ELECTROLYSIS OF THE AZIDE ION

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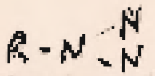
Foreward:

In writing this paper on the "Electrolysis of the azide ion," the writer has consulted all available information since 1885, when the azide ion was first discovered by Curtius. The writer started his search with the help of the two major science abstracting journals: The German Chemisches Zentrablatt, and the American Chemical Abstracts. The search in the American Chemical Abstracts started from the year 1907 to the present time, while Chemisches Zentrablatt was consulted from 1885 to 1907. Much of the information in this paper has been translated from German, French and Russian publications into English.

STRUCTURE AND ELECTRONIC CONFIGURATION

OF THE AZIDE ION

Three types of formulas are possible for the azides:[1,2]

(1) 

(2) $R-N \rightrightarrows N$

(3) $R-N \leftarrow N \equiv N$

For the azide ion, we have definite proof of an open-chair rectilinear formula from the crystal structures of the salts[3] (Hendricks and Pauling, J. Am. Chem. Soc., 1925, 47,2904). This can be formulated in two ways, since a valency angle of 180 degrees is compatible with either two double links or a single and a triple link: $\left[N = N \rightrightarrows N\right]^-$; $\left[N \leftarrow N \equiv N\right]^-$

The first is, from its greater symmetry much more probable. L.K. Frevel[4] redetermined the N to N distances in crystals of NaN_3 and KN_3 and found them to be 1.150A ± 0.016 and 1.145A ± 0.0.7, respectively. The N to N distance in $N \equiv N$ (N_2) is 1.10A and in $N = N$ is 1.26A, the difference being the same as that between $C = C$ and $C-C$. In view of the functional dependence on bond character for single- bond- double bond resonance (Cto C and other linkages), it appears resonable to extend the function to the double bond- triple bond resonance in N_3^- thus the N to N distance of 1.15A.

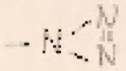
in corresponds to about 30% triple bond character.[4] The configuration of N_3^- may be represented as

$$:N:::\ddot{N}:\ddot{N}:^{-} \longleftrightarrow :\ddot{N}::\overset{+}{N}::\ddot{N}: \longleftrightarrow :\ddot{N}:\overset{+}{N}:::N:$$

The somewhat larger N to N distance of 1.165A ± 0.021 in NH_4N_3 (24% triple bond character) is due to the attachment of each terminal N of the N_3^- to its two nearest neighbors by H bonds. The linear structure for N_3^- was also confirmed by the work of A. Potier,[5] by the LCAO method (linear combination of atomic orbitals).

The calculated and observed physical properties agree well for N_3^- as well as for CO_2, NO_2^+ and CS_2. The predicted reactivities were also confirmed for the above mentioned ions and molecules.

DIPOLE MOMENTS

Lidgwick, Sutton, and Thomas[2] determined the dipole moments of the azides along with those of phenyl, p-tolyl, p-C_6H_4Cl, p-C_6H_4Br and p-$C_6H_4NO_2$, isocyanates and distributed diazomethanes containing these groups. The values indicated that the compounds exist either in the ring form  $-N\langle{N \atop N}$, or as a tautomeric mixture of the two linear forms, $-N=N\rightarrow N$ and $N\leftarrow N\equiv N$. Calculations based on the known heats of combustion favor the latter form, in confirmation with the work of Sidgwick, Sutton, and Thomas[2] as mentioned above.

Values of the extrapolated polarization P, the refraction R, and the dipole moment μ, detected in C_6H_6 solution at 25° degrees, for some organic azides, are:[6]

azide	P	R	
$N_3CH_2CO_2Et$	192.23	30.16	2.79
N_3CO_2Me	83.07	20.87	1.73
N_3Et	114.43	19.13	2.14
$N_3CH_2CH:CH_2$	100.69	23.76	1.92
$N_3CH_2CH_2OH$	149.91	20.82	2.49
N_3Ph	77.51	34.61	1.44
p-$N_3C_6H_4NO_2$	213.57	39.44	2.89
m-$N_3C_6H_4NO_2$	298.17	39.44	3.52
o-$N_3C_6H_4NO_2$	451.90	39.44	4.25
2,4-$N_3C_6H_3(NO_2)_2$	191.48	44.27	2.66
p-$N_3C_6H_4Br$	43.72	42.37	0.06
N_3Bz	180.34	39.36	2.60
1-$N_3C_{10}H_7$	91.44	53.01	1.36
2-$N_3C_{10}H_7$	106.00	53.01	1.60
1-NO_2-2-$N_3C_{10}H_6$	467.20	57.82	4.44
1-NO_2-4-$N_3C_{10}H_6$	260.36	57.82	3.12
8-NO_2-2-$N_3C_{10}H_6$	497.13	57.82	4.59

The mean R of the C-N_3 group in aliphatic azides is 9.4 as against 10.0 in N_3Ph and 10.4 in 1-$N_3C_{10}H_7$. The negative end of the CN_3 group dipole is evidently oriented in the direction of the outer N atom.

The dipole moment of $p\text{-}N_3C_6H_4Me$, 1.9 is near the sum of the moments of toluene and N_3Ph ; the C-N-N angle is apparently greater than in aliphatic azides. The highest μ of N_3Ph as compared with N_3Et must be due to a shift of electrons towards the ring owing to interaction with the N_3^- group.

MOBILITY OF AZIDE ION AND MEAN LIFE OF ELECTRONICALLY ACTIVATED NITROGEN

The azide ion is very mobile in a solution, and although the ions OCN and N_3 are very similar: the mobility of N_3 is greater than that of OCN.[7] Slow thermolysis, or electrolysis of aqueous solutions of azides (NaN_3, KN_3, HN_3) is accompanied by ultraviolet radiation, which is independent of the cation, and is due to deactivation of the Nitrogen.[8]

By electrolysis of an aqueous solution of NaN_3 with a special arrangement by which a circuit is periodically opened and closed the average life of the activated nitrogen is determined as $2.5 \pm 0.2 \times 10^{-3}$ sec An oscillograph attached to the cathode showed the existence of metastable state attributed without doubt to the molecule of nitrogen which was activated electrically. The ionic radius for the azide has been found to be $\alpha = 8.5A$.[9]

ELECTRON AFFINITY AND REACTIONS OF THE AZIDE ION IN AQ. SOLUTION

The absorption spectrum in the near ultraviolet of the N_3^- ion in aqueous solution has been detected. It is similar to that of the halogen ions and corresponds to an electron affinity spectrum. A value of 125 Kcal/g.mol . mol. is deduced for the sum of electron affinity and heat of hydration of the azide ion.[10] This value leads to an estimate of the N-H bond energy in N_3H of 3.3 ± ±0.3 ev. The reaction between N_3^- and Ce^{+4} ions is a simple mechanism, involving electrontransfer processes.

The reactions have been investigated which occur when an electric discharge is passed from a positive electrode to the surface of an aqueous electrolyte containing oxidizable substances such as ferrous azide, ferrocuanide, and cerous ions.[11] Electrolysis is accompanied by oxidation arising from the breakup of H_2O due to the bombardment of the solution by gaseous ions, and the chemical phenomena are analogous to the effects produced by ionizing radiations. An attempt has been made to develop a general mechanism of the process which will account quantitatively for the oxidation yields and their dependence on exceptional conditions.

IONIC CONDUCTANCE OF SOME SOLID METALLIC AZIDES.

