PHYSICS AND CHEMISTRY OF THE INORGANIC AZIDES

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Received February 25, 1959

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I. INTRODUCTION

In the series of solid inorganic azides KN_3 , TlN_3 , AgN_3 , and CuN_3 there is a marked variation in the stability to heat, light, and shock. Whereas potassium azide is a relatively stable solid, thallous azide decomposes at a measurable rate at temperatures close to its melting point. The decomposition of silver and cuprous azides can be rapid, and under certain circumstances explosion and detonation may result. Many of the inorganic azides form ionic or partly ionic

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solids, so that an electron-transfer mechanism must operate during some stage of the decomposition to metal and nitrogen gas. In order to explain the difference in stability it is necessary to know the electron energy band system in the solid concerned. On the other hand, the covalent azides such as hydrogen azide or hydrazoic acid, HN_3 , decompose by a free-radical mechanism. Here it is necessary to identify the transient intermediates before it is possible to write down the rate-determining step in the decomposition.

Most of the work on the inorganic azides prior to 1934 has been described by Audrieth (3). The pioneer work of Garner and his colleagues (63-68) and of others (10, 77, 94-97, 143-145) has given much valuable information on the kinetics and mechanism of decomposition. In recent years there has been a fairly comprehensive study of the physical and chemical properties of the inorganic azides. These include investigations of their synthesis, their structure, and their optical and electrical properties. Attempts have been made to follow the collapse of the solid lattice during decomposition. X-ray diffraction, electron diffraction, and electron microscopy have all been used with some degree of success. Reliable thermochemical data are also available, so that values for the lattice energies and heats of formation are known. It is thus now possible to estimate the electron energy levels for some of the azides and to relate these values to the measured kinetic data. From this correlation, a simple picture has emerged for the stability of the univalent azides. It therefore seems an appropriate time to review some of the current ideas which have been used to describe the behavior of azides. There are still a large number of gaps in our knowledge. In particular, the role of defects and dislocations in the decomposition of azides is not known and no attempt has been made to speculate on this aspect of the work. A good deal more is known about the fast explosive reaction in the inorganic azides, and this has been described in a recent monograph (21).

II. PREPARATION OF INORGANIC AZIDES

Audrieth (3) has reviewed the preparation of azides up to 1934. Details of some of these preparations are given in *Inorganic Syntheses* (17, 57). They concern aqueous hydrazoic acid and anhydrous hydrogen azide in ethereal solution (17); potassium azide by two routes (17, 57); ammonium azide by two routes (57); NaSCSN₃ (17), HSCSN₃ (17), and (SCSN₃)₂ (17). Since these preparations were described, interest has centered on the two regions of the Periodic Table below:

A. AZIDES OF THE LIGHT ELEMENTS

1. Hydrogen azide

Gaseous hydrogen azide, NH_3 , has been generated in a number of ways, among which the reaction of sodium azide with syrupy phosphoric acid (84, 123) and

with stearic acid (85) represents very convenient preparations. Stearic acid reacts only when molten, and this offers a readily controllable reaction. Small amounts of hydrogen azide have also been made by passing nitrogen gas through the aqueous solution, freeing from water with phosphorus pentoxide, and condensing the hydrogen azide in a liquid-nitrogen trap (147).

Liquid hydrogen azide is too dangerous for its applications to have been developed. Ethereal solutions of hydrogen azide have found applications (3, 57) where exclusion of moisture is important and have been widely employed in the new syntheses described below.

Aqueous hydrogen azide is safest when dilute; Audrieth recommends 3 per cent solutions. Joyner found (98) that aqueous solutions containing as little as 17 per cent hydrogen azide could detonate; solutions containing 50 per cent hydrogen azide have been used (129), although not without hazard.

2. Sodium azide and other alkali metal azides

The lattice of these solid azides is composed of ions. The common laboratory source of the azides is technical sodium azide, itself manufactured from sodium amide and nitrous oxide. The mechanism of this reaction has been investigated by isotope experiments, using ¹⁶N (26, 27), and the course of the reaction is summarized by the equations:

 $2NaNH_2 + O^{15}NN \xrightarrow{-NaOH} {}^{NaOH} {}^{Na^{15}NNN} (22 \text{ per cent}) \\ NaN^{15}NN (78 \text{ per cent})$

The reaction between calcium amide and nitrous oxide has also been studied (28).

A method for growing large crystals (4 x 6 x 1 mm.) of sodium azide has been described (41); large crystals of potassium azide (41) can be obtained more easily. Lithium azide forms a monohydrate (the phase diagram for the $\text{LiN}_3\text{-H}_2\text{O}$ system (132) has been described), which yields the pure anhydrous salt only with difficulty. Its preparation is aided by the use (75) of strong aqueous solutions of hydrogen azide or by carrying out the reaction in ether, and requires prolonged drying with phosphorus pentoxide.

3. Ammonium azide

The preparation of ammonium azide is described in *Inorganic Syntheses* (57). It may be made from an ethereal solution of hydrogen azide through which dry ammonia gas is passed. The ammonium azide precipitates from the ethereal solution as it is formed; the crystals obtained from ethanol are long needles.

Larger quantities of ammonium azide may conveniently be made by the reaction of 1 mole of sodium azide with 1 mole of ammonium chloride in 300-500 ml. of dimethylformamide at 100° C. When reaction is complete, the temperature is lowered to $60-70^{\circ}$ C. and ammonium azide and dimethylformamide are distilled at 30-35 mm. pressure. The azide is filtered off and washed with ethanol and ether.

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4. The azides of beryllium, boron, magnesium, aluminum, silicon, gallium, and tin(IV)

Wiberg and Michaud (153), in 1954, made a remarkable contribution to preparative azide chemistry. They treated solutions of hydrogen azide in ether or tetrahydrofuran with metal hydrides, usually at low temperatures:

$$BH_3 + 3HN_3 \rightarrow B(N_3)_3 + 3H_2$$

$$AlH_3 + 3HN_3 \rightarrow Al(N_3)_3 + 3H_2$$

$$SiH_4 + 4HN_3 \rightarrow Si(N_3)_4 + 4H_2$$

$$GaH_3 + 3HN_3 \rightarrow Ga(N_3)_3 + 3H_2$$

The metal alkyls reacted similarly, and anhydrous beryllium and magnesium azides were made in this way:

$$Be(CH_3)_2 + 2HN_3 \rightarrow Be(N_3)_2 + 2CH_4$$
$$Mg(C_2H_5)_2 + 2HN_3 \rightarrow Mg(N_3)_2 + 2C_2H_6$$

The structures of these azides have not been determined, and it is doubtful whether they are ionic solids.

In certain cases "mixed" azides could be produced in consecutive reactions and regulated by controlling the temperature. For example, lithium borohydride reacts as follows:

Similarly, aluminum trimethyl retains one methyl group per aluminum atom:

$$Al_2(CH_3)_6 + 4HN_8 \rightarrow 2CH_3Al(N_3)_2 + 4CH_4$$

By working in dry benzene solution aluminum, silicon, and stannic azides were made from the corresponding chlorides and sodium azide. Stannic chloride, however, produced a complex stanni-azide when sodium azide was in excess:

$$6NaN_3 + SnCl_4 \rightarrow Na_2Sn(N_3)_6 + 4NaCl$$

B. AZIDES OF THE HEAVY METALS

A number of heavy metal azides may be prepared by precipitation from aqueous solution and purified by recrystallization; this method is suitable for preparing the azides of silver, thallium(I), mercury(I), mercury(II), and lead(II). It does not lend itself to preparing copper(I) or copper(II) azide or the β -forms of lead(II) and mercury(II) azides, nor, without modification, to the preparation of cadmium azide.

1. Copper(I) and (II) azides

Cuprous azide is made (138) from 10 per cent aqueous sodium azide reacting with cuprous chloride dissolved in saturated aqueous potassium chloride. Acetic acid and a trace of potassium bisulfite must be present; cupric ion must be absent. Cuprous azide can be recrystallized as yellow-green needles and plates from its solution in saturated potassium chloride at 60°C.; about 0.1 per cent of potassium bisulfite is added to prevent oxidation.

Cupric azide (solubility = 0.0080 g./100 g. water at 15°C.) is readily precipitated from an aqueous solution containing cupric and azide ions. Straumanis and Cirulis (139) have described the salt and some of its complex ions.

2. Silver azide

Silver azide is readily prepared by precipitation from aqueous solutions containing silver and azide ions. It is conveniently recrystallized from aqueous ammonia to give colorless plates and needles.

3. Cadmium azide

Preparation of cadmium azide from aqueous solution requires special precautions (20, 129) to limit hydrolysis. Cadmium carbonate is dissolved in aqueous hydrazoic acid; to the hot solution 50 per cent hydrazoic acid is added, and cadmium azide separates on cooling as yellow crystals.

4. Gold(I) azide (aurous azide)

Attempts to prepare gold azide have so far been unsuccessful. A sodium gold azide has been described (130).

5. Mercury(I) and (II) azides

Mercurous and mercuric azides are both readily prepared by precipitation. Mercuric azide, $Hg(N_{\vartheta})_2$, is soluble in hot water and may be recrystallized from it in the α -form. The β -form is prepared in the same way as β -lead azide (Section III,B,7).

6. Thallium(I) azide (thallous azide)

Thallous azide is prepared by precipitation and purified by recrystallization from hot water. It forms pale yellow needles and plates.

7. Lead azide

Lead azide is readily prepared by precipitation. It is soluble in ammonium acetate and in acetic acid and crystals of the orthorhombic (α) form may be grown from these solutions.

The monoclinic (β) form is obtained by permitting lead and azide ions to diffuse together slowly. The same method produces an unstable form of mercuric azide. Experimentally (131), an upper layer of aqueous sodium azide is separated by aqueous sodium nitrate from a lower layer of aqueous lead nitrate. Azide ions diffuse down across the upper boundary and lead ions up across the lower. After about 1 hr. a faint haze appears in the nitrate layer nearer to the original azide boundary (figure 1). Crystals of β -lead azide now begin to grow on the walls of the container and into the solution. Growth continues rapidly for $\frac{1}{2}$ to 1 hr. until there is a small number of relatively large crystals in the system.



Fig. 1. The diffusion growth of β -lead azide crystals

The separation of solid then appears to cease completely for 1 to $1\frac{1}{2}$ hr. Now explosion may occur. If no explosion occurs during the quiescent period, crystallization recommences with the formation of a very large number of much smaller crystals as a dense mat, usually just above the original lead nitrate boundary. Crystallization continues downwards until the reagents are consumed. Some of the experimental conditions which lead to spontaneous explosions during growth from solution have been described by Bowden and Yoffe (21).

C. COMPLEX AZIDES

To the complex azides listed by Mellor (114) and discussed in outline by Audrieth (3) may be added the sodium hexazidostannate, $Na_2Sn(N_3)_6$ (153), and the complex copper azides (139). The latter are red-brown or blue compounds made by dissolving cupric azide in aqueous solutions of alkali metal azides and have the general formulae $M[Cu(N_3)_3]$, $M_2[Cu(N_3)_4]$, and $M[Cu_2(N_3)_5]$; the last formula is most common. As the atomic weight of M increases, so also do the stability and ease of crystallization. A sodium gold azide of the formula $NaAu_{1.43}N_{9.05}$ has been reported (130).

D. HALOGEN AZIDES

Audrieth (3) discusses a number of these. Subsequent work on chlorine azide (62) and fluorine azide (24) has been reported. When fluorine azide decomposes it does so by fission of the FN---N₂ bond and the fluorine analog of azomethane is formed (as cis and trans isomeric forms):

$2FN_3 \rightarrow 2FN + 2N_2 \rightarrow FN = NF + 2N_2$

Recently nitrosyl azide, ON_4 , previously postulated as an unstable intermediate in the decomposition of azides by nitrogen tetroxide (79) and nitrous acid, has been isolated as an unstable yellow compound (106).

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III. PHYSICAL PROPERTIES

A. CRYSTAL STRUCTURE OF THE INORGANIC AZIDES

On the basis of the experimental evidence available it seems possible to classify the azides into two distinct groups. On the one hand there are the organic type azides in which covalent bonding occurs, as shown by the asymmetry of the azide group. Secondly, there are the inorganic azides having a symmetrical azide group and some degree of ionic binding. The degree of ionic binding occurring in the inorganic azides diminishes with increasing ionization potential of the metal forming the azide (49).

1. Monovalent azides

The crystal structures of all the common monovalent azides have been determined. For the azides given in table 1 the azide group is linear and symmetrical. This is a characteristic feature of the inorganic azides, unlike the organic azides in which the azide group is asymmetric as regards nitrogennitrogen separation. The asymmetric form of the azide group in the organic azides is due to the covalent bond formed between the organic group and one "end" nitrogen (N_{II}) of the azide group. The symmetric azide group of the inorganic azides does not, however, mean that these azides are necessarily completely ionic. The crystal structures of the azides given in table 1 have been discussed by Evans and Yoffe (9).

