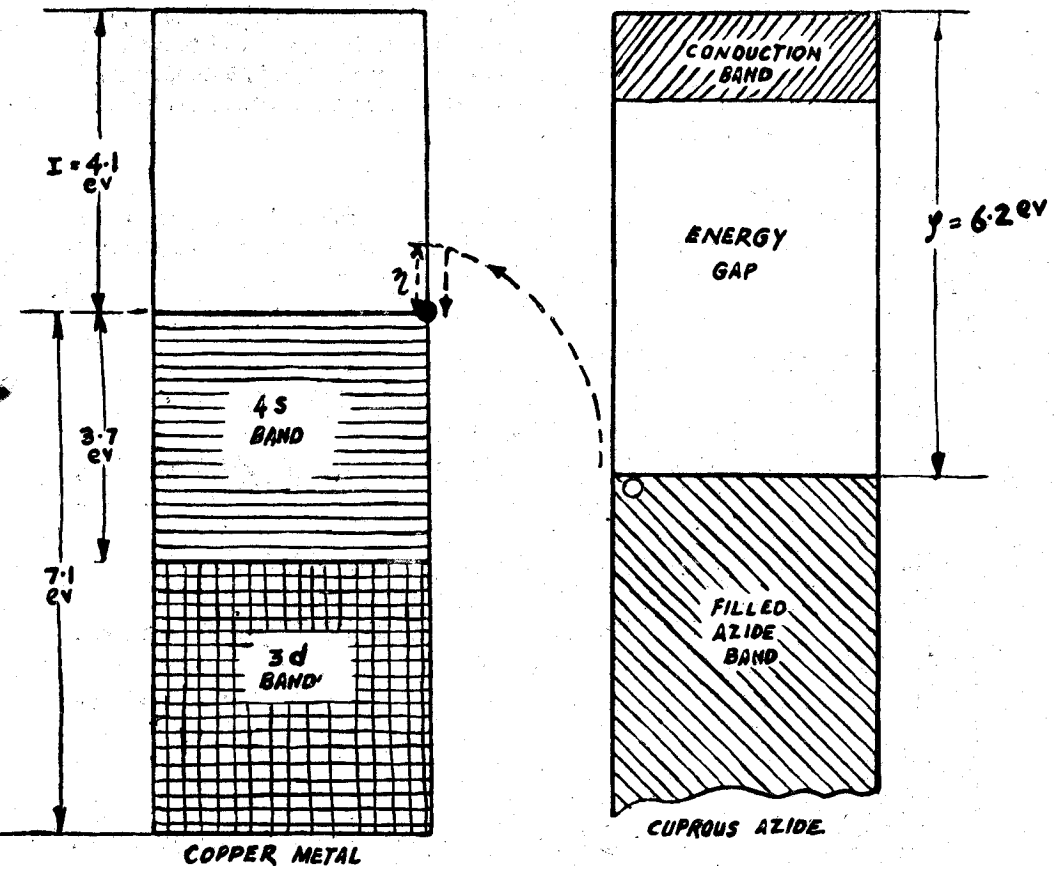


FIG. IX:—ENERGY LEVELS IN METALLIC COPPER AND CRYSTAL OF CUPROUS AZIDE

by Mott and Jones[12] that this absorption arises from transition of an electron from top of 3 d band to the Fermi level of copper. Friedel[13] has argued that Coulomb energy (E_c) of interaction between the electron and the hole created by light absorption plays a considerable role in this transition. Since on *thermal* excitation the lattice par ameters near the hole Cu^{++} contract by 10 per cent the value of E_c therefore increases by 10 percent. The energy required for thermal excitation of electron would therefore be 1·3 e.v. instead of 2·1 e.v. for optical transition. On thermal excitation of electrons from 3 d band of metallic nuclei, electrons from azide band of the crystal jump into holes left in the band. This leads to initiation of chain reactions shown in equations (1) and (4). Thus activation energy involved in thermal decomposition of cuprous azide works out to be 1·3 e.v. This value is very close to the value of activation energy 1·15 e.v. determined experimentally.

Gray and Waddington[6] in interpretation of their results on decomposition of silver azide ascribe no role to metallic nuclei. This does not appear to be a valid assumption. On the basis of the suggestions advanced in this paper it is easy to explain the thermal behaviour of other azides. As for example in

thermal decomposition of azides of transition metals vacant 'd' orbitals play an important role. In the case of alkaline earth azides the energy gap between first and second Brillouin zones in the principal crystallographic directions of metallic nuclei exert a great influence on thermal decomposition. These results will be presented in another paper.

Acknowledgment

Grateful thanks are due to Prof. D. S. Kothari, Scientific Adviser to the Minister of Defence, and Prof. C. H. Smith, Dean, Institute of Armament Studies, Kirkee, for encouragement during this investigation.

References

1. Wohler, L. and Krupko, W. Ber. 46, 2045, 1913.
2. Straumanis, M. M. Circulis, A. Z. Anorg. Chem. 251, 315, 1943.
3. Yoffe, A. D. Proc. Roy. Soc. 208A, 188, 1951.
4. Copp. J. L. Napier, S. E. Nash, T. Powell, W. J. Skelly, H. Ubbelohde, A.R. Woodward, P. Phil. Trans. Roy. Soc. London, 241A No. 831, 187, 1948.
5. Taylor, W. and Weale, A. Proc. Roy. Soc. 138 A, 92, 1932.
6. Gray, P. and Waddington, T. C. Proc. Roy. Soc. 241, 110, 1957.
7. Lukirsky, P. Gudris, N. and Kulikowa, L. Zeits. F. Phys. 37, 308, 1926.
8. Gudris, N. and Kulikowa, L. Zeits. F. Phys. 45, 801, 1927.
9. Marton, L. 'Advances in electronics' Vol. VII, 1·19 1955 (Academic Press).
10. Howarth, D. J. Proc. Roy. Soc. 220A, 513, 1953.
11. Dowden, D. A. J. Chem. Soc. 242, 1950.
12. Mott, N. F. and Jones, H. Theory of properties of metals and alloys (Clarendon Press Oxford) 1936.
13. Friedel, J. Proc. Phys. Soc. 65B, 769, 1952.