ELECTROLYSIS OF THE AZIDE ION

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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) $R-N\left\langle\begin{smallmatrix}N\\N\end{smallmatrix}\right.$

(2) $R-N=N$

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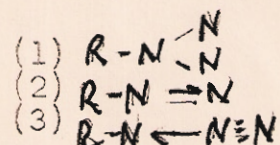
For the azide ion, we have definite proof of an open-chain cectilinear formula from the crystal structures of the salts[3] (Hendricks and Pauling, J. Am. Chem. Soc., 1925, 47,2904). This can be formulated in two ways, since a valency angle of 180 degrees is compatible with either two double links or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

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 (C to 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

$$:N::N:\ddot{N}:^- \longleftrightarrow :\ddot{N}::N::\ddot{N}: \longleftrightarrow :\ddot{N}:N::N:$$
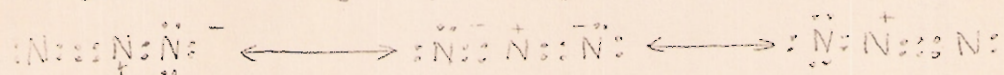
The somewhat larger N to N distance of 1.165A $\pm$ 0.021 in NH_4N_3 (24% triple bond character) is due to the attachment of each terminal N of the N_3^- to its two nearest neighbors by H bonds. The linear structure for N_3^- was also confirmed by the work of A. Potier,[5] by the LCAO method (linear 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-$C_6H_4B_2$ amd p-$C_6H_4NO_2$, isocyanates and distributed diazomethanes containing these groups. The values indicated that the compounds exist either in the ring form — $N\langle^N_N$, 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 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	23.26	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
$p-N_3C_6H_4B_2$	43.72	42.37	0.26
N_3B_2	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 $p-N_3C_6H_4Me$, 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 ultra-violet radiation, which is independent of the cation, and is due to deactivation of the Nitrogen.[6]

By electrolysis of an aqueous solution of NaN_3 with a special arrangement by which a circuit is period-ically 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 $\pm$
$\pm$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 acti-
vation energies for conductance obtained. All the
azide salts obey the equation: $\log K = \log A - \left(\frac{E}{2.303 \, RT}\right)$ (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 deter-
minations. 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	Ekcal/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	-5.99	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
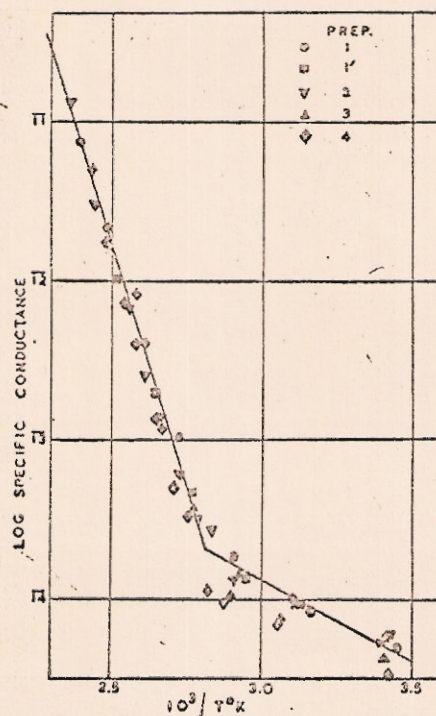cation impurities in KN_3 by co-precipitation were
unsuccessful.[12]