Figure 2 gives the projection on to the (001) plane of the silver and nitrogen in silver azide. This diagram is also applicable to potassium, rubidium, cesium, and thallous azides. The azide groups lie in planes parallel to (001) and are

Salt	Crystal Class	Cell Constants	Mole- cules per Unit Cell	Coördination	NI-NII	IIN-X	References
					A.	A.	
NaNs	Body-centered rhombohe- dral	$a_0 = 5.488 \text{ A.}$ = 38°43'	1	6:6	1.17 1.15 ± 0.016	2.48	(89a) (61)
KN:	Body-centered tetragonal	$a_0 = 6.094 \text{ A.}$ $c_0 = 7.056 \text{ A.}$	4	8:8	1.16 1.145 ± 0.017	2.96	(89a) (61)
RbN:	Body-centered tetragonal	$a_0 = 6.36 \text{ A.}$ $c_0 = 7.41 \text{ A.}$	4	8:8	1.13	3.11	(86)
CsN:	Body-centered tetragonal	$a_0 = 6.72 \text{ A.}$ $c_0 = 8.04 \text{ A.}$	4	8:8		3.34	(151)
T1N:	Body-centered tetragonal	$a_0 = 6.23$ A. $c_0 = 7.37$ A.	4	8:8		2.98	(86a)
AgN:	Orthorhombic	$a_0 = 5.59 \text{ A}.$ $b_0 = 5.91 \text{ A}.$ $c_0 = 6.01 \text{ A}.$	4	8:8 (4 closer in)	1.16	2.79 2.56	(23b, 124b) (152b)
CuN3	Tetragonal	$a_0 = 8.65 \text{ A}.$ $c_0 = 5.59 \text{ A}.$	8	4:4	1.17	2.23	(153b)
NH4N3	Orthorhombic	$a_0 = 8.93 \text{ A.}$ $b_0 = 8.64 \text{ A.}$ $c_0 = 3.80 \text{ A.}$	4	8:8 (4 closer in)	1.166	3.2 2.98	(61)

 TABLE 1

 Crustal structures of the inorganic monovalent azides



Fig. 2. The projection on to the (001) plane of the silver and nitrogen in silver azide

TABLE 2

 Ionic radius and ionization potential for the elements forming the azides listed in table 1

 Element
 Ionic Radius
 Ionization Potential
 Element
 Ionic Radius
 Ionization Potential

Element	Ionic Radius	Potential	Element	Ionic Radius	Potential
	A .	e.v.		A.	e.v.
Na	0.95	5.12	T1	1.51	6.07
K	1.33	4.32	Ag	1.26	7.54
Rb	1.48	4.16	Cu	0.96	7.68
Cs	1.69	3.87			

inclined at an angle of 45° to the (100) plane for those azides having a tetragonal structure. The variation in unit cell size and crystal class for the azides given in table 1 is due to the difference in properties between the metals. The ionic radius of the metal forming the compound will be one significant variable; another is the ionization potential (I) of the metal (or more strictly I - E, where E is the electron affinity of the azide radical) (49). Table 2 gives the ionic radius and ionization potential for the series of elements forming the azides listed in table 1.

(a) Alkali metal azides

The electron affinity of the azide radical is ca. 3.05 e.v. Table 1 shows that potassium, rubidium, and cesium azides all possess a tetragonal structure, and that an increase in the magnitude of a_0 and c_0 accompanies an increase in the ionic radius of the metal ion. The metal ion will be in contact with the end nitrogen, N_{II}, of the azide group. Denoting this contact radius of the azide group by r, then the value r = 1.63 A. satisfies the dimensions of X—N_{II} (table 1) for potassium, rubidium, and cesium azides. The small ionic radius of sodium results in a hexagonal structure for sodium azide.

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(b) Thallous azide

Thallous azide also has a tetragonal structure, but its unit cell dimensions are not satisfied by r = 1.63 A. A further point of interest is that whereas the value of c_0/a_0 increases in going from potassium azide to cesium azide, for thallous azide it is less than for cesium azide. This may be accounted for by supposing that the valence electron is still partly under the influence of the thallium (due to its higher ionization potential) and so retains some of its 6p orbital characteristics.

(c) Silver azide

Using the value of r given earlier for the contact radius of the azide ion (i.e., 1.63A.) gives the value of c_0 corresponding to the azide groups in contact along c_0 as 6.52 A. This is greater than the value of c_0 given for silver azide (table 1). The value of r applicable to the azide group in silver azide must therefore be different from that in potassium, rubidium, and cesium azides and obeys the relationship $4r \leq 6.01$ A. If 4r = 6.01 A. the azide groups are in contact along c_0 . The Ag-N_{II} distances are 2.56 and 2.79 A. Consequently, if r = 1.5 A. (as indicated by measurements on the refractive index of silver azide (49)), the separation of 2.56 A. is less than that corresponding to ionic binding. It is therefore assumed that the silver (as a result of its higher ionization potential) forms some degree of nonionic binding with the azide group, there being four bonds per silver ion lying approximately in the xz plane. An alteration in the value of r would be expected to accompany this change in charge distribution. The tendency of silver azide to cleave along planes parallel to the crystal surface supports the idea of bonding in the (010) plane.

(d) Cuprous azide

Cuprous azide, CuN_3 , possesses a tetragonal unit cell similar to that of potassium, rubidium, and cesium azides. However, cuprous azide has a different space group from that of potassium azide and thus a direct comparison cannot be made between the lattices of cuprous azide and potassium azide. The ionic radius of cuprous ion (table 2) is 0.96 A., and the crystal structure of the azide has a copper-nitrogen contact distance of 2.23 A. (table 1). The observed distance of 2.23 A. is thus considerably less than the distance of 2.59 A. expected if cuprous azide were an ionic compound. The chainlike nature of the molecular arrangement is another indication that cuprous azide extends the deviation from ionic structure exhibited by thallous and silver azides. This, it is suggested (47), is a natural consequence of the higher ionization potential of copper-

(e) Ammonium azide

Ammonium azide belongs to the space group D_{2h}^7 (or P_{man}) and is isomorphous with ammonium bifluoride (61). Its structure is essentially that of a distorted potassium azide lattice; whereas in potassium azide each potassium ion has eight equidistant nitrogen neighbors, in ammonium azide four of the eight azide ions surrounding the nitrogen atom of ammonium are drawn in tetrahedrally to the distance 2.98 A. by the formation of N—H····N hydrogen bonds. The other four are at about 3.2 A.

(f) Hydrazoic acid

The solid-state structure of this compound is unknown. Gaseous hydrogen azide exhibits covalent linking and gives rise to one bond, HN—NN, which is long (1.24 A.) and weak and another, HNN—N, which is short (1.10 A.) and strong. The crystal structure of the isoelectronic compound HNCO has been determined (37) and found to be orthorhombic, with the molecules linked into infinite zigzag chains by N—H…N hydrogen bonds. Solid hydrazoic acid may similarly be expected to give molecular bonding and therefore exhibit an extreme departure from the ionic condition.

(g) Halogen azides

Azides may be made even from such electronegative elements as the halogens. Thus IN₃, BrN₈, CNN₃, FN₃, ClN₃ are all known. Unfortunately, little is known about the halogen azides because these compounds form unstable solids at low temperatures and an investigation of their crystal structure may be difficult. The polarization in the solid is probably of the form $\text{Cl}^{\delta-}$ N₃^{\delta+}.

2. Divalent azides

These azides exist in the form $M(N_3)_2$. The only complete structural analysis that has been made is that of strontium azide (105). Of the other azides the cell constants and crystal classes only have been determined and these are listed in table 3.

Strontium azide has a space group F_{ddd} . The unit cell is orthorhombic (pseudotetragonal), having dimensions a = 11.82, b = 11.47, and c = 6.08 A. There are eight molecules per unit cell. The azide group is linear and symmetrical, the nitrogen-nitrogen distance being 1.12 A. The strontium ion has eight near neighbors which can be classified into two sets of four. In the first set the strontiumnitrogen separation is 2.63 A. and in the second set 2.77 A. The ionic radius of the strontium ion is 1.13 A., and the contact radius of the azide ion (ionic) is 1.63 A. The strontium-nitrogen distance of 2.77 A. thus corresponds to ionic bonding. The smaller strontium-nitrogen distance of 2.63 A. may, as for silver azide, indicate the presence of some type of directed bonding.

B. OPTICAL PROPERTIES OF THE INORGANIC AZIDES

Measurements of the optical properties of the inorganic azides have been made in order to determine the electron energy band structure of these solids. In order to perform such a calculation it is necessary to know (a) the high- and low-frequency dielectric constants and (b) the fundamental absorption spectrum.

The high-frequency dielectric constant, k_0 , is given by $k_0 = n^2$, where *n* is the refractive index of the compound. The relation $k_0 = n^2$ holds only outside the region of anomalous dispersion, i.e., for wavelengths at which there is no optical absorption by the compound.

Salt	Crystal Class	Cell Constants	Number of Molecules per Unit Cell	Reference	
Cu(Na)2	Orthorhombic	$ \begin{array}{c} A.\\ a = 9.23\\ b = 13.23 \end{array} $	8	(139)	
Ca(Ni)2	Orthorhombic	c = 3.07 a = 11.62 b = 10.92	8	(151)	
Ba(Na)2	Monoclinic	c = 5.66 a = 6.22 b = 29.29 c = 7.02	10	(86)	
Cd(N ₁) ₁	Orthorhombic	$\alpha = 105^{\circ}$ a = 7.82 b = 5.46	8	(10a)	
α-Pb(N3)2	Orthorhombic	c = 7.02 a = 6.63 b = 11.31	12	(6a, 124)	
β-Pb(N3)3*	Monoclinic	c = 16.25 a = 5.09 b = 8.84 c = 17.51	8	(124)	
		$\alpha = 90^{\circ}10'$			

 TABLE 3

 Cell constants and crystal classes of azides of divalent elements

* Grown by diffusion.

The low-frequency dielectric constant k (or more particularly the static dielectric constant) has been measured at frequencies in the megacycle region.

1. Refractive indices

Measurements of the refractive index, besides yielding the value of k_0 , give an indication of the type of electron bonding occurring in the crystal examined. These results therefore complement the semiquantitative discussion previously given on the crystal structure of the inorganic azides. In this respect the most useful results are those in which the refractive index has been measured as a function of wavelength throughout the visible spectrum (49).

(a) Sodium azide

This compound does not show dispersion in the visible region (50). For light propagated normal to the major parallel morphological faces the refractive index has been given as 1.38 (41) and 1.48 (50). When the vibration of the electric vector is normal to the crystal face the index of refraction is 1.52 (41).

(b) Potassium azide

Crystals of this compound may be grown with the major morphological faces containing the axes a and b of the unit cell (figure 2). When the electric vector of the incident light vibrates in the c direction the refractive index $n_c = 1.45$ (41). Similarly, $n_a (= n_b)$ is given as 1.66 (41) and exhibits slight dispersion as shown by the results (50) of table 4. These values for the refractive index are

Wavelength	Refractive Index, na	Wavelength	Refractive Index, na	
A. 4800 5500	1.5 1.51	A. 1.5 6000 1.51 6500		
REFRACTIVE INDEX, n 0 0 0 0 1 0 0 0	00000000000000000000000000000000000000		-0	
4500	5000	6000	7000	

 TABLE 4

 Variation of refractive index with wavelength for potassium azide

Fig. 3. The variation in refractive index with wavelength for silver azide: \circ , n_{\perp} ; \bullet , n_{\parallel} .

typical of ionic compounds. The crystallographic structure also suggests, as observed, that $n_a = n_b > n_c$, since polarization will occur at the azide ion (N₃⁻).

(c) Thallous azide

Measurements using the Becke line effect for sodium light give (50) n > 1.99. Thallous azide is a colored compound (pale yellow) and the associated dispersion means that direct optical examination can give only an approximate value for n.

(d) Silver azide

Silver azide, AgN₈, forms thin platelike crystals. The major surface is a composite of (010) and (100) planes, with (010) predominating. The variation of refractive index with wavelength has been determined (49) for all wavelengths in the visible region. The results are given in figure 3, where n_{\perp} and n_{\parallel} are the refractive indices for light having its electric vector along the a(x) and c(z)crystal axes, respectively. Also, the refractive index in the a(x) direction is different from that in the b(y) direction. The value of 1.8 obtained for n_{\parallel} sup-

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ports the idea of the azide groups being in contact at their centers along c (cf. Section III,A). The dispersion and larger values obtained for n_{\perp} also favor a charge distribution localized along the N_{II} -Ag(nearest) directions.

(e) Cuprous azide

The refractive index has been measured (50), using the Becke line method. This compound is pale yellow, so the measured value of n > 1.81 is necessarily only approximate.

(f) Triphenylmethyl azide

This compound has been included, as it is a truly covalent compound. The refractive index (52) is 1.43.

2. Low-frequency dielectric constant

These measured values are given in table 6, which also gives the frequency at which the measurements were made.

3. The optical absorption spectra of some inorganic azides

Potassium, thallous, silver, and cuprous azides exhibit a wide variation in stability to heat and light. In order to estimate the energetics of the electronic processes leading to decomposition it is necessary to determine the electron energy levels of the particular solid. For this reason measurements have been made of the absorption spectra of pure and decomposed samples of the azides. Potassium, thallous, and silver azides have received the most attention.

(a) Sodium azide

The position of the absorption edge has been approximately determined, using a reflection technique. Maximum absorption occurs (94) in the vicinity of 2400 A.

Azide	$k_0 \ (= \ n^2)$	Azide	$k_0 \ (= n^2)$	Azide	$k_0 \ (= \ n^2)$			
NaNs	2.19 2.25	TlNs AgNs	3.95 4.85	$\begin{array}{c} CuN_{\vartheta}.\\ (C_6H_{\vartheta})_{\vartheta}CN_{\vartheta}.\end{array}$	3.24 2.04			

 TABLE 5

 High-frequency dielectric constants of azides

TABLE 6	
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Low-frequency dielectric constants of azides

Azide	Dielectric Constant, k	Frequency	Reference	Azide	Dielectric Constant, k	Frequency	Reference
		mc./sec.				mc./sec.	
Na Ns	6.4	1.5	(111)	Hg2(N3)2	4.6	1.5-4.5	(35)
KN3	6.85	50	(111)	Ba(N₂)₂	7.74	1.5	(111)
T1N3	11.5	1.35	(47)	$Sr(N_2)_2$	8.3	1.5	(111)
AgN8	9.35	1.35	(111)	(C6H5)3CN8	2.1	1.2	(47)
CuN3	9.3	2-4.5	(50)				

(b) Potassium azide

The absorption edge of this compound exhibits no unusual features; maximum absorption occurs (50) at 2480 A. A detailed investigation of this compound has been made by Tompkins and coworkers (94, 148). New absorption bands may be produced by irradiation with ultraviolet light when the crystal is at liquid-air temperature (-196° C.). These bands are ascribed to the formation of F and V centers (148).

(c) Thallous azide

The absorption spectrum of this compound at room temperature has been measured by Evans and Yoffe (50) and is given in figure 4. The main features of the absorption spectrum are as follows: (a) There is a pronounced long wavelength tail extending into the visible region. This is responsible for the pale yellow color of thallous azide crystals. (b) The main absorption edge has a "shoulder" which arises from the overlapping of two absorption bands at the point A. (c) The two absorption peaks comprising this shoulder have maxima at 3200 A. and 2750 A., respectively. Beyond this the absorption rises steadily to the 2000 A. limit of measurement.

The absorption spectra of thallous azide after decomposition has been induced have also been measured by Evans and Yoffe (51); these results will be discussed in Section III,C.