The ionic conductance of solid Li, Na, K, Ca, Sr, and Ba azides has been measured by Jacobs[12] over as wide a temperature range as possible and the activation energies for conductance obtained. All the azide salts obey the equation; $\log K = \text{Log } A - (\frac{E}{2.303\ RT})$ (1)
(1) where k is the specific conductance in ohm^{-1} cm^{-1}, A is a constant, and E the activation energy for the conductance process in kcal/mole. The results are summarized in Table I, where each value of E and logA represents the mean of at least three series of determinations. The maximum deviations from the mean values of E are ± 0.3 percent for Li, Na, and K azides and ± 1.2 percent for Ca, Sr, and Ba azides, the accuracy being lower for the alkaline earths because of their lower specific conductance.

Table I. Values of the constants in the conductance equation

Salt	Temp. range °K	logA	E kcal/mole
LiN_3	300-370	0.840	19.1
NaN_3	375-490	0.490	25.0
KN_3	390-500	4.59	30.1
CaN_6	290-370	-9.56	5.3
SrN_6	300-380	-10.70	5.1
BaN_6	295-380	-8.99	11.6

The results for the potassium azide are shown separately in Fig. 1. The reproducibility is satisfactory for preparations precipitated from carefully neutralized solutions (phenol phthalein). Included in this plot are results obtained using KN_3 precipitated from solutions containing CO_3^{2-} ions. This has the effect of lowering the conductance, although the temperature coefficient remains unaltered. Many attempts to incorporate divalent cation impurities in KN_3 by co-precipitation were unsuccessful.[12]

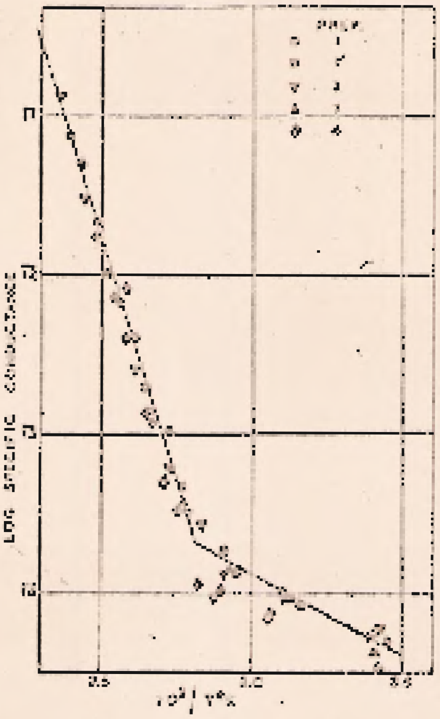


Fig. 1. Ionic conductance of various preparations of potassium azide as a function of temperature. Preparation 1, neutral solution; 1', same preparation as 1 but pre-irradiated with ultraviolet light; 2, excess acid; 3, neutral solution; 4, potassium carbonate added.

DISCUSSION

For many salts the plot of log k against 1/T shows two linear sections associated with activation energies E_1 (for the low-temperature region) and E_2. These have been related to the energies for migration of the mobile species (E_0) and for creation of defects (W_0) by the equations $E_1 = E_0$, $E_2 = E_0 + \frac{1}{2} W_0$. (2)

As a provisional hypothesis, it is assumed that in this temperature range the alkali azides are predominantly cationic conductors and that the conducting species are cation vacancies rather than interstitial cations. By comparison with the values for the alkali halides, the experimental activation energies E of 19.1, 25.0, and 30.1 kcal/mole for the Li, Na, and K azides appear to be E_2-values and this is supported by the plots of E_2 and E_1 against $1-1/\epsilon_0$, where ϵ_0 is the high-frequency dielectric constant, shown in Fig. 2.

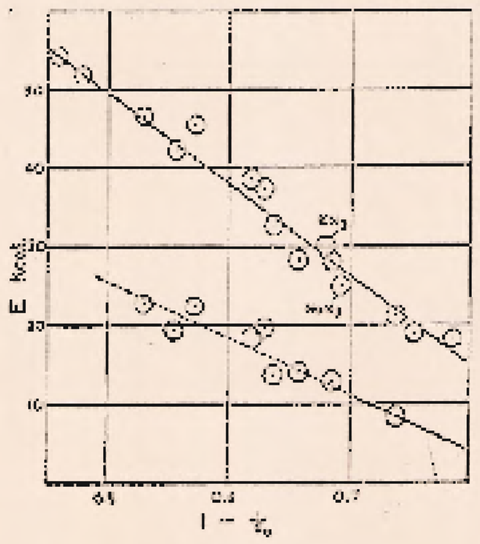


Fig. 2. Plot of the activation energies for ionic conductance against $1-1/\epsilon_0$.

The dielectric constants of KN_3 and NaN_3 were interpolated from the smooth curve obtained by plotting the wavelength of the ultraviolet absorption edge against ϵ_∞. The points for KN_3 and NaN_3 lie quite definitely on the E_2-line. Unfortunately, we have no knowledge of ϵ_∞ for LiN_3, but the value of E of 19.1 kcal is comparable with that of E_2 for LiI (21.2 kcal) but much larger than that of E_1 for this salt (8.4 kcal).[12]

The experimental E-values found for the alkaline earth azides are of a lower order of magnitude and could refer to E_1. In the other salts containing divalint cations for which transport numbers have been determined, the majority ($BaCl_2$, $BaBr_2$, BaI_2, $PbCl_2$, and $PbBr_2$) show an anion transport number of unity: E_1 may therefore be the activation energy for the mobility of the anoin vacancies in BaN_6 but the generally low values found for the divalent azides indicate that these are most probably for ions in special positions.

Since the corresponding values for KCl, KBr, and KI are 22.8, 22.4, and 19.6 kcal/mole, respectively the low temperature value of 4.5 kcal/mole in KN_3 is unlikely to be that for the activation energy for the bulk migration of cation vacancies. This is supported by an independent estimate of E_1. The energy required to create a pair of vacancies is given by $W_0 = W_L - W_p$ (3) where W_L is the lattice energy per ion pair and W_p the total polarization energy $(W_p^+ + W_p^-)$. The lattice energy of potassium azide can be calculated from the following thermochemical data:

$\Delta H^\circ_f\, KN_3\,(c) = -1.4$ kcal/mole[6]

$\Delta H^\circ_f\, N_3^-\,(g) = 37$ kcal/mole[6]

$\Delta H^\circ_f\, K^+\,(g) = 122.9$ kcal/mole.[7]

Using a Born-Haber cycle, we find $W_L = 153$ kcal/mole. The polarization energy W_p may be estimated only indirectly. In general, two methods exist for the calculation of W_p. In that due to Jost,[13] the creation of a vacant site is regarded as equivalent to scooping out a hole of radius R in a medium of uniform dielectric constant ϵ_0. The polarization energy resulting is

$$W_p = \left(1 - \frac{1}{\epsilon_0}\right)\frac{e^2}{2R} \qquad (4)$$

This method should be independent of the type of crystal lattice, but the difficulty lies in choosing values for R^+ and R^-. Mott and Littleton[14] have improved Jost's method by calculating the dipoles on the nearest and next-nearest neighbors directly in a NaCl-type lattice, and applying Jost's formula to the rest of the lattice. Their method involves a great deal of calculation. Accordingly, the polarization energy was estimmted indirectly by plotting the experimental values for the alkali and silver halides given by $W_L - 2(E_2 - E_1)$ against $(1 - 1/\epsilon_0)\ 1/a$, where a is the anion-cation distance. If $R^+ + R^-$ is proportional to a, these results should all lie on a straight line. As shown in Fig. 3, this is approximately true, particularly at the higher values of the dielectric constants, the maximum deviation being ± 5 percent for NaCl. The polarization energy in KN_3 obtained by interpolation from Fig. 3 is 134 kcal. Hence W_3 = 11 kcal and E_1 = 20.5 kcal, which is of the order expected. It is therfore most unlikely that the experimental value of 4.5 kcal refers to E_1 and it is concluded that this energy refers rather to the mobility of surface vacancies, as first suggested by Smekal.[15] The low values found in Ca, Sr, and Ba azides are also considered to refer to surface conductance.