Fig. I. 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 logk 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 $E_1 = E_0$, $E_2 = E_0 + \frac{1}{2}W_0$. $\qquad$ (2)
As a provisional hypothesis, it is assumed that in
this temperature range the alkali azides are predominantly
catonic 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
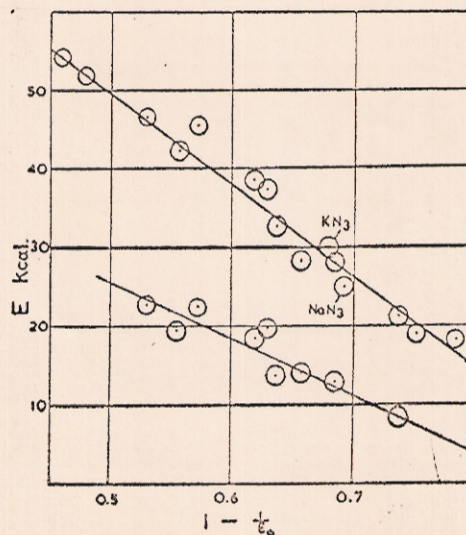dielectric constant, shown in Fig. 2.

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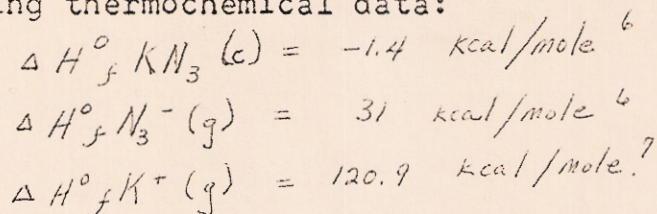conductance against $1-1/\epsilon_0$.

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_0. The points for KN_3 and NaN_3 lie quite definitely on the E_2-line. Unfortunately, we have no knowledge of ϵ_0 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 $W_c = W_L - W_p$ (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:

$$\Delta H^o_f\ KN_3\ (c) = -1.4\ \text{kcal/mole.}\ [6]$$

$$\Delta H^o_f\ N_3^-\ (g) = 31\ \text{kcal/mole}\ [6]$$

$$\Delta H^o_f\ K^+\ (g) = 120.9\ \text{kcal/mole.}\ [7]$$

Using a Born-Haber cycle, we find $W_L = 153$ kcal/mole.
The polarization energy $W\rho$ may be estimated only indirectly.
In general, two methods exist for the calculation of $W\rho$.
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_o. The
polarization energy resulting is

$$W\rho = \left(1 - \frac{1}{\epsilon_o}\right)\frac{e^2}{2R} \tag{4}$$

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 calcualting the dipoles on the neraest 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 estimated indirectly by plotting
the experimental values for the alkali and silver
halides given by $W_L - 2(E_2 - E_1)$ against $(1 - 1/\epsilon_o)$ 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 $W_0 = 19$ 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
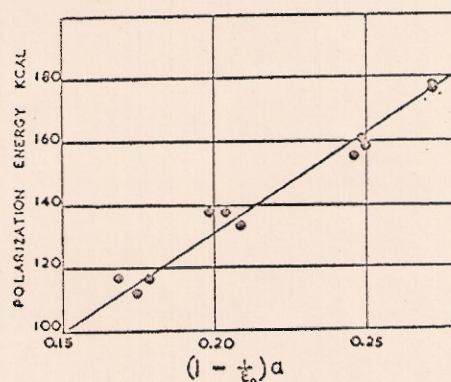Ca, Sr, and Ba azides are also considered to refer to
surface conductance.

Fig. 3. Plot of the polarization energy, calculated
from the lattice energies and activation energies for
conductance, against $(1-1/\epsilon_0)a$.

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 energy 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 than 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

$$N_3^- + 3H = N_2 + NH_3 + e^-.$$
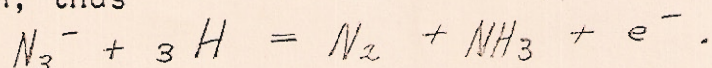
In the prescence of platinum black, sodium azide is hydrolysed to ammonia and nitrogen, the rate of hydrolysis being greatly increased if the platinum surface is saturated with hydrogen.[21] Both these reactions are catalysed by the metal surface, and as only one atom of nitrogen is liberated as ammonia, it seems likely that one nitrogen atom in the ion behaves differently from the other two, and that the ion decomposes thus