FIG. 4. Absorption spectrum of thallous azide at room temperature

(d) Silver azide

The absorption spectrum of a single crystal of silver azide at a series of temperatures has been determined by McLaren and Rogers (113) and is given in figure 5. The absorption band resolved at low temperatures has its maximum at 3590 A. New absorption bands are formed when silver azide is partially decomposed by heat or light; these will be considered in Section III,C.



FIG. 5. The absorption spectra of silver azide. Curve 1, at room temperature; curve 2, at -80° C.; curve 3, at -175° C.



FIG. 6. The absorption spectrum of cuprous azide at room temperature

(e) Cuprous azide

The absorption spectrum of a small single crystal of cuprous azide has been measured by Evans and Yoffe (50) and is given in figure 6. At 5500 A. the percentage transmission is 16 per cent, diminishing to 1 per cent at 3800 A.

(f) Mercurous azide

The absorption spectrum of a thin evaporated film of mercurous azide has been measured at room temperature by Deb (35). The onset of maximum absorption occurs at 3900 A.

(g) Barium azide

The absorption edge has been approximately located (94) by measuring the reflection spectrum. Maximum absorption occurs in the vicinity of 2200 A.

(h) Lead azide

The absorption spectrum at room temperature of a single crystal of lead azide has been measured by McLaren (111). The absorption edge occurs at 4000 A.

C. ELECTRICAL PROPERTIES OF THE AZIDES

1. Photoconductivity

This section describes the results that have been obtained from measurements of photoconductance in pure and decomposed samples of the azides. Potassium, thallous, and silver azides have received the most attention. On the basis of such measurements it is possible to suggest a mechanism by which the azide undergoes decomposition (photochemical or thermal). There has unfortunately been a tendency to invoke concepts in the theory which at present have little experimental basis.

(a) Potassium azide

A pellet of potassium azide when irradiated by a mercury vapor lamp does not give rise to any detectable photocurrent (94). Potassium azide is reported (149) to be a photoconductor when irradiated at wavelengths well within the absorption edge. When single crystals of potassium azide at liquid-nitrogen temperature are irradiated with ultraviolet light they become lilac in color (148). By analogy with potassium chloride this new absorption band is described as an F center band. Subsidiary bands on the short and long wavelength side of this band are similarly attributed to V and M, R type centers, respectively.

The F band arises from the absorption by centers consisting of a single electron trapped at an anion vacancy. When crystals irradiated at -196 °C. are warmed in the dark to between 0 °C. and 25 °C., the F band diminishes with the simultaneous formation of a broad band with a peak at ca. 7500 A. This new absorption band, identified as an R' band, may also be produced by irradiating a pure crystal at room temperature. The R' band is considered to arise from the aggregation of F centers.

When a crystal containing an R' band is heated to 60°C., the F centers dissoci-

ate to form thin layers and filaments of metallic potassium within the crystal. At this stage the R' band disappears and a new absorption band is formed which has a peak at 4400 A. The crystal in this condition now exhibits photoconductivity and this is attributed to photoemission from the metallic potassium into the conduction band of the potassium azide. The band at 4400 A. is the corresponding absorption process.

If the crystal is further heated to 276° C., the absorption spectrum then consists of a strong band at 7250 A. plus the selective photoemission peak at 4400 A. The band at 7250 A. is due to light scattering by colloidal particles of potassium.

(b) Thallous azide

The optical properties of thallous azide have been studied by Evans and Yoffe (50, 51). At room temperature pure crystals of thallous azide show marked photoconduction when irradiated with light within the absorption spectrum. The spectral distribution of photocurrent when the crystal is irradiated on a major morphological face is given by curve A of figure 7. There is a subsidiary maximum in the photocurrent at 4300-4350 A. At wavelengths less than 4000 A. the photocurrent increases rapidly. The subsidiary maximum at 4300–4350 A. may be identified with the thermal dissociation of optically formed excitons. The optical transition of electrons from the full band to the exciton band of the crystal gives rise to the "shoulder" at ca. 3000 A. shown by the absorption spectrum of figure 4. This subsidiary photoconduction maximum is temperature dependent and has an activation energy of 0.33 e.v. This corresponds to the thermal energy of dissociation of excitons in this compound. The steep rise in photocurrent for wavelengths less than 4000 A. (figure 7) corresponds to optical transitions of electrons from the full to the conduction band of the crystal. Curve B of figure 7 shows the spectral distribution of photocurrent in a photochemically decomposed crystal of thallous azide. The short wavelength rise in photocurrent due to fullconduction band transitions has been eliminated, and it has been suggested that this is due to the photolytic thallium metal which acts as an electron trap. This is also responsible for the movement of the subsidiary photocurrent maximum to shorter wavelengths, i.e., to 4250 A. Photoconduction in thermally and "radioactively" decomposed thallous azide has also been studied (51), and the results enable the following interpretation to be given of the spectral distribution of photocurrent in pure thallous azide (curve A, figure 7). Let C_x be the photocurrent due to the thermal dissociation of excitons and C_s the photocurrent due to the direct optical formation of conduction band electrons. At long wavelengths, i.e., ca. 5000 A., the photocurrent is due to $C_x + C_s$. The absorption steadily increases with decreasing wavelength, and the subsidiary maximum at 4300-4350 A. is achieved when electron-positive hole recombination limits the rapidly increasing value of C_x . C_x then decreases to zero at 3980 A. (3.1 e.v.). For wavelengths less than 3980 A, the photocurrent is entirely due to C_s and this component is then unaffected by electron-positive hole recombination until 3600 A. (3.44 e.v.). This discussion on thallous azide has been restricted to the case when the major morphological crystal face is irradiated with light. It has



FIG. 7. Spectral distribution of the photocurrent in thallous azide at room temperature calculated for an equal intensity at each wavelength. Curve A, \circ , undecomposed crystal; curve B, +, photochemically decomposed crystal.

been found (51) that the minor crystal faces (presumably due to their higher surface energy) are far more sensitive to photochemical decomposition.

(c) Silver azide

Pure crystals of silver azide are photoconductors at room temperature when irradiated with light of the appropriate wavelength.

The photoconductive properties of undecomposed silver azide have been studied by McLaren and Rogers (113). The spectral distribution of photocurrent at room temperature is shown in figure 8. It is believed that, as in the case of thallous azide, the photocurrent arises from the thermal dissociation of optically formed excitons. The corresponding exciton absorption band was given in figure 5. The maximum photocurrent occurs at 3800 A. By measuring this maximum photocurrent as a function of temperature the activation energy of exciton dissociation was found to be 0.38 e.v. When a single crystal of silver azide is heated at a temperature greater than 100°C. it undergoes thermal decomposition and a new absorption band develops which has a maximum at 4900 A (112). This absorption band is due to the formation of colloidal particles of silver within the silver azide as a result of the thermal decomposition. Silver azide which has been photochemically decomposed also exhibits this absorption band at 4900 A., but in addition there is another band at ca. 4200 A. (10), which can be bleached by infrared light. After such bleaching photoconductance is observed in the near infrared. The photoresponse curve of this latter effect exhibits two bands of sensitivity, one having a threshold frequency of ca. 2.75 e.v. and the other having a threshold frequency of 1.65 e.v. This latter value of 1.65 e.v. is





interpreted as the energy required to excite electrons optically from colloidal particles of silver to the conduction band of the silver azide. In Section III,C,2 it is stated that the apparent thermal activation energy of electronic conductance in partially decomposed orthorhombic silver azide is 0.39 e.v. This is the same value as that obtained for the activation energy of thermal dissociation of excitons in this compound. The "dark" electronic conductance is considered to arise from the thermal ionization of colloidal silver. The corresponding optical process is photoemission from colloidal silver, which gives rise to a photocurrent in the near infrared, as already described.

(d) Cuprous azide

Cuprous azide deviates from an ionic structure to an even greater extent than silver azide. Consequently one would expect cuprous azide to be a very good photoconductor. However, photoconduction has not been observed in single crystals of cuprous azide (50), but there is a complex dark current effect. The absence of a detectable photocurrent has been attributed to the very short lifetime of the photoelectrons.

(e) Mercurous azide

There is no evidence of photoconduction in thin evaporated films of mercurous azide (35).

(f) Lead azide

Lead azide is a weak photoconductor. Measurements have been made on single crystals of this compound (50), using a mercury vapor lamp as a light source. The maximum in the spectral distribution of photocurrent occurs at a wavelength of ca. 3650 A. McLaren and Rogers (113) have found that the primary photocurrent diminishes with time of irradiation, owing to the formation of a space charge. This space charge may be removed by irradiating the crystal with red light without any applied electric field on the crystal.

2. Conductivity and electrical breakdown

Measurements on conductivity in solids provide useful information concerning the nature and movement of charge carriers. They are also useful in considering the mechanism of decomposition. The conductivities of a number of azides have been measured; however, only potassium azide and silver azide have been studied in any detail.

Jacobs and Tompkins (94) used pellets of potassium azide in a vacuum and measured the specific ionic conductance K (ohm⁻¹ cm.⁻¹) between 396° and 474.5°K. They found that potassium azide is a cationic conductor, and that the relation for ionic conductance is

$\log_{10} K = 6.07 - 33.75 \text{ kcal.}/4.576T^{\circ}\text{K.}$

This expression refers to the non-structure-sensitive region (126). At lower temperatures a structure-sensitive region depending on surface conductance has been observed. The activation energy for this region is 4.5 kcal.^2

The dark conductivity of silver azide (10, 149, 159) and cuprous azide (50) is a complex phenomen. Bartlett, Tompkins, and Young (10) have estimated the activation energy for ionic conductance of a sintered mass of silver azide as 25 kcal. for temperatures below the transition temperature (190°C.). The conductivity is probably due to mobile interstitial silver ions. In partly decomposed silver azide the conductivity is predominantly electronic in nature. Below the transition temperature (orthorhombic form) the activation energy for electronic conduction is 9 kcal.; above the transition temperature it is 6.4 kcal. They have also estimated the relative contributions due to interstitial silver ions and to electrons at 190°C. The specific conductance at 190°C. due to silver ions is 10^{-6} ohm⁻¹ cm.⁻¹ and the electronic contribution (*n* type) is 10^{-5} ohm⁻¹ cm.⁻¹ They consider that the conduction electrons are obtained during thermal ionization of colloidal centers of silver in the partly decomposed silver azide.

Some values for the specific resistance at room temperature of single crystals of a number of azides are listed in table 7 (35, 50, 113). The breakdown voltage —namely, the voltage at which a high current and explosion is observed—is also given in the table.

² Energies in this review are given in electron volts and kilocalories. The conversion factor is 1 e.v. = 23.05 kcal.

THE INORGANIC AZIDES

ΓА	В	I	ε	7	
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Compound	Specific Resistance at Room Temperature	Breakdown Voltage per Centimeter at Room Temperature
	ohm ⁻¹ cm. ⁻¹	
TlNs	ca. 8×10^{12}	· · _
AgN8	ca. 3×10^{3}	ca. 300 v.
CuNs	Complex dark current effect	ca. 2.5 k.v.
Hg2(N3)2		High
Hg(N ₈) ₂	ca. 1.7×10^{10}	ca. 100 k.v.
Pb(N ₃) ₂	ca. 1.5×10^{18}	—

Specific resistance and breakdown voltage of some inorganic azides

Breakdown voltage: When a silver azide crystal is placed between two electrodes, breakdown and explosion is observed when the D.C. field is in the region 250-300 v./cm. (19). The breakdown voltage increases with decreasing temperature. The time to explosion also increases with increasing frequency if an A.C. field is applied. Just prior to explosion the current passing through the crystal increases; for example, a current of 150 μ A has been measured when a crystal is placed in a field of 900 v./cm. Experiments have shown that the breakdown is not due to the formation of a silver thread in the crystal by electrolysis. McLaren has suggested that the silver azide is polarized during the application of a D.C. field, and that breakdown occurs when the polarization reaches a critical value. The space charge fields set up in the crystal are now strong enough to cause a flow of electrons into the crystal from the cathode. If the electrons enter the crystal with sufficient energy, decomposition and explosion may result. A similar mechanism has been suggested for cuprous azide by Evans and Yoffe (50).

D. ELECTRON ENERGY LEVELS IN SOME INORGANIC AZIDES

In order to estimate the electron energy levels in a solid it is necessary to have information on the optical and electrical properties of the compound. Such information is available only for potassium, thallous, and silver azides. Cuprous and mercurous azides will be briefly considered, but these compounds have not received much attention. In the case of potassium, thallous, and silver azides thermal and photochemical decomposition is generally considered to take place by the reaction

$$2MN_3 \rightarrow 2M + 2N_3$$
$$2N_3 \rightarrow 3N_2 + Q$$

The heat of reaction, Q, contributes to the exothermicity of the overall reaction which may lead to the explosion and detonation of the solid (*cf.* Section IV). The first step in the decomposition of these azides is therefore the formation of neutral azide radicals, N_{3^0} . In Section III,A it was shown that the order of decreasing ionic character is $KN_3 > TlN_3 > AgN_3$, this change being due to the increasing ionization potential of the metal atom in this series (49). Figure 9 shows the electron levels of a solid of the type which will be considered in this section. The optical energy, E_1 , required to promote an electron from the full band to



FIG. 9. Energy level diagram of an azide of a monovalent element. The zero is the energy of an electron at rest outside the crystal.

the exciton band of the crystal may be obtained from the absorption spectrum of the azide. The energy required to dissociate the exciton, and so promote an electron to the conduction band, may be determined from the photoconductive behavior (if any) or calculated. The optical energy, E_2 , necessary to dissociate an exciton is given by

$$E_2 = \frac{hcR_{\rm H}}{k_0^2}$$

where $R_{\rm H}$ is the Rydberg constant and k_0 is the high-frequency dielectric constant. The corresponding thermal energy, E_i , for any of these processes is given approximately by

$$E_{i}\cong\frac{k_{0}}{k}E$$

where E is the optical energy and k is the low-frequency dielectric constant.