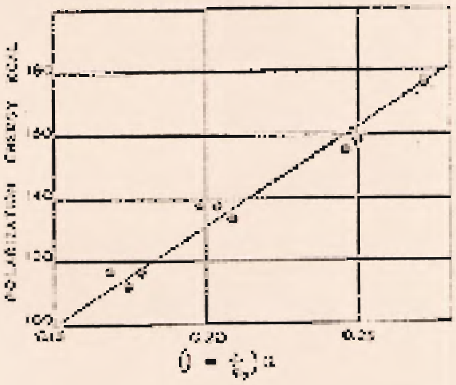


Fig. 3. Plot of the polarization energy, calculated from the lattice energies and activation energies for conductance, against $(1-1/\varepsilon_0)a$.

On this basis, one would expect three regions corresponding to surface conductance, the usual bulk structure-sensitive conductance, and the characteristic conductance of the salt, with activation energies of 4.5 kcal, about 20 kcal and 30 kcal, respectively. In practice only the first and last of these two can be differentiated, although the transition region is somewhat diffuse (Fig. 1). It may be that the bulk structure-sensitive conductance is not differentiated, because of a fortuitous combination of the values of the activation energies and the number of vacant sites. If the value of the activation evergy necessary for bulk conductance such that this represents one percent of the surface conductance at the temperature at which the characteristic conductance begins to be appreciable then is calcualted, a value of 18 kcal in substantial agreement with the value estimated from the polarization energy is found. The hypothesis of surface conductance has received further confirmation from the agreement between the number of vacant sites in the surface layers calcualted from the conductance data and from the rate of photolysis of potassium azide.[16]

The conditions of preparation of the azide would be expected to cause variation in surface conductance. In presence of CO_3^{2-}, or with excess OH^- in presence of air, leading to CO_3^{2-}, the divalent anion is preferentially attached to normal surface anion sites producing additional anion vacancies (to maintain electroneutrality) and reducing the number of cation vacancies by pair formation. The number of mobile charged carriers is thus reduced and consequently the conductance is smaller then in the "neutral" salt.

THE KINETICS OF THE ELECTROLYSIS OF THE AZIDE ION

The kinetics of the electrodeposition of hydrogen and oxygen from aqueous solution have been studied exhaustively, and a number of theories as to the precise nature of the reaction have been put forward. These reactions are peculiar in that in each case the products are constituents of the solvent, and in addition complications arise owing to the fact that hydrogen and hydroxyl ions are hydrated in solution, might, therefore, be expected to follow a different course from the deposition of hydrogen and oxygen. According to the theory of ionic solution put forward by Bernal and Fowler,[17] univalent ions of radius greater then 1·6A. are to be regarded as unhydrated in aqueous solution, in the sense that they do not carry along a co-ordinated shell of water molecules. The azide ion comes in this category, and although it has been shown that the electrodeposition of the ion is an irreversible process,[18, 19] no detailed investigation of the kinetics of the reaction appear to have been made. The following series of experiments were carried out by H. Stout in an attempt to elucidate further the nature of the deposition process.

Nature of the Electrode Reaction.- On electrolysis of an aqueous solution of sodium azide using a platinum anode, nitrogen is evolved in amount corresponding to

the reaction.[20] $N_3^- = 3/2\ N_2 + e^-$.
At an aluminum electrode-- however, only two-thirds of the theoretical amount of nitrogen is evolved, the remaining one-third appearing in the form of ammonia. This is presumably due to the reduction of the azide ion by nascent hydrogen formed by solution of the anode in the electrolyte, which gives a slightly alkaline reaction, thus

$$N_3^- + 3H = N_2 + NH_3 + e^-.$$

In the presence of platinum black, sodium azide is hydrolysed to ammonia and nitrogen, the rate of hydrolysis being greatly increased if the platinum surface is saturated with hydrogen.[21] Both these reactions are catalysed by the metal surface, and as only one atom of nitrogen is liberated as ammonia, it seems likely that one nitrogen atom in the ion behaves differently from the other two, and that the ion decomposes thus

$$N_3^- = N_2 + N + e^-$$

the nitrogen atom being adsorbed on the metal surface. Hydrogen on the surface would then react with the absorbed atom to form ammonia. The rate of reaction would, of course, be controlled by the rate of removal of adsorbed nitrogen atoms. This is in accord with the fact that hydrogen catalyses the exchange reaction between the two isotopic nitrogens, N_2^{14} and N_2^{15}, on an iron surface, ammonia, or at least an imido bond, being formed as an intermediate product.[22]

Free Energy of Formation of N_3^- aq. -- The free energy of formation of the azide ion in solution is the free energy change in the reaction

$$\tfrac{1}{2} H_2 + \tfrac{3}{2} N_2 + aq. + H^+ aq. \quad \cdot \quad \cdot \qquad (5)$$

A search of the literature has failed to reveal sufficient data for the exact calculation of ΔF°, but an approximate value may be estimated from the free energy changes in the following reactions:--

$$\tfrac{1}{2} H_2 + \tfrac{3}{2} N_2 = HN_3 (gas). \quad \Delta F^\circ = 78.5 \text{ K.cal.}^{23} \qquad (6)$$

$$HN_3 (gas) + aq. = HN_3 \; aq. \qquad (7)$$

The heat of formation of hydrazoic acid gas is 71.9 K.cal.[24] and of aqueous hydrazoic acid 54·6 K.cal.[25], which gives ΔH° for reaction (7) as -17·3 K.cal. The corresponding entropy change ΔS° may be estimated roughly by comparison with the ΔS° for the solution of nitrous oxide

$$N_2O \; gas + aq. = N_2O \; aq. \quad \Delta F^\circ = 2.184 \text{ K.cal}^{26} \quad \Delta H^\circ = -6.25 \text{ K.cal.} \qquad (8)$$

The ΔS° of this reaction is therefore -28·3 cal. per degree. As nitrous oxide has a linear structure corresponding[17] to resonance between $\overset{-}{N}=\overset{+}{N}=O$ and $N\equiv\overset{+}{N}-\overset{-}{O}$ [*], the entropy change on solution would be expected to be of the same order in each case, and so the entropy of solution HN_3 gas may be taken as about -30 cal. per degree. The free energy change ~~of energy~~ on solution of HN_3 gas will therefore be about -8·4 K.cal. for gas at one atmosphere pressure and unit activity of acid.

$$HN_3 \; aq. \rightleftharpoons H^+ aq. + N_3^- \; aq. \quad \cdot \qquad (9)$$

The dissociation constant[28] of hydrazoic acid is 2·8 x 10^{-5},

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[*] (and as hydrazoic acid gas contains the linear group -NNN corresponding to resonance between $-\overset{-}{N}-\overset{+}{N}\equiv N$ and $-N=\overset{+}{N}=\overset{-}{N}$)

and so the free energy change for reaction (9) is 6·2 K.cal. The free energy change in reaction (5) is equal to the sum of the free energy changes in reactions (6), (7), and (9) and is therefore 76·3 K.cal. and this is the free energy of formation of the azide ion. It will be noted that the error introduced in estimating the entropy of solution of HN_3 is not of great importance as the contribution of reaction (7) amounts to only 11% of the whole. It will also be seen that the free energy of formation of HN_3 aq. is 70·1 K.cal. which is rather greater than the value of 65·3 K.cal. given by Latimer[27] but as the latter is based on an entropy of 48 cal. per degree for HN_3 estimated by comparison with a value of 50 cal. per degree for HNO_2, it is probably less accurate than the former estimate.