$$N_3^- = N_2 + N + e^-$$
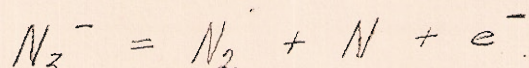
the nitrogen atom being adsorbed on the metal surface. Hydrogen on the surface would then react with the absorbed atom to form ammonia. The rate of reaction would, of course, be controlled by the rate of removal of adsorbed nitrogen atoms. This is in accord with the fact that hydrogen catalyses the exchange 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

$$\tfrac{1}{2}H_2 + \tfrac{3}{2}N_2 + aq. + H^+ aq. \qquad \cdot \qquad \cdot \qquad (5)$$
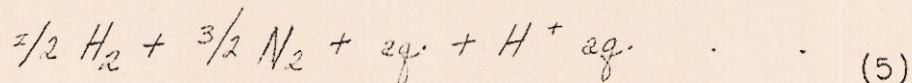
A search of the literature has failed to reveal sufficient data for the exact calculation of ΔF°, but an appro--ximate value may be estimated from the free energy changes in the following reactions:--

$$\tfrac{1}{2}H_2 + \tfrac{3}{2}N_2 = HN_3 (gas). \quad \Delta F^\circ = 78.5 \; K.cal.^{[23]} \quad (6)$$
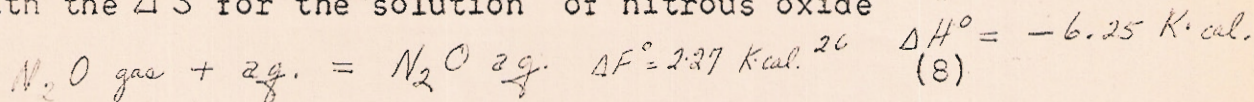
$$HN_3 (gas) + aq. = HN_3 \; aq. \qquad\qquad (7)$$
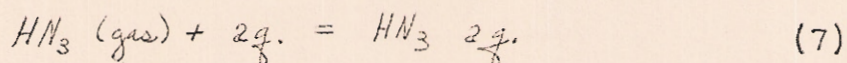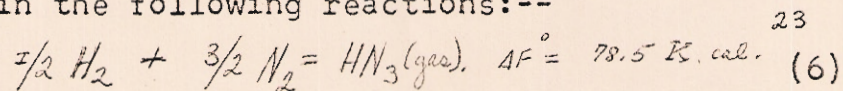
The heat of formation of hydrazoic acid gas is 71.9 K.cal.[24] and of aqueous hydrazoic acid 54.6 K.cal.,[25] which gives ΔH° for reaction (7) as -17.3 K.cal. The corresponding entropy change ΔS° may be estimated roughly by comparison with the ΔS° for the solution of nitrous oxide

$$N_2O \; gas + aq. = N_2O \; aq. \quad \Delta F^\circ = 2.27 \; Kcal.^{[26]} \quad \Delta H^\circ = -6.25 \; K.cal. \quad (8)$$

The ΔS° of this reaction is therefore -28.3 cal. per degree. As nitrous oxide has a linear structure corresponding[27] to resonance between $N = \overset{+}{N} = O$ and $N \equiv \overset{+}{N} - O \; \circledast$, 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.

$$HN_3 \; aq. \rightleftharpoons H^+ aq. + N_3^- \; aq. \qquad \cdot \qquad (9)$$
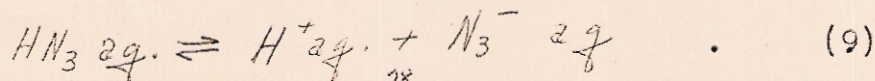
The dissociation constant[28] of hydrazoic acid is 2.8×10^{-5}, (and as hydrazoic acid gas contains the linear group -NNN corresponding to resonance between $-N = \overset{+}{N} = N$ and $-N - N \equiv N$)