(a) Potassium azide

The most complete measurements of the absorption spectrum of this compound are those due to Evans and Yoffe (50). The short wavelength limit of absorption is given as 5.08 e.v., which approximates to the optical energy required to form an exciton. From the measured value of k_0 the optical energy required to dissociate the exciton is calculated as 2.68 e.v. (50) and the corresponding thermal energy is 0.9 e.v. This large value of 0.9 e.v. accounts for the fact that potassium azide does not photoconduct when irradiated in the exciton band (Section III,C). The optical energy required to promote directly an electron from the full band to the conduction band of the crystal is 5.08 + 2.68 = 7.76 e.v. (ca. 1600 A.). Excluding the case of irradiation with light of wavelength ca. 1600 A. it is impossible to promote an electron to the conduction band and so form a positive hole N₃⁰. This difficulty was first overcome by Jacobs and Tompkins (94), who considered that the exciton was dissociated in the vicinity of an anion vacancy to form an *F* center and a positive hole. At 60°C. the *F* centers dissociate by the transfer of electrons to adjacent potassium ions (Section III,C).

(b) Thallous azide

From the absorption spectrum of thallous azide it was estimated that the maximum of the exciton band is at 3200 A., i.e., 3.9 e.v. is the optical energy required to form an exciton. The optical energy necessary to dissociate the exciton may be calculated as 0.85 e.v., which corresponds to a thermal energy of 0.3 e.v. The long wavelength photocurrent in thallous azide is considered by Evans and Yoffe (50) to arise from the thermal dissociation of excitons. This thermal energy has been measured experimentally and found to be 0.33 e.v., a value which is in good agreement with the calculated value just given. In the absence of any other kind of electron trap it has been shown that recombination of electrons and positive holes normally occurs. Thus initially there is very little photochemical decomposition during irradiation. However, once product specks of a metal have been formed in the crystal, these act as traps for positive ions which in turn generate electron traps. Hence in partly decomposed thallous azide an electronacceptor level exists below the conduction band and this increases the lifetime of the positive holes. The optical energy necessary to promote an electron from the full band to the conduction band is 4.8 e.v., a value which corresponds to a thermal energy of ca. 1.65 e.v.

(c) Silver azide

This azide is also a photoconductor at room temperature and, as in the case of thallous azide, the photocurrent is considered to be due to the dissociation of excitons by the thermal energy of the lattice. From the absorption spectrum it was found (113) that the optical energy required to form an exciton in silver azide is 3.5 e.v. The calculated value of the optical exciton dissociation energy is 0.77 e.v. The thermal activation energy of exciton dissociation was found experimentally to be 0.38 e.v. This corresponds to an optical activation energy of 0.88 e.v., which may be compared with the calculated value of 0.77 e.v. During decomposition specks of metal product are produced in the crystal which may act as electron traps in the manner described for thallous azide. In Section III,C it was noted that photoemission occurs from silver metal specks into the conduction band of the silver azide; hence in partially decomposed silver azide an electron-donor level is introduced 1.65 e.v. below the conduction band.

(d) Cuprous azide

For this compound only approximate estimates have been made of the energy levels of the solid (50). The optical energy necessary to form an exciton is given as 3.25 e.v. and the optical energy to dissociate the exciton as 0.8 e.v. The corresponding thermal energy required to dissociate the exciton is 0.35 e.v.

Table 8 gives the summarized values of the results discussed in this section. An interesting feature of table 8 is that the thermal energy necessary to dissociate an exciton in thallous, silver, and cuprous azides is approximately the same. However, the total energy required to promote an electron from the full band to the conduction band diminishes in going from potassium azide to cuprous

Azide	Optical Energy Required to	Optical Energy to Dissocia Energy the Exciton Required to		Azide	Optical Energy Required to	Energy to Dissociate the Exciton	
	Form an Exciton	Optical	Thermal		Form an Exciton	Optical	Thermal
	e.v.	e.v.	6.9.		6.1.	e.t.	e.v.
KNs	5.08	2.68	0.9	AgN8	3.5	0.77	0.33
T1N3	3.9	0.85	0.3	CuN3	3.25	ca. 0.8	ca. 0.35

TABLE 8

azide. The energy required to form a neutral azide radical therefore diminishes in this order.

E. VIBRATION FREQUENCIES AND FORCE CONSTANTS IN THE AZIDES

The information afforded about bond lengths and angles by x-ray diffraction, electron diffraction, far infrared and microwave absorption (Section III, A and B) and about electron distribution and energy levels by ultraviolet absorption spectra has been supplemented by a study of the fundamental vibration frequencies. It is convenient to discuss the results in three main groups: (1) the azides of the alkali and alkaline earth metals, which are undisputedly ionic; (2) the heavy metal azides; and (3) hydrogen azide. The isolated azide ion, N_3^- , free from any lattice, is not accessible to measurement; azides such as the organic azides and coördination compounds are too complex for a complete treatment.

Of the three fundamental frequencies of a linear, triatomic group the bending frequency, ν_2 , and the asymmetric stretching frequency, ν_3 , are active in infrared absorption. The symmetric stretching frequency, ν_1 , is normally inactive, although this selection rule may be relaxed under the perturbing influence of neighboring ions; it can, of course, contribute to such combination tones as $\nu_1 + \nu_2$ and $\nu_3 - \nu_1$. In Raman scattering, ν_1 is an allowed vibration and so is the overtone $2\nu_2$.

The three fundamental frequencies of the azide ion permit the calculation of the three force constants required in the most general description of a linear triatomic XY₂ molecule. In the language of the valence-force field these are stretching (k_1) , bending (k_3/l^2) , and stretching-stretching interaction (k_{11}) constants. (Stretching and bending which belong to different symmetry classes do not interact.)

1. The azide ion in the azides of Group IA and Group IIA metals

The most extensive investigations of these azides are those made by Gray and Waddington (74) on infrared absorption spectra and by Kohlrausch and Wagner (103) on Raman spectra. Table 9 summarizes these results. Earlier measurements refer to sodium azide (8, 99, 104, 150) and to the aqueous azide ion (99, 104, 150). The whole range of frequencies encountered in the alkali metal and alkaline earth metals is similar and the difference is only a few per cent.

The symmetrical stretching frequency (ν_1) , occurring near 1350 cm.⁻¹, does

a 1		Frequen	cy†		Force Constant			
Sait -	V1 V2		V2 V3		<i>k</i> 1	k11	k 8/l2	
	cm1	cm1	cm1	cm1	10 ⁵ dynes cm. ⁻¹	10 ³ dynes cm. ⁻¹	10 ⁵ dynes cm.	
LiNs	1368.7	635	2092	1277	13.94	1.73	0.56	
Na Na	1358.4	639	2128	1267	13.92	1.30	0.57	
KN8	1343.6	645	2041	1273	13.36	1.74	0.58	
RbNs	1338.8	642	2024	1271	13.21	1.78	0.57	
CsNs	1328.6	635	2062	1267	13.31	1.45	0.56	
DaN6	1380.5	638	2114	1267	14.21	1.74	0.57	
SrN6	1372.7	635	2096	1273	14.01	1.75	0.56	
BaN6	1354.4)	650 ∫	2123	1278	14.15*	1.97*	0.55*	
	Ì	637 \	2083					
NH4N3	1345	661 650	2041	-	13.36	1.74	0.59	

TABLE 9 Fundamental vibration frequencies and force constants of the azide ion, N_{s}^{-} (74)

* Mean values.

† In this table values of \$1 and 2\$2 come from Raman spectra and values of \$2 and \$3 from infrared spectra.

not show appreciable Fermi resonance with the harmonic $2\nu_2$, since the frequency of this harmonic as observed in Raman spectra is closely equal to twice that of the fundamental, ν_2 , active in the infrared. Moreover, there is little intensity borrowing such as occurs, e.g., in the isoelectronic molecule carbon dioxide (90). This bending frequency, ν_2 , occurs near 645 cm.⁻¹, lying just beyond the convenient rock salt range. The asymmetrical stretching frequency lies near 2070 cm.⁻¹

If varying polarizing power and ionization potential are of importance in this series one should expect to discover significant trends within the two series Li, Na, K, Rb, Cs and Ca, Sr, Ba. There are, however, no marked trends from member to member; even in the salts potassium azide, rubidium azide, and cesium azide, which are actually isomorphous, the asymmetric stretching frequency varies irregularly and in this group none of the fundamentals shift by as much as 2 per cent. Vibration frequencies in another isomorphous (151) pair, calcium azide and strontium azide, are even closer. Thus, any regular variation due to varying cationic polarizing power, which might be present, has been masked by other variations, such as those arising from the different lattice spacings. The relative complexity of the barium azide spectra (both bending and stretching frequencies are split in barium azide though not in calcium azide and strontium azide) has been ascribed (74) to the more complex crystal lattice. A detailed account of lattice-ion interactions of some azides has been given by Moore (117).

2. The azide ion in solid ammonium azide

The detailed vibrational assignment of the observed frequencies of solid ammonium azide has been made (40) and the known crystal structure (61) used to interpret observations. The azide ions are linear and symmetric $(D_{\infty h})$ and are distributed equally between two sets of sites each having C_{2h} symmetry. Each set of azide ions gives rise to four nondegenerate vibrations, two being derived from bending motion ν_2 . This splitting of ν_2 into two components is the only complication observed (40, 74) in the anion spectrum. Gray and Waddington (74) interpret the removal of degeneracy in terms of hydrogen bonding, but this is open to other interpretations.

3. The azide ion in the heavy metal azides

Spectroscopy of the heavy metal azides is in a less developed state, although lead azide (65) was the first azide to be examined. Their explosiveness has discouraged most workers from handling single crystals, and although work with mulls and potassium bromide discs is safer, these azides often cannot be ground up and the spectra are less satisfactory. Table 10 lists the data reported. Some of the lines observed in the past (36) which did not correspond to fundamentals, harmonics, or combination tones of frequencies met with in stable azide salts were interpreted as indicating the presence of highly unsymmetrical ions with two different nitrogen-nitrogen bond distances. Today some of these lines would be ascribed to the presence of other chemical species.

4. The hydrogen azide molecule

The structure of the hydrogen azide molecule is known from the rotational fine structure of the N—H stretching frequency (53) and the microwave spectrum (2). The molecule is planar with symmetry C_s . The three nitrogen atoms are collinear and the H—N—N interbond angle is 112°. The molecule has five inplane (A') vibrations and one out-of-plane vibration (A''); all vibrations are active in both Raman and infrared. The infrared spectrum has been observed in the gas phase (32, 54), in aqueous solution (25), in carbon tetrachloride (38), and in the solid (38). The Raman spectrum of the gas phase (46) has also been examined.

	Frequency						
Azide -	¥1	24	νs	222	Unassigned	Kelerence	
	cm. ⁻¹	cm1	cm1	cm1	cm1		
T1N:		636	1941		1602	(36)	
AgNs		644	2173		619, 1634 .	(36)	
-	1334	631	2073, 1960			(117)	
CuNs.		680			570, 1242, 1514	(36)	
	1337	615	2110	[(35)	
Hg:Ne		642		1268	1579	(36)	
-	1300	620	2080			(35)	
HgN ₀	1313	675, 644, 642	2070	1		(35)	
		584					
2-PbN6	1352	630			607, 1602	(36)	
	1350, 6	628	2006	1254		(103)	
			2080			(65)	
9-PbN₀	1352		2040			(65)	
Zn(OH)N:	1334			1269	603	(103)	

TABLE 10Vibration spectra of heavy metal azides

TABLE 11

Vibration	Approvimate Description	Frequency		Wibsotias	Approximate	Frequency	
	Approximate Description	HN3	DN:	VIDIATION	Description	HN3	DN:
		cm1	cm1			cm1	cm1
»1 (A')	H-N stretching	3336	2480	14 (A')	H-N-N bending	1150	955
¥2 (A')	N—N—N asymmetrical stretching	2140	2141	26 (A')	N—N—N bending	522	498
¥8 (A')	N-N-N symmetrical stretching	1274	1183	ν6 (A")	N-N-N bending	672	638

Fundamental frequencies in hydrogen azide (gas)*

• Fundamental frequencies in solid HNs and DNs are discussed in reference 38.

The assignment made by Dows and Pimentel (38), which adopts new skeletal frequencies, is listed for HN_3 and DN_3 in table 11. It calls for a revision of Thomas' force constants (146).

5. Force constants in azides and in some isosteric (isoelectronic) molecules and ions

Values of the three force constants (74) for stretching, interaction, and bending in the saltlike azides are listed in table 9. Mean values and standard deviations (dynes cm.⁻¹) are: k_1 , 13.67 \pm 0.13; k_{11} , 1.70 \pm 0.60; k_{δ}/l^2 , 0.57 \pm 0.01. The interaction force constant k_{11} is subject to the largest error because it is determined as a small difference. The small scatter in stretching and bending force constants reflects the small frequency range and the insignificant differences in nitrogen-nitrogen bond lengths in these azides (Section III,A). Two isosteric series are of especial interest in discussing force fields in the azide ion. The first comprises the ions NO_2^+ , CO_2 , N_3^- , and CN_2^{2-} , which are all symmetrical YX_2 molecules differing from one another by one unit of charge. The second series is the triad N_3^- , N_2O , HN_3 . Nitrous oxide forms a bridge between the free azide ion and the covalently bound azide group: if O is replaced by the isoelectronic N^- , the azide ion results; if O is replaced by NH, hydrogen azide results. Fundamental frequencies (see table 13) reflect differences which are due partly to force fields and partly to mass differences; force constants (which reflect only forcefield differences) for some isoelectronic species are listed in table 12.

In the series NO₂⁺, CO₂, N₃⁻, CN₂²⁻ the nuclear charge decreases while the number of electrons remains the same. Accompanying this there is a steady decrease in the stretching force constant k_1 , indicating that the molecule as a whole is less tightly bound. In the same series, the interaction constant k_{11} increases, indicating that the stretching of one bond has an increasing influence on the stretching of the other in the order NO₂⁺, CO₂, N₃⁻, CN₂²⁻. There is a similarly marked difference between the bending force constants; N₃⁻ and CO₂ both resist bending more strongly than NO₂⁺ does.