The Reversible Potential of the N_3^- - N_2 Electrode.- The reversible potential of the normal azide-nitrogen system measured against a normal hydrogen electrode is the E.M.F. of the cell

$$N_2 \,|\, N_3^- \text{ aq.} \,\|\, H^+ \text{ aq.} \,|\, H_2$$

for unit activity of both ions and at one atmosphere pressure. As the free energy change in the reaction is 76·3 K.cal., the E.M.F. of the cell is 3·3 volts, hydrogen being positive, and so the reversible potential of the normal azide-nitrogen electrode is -3·3 volts against the normal hydrogen electrode.

Entropy of N_3 - Ion.--For the reaction

$$\tfrac{1}{2} H_2 + \tfrac{3}{2} N_2 + aq. = H^+ aq. + N_3^- aq.$$

ΔH° is 58·4 K.cal.,$^{25^\circ}$ ΔF° is 76·3 K.cal., and so ΔS° = -60 cal. per degree. Taking absolute entropy[30] of H_2 as 29·7 of N_2 as 45·9, and of[31] H^+ as -4·6 , all in cal. per degree it follows that the absolute entropy of N_3^- aq. must be appro approximately 28 cal. per degrees.

Entropy of N_3^- (gas).--It is interesting to compare this value for the entropy of the azide ion in solution with the entropy calculated for a hypothetical gaseous ion N_3^-. Taking the ion as linear and symmetrical with the N-N distance 1·15 A., the moment of inertia is 4·56 X 10^{-39} g. $cm.^2$, and the rotational entropy given by

$$\frac{S_{rot}}{Nk} = \ln \frac{4\pi^2 IkT}{h^2} + 1$$

becomes S_{rot} = 12·2 cal. per degree per g. mol. at 298° degree K. The translational entropy is given by

$$\frac{S_{vib}}{Nk} = \sum\left[\frac{h\nu}{kT}\left(\frac{e^{-h\nu/kT}}{1-e^{-h\nu/kT}}\right) - \ln\left(1-e^{-h\nu/kT}\right)\right]$$

and so S_{trans} = 32·6 cal. per degree per g. mol. at 298° degree K. The frequencies of vibration of the gaseous ion are unknown, but taking them equal to those in solution, namely, ν_1 = 1350, ν_2 = 630, and ν_3 = 2080, the entropy of vibration given by

$$\frac{S_{trans}}{Nk} = \ln \frac{(2\pi MkT)^{3/2}}{h^3} \cdot \frac{kT}{P} + \frac{5}{2}$$

becomes S_{vib} = 0.32 cal. per degree per g. mol. at 298° K. The total entropy of the gaseous ion is thus 45·1 cal. per degree per g. mol., and comparing this with the value of 28 cal. per degree per g. mol. for the aqueous ion, it appears that the hypothetical entropy of solution of the N_3^- ion is about -17 cal. per degree per g. mol.

EXPERIMENTAL

For the above mentioned calculations, Stout used the electrolytic cell shown diagrammatically in Fig. 4, was made of soda glass and consisted of an anode compartment C, seperated by an ungreased tap T_2. When closed, the latter effectively prevented diffusion of hydrogen from cathode to anode without seriously obstructing the current flow. A capillary tube B, carrying an ungreased tap T_1, was sealed through the wall of the anode compartment and the end drawn out to a fine tip. The other end dipped into a beaker containing a saturated solution of potassium chloride, and this was connected by a salt bridge to a saturated calomel half cell. The anode, a piece of platinum, palladium, or iridium foil, was welded to a wire of the same metal, which in turn was welded to a length of platinum wire. This was sealed into a galss tube, D, which fitted into a ground glass joint, J, at the top of the anode compartment, the length of wire being such that the foil was about 1 mm. from the tip of the capillary tube. The cathode compartment was open to the atmosphere and had a length of platinum wire sealed into it as the electrode. To fill the cell, electrolyte was blown in from a flask through the tube, E, by nitrogen under pressure from a cylinder, all the taps except T_4 being open. After filling the anode and cathode compartments and the capillary tube B, which required about 15 c.c. of

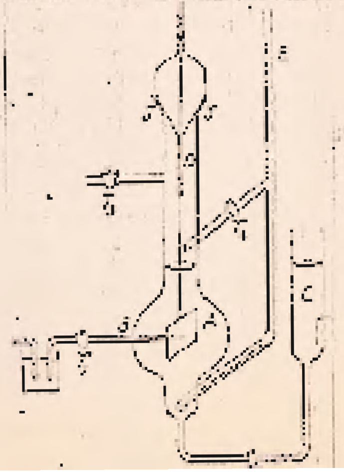


Fig. 4- The electrolytic cell.

solution, all taps were closed and the nitrogen supply connected directly to the tube E. On opening T_2 the solution could be stirred by blowing through it a stream of gas, and by opening T_3 and T_4 a stream of nitrogen could be passed through the gas space in the anode compartment. The electrodes were prepared by cleaning in strong nitric acid, followed by heating to a high temperature. Before use the cell was cleaned with chromic acid and washed with distilled water.

Solutions of sodium and ammonium azides were used as electrolytes. Commercial sodium azide was purified by dissolving in distilled water and precipitating with alcohol, the precipitate being dried and finally recrystallised from distilled water. Ammonium azide was prepared from barium azide solution by double decomposition with excess of ammonium sulphate. After filtering off the precipitated barium sulphate, the filtrate was treated with alcohol, when ammonium azide was precipitated. The precipitate was then dried in a desiccator under reduced pressure.

The water used in making up the solutions was distilled twice, the final product having a conductivity of between 10^{-6} and 10^{-10} reciprocal ohms per c.c. Before use the solutions were saturated with nitrogen, purified from oxygen by passing over heated copper.

The electrical circuit was similar to that used by Bowden and Rideal.[33] Potentials were measured on a

Cambridge potentiometer used in conjunction with a Compton electrometer as a null instrument. The current, supplied by a high tension battery and controlled by a series of grid leak resistances, was determined from the potential drop across a standard resistance in series with the cell.