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[29]
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

$$N_2 \mid N_3^- \text{ aq.} \parallel H^+ \text{ aq.} \mid H_2$$

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^c is 58·4 K.cal.[25], ΔF^o is 76·3 K.cal., and so $\Delta S^o = -60$ cal. per degree. Taking absolute entropy[30] of H_2 as 29·7 of N_2 as 45·9, and of $H+$[31] 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

$$\frac{S_{ROT}}{Nk} = \ln \frac{4\pi^2 I k T}{h^2} + I$$

becomes $S_{rot} = 12\cdot2$ cal. per degree per g. mol. at 298° degree K. The translational entropy is given by

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

and so $S_{TRANS} = 32\cdot6$ 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, $\nu_1 = 1350$, $\nu_2 \sim 630$, and $\nu_3 \sim 2080$, the entropy of vibration given by

$$\frac{S_{TRANS}}{Nk} = \ln \frac{(2\pi M k T)^{3/2}}{h^3} \cdot \frac{kT}{P} + \frac{5}{2}$$

becomes $S_{VIB} = 0\cdot32$ 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,
separated 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.
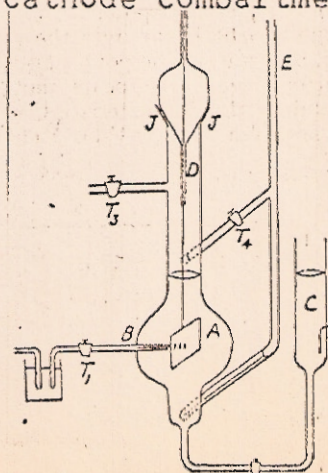
solution, all taps were closed and the nitrogen supply connected directly to the tube E. On opening T_3 the solution could be stirred by blowing through it a stream of gas, and by opening T_3 and T_4 a stream of nitrogen could be passed through the gas space in the anode compartment. The electrodes were 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 $2\text{-}8 \times 10^{-5}$.

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
$(= \frac{2.3RT}{\beta F})$.   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^{-7} 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.
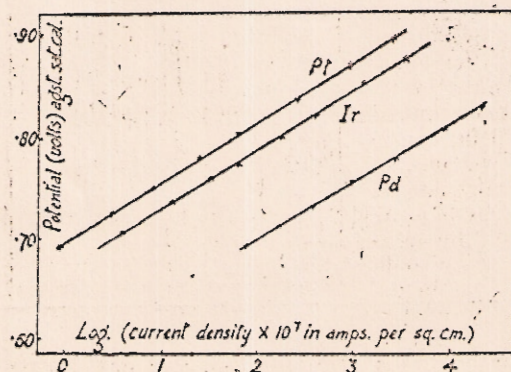
(b) Palladium and Iridium Anodes.- A palladium electrode substituted for the platinum electrode gave a similar V--log i curve, but in this case the slope was 54 mv. corresponding to $\alpha = 1.1$. At a given potential, however, the current density was about 100 times greater than on platinum. With an 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 shoen 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 wach 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 con-
sequently oxygen and not nitrogen is evolved at the anode.

Fig. 6.
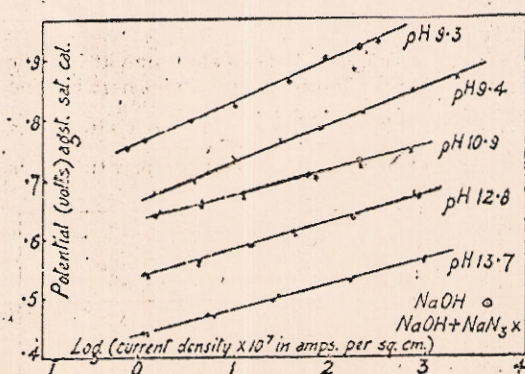
Effect of Varying Azide Ion Concentration.- A series
of V-log i curves for sodium azide solutions of strength
N, N/10, and N/100, was obtained using the same platinum
anode in each case. Typical curves are shown in Fig.
7, from which it will be seen that at a given potential
a tenfold increase in azide ion concentration causes a
tenfold increase, approximately, in the rate of deposition.