In the series N_3^- , N_2O , HN_3 the number of general quadratic force constants required varies and a formal comparison is complex (74, 90, 146). However, if the two of the six fundamental frequencies of HN_3 which are essentially N—H

TABLE 12

Force constants of some isoelectronic molecules and ions 1. Linear YX_2 molecules (sixteen valency electrons)

0	Force Constants	of General Quad	ratic Force Field	
Species	k1	k11	k 5/l2	Keierence
	10 ⁵ dynes cm. ⁻¹	10 ⁵ dynes cm. ⁻¹	10 ⁵ dynes cm. ⁻¹	
NO ₂ +	17.4	1.04	0.41	(79)
CO ₂	16.8	1.3	0.57	(90)
Na	13.7	1.74	0.57	(74)
CN ₂ ²	12.2	2.05	0.49	(34)

2. The azide ion, nitrous oxide, and hydrogen azide (sixteen valency electrons)

Constant of the second s		Force C	onstants		Deferre
Species	k1	k 2	k12	k 8/l1l2	Kelerences
	10 ⁵ dynes cm. ⁻¹				
Ns ⁻ (g.q.f.f.)	13	.7	1.74	0.57	(74)
NNO (s.v.f.f.)	14.6	13.7	-	0.49	(90)
NNH (g.q.f.f.)	17.8	10.1	1.74	0.71	(74) (25, 32, 38, 46, 54, 146)

TABLE 13

Comparison of vibration frequencies in hydrogen azide, nitrous oxide, and the azide ion

	Frequency			
Approximate Description -	HN:	N _{\$} O	Nı-	
	<i>cm</i> . ⁻¹	cm1	cm1	
(HN)—N _I —N _{II} symmetrical stretching	1274	1285	1360	
(HN)—N _I —N _{II} bending	522 (A')	589	650	
	672 (A")			
$HN-N_I-N_{II}$ asymmetrical stretching	2140	2240	2040	

vibrations are set aside, skeletal vibrations and force constants (see table 12) in the three molecules may be compared.

In nitrous oxide, two stretching force constants replace the single one of the symmetrical azide ion; the oxygen atom is less tightly bound than the nitrogen of nitrous oxide. The same process is more marked in hydrogen azide: one bond, HN—NN, is long (1.24 A.) and weak and the other, HNN—N, is short (1.10 A.) and strong, whereas in the ion N₃⁻ both are the same (1.15 A.). Two force constants referring primarily to N—N stretching, 10.1×10^5 dynes cm.⁻¹ and 17.3×10^5 dynes cm.⁻¹, replace the one N—N force constant, 13.7×10^5 dynes cm.⁻¹, of N₃⁻.

F. THERMAL CONSTANTS

Relatively few measurements have been made on the thermal constants of the azides. Some values have been published for the melting points, specific heats, and thermal conductivities. The accuracy of the measurements, however, is not good, and the investigations are not sufficiently extensive to allow detailed calculations to be made on the effect of temperature on the solid lattice.

1. Melting points

All univalent azides have been found to melt prior to explosion (50). Melting has also been observed with some divalent azides (35, 50). Some of the melting points are given in table 14. The table shows that the melting point is lowered as one proceeds along the series potassium, thallium, silver, copper. The melting point is of course related to the structure and coördination number of the azide. These will depend on the cation radius, and also on the extent of valence electron sharing discussed in Sections III, B, C, and D. In general, for equal cation radii the higher the ionization potential of the metal atom, the lower the melting point of the azide. The melting point is lowered in spite of the fact that the lattice energy increases along the series (see table 20).

2. Specific heat

Yuill (160) has determined the specific heats of silver azide and lead azide. The values are: silver azide at 250°C., 0.117 cal./g./°C.; lead azide at 100°C., 0.10 cal./g./°C.; lead azide at 250°C., 0.116 cal./g./°C.

3. Thermal conductivity

No measurements have been made on single crystals. The thermal conductivity of a number of azides in the form of pressed pellets has been measured by McLaren (111); the values are given in table 15.

Azide	Melting Point	Reference	Azide	Melting Point	Reference
	°C.	-		°C.	
HNa.	-80; 37 (b. pt.)	(3)	AgN3	ca. 250 (d.)	(50)
KN3	343, 350	(3)	CuN3	ca. 205 (d.)	(50)
RbNa	300, 321	(3)	Hg2(N8)2	ca. 210 (d.)	(35)
CsN2	320, 326	(3)	Ba(Ns)2	ca. 275 (d.)	(50)
NH4N8	160	(3)	Hg(Na)2	ca. 195 (d.)	(35)
T1N3	ca. 334 (d.)	(50)			

 TABLE 14

 Melting points of some inorganic azides

TABLE 15	
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	Thermal	conductivity	of	pressed	pellets	of	' azides
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Compound	Mean Temperature	Pellet Density	Thermal Conductivity
	°C.	g./cc.	c.g.s. units
NaNs	68	1.77	$25 imes 10^{-4}$
T1N3	65	4.6	8×10^{-4}
Ba(N ₃) ₂	80	2.75	11×10^{-4}
Pb(N ₃) ₂	45	3.62	4×10^{-4}

IV. THERMOCHEMISTRY OF THE AZIDES: HEATS OF FORMATION

AND LATTICE ENERGIES

Azide thermochemistry may conveniently be divided into three parts. The first deals with experimentally accessible quantities, such as heats of combustion and decomposition, and may be described as classical thermochemistry. The second is concerned with lattice energies of the inorganic azides, i.e., with quantities not immediately accessible by experiment but, in principle at least, susceptible to theoretical calculation. The third, which may be called radical thermochemistry, deals with the dissociation energies of chemical bonds and the electron affinity of free radicals.

Thermochemical magnitudes belonging to these different classes are of course related; e.g., we shall even meet "experimental" values for lattice energies and the division is only one of convenience. Experimental thermochemistry and lattice energies are considered in this section; bond energies and thermochemistry of the azide radical in Section V. The principal part of azide thermochemistry concerns heats; where entropies and free energies are known reliably, full reference is given. These data, although desirable, are sparse.

A. EXPERIMENTAL THERMOCHEMISTRY OF THE AZIDES

Thermochemical determinations, such as the heat of combustion of ammonium azide, which relate the heat of formation of an azide to molecular nitrogen and to its other constituent elements, are here called primary data; thermochemical interrelations between one azide and another, such as the heat of neutralization of hydrazoic acid, are called secondary data. In general, among inorganic azides, secondary data are easier to determine than primary and their precision is higher. Establishment of accurate azide thermochemistry makes its severest demands therefore on the primary determinations.

1. Organic azides

The heats of combustion of phenyl azide (133) and ethyl azidoacetate (133) were measured in 1929. Since then only cyanuric triazide (121), 2-triazoethanol

Azide	Heat of Combustion $-\Delta U_c^{\circ}$, 298	Enthalpy of Formation ΔH_{f}° , 298	Reference
	kcal. mole ⁻¹	kcal. mole ⁻¹	
Methyl azide		57 (g)*	(59)
Cyanuric azide		219 (s)	(121)
2-Hydroxyethyl azide	381.92 ± 0.23	22.47 (1)	(55)
Cyclopentyl azide	820.04 ± 0.22	42.79 (1) 53 (g)*	(56)
Cyclohexyl azide	965.22 ± 0.10	25.90 (1) 37 (g)*	(56)
Phenyl azide	817.3	82.3 (1)	(133)
Sthyl azidoacetate	582.4	33.3 (1)	(133)

TABLE 16

Corrected heats of combustion and standard enthalpies of formation of the organic azides

* Estimated value.

(55), and cyclopentyl and cyclohexyl azides (56) have been examined. Their corrected heats of combustion $(-\Delta U_{298}^{\circ})$ and the corresponding enthalpies of formation at 25°C. (ΔH_{298}°) are listed in table 16. The entry for methyl azide is quoted (59) as being derived from a group-energy term treatment of the experimental data for the two cyclic azides. However, a group-energy term treatment (70) reveals apparent abnormalities within the three azide determinations coming from the same laboratory (55, 56) and raises doubts about the precision claimed.

2. Hydrogen azide and the aqueous azide ion

The heat of formation of hydrogen azide was first determined directly by measurement of the heat of explosive decomposition of the gas (85). Heats of vaporization and solution in water were reported at the same time. Prior to these experiments the only wholly experimental value for aqueous hydrogen azide came from work by Berthelot and others (7, 12) in the nineteenth century. Arithmetical errors in these old papers have been discovered (75) and an apparent disagreement resolved. The most precise values come from measurements (75) of the heat of formation of the aqueous azide ion and of its heat of neutralization combined with earlier heats of solution and vaporization (85) of hydrogen azide.

For gaseous hydrogen azide Dows and Pimentel (38) have calculated the thermodynamic properties (in the perfect gas state) of C_p° , $(H^{\circ} - H_0^{\circ})/T$, $(F^{\circ} - H_0^{\circ})/T$, and S° at 0° and 25°C. and at 100° intervals from 100°K. to 1500°K. Their calculations are based on a microwave determination of the structure of hydrogen azide (2) leading to $I_1 I_2 I_3 = 6963 \times 10^{-120}$ g.³ cm.⁶ and on their own frequency assignment. These calculations supersede earlier work (54); some of the results are included in table 17.

The aqueous azide ion and the aqueous acid are thermochemically related (75) by the ionization:

$$HN_{3aq} \rightleftharpoons H_{aq}^+ + N_{3aq}^- \Delta H_{238}^\circ = 3.60 \text{ kcal. mole}^{-1}$$

State	ΔH_f°	State	ΔH_f°
	kcal. mole-1	·	kcal. mole ⁻¹
Gaseous HN: Liquid HN:	71.66 64.37	Aqueous H ⁺ + Ns ⁻ , ∞H2O HNs undissociated, ∞H2O	65.53 61.93

 TABLE 17

 Heat of formation of hydrogen azide and the azide ion at 25°C.

Spectroscopic values (38) of thermodynamic functions of gaseous HN₃ in perfect gas state at 25°C.

C _p	$(H^{\circ} - H^{\circ}_{0})/T$	$-(F-H_0^\circ)/T$	S°
10.443	8.721	48.366	57.083

Recent (75) and old (7, 12) values of the heat of ionization are in substantial agreement. The standard heat of formation of the aqueous azide ion (65.53 kcal. mole⁻¹) determined by Gray and Waddington (75) thus offers the most accurate route to the thermochemistry of hydrogen azide and to that of the other inorganic azides dealt with in Section 3.

The standard free-energy change on ionization, ΔG_{298} , can be obtained, in principle, from any of the determinations (23, 92, 125, 152) of the acid ionization constant. The best value for ΔG_{298} appears to be about 6.20 kcal. mole⁻¹ with ΔS_{298}° equal to -8.72 cal. deg.⁻¹ mole⁻¹ (69). (For further information on entropies and free energies see reference 75.)

3. Azides of electropositive metals of Groups Ia and IIa

The enthalpies of formation of the crystalline azides of lithium, sodium, potassium, rubidium, cesium, calcium, strontium, and barium have been obtained by combining experimental measurements (75) of the enthalpies of solution, S, of the salts with tabulated enthalpies of formation (122) of the corresponding aqueous cations:

$$\begin{split} \mathbf{M}(\mathbf{N}_3)_s + \mathbf{a}\mathbf{q} &\to \mathbf{M}_{\mathbf{a}\mathbf{q}}^{s+} + z\mathbf{N}_3^{-}_{\mathbf{a}\mathbf{q}} \quad \Delta H = S\\ \Delta H_f^{\circ} \left[\mathbf{M}(\mathbf{N}_3)_s\right]_{zt} &= \Delta H_f^{\circ} \left[\mathbf{M}_{\mathbf{a}\mathbf{q}}^{z+}\right] + z\Delta H_f^{\circ} \left[\mathbf{N}_3^{-}_{\mathbf{a}\mathbf{q}}\right] - S \end{split}$$

Values of heats of solution and enthalpies of formation are listed in table 18. Ammonium azide is included with the other soluble azides.

4. Azides of the heavy metals

Heats of explosion of the heavy metal azides provide (13, 110, 155–157) primary determinations of their heats of formation. However, two experimental difficulties have made some of these direct determinations less than normally

Salt M(Ns)s	Enthalpy of Solution	Standard Enthalpy of Formation of Crystalline M (N ₂)z	Salt M(Ns)z	Enthalpy of Solution	Standard Enthalpy of Formation of Crystalline M(N ₈) _z
	kcal. mole ⁻¹	kcal. mole ⁻¹		kcal. mole ⁻¹	kcal. mole ⁻¹
LiNa	-2.60	2.58	AgNa.	16.67	74.17
NaNa.	3.17	5.08	TIN:	11.13	55.78
KN:	5.82	-0.33	Hg2Ne	29.87	141.5
RbNs	6.70	-0.07	CuN6	3.59	140.4
CsNs	8.70	-2.37	α-PbN6	15.94	115.5
NH4N3	7.02	26,79	β-PbN6		115.8†
CaNe	-9.74	11.03	NiN6·H2O	_	31.7
SrNs	-1.04	1.72	MnNs		94.0
BaN6	7.71	-5.32	ZnN6		50.8
CuN3		67.23*	CdN6		106.2

TABLE 18

Enthalpies of solution and enthalpies of formation of inorganic azides at 25°C.

* From cell experiments (140).

† From cell experiments (72).

reliable: fragmentation of the azide during decomposition, leaving unchanged material behind, and nitride formation in side reactions.

The inconsistencies were first apparent in the American (141) and Japanese (72, 140) work on metal-metal azide electrodes, which provided a number of cross-checks and eventually (140) enabled the thermochemistry of cuprous, silver, thallous, mercurous, and lead azides to be related to that of hydrazoic acid. New values for these five azides and for cupric azide were later obtained from heats of precipitation (75); these values are entered in table 18. They are consistent with the cell data (140) and with the most recent data on the heat of explosion (110) of thallous azide.

B. HEATS OF DECOMPOSITION

When a simple azide, XN_3 , decomposes it may yield either nitrogen and the element X or nitrogen and the nitride X_3N :

$$XN_3 \rightarrow 1.50N_2 + X \ (or \ 0.50X_2) \qquad \qquad \Delta H_1 \qquad (1)$$

$$XN_3 \rightarrow 1.333N_2 + 0.333X_3N \qquad \Delta H_2 \qquad (2)$$

Stoichiometrically, decomposition lies between the extremes above, and the heat of reaction varies accordingly between the appropriate values. These considerations apply equally to hydrogen azide and the metal azides and, *mutatis mutandis*, to some nonmetallic azides, such as BN_9 . These heats of decomposition are important even without further detailed knowledge, since exothermic decomposition is a prerequisite of explosion. They are also required in assessing the probability and extent of self-heating in exothermic decompositions (see Section VI). Garner (63) made an early application of thermochemistry to interpreting explosions of azides, and a recent detailed examination of self-heating in lead azide has been made by Groocock (81).