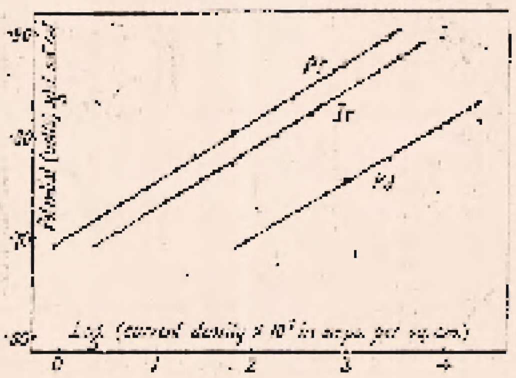
ph of Azide Solutions.- Owing to the catalytic decomposition of an azide solution by platinised platinum, a reversible hydrogen electrode cannot be used for measuring the ph of such a solution, and a glass electrode filled with Normal hydrochloric acid saturated with quinhydrone was used by Stout in its stead. Calibration was carried out against a hydrogen electrode in a series of buffer solutions. In this way the ph of N/10 sodium azide was found to be 9·4, and of N/10 ammonium azide 7·2, both of which are of the order expected in view of the fact that hydrazoic acid is a weak acid with a dissociation constant of 2·8 X 10^{-5}.

RESULTS

Electrolysis of sodium azide solutions at-

(a) Platinum anodes.--N/10 solutions of sodium azide were electrolysed at room temperature over a range of current densities, and the potential of the platinum anode measured against a saturated calomel cell. The relation between potential and the logarithm of the current density was found to be linear over the range from 10^{-7} to 10^{-4} amp. per apparent sq. cm., and as the potentials were unaffected by stirring the solution with nitrogen gas, it appears that the electrode reaction is irreversible and exhibits the characteristics of "activation overpotential."[34] In Fig. 5 is shown a typical V-log i curve. the slope, b, being 58 millivolts corresponding to a value of 0.98 for the factor α ($= \frac{2.3RT}{bF}$). Actually the slope was found to vary between 57 and 60 millivolts according to the particular electrode used, and so α may be slightly greater than 1.0. The V-log i curves were extremely reproducible, the difference between consecutive runs on the same anode rarely being greater than two or three millivolts. Consecutive runs on different anodes showed variations up to about 15 millivolts at the same current density. At currents below 10^{-4} amp. per sq. cm. the potential fell steeply to more negative values, probably owing to the presence of oxidisable impurities in the solution.

Fig. 5.



(b) Palladium and Iridium Anodes.- A palladium electrode substituted for the platinum electrode gave a similar V--log i curve, but in this case the slope was 54 mv. corresponding to $\alpha = 1{\cdot}1$. At a given potential, however, the current density was about 100 times greater than on platinum. With an iridium electrode, the slope of the V-log i curve was 60 mv., equivalent to a value of α rather less than 1·0. The current density, however, was then only 2 or 3 times as great as on platinum. V--log curves of i are shown in Fig 5 for these metals.

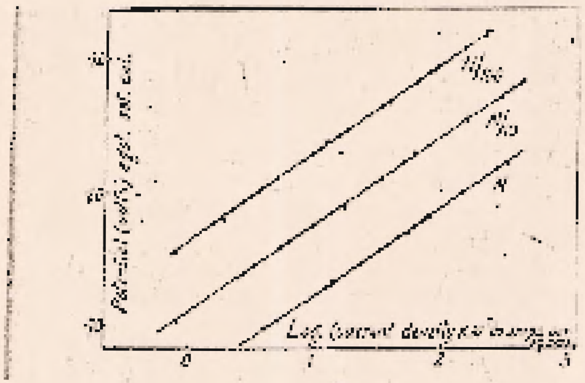
Effect of Varying ph.- The electrolysis of solutions of sodium azide in aqueous hydrazoic acid has been investigated by Reisenfeld and Muller, who found no change in the rate of deposition at constant potential over the ph range of 2 to 6. In order to extend this range to the alkaline side of neutrality, a series of solutions of various ph values was made up from mixtures of sodium azide and sodium hydroxide, and V-log i curves determined in the usual way. These curves were then compared with the V-log i curves obtained for solutions of sodium hydroxide only, of similar ph, the ph value in each case being measured with the glass electrode. Between ph 13·7 and 10·4 the two sets of V-log i curves, for the same platinum electrode were identical and analysis of the evolved gases showed these to be oxygen in each case. The V-log i curve for sodium hydroxide of ph 9·4, however, was found to lie above the corresponding curve for N/10 sodium azide solution which also has a ph of 9·4 i.e. the current at a given potential is greater for the latter solution than the former. In the case of the azide solution the gas evolved is, of course, nitrogen and not oxygen. Ammonium azide solution of strength N/10 with a ph of 7·2, gave a V-log i curve practically identical with that for N/10 sodium azide. In Fig. 6 is given a series of V-log i curves covering the ph range 9·4 to 13·7, all the curves being obtained with the same platinum anode.

It appears from the foregoing that, at a given potential, the rate of deposition of the azide ion from solutions tenth normal with respect to this ion, is independent of ph between 7·2 and 9·4 and this, taken in conjunction with Reisenfeld and Muller's work, indicates that the rate of deposition is independent of ph over the range 2 to 9·4. For ph greater than about 10, in solutions tenth normal with respect to the azide ion, the rate of deposition of oxygen is greater than that of the azide ion at the same electrode potential, and consequently oxygen and not nitrogen is evolved at the anode.

Fig. 6.

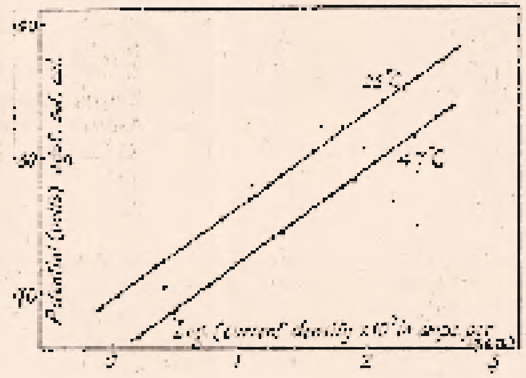
Effect of Varying Azide Ion Concentration.- A series of V-log i curves for sodium azide solutions of strength N, N/10, and N/100, was obtained using the same platinum anode in each case. Typical curves are shown in Fig. 7, from which it will be seen that at a given potential a tenfold increase in azide ion concentration causes a tenfold increase, approximately, in the rate of deposition.

Fig. 7



Effect of Temperature on α.- A series of V-log i curves was determined also by Stout at two different temperatures in order to observe the effect of this variable on azide deposition. The cell was placed in an air thermostat maintained at either 25 degrees C. or 47 degrees C. the actual temperature of the electrode being measured by means of a copper--constantan thermocouple. One junction was enclosed in the thin-walled tube being filled with toluene to ensure good thermal contact. The cold junction was in ice, and the temperature was obtained from readings of a milliboltmeter in series with the thermocouple. It was found that raising the temperature decreased the electrode potential, the current being held constant, but the slope of the V-log i curve appeared to be unchanged. Two representative curves for 25° C. and 47° C. are shown in Fig. 8. Alternate heating and cooling had no appreciable effect on the reproducibility of the curves.

Fig. 8.



The fact that the slope is the same at both temperatures indicates that α increases with temperature, for otherwise the slope would be expected to increase ($b = \frac{2.3\,RT}{\alpha F}$). As the change in α is only of the order of a few percent. for a 20° C. rise in Temperature, it is necessary to test whether it is really significant in the statistical sense, or whether it may be ascribed to experimental error. This may be done by calculating the regression coefficients for the lines of regression of $\frac{2.3\,RT}{F}$ log i on electrode potential at the two temperatures, and then applying Fisher's "t" test for the significance of the difference of the two coefficients.[35] The regression coefficients are equal to the value of α at each temperature, and putting

$$\frac{2{\cdot}3\,RT}{F}\log i = \theta, \text{ gives}$$

$$\alpha_T = \frac{\Sigma\,(V-\bar{V})\ (\theta-\bar{\theta})}{\Sigma\,(V-\bar{V})^2}$$

where $\bar{\theta}$ and $\bar{V}$ are the mean values of θ and V.