Fig. 7
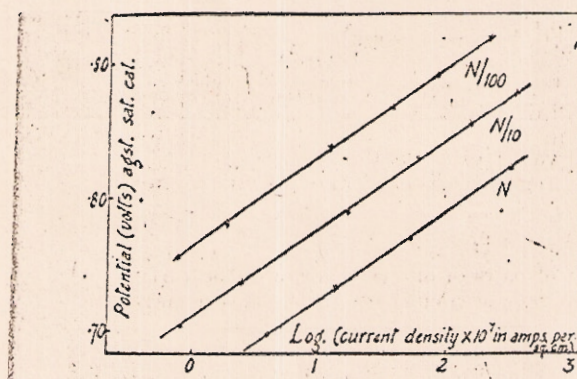
Effect of Temperature on x.- A series of V-log
i curves was determined also by Stout at two different
temperatures in order to observe the effect of this
variable on azide deposition. The cell was placed in
an air thermostat maintained at either 25 degrees C.
or 47 degrees C. the actual temperature of the electrode
being measured by means of a copper--constantan ther-
mocouple. 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.
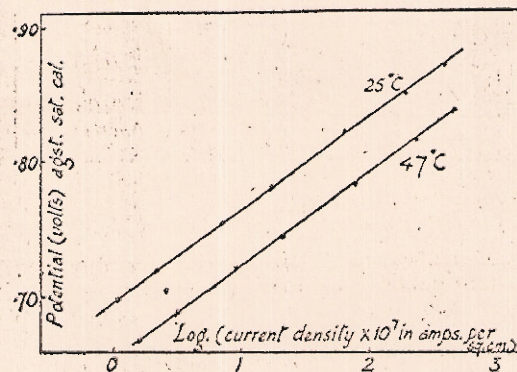
The fact that the slope is the same at both temp-
eratures indicates that α increases with temperature, for
otherwise the slope would be expected to increase
$(b = \frac{2 \cdot 3\ RT}{\alpha F})$. As the change in α is only of the order
of a few percent. for a 20° C. rise in Temperature,
it is necessary 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 $\frac{2 \cdot 3\ RT}{F}$ log i on electrode potential at the
two temperatures, and then applying Fisher's "t"
test for the significance of the difference of the

35

two coefficients. 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

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

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

$$S_{T_1, T_2}^2 = \frac{n_1 S_{T_1}^2 \, \Sigma (V_1 - \bar{V}_1)^2 + n_2 S_{T_2}^2 \, \Sigma (V_2 - \bar{V}_2)^2}{n_1 + n_2}$$
$$\times \left[\frac{1}{\Sigma (V_1 - \bar{V}_1)^2} + \frac{1}{\Sigma (V_2 - \bar{V}_2)^2} \right]$$

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

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

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 I% 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 I%, 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 dx/dT over this range of

4×-10^{3} degrees^{-1}.

Table I.- Variation of Regression Coefficient of

$2 \cdot 3 \cdot \frac{RT}{F}$ 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 $\frac{2 \cdot 3\, RT}{F} \log \cdot i = \theta_T$	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. $\alpha_T = \dfrac{\Sigma(V-\bar{V})(\theta_T-\bar{\theta}_T)}{\Sigma(V-\bar{V})^2}$	1·023	0·919	1·058	1·005

Table I. cont.