Hydrogen azide may give either hydrogen and nitrogen, as happens in its explosive decomposition (73, 85), or nitrogen and ammonia as in heterogeneous decomposition. In the presence of oxygen, complete combustion occurs:

	ΔH kcal. mole ⁻¹
$HN_3 = 0.50H_2 + 1.50N_2$	-71
$HN_{3} = 0.333NH_{3} + 1.333N_{2}$	75
$HN_3 + 0.25O_2 = 0.50H_2O + 1.50N_2$	-100

The nitrides and oxides of the alkali metals and alkaline earth metals are very exothermic (ΔH_f negative) compounds, and the amount of heat evolved in the decomposition of their azides varies rapidly with the relative proportions of metal and nitride formed. Table 19 summarizes typical thermochemical details for some azides and it is seen that, if barium azide decomposes to the nitride, heat is evolved, whereas decomposition to the metal is endothermic. When the azides are decomposed in air or oxygen, decomposition is correspondingly more violent, as has been observed by Yoffe (158).

		Exothermicity	cxothermicity				
Azide	Decomposition to metal	Decomposition to nitride	Oxidation to oxide				
	kcal. mole ⁻¹	kcal. mole ⁻¹	kcal. mole ⁻¹				
LiN ₃	2.6	18.8	74.3				
CaN ₆	11.0	45.4	162.9				
SrN ₆	1.7	32.8	142.7				
BaNs	-5.3	23.6	121.0				

TABLE 19 Exothermicity $(-\Delta H)$ of decomposition and oxidation of four azides

C. LATTICE ENERGIES

1. The Born cycle for the azides

Interpretation of the physical and chemical properties of inorganic azides requires knowledge of the lattice energies of the solids and of the electron affinity of the azide radical. These quantities are related to one another and to experimentally measurable quantities by the extended Born cycle (given below in terms of enthalpy changes at 25°C. for MN_3 , where M is a univalent metal):



Here U is the lattice (internal) energy of MN_3 at 25°C.; U + 2RT is the corresponding lattice enthalpy; H is the standard enthalpy of hydration of the two gaseous ions; S is the standard enthalpy of solution of the crystalline azide; E is the electron affinity of the gaseous azide radical; Q is the enthalpy of formation of the gaseous azide radical; and the other symbols have their usual meanings.

The four unknowns U, H, Q, and E are related by two independent equations: (a) between lattice energy and ion-pair heats of hydration

$$U = -H + S - 2RT \tag{1}$$

(b) between lattice energy and electron affinity

$$Q - E = U + 2RT - I - L + \Delta H_{f}^{\circ}(MN_{3})(s)$$
(2)

It is important to note that lattice energy U, although not directly measurable, is unambiguously defined by these equations and is expressible in terms of measurable quantities; it is *not* a quantity peculiar to an ionic lattice. Of course, if a solid is ionic, calculation of its lattice energy becomes a problem in electrostatics and, in principle, is always possible.

2. Calculation of lattice energies term by term

When the constituent ions of a solid are spheres, term-by-term calculation of the lattice energy is straightforward, though it may be tedious. Such a model was used by Jacobs (93) in his calculation of the lattice energy of potassium azide. However, the azide ion is not spherical and this treatment is approximate. Gray and Waddington (76) treated the azide ion as an ellipsoid of revolution with a charge distribution (15) that could be better represented by the superposition of a point charge and an extended quadrupole.

$$N-N-N$$
 $N-N-N$ $0 -e$ 0 $-0.83e$ Point chargeQuadrupole

They calculated lattice energies in this way for the three isomorphous (tetragonal) azides of potassium, rubidium, and cesium; they were not able to extend these calculations to more complicated azides. The values (kcal. mole⁻¹) of the constituent terms (76) of the lattice energy U of potassium azide are as follows: coulombic attraction, 161.7; quadrupole-quadrupole interaction, 9.0; van der Waals (dispersion) term, 6.2; zero-point energy, -1.3; repulsive interaction, -19.5; specific heat correction, 0.9: net value of U, 157.

3. Lattice energies from empirical relations

In addition to direct calculation an equation due to Kapustinsky (100), which essentially ignores all contributions save the Coulomb and repulsion terms, offers a route to lattice energies. For the azides

$$U = 287.2 \frac{\nu z_1 z_2}{r_1 + r_2} \left\{ 1 - \frac{0.345}{r_1 + r_2} \right\}$$

where ν is the number of ions in the chemical molecule, z_1e and z_2e are the charges on cation and anion, and r_1 and r_2 are the Goldschmidt radii of cation and anion. It appears to give results which are 2-3 per cent low for the azides (76).

4. Lattice energies from heats of hydration

Equation 1 of Section IV,C,1 expresses the fact that the heat of solution of an ionic solid is the difference between the energy needed to disperse it into its constituent ions and the energy freed when the dispersed ions are hydrated. Heats of hydration have been used successfully (76) to obtain good values of lattice energies for lithium, sodium, potassium, rubidium, and cesium azides. This method for obtaining lattice energies, first used by Gray and Waddington, has since been extensively exploited by Morris (118).

5. Numerical values of lattice energies of inorganic azides

Once one value of lattice energy has been established, equation 2 of Section IV,C,1 leads to a value of 34.8 kcal. mole⁻¹ for Q - E, a quantity which is the

TABLE 20Lattice energies of azides (76)All values internal energies at 25°C.

Azide	Lattice Energy Azide		Lattice Energy		
	kcal, mole ⁻¹		kcal. mole ⁻¹		
LiNs	194	CaNs	517.4		
NaNs	175	SrN6	493.8		
KN3	157	BaNs.	468.8		
RbN ₃	152	CuN3	227.2		
CsN3	146	AgN ₈	204.7		
		T1N3	163.5		
NH4N8	175	α-PbN.	433.7		

same for all azides. Q - E (or Q_{-}) is the enthalpy of formation of the gaseous azide anion, N₈-(g). This value of Q - E may then be used to derive lattice energies for all other azides for which enthalpies of formation etc., are known. In this way the lattice energies for ammonium, cuprous, silver, thallous, calcium, strontium, and barium azides listed in table 20 have been obtained. As emphasized above, the *existence* of a lattice energy does not require even the existence of ions in the solids concerned; much less does it imply wholly ionic bonding.

V. THE AZIDE RADICAL

Formation of the neutral azide radical from an azide ion is accepted (10, 50, 64, 77) as the key to the interpretation of decompositions of ionic azides. Its physical and chemical properties are correspondingly important and are summarized here. An outline of the corresponding properties of the ionic species N_{3}^{+} and N_{3}^{-} and of the molecule HN₃ is also given.

A. OCCURRENCE OF THE AZIDE RADICAL

In the gaseous phase formation of the azide radical³ has been reported in flash photolysis and in electron-impact experiments. Thrush (147) obtained the absorption spectrum of the same triatomic species from flash photolysis of both HN_3 and DN_3 and suggested that it was the N_3 molecule, formed in secondary reactions rather than by the primary photochemical act:

$$\begin{array}{l} \mathrm{HN}_{3} \; (\mathrm{or}\; \mathrm{DN}_{3}) \rightarrow \mathrm{HN} \; (\mathrm{or}\; \mathrm{DN}) \; + \; \mathrm{N}_{2} \\ \\ \mathrm{HN} \; + \; \mathrm{HN}_{3} \rightarrow \mathrm{NH}_{2} \; + \; \mathrm{N}_{3} \end{array}$$

Such reactions do not conflict with observations on the slow photolysis and though it must be stressed that identification of N_3 is tentative, it is supported by similar work (555) on the flash photolysis of HNCO. Azide radicals do not appear to play distinctive roles during the thermal decomposition of hydrogen azide or of the organic azides; they are commonly assumed to be absent (73).

³ At one time the name "nozone" was suggested by G. B. Kistiakowsky for N_3 by analogy with the name "ozone" and by way of expressing scepticism of its alleged (60) role in the nitrogen afterglow. Masses 42, 43, and 44 have been detected in mass-spectrometric studies of N_2 .

Electron-impact experiments on hydrogen azide and methyl azide (59) have also given mass-spectrometric evidence for the formation of the azide radical and its positive and negative ions.

In the *liquid phase* azide radicals are formed optically by electron transfer from dissolved azide ions. In aqueous solution of, e.g., sodium azide, an ultraviolet absorption maximum (observed as an inflection) at 2250–2300 A. (42) is attributed to electron transfer to the water. The characteristic red coloration of the ferric ion-azide ion is due to absorption in the visible region (76) when the electron transfer is to the ferric ion.

In the solid phase azide radicals (positive holes) are formed (1) by ultraviolet irradiation in photoconductivity experiments (10, 50, 51, 113) when the electron enters the conduction band; (2) by electron bombardment (20, 83, 135, 148); by x-ray (81, 82, 88) and γ -ray (41, 82, 89, 102) irradiation. They are the precursors of molecular nitrogen in thermal decompositions (4-6, 10, 50, 64, 77).

Spectroscopic evidence for the existence of more than one form of triatomic nitrogen in a solid matrix at very low temperature has been obtained. The linear symmetrical N₃ radical is said to be formed when nitrogen atoms formed by a discharge through nitrogen are trapped at 20°K. (115a) and when hydrogen azide, dispersed in a solid matrix, is photolyzed (10c). A weakly bound, triatomic molecule, N—N₂, has been identified (123a) as the species responsible for the glow emitted by solid nitrogen near 4°K. condensed from a gas discharge or bombarded by an electron beam.

B. STRUCTURAL PROPERTIES OF N_3

The spectrum ascribed (147) to N_3 is too diffuse to yield detailed information about the structure. However, the azide radical is isoelectronic with the molecular ion CO_2^+ and comparison may yield useful information. Thus N_3 will also be expected to be linear and have an inverted ${}^2\Pi_g$ ground state; similar expectations may be true of the analogous cyanate (OCN) and fulminate (ONC) radicals and of the N_2O^+ ion.

For CO₂⁺ Mrozowski (120) has summarized the relation of vibration frequencies to those in the parent molecule as follows: ν_1 (CO₂⁺), 1280 cm.⁻¹ (1360 in CO₂); ν_2 (CO₂⁺), ~632 (673 in CO₂); ν_3 (CO₂⁺) ~2305? (2379 in CO₂).

The carbon-oxygen bond length is 1.177 A. (1.163 in carbon dioxide). Similar differences are to be expected between the azide radical and anion. The isoelectronic cyanate radical, OCN, has also been recognized (91) in flash photolysis and by its fluorescence spectrum. Its rotational constants in the ground and excited electronic states $B_{000}^{"}$ and $B_{000}^{"}$ have been determined.

Values (cm.⁻¹) of 2150 (115a), 2140 (10c), and 1700 (123a, 147) have been identified as vibration frequencies characteristic of linear symmetric N_3 .

c. The electron affinity and ionization potential of N_3

In Section 4 the reaction thermochemistry of N_3 is discussed; its enthalpy of formation, Q, is the basis. Evaluation of Q is linked closely with the determination of the electron affinity of N_3 and, equivalently, with the enthalpy of formation

TABLE 21

 $\begin{array}{l} Thermochemistry \ of \ the \ azide \ radical \ and \ its \ ions\\ E(N_{3}) \ = \ 70 \ \pm \ 3 \ kcal. \ mole^{-1}; \ I(N_{3}) \ \leq \ 283 \ \pm \ 6 \ kcal. \ mole^{-1}*\\ 1 \ e.v. \ \equiv \ 23.05 \ kcal. \ mole^{-1} \end{array}$

Species	N2 ⁺	N3	N3-
Term symbol ΔH_f (kcal. mole ⁻¹)	$52g^{-} \leq 388 \pm 5^{*}$	$^{2}\Pi_{\sigma}$ 105 ± 3	$\begin{array}{c} {}^{1\Sigma_{g}^{+}}\\ 35 \pm 1\end{array}$

* Upper limit.

 Q_{-} (= Q - E) of the gaseous azide ion N₃⁻. Similarly, combination of the heats of formation Q and Q_{+} of the radical and of the positive azide ion N₃⁺ yield the ionization potential. Table 21 summarizes the existing data; their derivation is discussed below.

1. The ionization potential of N_3

The ionization potential $I(N_3)$ is derived by combining values of the enthalpies of formation of the radical (see V,C,4 below) and of the positive ion.

The enthalpy of formation, Q_+ , of the azide ion N₃⁺ has been derived (59) from the appearance potential (16.0 \pm 0.2 v.) of N₃⁺ from HN₃ as $Q_+ \leq 388 \pm 5$ kcal. mole.⁻¹ A value for Q_+ cannot (59) be derived from similar experiments on methyl azide, as excess kinetic energy is involved. This value of Q_+ corresponds to an ionization potential of 283 \pm 6 kcal. mole⁻¹.

2. The electron affinity of N_3

The electron affinity, E, of the azide radical has been derived (76) from ultraviolet absorption spectra data (16), since replaced by more reliable values (42) and recalculated (70) as $E = 67 \pm 5$ kcal. mole⁻¹. A second value, $E = 73 \pm 5$ kcal. mole⁻¹, has been obtained from the visible absorption (charge transfer) spectrum (76) of the Fe³⁺N₃⁻ ion-pair in aqueous solution. These values are essentially interpolations using the halogens as standards; their true dependence on heats of hydration is slight.

A completely independent value, $E = 69 \pm 7$, can be derived (70) from electron-impact data (59) reported for methyl azide. This value is derived from the differences in the appearance potentials of CH₃⁺ and N₃⁻ and depends only on the ionization potential of the methyl radical (and not on an assumed heat of formation for methyl azide).

The mean value for E suggested by these results is 70 kcal. mole⁻¹ with a probable error of about 3 kcal. mole⁻¹. Waddington's estimate (private communication) is higher by a few kilocalories than this mean value.

3. The heat of formation of the negative azide ion N_3^-

This quantity $(Q_{-} \text{ or } Q - E)$ is derived below as a first step; it is 35 kcal. mole⁻¹.