The variance, S_T^2, of the regression coefficient is estimated from the equation

$$S_T^2\,.\,n\,\Sigma\,(V-\bar{V})^2 = \Sigma\,(\theta_T-\bar{\theta}_T)^2 - \alpha_T^2\ \Sigma\,(V-\bar{V})^2$$

where $(n+2)$ is the number of pairs of observations, and the variance of the difference between the regression coefficients at the two temperatures is then given by

$$S^2_{T_1,T_2} = \frac{n_1 S^2_{T_1}\,\Sigma(V_1-\bar{V}_1)^2 + n_2 S^2_{T_2}\,\Sigma(V_2-\bar{V}_2)^2}{n_1 - n_2}$$

$$\times\left[\frac{1}{\Sigma(V_1-\bar{V}_1)^2}+\frac{1}{\Sigma(V_2-\bar{V}_2)^2}\right]$$

The required value of "t" may then be calcualted from

$$t = \frac{\alpha_{T_1}-\alpha_{T_2}}{\sqrt{S^2_{T_1,T_2}}}$$

and the probability of this being exceeded purely by chance for two sets of observations differing only through sampling errors may be obtained from tables.[36] The number of degrees of freedom with which the tables are to be entered is simply (n_1+n_2). In Table I are given the details of the calculation of the regression coefficients for temperatures of 25 °C. and 47 °C. and for two different platinum electrodes. For the first electrode with 34 degrees of freedom the value of "t" is 6·13, and for the second electrode with 62 degrees of freedom, t 3·12. Referring to the tables of "t", the 1% level of significance for 34 degrees of freedom is found to be about 2·75, and for 62 degrees of freedom about 2·6. The actual values of "t" obtained thus represent a higher significance level than 1%, and consequently the increase in α with temperature must be regarded as a definite "effect." Taking the mean change in α for both electrodes, it appears that a rise in temperature from 25° C. to 47° C. produces an increase in α of about 8%, giving an estimate for dα/dT over this range of 4×-10^{3} degrees^{-1}.

Table I.- Variation of Regression Coefficient of $2{\cdot}3\frac{RT}{F}$ Log I on Potential With Temperature.

	Electrode I.		Electrode 2.	
Temp. °C.	47	25	47	25
Mean pot. agst. cal. $\bar{V}$ mv.	773·3	808·7	753·7	795·2
Mean $\frac{2{\cdot}3\,RT}{F}\log i = \theta_T$	1·681	1·694	1·658	1·688
$\Sigma(V-\bar{V})^2$	$35{\cdot}67 \times 10^{-3}$	$34{\cdot}26 \times 10^{-3}$	$66{\cdot}83 \times 10^{-3}$	$90{\cdot}90 \times 10^{-3}$
$\Sigma(\theta_T-\bar{\theta}_T)^2$	$37{\cdot}34 \times 10^{-3}$	$28{\cdot}98 \times 10^{-3}$	$74{\cdot}94 \times 10^{-3}$	$92{\cdot}32 \times 10^{-3}$
$\Sigma(V-\bar{V})(\theta_T-\bar{\theta}_T)$	$36{\cdot}48 \times 10^{-3}$	$31{\cdot}48 \times 10^{-3}$	$70{\cdot}69 \times 10^{-3}$	$91{\cdot}37 \times 10^{-3}$
Regression coeff. $\alpha_T = \frac{\Sigma(V-\bar{V})(\theta_T-\bar{\theta}_T)}{\Sigma(V-\bar{V})^2}$	1·023	0·919	1·058	1·005

Table I. cont.

	Electrode I.		Electrode 2.	
No. of pairs of observations	18	18	24	40
$n[\Sigma(V-\bar{V})^2] \cdot S_r^2$	0·10 X 10^{-3}	0·06 X 10^{-3}	0·16 X 10^{-3}	0·53 X 10-
$S^2_{r_1 r_2}$	0·270 X 10^{-3}		0·289 X 10^{-3}	
$t = \frac{\bar{r}_1 - \bar{r}_2}{\sqrt{S^2_{r_1 r_2}}}$	6·13		3·12	
No. of degrees of freedom	34		62	
Value of t. for P = 1%	2·75		2·6 approx.	

The Energy of Activation.- The discharge of an azide ion is a process which must occur in several stages, each stage probably requiring a certain energy of activation. The reaction rate as measured by the current density will, however, be controlled by the slowest stage, and the energy of activation of the reaction as a whole will be that corresponding to this slowest stage. If at temperature T °K. and potential V volts, the energy of activation is E_V cal. per g. mol. then assuming a Maxwellian distribution of energy amongst the reactants it follows that the current density $i_{T,V}$, is given by

$$i_{T,V} = k \, . \, e^{-H_v/RT}$$

where k is a constant for the particular reaction concerned.

Assuming the energy of activation is a function of the electrode potential and that increasing the potential by ΔV volts decreases the energy of activation by $\alpha_T \Delta V . F$, where α_T is a constant at constant temperature, then

$$i_T = k \, . \, e^{(-H_v + \alpha_T \Delta V . F)/RT}$$

and therefore

$$\left[\frac{\partial (\ln i)}{\partial V}\right]_T = \frac{\alpha_T F}{RT}$$

The energy of activation is given by

$$\left[\frac{\partial (\ln i)}{\partial T}\right]_V = \frac{H_v}{RT^2} .$$

and the temperature coefficient of potential by the quantity $\left(\frac{dV}{dT}\right)_i$ and as

$$\frac{d(\ln i)}{dT} = \left[\frac{\partial (\ln i)}{\partial T}\right]_V + \left[\frac{\partial (\ln i)}{\partial V}\right]_T . \left(\frac{dV}{dT}\right)_i$$

at constant i,

$$0 = \left[\frac{\partial (\ln i)}{\partial T}\right]_V + \left[\frac{\partial (\ln i)}{\partial V}\right]_T . \left(\frac{dV}{dT}\right)_i$$

i.e.

$$H_v = - \alpha_T F T \left(\frac{dV}{dT}\right)_i$$

Thus the calcualtion of the energy of activation requires a knowledge of the value of α_T, and the temperature coefficient of potential at constant current.

Temperature Coefficient of Potential.- The temperature coefficient of potential at constant current was determined by Stout[32] from the change in potential of the electrode on alternate heating and cooling of the cell. Heating was carried out in an air thermostat, and cooling effected by placing a jacket of ice round the cell. Temperatures were measured by means of the thermocouple previously described. The cell was heated rapidly over a range of 15° C., then cooled to room temperature and reheated, the whole process being repeated several times until the potential at a given temperature became approximately constant. The potentials and temperatures were read at two-minute intervals, and plotted on temperature vs. time and potentials vs. time graphs as shown in Fig. 9. The peak potentials correspond to the peak temperatures, and comparison of the times at which these were attained shows that there was no appreciable lag between the actual electrode temperatures and the thermocouple temperatures. From the graphs the potentials at 20° C. and 30° C. were read off for each heating and cooling, and the mean potential change for this temperature interval calculated, from which the temperature coefficient of potential was obtained. The value of the latter is, of course, dependent on the current density at which the measurements are carried out, and in Table II. are given the values of dV/dT for three different platinum electrodes in N/10 azide solution, together with an estimate of the variance.