	Electrode I.		Electrode 2.	
No. of pairs of observations	18	18	24	40
$n\left[\Sigma(v-\bar{v})^2\right].S_T^2$	0.10×10^{-3}	0.06×10^{-3}	0.16×10^{-3}	0.53×10^{-3}
$S^2_{T_1,T_2}$	0.270×10^{-3}		0.289×10^{-3}	
$t = \dfrac{\alpha_{T_1}-\alpha_{T_2}}{\sqrt{S^2_{T_1,T_2}}}$	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 H_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

$$i_{T,V} = k \cdot e^{-H_V/RT}$$

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 $\alpha_T \Delta V \cdot F$, where α_T is a constant at constant temperature, then

$$i_T = k \cdot e^{(-H_V + \alpha_T \Delta V \cdot F)/RT}$$

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

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

at constant i,

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

i.e.

$$H_V = -\alpha_T FT \left(\frac{dV}{dT} \right)_i$$

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
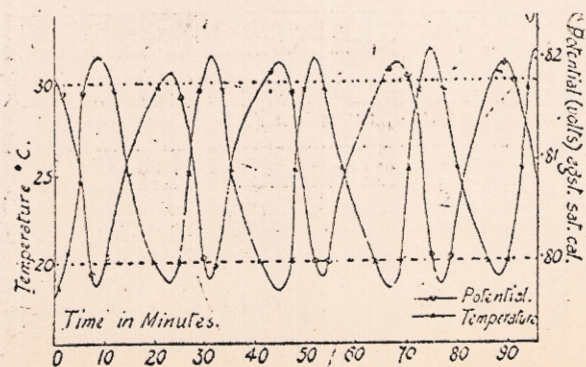with an estimate of the variance.

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	2.5×10^{-5}	12	-176	1644
2	2.0×10^{-5}	7	-199	110
3	2.0×10^{-5}	10	-184	356

Mean value of dV/dT = -185 mv. per $^{\circ}$C

Mean variance from 29 degrees of freedom = 73 (mv. per $^{\circ}$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 0.81 volt against saturated calomel.

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

$$\frac{i}{F} = p n \sqrt{\frac{RT}{2 \pi M}} e^{-H_v/RT}$$

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 0.14, 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
I on some platinum electrodes down to 10^{-5} on mercury.

DISCUSSION

The salient points emerging from the foregoing
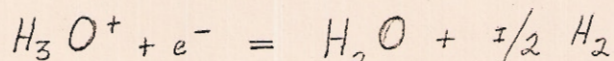are that the anodic deposition of the azide ion is a
reaction showing the characteristics of activation
overpotential, giving a linear V-log i curve with α
approximately equal to unity. The reaction occurs at
measureable rates only at the extremely high overpotential
of ca. 4 volts, the reversible potential in N solution
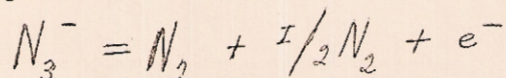being - 3 3 volts against saturated calomel. Increase

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
$$H_3 O^+ + e^- = H_2 O + {}^1/_2 H_2$$
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
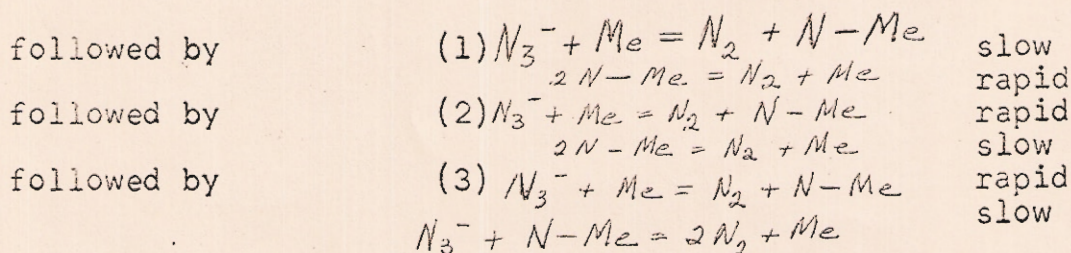will occur again in stages, the slowist being rate
determining.