THE INORGANIC AZIDES

4. The enthalpy of formation of N_3

The enthalpy of formation, Q, of the azide radical comes from combination of the electron affinity with the heat of formation Q - E (or Q_{-}) of the azide ion; Q_{-} appears to be the most precisely known of all these quantities. Theoretical calculations of lattice energies (76) and empirical correlations with heats of solvation (76) lead to the value Q - E or $Q_{-} = 34.8 \pm 1.0$ kcal. mole⁻¹.

An independent but less precise value comes from electron-impact experiments on hydrogen azide (59), which lead to $Q_{-} \leq 45 \pm 5$ kcal. mole⁻¹. A third value for Q_{-} can be obtained from similar experiments on methyl azide (59) only if a guess is made about the heat of formation of methyl azide.

These values for Q - E, when combined with the value $E = 70 \pm 3$, lead to $Q = 105 \pm 3$ kcal. mole⁻¹ for the standard enthalpy of formation of the azide radical. A recent semiempirical study by Singh (137) leads to Q = 113 kcal. mole⁻¹.

It should be noted that the new value (Q = 105) reported here is 10 kcal. mole⁻¹ lower than the previous "best" value. The origin of the difference lies in the new work reported (42, 59, 70); it is also reflected in the lower bond-dissociation energies $D(X-N_3)$ in the covalent azides.

5. The stabilities of N_3^- , N_3 , and N_3^+

Comparison (59) of the minimum enthalpies of dissociation into ground state products of the three species N_3^- , N_3 , and N_3^+ shows that, whereas N_3 is apparently weakly bonded, the bonds in both N_3^+ and N_3^- are firm; either adding or removing an electron from N_3 leads to a strengthening of the bonds.

$$N_{3}^{+} \rightarrow N_{2}^{+} + N \cdots D_{+} \cdots D_{+} > D$$

$$N_{3}^{-} \rightarrow N_{2}^{-} + N \cdots D_{-} \cdots D_{-} > D$$

d. Thermochemistry of N_3 reactions

The value for the enthalpy of formation of the gaseous azide radical, $Q = 105 \pm 3$ kcal. mole⁻¹ (see Section V,C,4), is the basis of its reaction thermochemistry. Figure 10 illustrates some of the energy relationships in N₃ and in HN₃; individual reactions are discussed briefly below. The data refer strictly to the gaseous phase but are also of value in interpretation of condensed-phase reaction thermochemistry.

1. Decomposition of the azide radical

Unimolecular decomposition of the ground-state $({}^{2}\Pi_{g})$ azide radical to form a molecule and an atom of nitrogen also in their ground states requires only 7.5 kcal. mole⁻¹ but is forbidden by the correlation (spin conservation) rules. Dissociation into products in excited states is permitted but requires at least 62 kcal. mole⁻¹. For these reasons unimolecular decomposition is not expected to be important at ordinary temperatures.



FIG. 10. Enthalpy relations in hydrogen azide and the azide radical. Heats of formation and bond-dissociation energies (in kilocalories per mole at 25°C.) refer to gaseous species in ground states.

	ΔH kcal. mole ⁻¹
Forbidden: N ₃ (² Π_{g}) \rightarrow N (⁴ S ₂) + N ₂ (¹ Σ_{g} ⁺)	7.5 ± 3
Permitted: N ₃ (² II _g) \rightarrow N (² D) + N ₂ (¹ Σ _g ⁺)	62.3 ± 3
Permitted: $2N_{3}$ (${}^{2}\Pi_{g}$) $\rightarrow 3N_{2}$ (${}^{1}\Sigma_{g}^{+}$)	-210 ± 6

Bimolecular decomposition to molecular nitrogen involving only ground-state species can occur, however. Moreover, it is a highly exothermic reaction and is expected to be the principal mode of degradation in the *ionic* azides. In the covalent azides RN_3 , fission of the RN— N_2 bond offers an alternative route.

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2. Decomposition of hydrogen azide

Unimolecular decomposition of hydrogen azide to a (ground state) hydrogen atom and an azide radical is not forbidden by correlation rules, but the energy required $D(\text{H}-N_3)$ is large (85 kcal. mole⁻¹) and decomposition by this mode is unlikely. Dissociation energies of other hydrogen-nitrogen bonds may be derived (1, 70, 151) from existing experimental data. They are (ΔH , in kcal. mole⁻¹): $D(\text{H}-N\text{H}_2) = 104 \pm 2$; $D(\text{H}-N\text{H}) = 86 \pm 5$; $D(\text{H}-N) = 90 \pm 2$. Thus the dissociation energy $D(\text{H}-N_3)$ lies close to those of other bonds between the same atoms.

	ΔH kcal. mole ⁻¹
Permitted: HN ₃ (¹ A') \rightarrow H (² S _g) + N ₃ (² \Pi _g)	85 ± 3
Forbidden: HN ₃ (¹ A') \rightarrow NH (³ Σ^{-}) + N ₂ (¹ Σ_{g}^{+})	5 ± 2
Permitted: HN_3 (¹ A') \rightarrow NH (¹ Δ) + N ₂ (¹ Σ_g^+)	33 ± 2

Unimolecular decomposition of hydrogen azide to the imine radical and molecular nitrogen would require only 5 ± 2 kcal. mole⁻¹ if all species were in their ground states. This however is a forbidden reaction. If excited states of NH are invoked, then, for the easiest permitted reaction (59), about 33 kcal. mole⁻¹ are required.

This figure, $\Delta H = 33$ kcal. mole⁻¹, is a minimum value for the activation energy of decomposition of hydrogen azide if pyrolysis is controlled by HN—N₂ bond fission.

3. Decomposition of organic azides

The dissociation energies of some carbon-azide bonds derived previously (76) and amended by the new heat of formation of the azide radical are listed in table 22. The mean value is 72 kcal. mole⁻¹ but the scatter is large and reflects the poor quality of the thermochemistry of the organic azides.

Organic azides normally decompose by $RN-N_2$ bond fission. This process has to satisfy correlation requirements similar to those satisfied by hydrogen azide, but for the organic radicals RN < there are no thermochemical data and, thermochemically, the picture is correspondingly less complete. Information on the course of the reaction may be found in standard texts or recent references (e.g., 22, 134).

			TABLE 22				
Dissociation	energies	of	carbon-azide	bond	in	organic	azides

Azide	Cyclopentyl Azide	Cyclohexyl Azide	2-Triazo- ethanol	Ethyl Azido- acetate	Phenyl Azide
$D(R-N_3)$ (kcal. mole ⁻¹)	75	81	61	67	78

Mean value = 72 kcal. mole⁻¹.

VI. THERMAL DECOMPOSITION OF AZIDES

The thermal decomposition of a number of simple azides results in the formation of metal and nitrogen:

$2MN_3 \rightarrow 2M + 3N_2$

In many cases the decomposition is an exothermic one. Values for the heat of reaction have been listed in Section IV. During the decomposition of azides such as calcium azide, however, some nitride is also formed (2a). The experiments of Tompkins and Young (149) suggest that the nitride is not an intermediate in the decomposition but arises from the reaction of metallic calcium with gaseous nitrogen formed during the decomposition. When crystals of silver azide, thallous azide, cuprous azide, barium azide, etc. are heated, metallic nuclei form on the surface of the crystal. It has been shown (64) that decomposition can proceed with a lower activation energy at the metal-azide interface. A study of the formation and growth of nuclei at the surface is therefore important, and this has been investigated both from the theoretical (97) and experimental (109, 135, 154) point of view.

The simplest way to follow decomposition in the azides is to measure the pressure of nitrogen gas liberated as a function of time. The early studies of Garner and his colleagues (63–68) and later work by Tompkins and his coworkers (e.g., 10,149) and others (35, 77) used this method. In general, however, the decomposition cannot be described by a simple law, and a variety of equations have been used to fit all or part of the pressure-time curves (see table 23). There does not seem to be complete agreement on which particular equation should be used and the reader is referred to the original papers. From the kinetic data it has been possible to estimate the activation energy for decomposition and some selected values are given in table 24.

If one considers the series of univalent azides potassium, thallous, silver, and cuprous one finds that the activation energy decreases in the order given. This is the order to be expected from the discussion on the electron energy levels given in Section III.

The results described above tell very little about the collapse of the solid azide lattice during decomposition to give the final metal product. An attempt has been made by Sawkill (135) to follow this collapse in silver azide by the combined use of electron diffraction and electron microscopy. Unfortunately, silver azide decomposes in the electron beam of the electron diffraction camera and a thermal and electron excitation mechanism apply. It is not at present possible to separate the two effects. The size and shape of surface silver nuclei formed during the thermal decomposition of silver azide have, however, been determined by McAuslan (109) and Camp (referred to in reference 21), using replica techniques and electron microscopy. The nuclei vary in size from less than 10 A. in width to more than several thousand Ångström units. The silver nuclei are not ordered relative to the silver azide lattice. The breakup of azide crystals during heating has been followed, using a scanning electron microscope (18). When a crystal of silver azide is heated to temperatures higher than the

TABLE 23

Kinetic equations used to fit pressure-time curves obtained from the thermal decomposition of some solid inorganic azides

Compound	Equation Used	Comments	Reference
KNs NaNs	p = kt $p = kt$	Initially there is a unimolecular decomposition	(95) (67)
AgN3 {	$\frac{\mathrm{d}(\mathbf{N}_2)}{\mathrm{d}t} = k[\mathrm{Ag}\mathrm{N}_3]^{\frac{2}{3}}$	No induction period	(77)
	$\begin{aligned} & \int_{1}^{0} -(1-p/p_{f})^{\frac{1}{2}} = kp_{f}^{-\frac{1}{2}}t \\ & 1-\alpha = \left(1-\frac{2kt}{a}\right)^{\frac{1}{2}} \\ & \alpha = \text{fraction decomposed in} \\ & \text{time } t; \ \alpha = \text{average linear} \\ & \text{dimension of the crystal} \end{aligned}$	This equation fits the decay process (10-95% de- composition). It is the equation for a contract- ing envelope and is of an equivalent form to that given in reference 7. Single crystals do show an induction period,	(10)
CuN3	$p^{\frac{1}{3}} = k(t - t_0')$	Sigmoid curves; t'_0 represents the induction period	(138)
T1N:	$\log\left(\frac{p_f}{p_f-p}\right) = kt$	First-order plot for molten TIN:	(78, 151)
CaN6	$p = k^3 (t - t_0)^2$ $\log p = kt + C$		(68a, 149) (108)
SrN6	$p = k^{\frac{3}{2}}(t - t_0)^{\frac{3}{2}}$ $\log p = kt + C$		(68a) (107)
BaNs	$p = C(t-t_0)^{\mathfrak{s}}$	"Fresh material"; to is the time preceding the onset of growth of "normal" nuclei; surface nuclei have been studied as a function of time by Wischin (154)	(64, 97, 143, 144, 149, 154)
	$p = C(t-t_0)^{\mathfrak{s}}$	"Aged" sample	(149)
D1 17	$\log p = kt + C$	—	(87)
PDNs	Unimolecular decomposition	· · · · · · · · · · · · · · · · · · ·	(00; cj. also 80)

TABLE 24

Activation energy,	E, j	for there	nal d	decompositio	n of	some	solid	inorganic	azides	(cf.	64)
--------------------	------	-----------	-------	--------------	------	------	-------	-----------	--------	------	----	---

Compound	Е	Reference	Compound	E	Reference	
	kcal. mole ⁻¹	-		kcal. mole ⁻¹		
ſ	49 in vacuo	(95)	CuNs	27	(138)	
KN:	41 in 16.4 mm. K vapor	(95)				
Į	36 in 24.8 mm. K vapor	(67)				
Na Na	34	(67)	Ca(Ns) 2	18-19	(108)	
LiN:	19	(9)	Sr(N3)2	ca. 20	(107)	
TlN:	ca. 40 (liquid phase)	(78)	Ba(Na)	21 - 27	(87)	
1 - N.	44 below 190°C.	(10)	Pb(Ns):	37-38	(65)	
HE112	31 above 190°C.	(10)				

transition temperature (ca. 190°C.), it breaks up into small blocks about 1 micron across. The blocks of silver azide continue to decompose to give metallic silver. The actual surface area is, however, much greater than the apparent surface area of the crystal.

The detailed mechanism for the decomposition of the inorganic azides is not known. The main outline can, however, be given for potassium, silver, and hydrogen azides. These three compounds correspond to an ionic azide, an azide with some measure of directed bonding, and a covalent azide.

According to Bartlett, Tompkins, and Young (10) the rate-determining step

in the thermal decomposition of silver azide is the thermal excitation of an electron to the conduction band. The initial step in the decomposition can therefore be represented as:

$$N_3^- \rightleftharpoons N_3 + e \tag{1}$$

Nitrogen gas will be formed by the reaction of two azide radicals at the surface.

$$2N_3 \rightarrow 3N_2 + 210 \text{ kcal.} \tag{2}$$

If any azide radicals are formed internally during the heating, these can appear at the surface by an electron-transfer mechanism. Metal will be formed according to the mechanism suggested by Mitchell (116).

$$Ag_n + Ag^+ + e \to Ag_{n+1} \qquad (n > 2)$$
(3)

There is at present no good experimental evidence that silver is formed internally in a crystal along dislocations.

For the decomposition of the low-temperature (orthorhombic) modification of silver azide the experimental value for the activation energy is in good agreement with the energy required to raise an electron from the valence to the conduction band. This has already been discussed in Section III,D.

Both the rate and the mechanism of decomposition in solids can be altered by the presence of impurities, defects, and dislocations. It is clear that they will also influence the decomposition of silver azide. There is, however, little quantitative data available on these effects (21, 33, 34, 77, 151). More is known about the sensitization of explosion in silver azide by impurities (see Section VIII).

It has been seen in Section III,D that the thermal energy required to dissociate an exciton in potassium azide is high. It is therefore unlikely that the mechanism described for silver azide applies to potassium azide. Jacobs and Tompkins (94–96) in fact suggest that the rate-determining step in the decomposition of potassium azide is the formation of an exciton which readily dissociates to form an F center. The resulting free positive holes that are formed will lead to decomposition and the formation of nitrogen gas. One factor in the decomposition of potassium azide which should be kept in mind is that both the products of decomposition

$$2KN_3 \rightarrow 2K + 3N_2$$

are volatile. A number of interesting effects have been observed on the influence of potassium vapor on the optical properties and decomposition behavior of potassium azide (95). The rate of decomposition is increased by the presence of potassium vapor; this has been attributed to a reduction in the activation energy for decomposition. Jacobs and Tompkins interpret their results in terms of the electron energy band system of potassium azide containing adsorbed potassium metal.