Fig. 9.

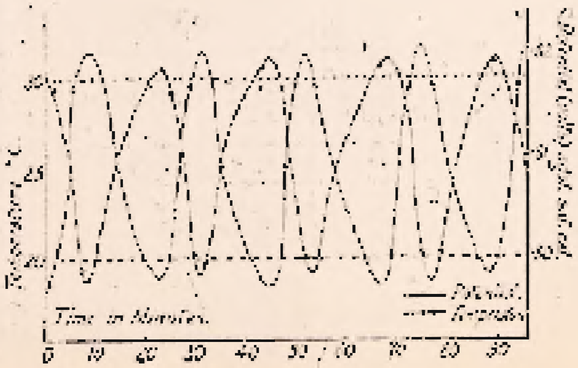


Table II.- Temperature Coefficient of

Potential for Platinum Electrodes in N/10 Sodium Azide Solution

Electrode	Current density amps. /sq. cm.	Degrees of freedom	mean value of dV/dT. mv. per C.	Sum of squares of deviation from mean.
1	$2 \cdot 5 \times 10^{-5}$	12	-176	1644
2	$2 \cdot 0 \times 10^{-5}$	7	-199	110
3	$2 \cdot 0 \times 10^{-5}$	10	-184	356

Mean value of dV/dT = -185 mv. per °C
Mean variance from 29 degrees of freedom = 73 (mv. per °C.)

The mean value of α for these electrodes was found to be 0·95, and so taking the mean temperature as 25° C., and the mean dV/dT as - 185 mv. per degree the energy of activation is 12·0 K.cal. per g. mol. at a potential of 0·51 volt against saturated calomel.

The Steric Factor.- The steric factor for the reaction may be evaluated by substituting in the equation

$$\frac{i}{F} = pn\sqrt{\frac{RT}{2\pi M}}\, e^{-H_1/RT}$$

where F is the Faraday, n the number of g. ions per c.c., M the ionic wt., and p the steric factor. The mean value of p calculated in this way for the three electrodes of Table II is 6·14, referring to platinum in N/10 solution at a potential of 0·81 volt against saturated calomel. This is of the same order as for hydrogen deposition at a cathode, where p varies from about 1 on some platinum electrodes down to 10^{-5} on mercury.

DISCUSSION

The salient points emerging from the foregoing are that the anodic deposition of the azide ion is a reaction showing the characteristics of activation overpotential, giving a linear V-log i curve with α approximately equal to unity. The reaction occurs at measureable rates only at the extremely high overpotential of ca. 4 volts, the reversible potential in N solution being - 3·3 volts against saturated calomel. Increase in temperature causes a small but significant increase in α, and the rate of reaction varies with different electrode metals and with varying concentrations of azide ion.

The kinetics of the reaction are similar in some respects to those for the cathodic deposition of hydrogen, for the latter also gives a linear V-log i curve and the rate of reaction varies with different electrode metals and with varying concentration of hydrogen ion. In other respects the two reactions are rather different, for α in the case of hydrogen deposition ranges between about 0·25 and 2·0 according to the particular electrode and solution used, and there seems to be no evidence to show that it varies with temperature. Moreover hydrogen deposition on platinum takes place at an appreciable rate at the reversible potential.

The overall reaction for hydrogen deposition is

$$H_3O^+ + e^- = H_2O + 1/2\, H_2$$

but this will take place in stages, the slowest of which will determine the rate of reaction. Similarly, for the deposition of the azide ion the overall reaction may be reagrded as

$$N_3^- = N_2 + 1/2\, N_2 + e^-$$

considering the ion to be unhydrated, although this will occur again in stages, the slowist being rate determining.

Many theories have been advanced to describe the slow process in the deposition of hydrogen, but these fall broadly into two classes postulating (a) the neutralization of the ion or (b) the formation of the H-H bond, as the rate determining step.[34, 37] The stage (b) may take place either by the direct desorption of two adsorbed atoms, or by the combination of an adsorbed atom with a hydrogen ion in solution. Analogously, three possible mechanisms for the azide reaction may be postulated :-

followed by	(1) $N_3^- + Me = N_2 + N-Me$	slow
	$2N-Me = N_2 + Me$	rapid
followed by	(2) $N_3^- + Me = N_2 + N-Me$	rapid
	$2N-Me = N_2 + Me$	slow
followed by	(3) $N_3^- + Me = N_2 + N-Me$	rapid
	$N_3^- + N-Me = 2N_2 + Me$	slow

Process (1) has the neutralisation of the ion as the rate determining step, with the desorption of N/atoms taking place relatively rapidly. (2) and (3) both postulate the neutralisation of the ion as occurring rapidly the slow process being the desorption of atoms, which will take place by the faster of the two alternative methods available. In all these processes, however, the neutralisation of the ion is considered to result in the formations of a nitrogen molecule and an adsorbed nitrogen atom, instead of three adsorbed nitrogen atoms, in accordance with the evidence given previously indicating that one nitrogen atom behaves differently from the other two.

Considering first the neutralisation of the ion as the slow process, it appears that in general α will be determined by the ratio of the slopes of two Morse curves, and as Adam[32] has pointed out cannot exceed unity. This process cannot, therefore, be rate determining in the azide case, but must be regarded as occurring rapidly compared with the desorption of atoms.

Although the neutralisation of the ion may occur rapidly, it is likely to be a rather irreversible process, and the reverse reaction at best will only take place at a very slow rate. Consequently, it is probable that the concentration of nitrogen atoms on the electrode surface will approach the saturation value, and under these conditions the simple desorption mechanism (2) would be expected to give a very small value of α, much less than unity. To account for $\alpha = 1$ on this hypothesis would require a surface only partially saturated with nitrogen atoms, the extreme case of a very sparsely covered surface corresponding to $\alpha = 2$. If the surface is only partially saturated, however, then presumably the formation of ions from adsorbed atoms must proceed at a rate comparable with the neutralisation of ions, and this would seem rather unlikely.

The alternative mechanism for desorption, involving combination for an adsorbed atom with an ion, also leads to difficulties over the value of α. The current will be given by

$$i = k[N_3^-][N - N_a]e^{\alpha VF/RT}$$

and if the surface is approaching saturation, $(N - N_a)$

will be approximately constant. The value of α will presumably depend on the relative slopes of the Morse curves for the approach of an N_3^- ion to the electrode, and for the separation of two nitrogen molecules from the electrode, and just as in the case of the ion neutralisation reaction would be expected to be less than unity. Should the surface be only partially saturated, then the (N-Me) would be expected to increase with potential, and $i = k\,[N_3^-]\,e^{VF/RT}\,e^{\alpha_1 VF/RT}$ where the first exponential gives the change in concentration of adsorbed atoms, and the second the change in activation energy. The observed value of α is then $(1 + \alpha_1)$ and should be greater than unity.[37] There seems no reason why α_1 should be extremely small, however, as would have to be the case. It appears, therefore, that neither the neutralisation nor the desorption mechanisms lead satisfactorily to the experimentally observed value of α.

The temperature variation of α is also difficult to account for although a possible explanation may lie in a change in the mobility of the adsorbed layer. Roberts[42] has shown that the heat of adsorption for a mobile layer is less than for an immobile layer, and thus if the mobility of the adsorbed layer of nitrogen atoms increases appreciably with temperature, the heat of adsorption would be expected to decrease. In this event, the slope of the appropriate Morse curve might be changed, and this would lead to a change in the value of α. This situation could, of course, arise in any of the above processed, as they all involve the adsorption of atoms.