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 $\quad$ (1) $N_3^- + Me = N_2 + N-Me$ $\quad$ slow
$\qquad\qquad\qquad\quad 2N-Me = N_2 + Me$ $\quad$ rapid

followed by $\quad$ (2) $N_3^- + Me = N_2 + N-Me$ $\quad$ rapid
$\qquad\qquad\qquad\quad 2N-Me = N_2 + Me$ $\quad$ slow

followed by $\quad$ (3) $N_3^- + Me = N_2 + N-Me$ $\quad$ rapid
$\qquad N_3^- + N-Me = 2N_2 + Me$ $\quad$ 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[38] 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

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

and if the surface is approaching saturation, $(N\!-\!Me)$

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 neutral-
isation 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.[39] 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[40] has shown that the heat of adsorption for a
mobille 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

$$I = k\,[A^-]_e - \frac{W - aF(V_o + n)}{RT}\left[1 - e^{-\frac{(a+b)F_n}{RT}}\right] \quad (1)$$

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:

$$Log\,I = log\,k\,[A^-] - \frac{0.43W}{RT} + \frac{0.43\alpha F V_o}{RT} + \frac{0.43\alpha F_n}{RT}$$

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

By designating $\int$ the point where the axis of the ordinance is met by curves of NaN_3 in the diagram below, we have..

$$y = \log k [A^-] - \frac{0.43 W}{RT} + \frac{0.43 \alpha F V_0}{RT}$$

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

+2.5

57° c
41° c
0.5
21° c
1.4° c

+1
0
0.6   0.3

OVERVOLTAGE IN VOLTS
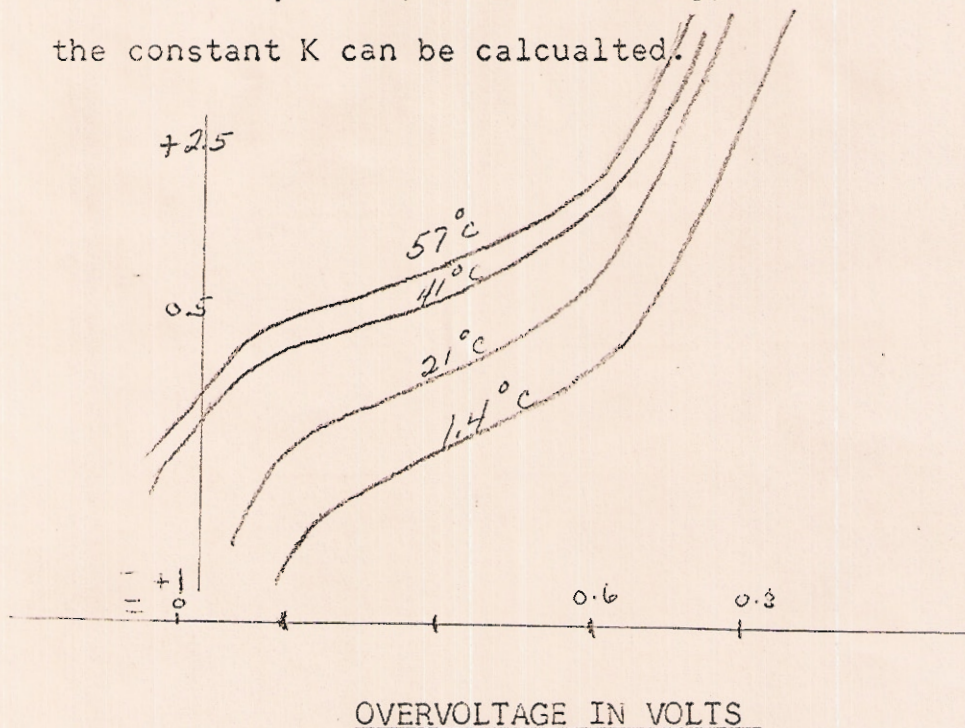
The rate of reaction at a given potential varies with the electrode metal and with concentration of solution, but is independent of PH from 2 to 9.4. At higher Ph, O_2 is preferentially evolved from solutions 0,1N in azide ion. At a given potential a 10-fold increase in N_3 - concentration causes about 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]

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

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. Tridium, 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 bonds 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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