The mechanism of the homogeneous decomposition of gaseous hydrazoic acid is entirely different. This covalent compound decomposes by a free-radical mechanism, and it is generally agreed that the initial step is fission of the longest nitrogen-nitrogen bond (cf. Section V):

$$HN_3 \rightarrow NH + N_2$$

The energetics of this step has also been considered in Section V. The subsequent reactions of the NH radicals which can result in the formation of nitrogen, hydrogen, and ammonia is the subject of some controversy (39, 58, 127), and it does not seem profitable to speculate on them at the present time. Experimental studies are made difficult by the heterogeneous decomposition. The decomposition of hydrogen azide by flash photolysis has been studied by Thrush (147).

VII. PHOTOCHEMICAL DECOMPOSITION OF SOME INORGANIC AZIDES

When a crystal of an inorganic azide is irradiated with light of wavelength corresponding to the absorption band of the solid, photochemical decomposition takes place. The products of decomposition are metal and nitrogen gas. An optical transition from the full band to the exciton band of an ionic azide (cf. Section III,D) corresponds to the formation of an excited azide ion in the lattice. The dissociation of an exciton to give, for example, an electron in the conduction band of the crystal would result in the formation of an azide radical, N₃. In considering the photochemical decomposition of the solid ionic azides it is convenient to consider optical transitions between electron energy levels of the solid in terms of excitation of the azide ion.

The photochemical decomposition of the azides has been studied by measuring the rate of evolution of nitrogen during irradiation of the azide. Nitrogen gas is formed by the reaction

$$2N_3 \to 3N_2 + Q \tag{1}$$

However, in all the photochemical decompositions that have been studied the wavelength of irradiation used does not produce azide radicals directly by absorption, i.e., in the manner

$$N_{8}^{-} + h\nu \to N_{8} + e \tag{2}$$

but by the series of reactions

$$N_3^- + h_\nu \to N_3^{-*} \tag{3}$$

$$N_{3}^{-*} + q \to N_{3} + e \tag{4}$$

where N_{s}^{-*} denotes an excited azide ion which is dissociated by the thermal energy q. It is probable that decomposition by equation 2 could be produced if absorbed quanta of sufficient energy were used. Once azide radicals, N_{s} , have been formed, it is necessary for these radicals to diffuse into adjacent positions where they can react according to equation 1. In the solid state this will occur at the surface of the crystal. However, in the absence of any other form of electron trap, recombination of electrons and positive holes will occur (50, 51).

$$N_3 + e \to N_3^- \tag{5}$$

Hence the efficiency of decomposition, as given by the fraction of reacting azide radicals, will be small. The introduction of electron-acceptor levels in the crystal will inhibit recombination of electrons and positive holes. During the corresponding increased lifetime of the radical more of the azide radicals can react according to equation 1 and hence the efficiency of photochemical decomposition is increased (50).

A. POTASSIUM AZIDE

A detailed study of the photochemical decomposition of potassium azide has been made by Jacobs and Tompkins (94). The results obtained show that (1) the rate of nitrogen evolution at constant decomposition temperature and intensity of irradiation is constant; (2) the quantum yield is low (ca. 0.001); (3) the rate at constant temperature varies as the square of the intensity of irradiation; (4) at constant intensity, the rate r as a function of temperature is given by the equation

$r = 1900 \left\{ 7.71 \times 10^{-4} + \exp(-4080/RT) \right\}$ (6)

where 4080 cal. mole⁻¹ is the experimentally determined activation energy of photochemical decomposition. The excitons produced by irradiation are trapped in bimolecular combinations at surface cation vacancies. These pairs of excitons may decompose, to form nitrogen, either (a) with zero activation energy or (b) with an activation energy of ca. 4.1 kcal. mole⁻¹. The steric relationships of the excitons determines the activation energy with which the excitons will decompose. If s_1 and s_2 are the steric factors corresponding to zero or 4.1 kcal. mole⁻¹ activation energy, respectively, then it has been shown that $s_1/s_2 \simeq 10^{-5}$ and $s_1 \simeq 10^{-4}$. The constant term in equation 6 therefore refers to decomposition (with low probability) of excitons involving zero activation energy and the exponential term to the predominant mode of exciton decomposition requiring an activation energy of ca. 4.1 kcal. mole⁻¹.

The various absorption centers produced during, and as a result of, irradiation have been considered in Section III,C. Unlike thallous and silver azide the photochemical decomposition of potassium azide results from the dissociation of excitons to give F centers and nitrogen gas. Thus it is not necessary to promote an electron to the conduction band of the solid, and the energy of photochemical decomposition corresponds to that necessary to form an F center in potassium azide.

B. THALLOUS AZIDE

The photochemical decomposition of thallous azide has been followed by measuring the pressure of the nitrogen gas evolved during irradiation (35). Measurements were made on compressed pellets of thallous azide irradiated with the full output of a mercury vapor lamp. The activation energy of photochemical decomposition over the temperature range -25° C. to 40° C. was found to be 7.2 kcal. mole⁻¹.

In Section III,D it was stated that the thermal energy necessary to dissociate

an exciton in thallous azide is 0.33 e.v. (ca. 7.6 kcal. mole⁻¹). This is in reasonable agreement with the value given for the activation energy of decomposition. Therefore under these experimental conditions the predominant mode of decomposition is that given by equations 3 and 4.

C. SILVER AZIDE

Photochemical decomposition of silver azide at room temperature results in the formation of discrete silver nuclei and the evolution of nitrogen gas. The activation energy of room-temperature photolysis (using light of wavelength 3650 A.) is given as ca. 6 kcal. mole⁻¹ (Young, private communication (113)). This is close to the value of 7.6 kcal./mole⁻¹ calculated as the thermal energy necessary to dissociate an optically formed exciton. In the initial stages of decomposition, when there are few metal particles to act as electron traps, recombination of electrons and positive holes will normally occur. The quantum efficiency of photochemical decomposition is low, ca. 0.1 (43). It seems that the rate of photolysis is proportional to the square of the intensity of irradiation (10).

D. MERCUROUS AZIDE

Mercurous azide is very sensitive to light. Its photochemical decomposition at room temperature results in the evolution of nitrogen gas and the formation of a solid brown product which is probably a nitride. In this respect mercurous azide differs from thallous and silver azides, where the solid product of decomposition is in the form of metallic nuclei. In view of the pronounced "nonionic" character of mercurous azide, photochemical decomposition probably takes place by bond fission within the azide group. Experiments by Deb (35) have shown that the rate of photolysis is approximately proportional to the intensity of irradiation. The activation energy of photochemical decomposition is ca. 8.4 kcal. mole⁻¹.

E. BARIUM AZIDE

The photodecomposition of barium azide has been studied by Thomas and Tompkins (143), who measured the rate of evolution of nitrogen during irradiation of the salt. Above 45°C. barium azide undergoes thermal decomposition; consequently observations on the rate of photolysis with temperature were restricted to temperatures less than 45°C. The experimental results showed that (1) there is a constant rate of evolution of nitrogen at constant temperature and constant intensity; (2) this rate varies as the intensity squared at constant temperature; (3) the rate increases in a complex manner with temperature at constant intensity. The rate of decomposition r is given by

$$r = \text{const.} \{ 1.9 \times 10^{-5} + \exp(-5350/RT) \}$$
(7)

As in the case of potassium azide, it is assumed that the decomposition mechanism consists of the trapping of optically formed excitons at cation vacancies. Steric effects determine whether the excitons will decompose with zero activation energy or with the experimental activation energy of 5350 kcal. mole⁻¹.

F. HYDROGEN AZIDE

Hydrogen azide is a covalent compound, and in the gas phase photochemical decomposition develops by a free-radical mechanism in which the initial step is fission of the longest nitrogen-nitrogen bond (cf. Section V). Recent work by Thrush (147) has led him to postulate the following mechanism for the decomposition of hydrogen azide during flash photolysis:

$$HN_{3} + h\nu = HN + N_{2}$$

$$HN + HN_{3} = NH_{2} + N_{3}$$

$$NH_{2} + HN_{3} = NH_{3} + N_{3}$$

$$2N_{3} = 3N_{2}$$

The overall equation is

$$3HN_3 \xrightarrow{n\nu} NH_3 + 4N_2$$

The photolysis of hydrogen azide suspended in inert gases at 20°K. has been studied by Becker, Pimentel, and Thiel (106).

VIII. IGNITION OF INORGANIC AZIDES

Inorganic azides such as silver and lead azide are perhaps best known for their ability to explode and detonate when subjected to shock. An explosion can be initiated in the azides in a variety of ways. These include heat, shock, light, and electric discharge. A detailed account of the explosion process has been given by Bowden and Yoffe (21), and for this reason only the essential features will be noted.

In general, the *initiation* of explosion in azides is concerned with the decomposition of a small volume of material (ca. 10^{-3} cm. radius) at a high temperature (ca. 500°C.) and in a short time (several microseconds). If the heat liberated during the decomposition of this small volume of material is sufficiently large, then a self-propagating reaction will develop and an explosion and finally a detonation will result. The phenomenon of detonation may thus be separated into two phases: (1) initiation of reaction; (2) growth to explosion and detonation.

It appears that the initiation of explosion by shock is thermal in origin. That is, if an explosion is brought about by impact or friction, then the mechanical energy must first be degraded into heat in a localized region of the material and the explosion grows from the hot region or "hot spot" by a thermal mechanism. It is perhaps an oversimplification to say that all explosions initiated by shock are thermal in origin, and criticisms of this point of view have been put forward by a number of investigators; nevertheless a thermal mechanism can be used to describe many of the experimental observations.

An explosion can also be initiated by a high-intensity short-duration light flash. Eggert and his colleagues (11, 43, 44) and Courtney-Pratt and Rogers (31) have suggested that even in this case the initiation of explosion is thermal. The azide is excited electronically, and this excitation energy is degraded into heat. Recent work by Evans and Yoffe (50), however, shows that the primary act in the initiation of decomposition is a true photochemical one, at least for thallous, silver, and copper azides. The growth to explosion, however, is thermal. The primary step is the final formation of azide radicals by absorption of light quanta (cf. Section VII)

$$N_3^- \xrightarrow{h_\nu} N_3 + e$$
 (1)

followed by the exothermic step which controls the growth to explosion.

$$2N_3 \rightarrow 3N_2 + 210 \text{ kcal.} \tag{2}$$

The complete equation for decomposition is of course given by the equation

$$2\mathrm{MN}_3 \to 2\mathrm{M} + 3\mathrm{N}_2 + Q \tag{3}$$

and the heat, Q, liberated during this decomposition may be obtained from table 19 (Section IV).

Silver azide can be sensitized to light by the presence of metal particles such as gold and silver (33, 50). The light energy required for ignition is also decreased. This sensitization may be explained in a simple way. The metal particles act as electron traps and so the concentration of azide radicals necessary for step 2 is increased.

Table 25 lists the light energy necessary for the explosion of a number of azides (35). It will be seen that the energy decreases in the order KN_3 , TIN_3 , AgN_3 , CuN_3 . Although these energies have not been related to the absorption spectra of the azides, the results show qualitatively that the sensitivity to light initiation increases as the ionization potential of the metal is increased (cf. Section III,D).

Experiments with silver azide also show that a molten layer is formed at the surface of the azide prior to explosion. This is true for ignition by heat as well as by light (48). It is suggested (50) that this molten layer is a necessary step in the initiation of explosion. In the solid state the reaction of azide radicals takes place mainly at the surface and the rate of the surface reaction is not sufficient to support a self-accelerating reaction. All the evidence indicates that it is necessary to decompose a volume of material large on the molecular scale for an explosion to develop. In the molten state, however, decomposition can also occur in the bulk of the material. The heat is liberated during this liquid-phase decomposition sufficiently rapidly for an exothermic explosion and detonation to grow.

Detonation, in fact, occurs within a very short time for materials such as silver azide. High-speed photographic methods (30) show that this time is less than 10^{-7} sec. The actual detonation velocity depends on the particular azide, the diameter of the sample, and whether the material is confined. The values usually range from ca. 1000 m./sec. for very thin films ca. 0.1 mm. thick to ca. 5000 m./sec. for the stable high-velocity detonation. The detonation velocity does not seem to be dependent to any marked extent on the structure of the azide in the solid state (21, 35). The absence of any extended burning region (except in certain circumstances (48)) in the azides is due to the fact that the decomposition takes place in a few steps and the heat of decomposition is liberated rapidly (21).

Compound	Critical Light Energy	Compound	Critical Light Energy			
KN8	joules*	Hg2(N3)2	<i>joules</i> * ca. 164			
TlN8 AgN3 CuN3	92 (confined) 39 12	$\begin{array}{c} Pb(N_3)_2. \\ Hg(N_3)_2. \\ \end{array}$	са. 29 са. 90			

TABLE 25

Ignition of inorga	nic azides by a	ı light flash of c	а. 50 µsec.	duration	(35)
				·····	

*Total energy of light flash.

One explosion phenomenon which has not been explained is the incidence of spontaneous explosion observed during the growth of lead azide and mercuric azide from solution (35, 101, 115, 131, 142). Explosions may be obtained, for example, with lead azide either during growth by the diffusion process (115, 131) or during crystallization from ammonium acetate solutions (101, 142). Perhaps the best controlled investigations are those by Taylor and Thomas (142). They are able to predict times to explosion fairly accurately and have shown that the crystals formed during growth from an ammonium acetate solution do not explode. It is the liquid phase which is responsible for the spontaneous explosions, and it seems that the explosions occur during the very early stages of the growth process. Further work is, however, necessary on this topic.

A study of detonation in solids such as the azides is a difficult matter. The reactions are complete in times which can be less than a microsecond. The reaction zone itself can be very narrow (less than a millimeter) and the pressures and temperatures are high. It is also a region of intense ionization and high electron density (29). It is therefore not surprising that very little is known about the reactions which occur in the detonation zone. However, a number of experimental techniques are currently being developed which should be of considerable help in this connection, and many of the outstanding problems should soon be solved.

The authors thank Dr. F. P. Bowden, F.R.S., for his encouragement and for many stimulating discussions, and also Dr. T. C. Waddington for frequent discussions.

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