OVERVOLTAGE OF AZIDE ION

In the process of discharge the activation of ions and the intensity I of the current is bound to the potential V of the electrody by the dollowing relation:[41]

$$I = K[A^-]_e^{-\frac{W - aF(V_0 + n)}{RT}}\left[1 - e^{-\frac{(a+b)Fn}{RT}}\right] \quad (1)$$

where K is a Kinetic constant. (A-) is the concentration of the ion in solution "W" is the energy of activation of the discharging reaction V is the potential of the electrode,n is the suspension.

a and b are the coefficients of transmission for the Kinetic energy of discharging reaction F,R,T have the usual significance. This theory not only applies to the anodic polarisation of a number of metals such as (Al, Si, Mg, and Ta), but also applies equally well to the overvoltage of azides as well as hydroxyl ions.

The study of the anodic overvoltages of those ions as a function of the intensity of current was made by electrolysis between platine electrodes in solutions of NaN_3 and NaOH in many temperatures, and concentrations with currents ranging from 5.10^{-9} to 10.10^{-3} amperes.

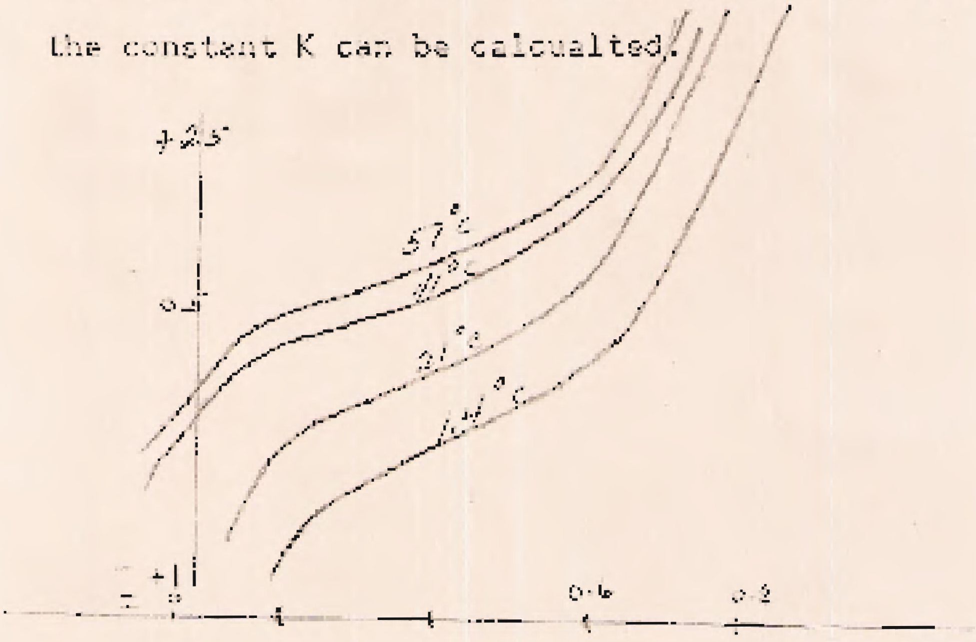
Disregarding the ionization reaction equation (1) can be written as follows:

$$\log I = \log K[A^-] - \frac{0.43W}{RT} + \frac{0.43\alpha F V_0}{RT} + \frac{0.43\alpha F n}{RT}$$

where Log I= f (n). In this equation the absolute potential between metal-liquid is overlooked.

By designating γ the point where the axis of the ordinance is met by curves of NaN_3 in the diagram below, we have.. $\gamma = \log k [A^-] - \frac{0.43 W}{RT} + \frac{0.43 \alpha F V}{RT}$

From this equation, both the energy of activation and the constant K can be calcualted.



OVERVOLTAGE IN VOLTS

The rate of reaction at a given potential varies with the electrode metal and with concentration of solution, but is independent of PH from 2'9.4. At higher Ph, O_2 is preferentially evolved from solutions 8,1N in azide ion. At a given potential a 10-fold increase in N_3 - concentration causes about a 10-fold increase in the rate of deposition. The Kinetics are similar in some respect to those for the cathodic deposition of H_2, which also gives a linear V vs.

log i curve, and a rate of reaction which varies with different electrode metals and with varying concentration of H^+. In other respects the two reactions are rather different.

The potentials were measured as Na azide solution was being electrolyzed at 0.005- 1.60 amp. /sq. cm. without catalyst and with polished Pt electrode. The potential followed the equation.[42]

$$E = a + b \log i$$

where a-1.10
      b-0.59

Addition of KCNS to the electrolysing solution lowers the potential considerably.

Riesenfeld and Muller[43] performed 14 experiments with plain and platinized Pt electrodes and NaN_3 solutions of various concentrations, and with a reversible AgN_3 electrode. With plain platinum electrode against a hydrogen electrode at 0° a potential of 1.211v was found; Platinized Pt gave about 0.06 v. lower. Iridium, pure Nickel and iron electrodes gave values close to plain Pt electrode. The temperature coefficient of the emf with plain Pt electrode, was -0.0017v per degree. The AgN_3 coated Ag anode, with the hydrogen electrode at 21° gave a value of 0.384v., and a temperature coefficient of -0.006v. per degree.

POLAROGRAPHIC STUDY OF THE AZIDE ION

The azide ion behaves in many respects like Cl^-. This can be detected by polarography with a dropping Hg electrode owing to the formation of an insoluble Hg compound.[44] The high volatility and low dissociation constant make it advisable to study neutral solution (0.1 N KNO_3) and to use a separate control electrode Hg - Hg SO_4 - 1N. Na_2SO_4. This experiment was conducted by R. Haul and E. Scholz. They used a relatively large Hg surface: The diameter of the capillary was 0.1 mm., and the drop period 1 second. The potential of the half-step of N_3^- - agreed well with that of Cl^- + 0.20 v., as compared with 0.17V., both in 0.001N solution relative to the calomel electrode. With increasing concentrations it shifted to negative values.

EFFECTS ACCOMPANYING THE ELECTROLYSIS OF THE AZIDE ION

Following the electrolysis of an azide solution, there is an increase in the intensity of rays produced by HN_3 and NaN_3 , on addition of $NH_2OH.HCl$ nitrides, nitrates, and sulfates, and a decrease with the addition of sulfites, hyponitrites, and hydroquinone.[45] The spectrum of the emission between 1900 and 2800A is

constituted of bonds situated at 1990, 2130, 2270, 2425 and 2550A, essentially the same as those obtained on the thermal dissociation of the azides of Na, Ag, Tl and Hg. The intensity of the various bands has been detected by means of a photon counter and compared with a number of molecules decomposed at the anode, giving a value of 10^{-10} to 10^{-11} photons per mol.
Gases such as N_2, H_2, A, N_2O and air were introduced with both the gas phase and liquid phase in the anode-compartment, where an azide solution was electrolyzed and which was separated from the cathode by a porous cup. The intensity of ultraviolet radiation was increased by N_2 and H_2 decreased by O_2, and was not affected by A, N_2O, and air. The intensity increased logarithmically with applied voltage.[46]

The ultraviolet emission accompanying electrolysis of HN_3 and NaN_3, is increased 500-600 times in presence of N_2 or H_2 (bubbled through anodic electrolyte), white A and N_2O are without influence and O_2 inhibits the emission.[47]

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