

1024. *Glow-discharge Electrolysis. Part IV.¹ The Formation of Hydrazine in Liquid Ammonia.*

By A. HICKLING and G. R. NEWNS.

The glow-discharge electrolysis of electrolyte solutions in liquid ammonia has been investigated over a wide range of conditions. The main product in solution is hydrazine in amount dependent upon the quantity of electricity passed. The yield initially when the glow-discharge electrode is an anode is 2.5 moles/faraday, but it decreases somewhat as hydrazine accumulates in the solution and a stationary concentration of about 2M is ultimately reached; the hydrazine yield is substantially independent of most other experimental variables. It is considered that the reactions are initiated by positively charged gaseous ions which are accelerated in the cathode fall near the liquid surface. On entering the liquid phase these are involved in both charge- and energy-transfer reactions producing NH_2 radicals. The proportions of the products formed are then considered to depend upon the competition of the various possible reactions of these radicals, and on this basis a quantitative interpretation of the results is possible.

In the previous parts of this series¹ the glow-discharge electrolysis of a variety of aqueous electrolytes has been investigated. It has been shown that, with the anode in the vapour phase, current is carried to the liquid surface by gaseous ions.² These are accelerated in the cathode fall of approximately 415 v which occurs within 0.05 cm. of the water surface, and they enter the solution with energies which the experimental results suggest are of the order of 100 ev. Thus in addition to bringing about oxidation by charge transfer, they may also cause dissociation of water molecules, and the process is analogous to the action of an ionising radiation where the energies of the bombarding particles are relatively small but where the dose rate can be extremely high. The experimental results agree with a scheme whereby 7—8 equivalents of OH radical are formed for each faraday of electricity passed, and the proportions of the products formed depend upon the competition of the various possible reactions of these radicals.

The present investigation was undertaken to extend the work to a non-aqueous solvent, and liquid ammonia was selected as providing a convenient system of considerable intrinsic interest. Preliminary work showed³ that the main product formed was hydrazine, and its production has been comprehensively studied and the mechanism of the process investigated.

EXPERIMENTAL

The cell used is shown in Fig. 1. It consisted of a large Pyrex test tube topped by a B34 socket. This connected it to a head through which anode and cathode were introduced by B14 joints, and which led through a spiral reflux condenser to a vacuum system containing a float manostat so that the pressure in the apparatus could be maintained constant over long periods. The anode was a platinum wire and the cathode was a small sheet of platinum foil, and they were so arranged that with a given volume of solution in the cell the cathode was completely immersed and the anode was a predetermined distance above the liquid surface. To maintain a constant temperature the cell was surrounded by a vacuum flask containing a suitable coolant, usually solid carbon dioxide in alcohol, and this was also used in the reflux condenser above the cell.

Current was supplied by a Leland rectifier unit of adjustable voltage (0—1500 v) through a suitable ballast resistance (5000—9000 Ω), a calibrated milliammeter, and a gas coulometer. The discharge was initiated by a pulse from an induction coil; once started it required about

¹ Parts I—III, Davies and Hickling, *J.*, 1952, 3595; Hickling and Linacre, *J.*, 1954, 711; Denaro and Hickling, *J. Electrochem. Soc.*, 1958, **105**, 265.

² Dewhurst, Flagg, and Watson, *J. Electrochem. Soc.*, 1959, **106**, 366.

³ Hickling and Newns, *Proc. Chem. Soc.*, 1959, 368.

600 v and the current could be maintained steady at any desired value between 0.01 and 0.1 A. Various electrolytes have been used in this work; that most commonly employed was 0.01M-ammonium nitrate, and it was made by adding the appropriate volume of liquid ammonia to a weighed quantity of the "AnalaR" salt. Liquid ammonia was usually used direct from the cylinder; in some experiments it was purified by distillation from sodium and introduced into the cell without exposure to air, but the results were not appreciably different from those obtained with the commercial product which contains a little water. The standard experimental conditions employed except where otherwise stated were: electrolyte, 20 ml. of 0.01M-solution of ammonium nitrate in liquid ammonia, exposing a surface of 9 sq. cm.; anode to surface distance, 0.5 cm.; pressure, 100 mm. mercury; temperature of the electrolyte, *ca.* -75° ; current, 0.025 A; voltage drop across the discharge, *ca.* 600 v.

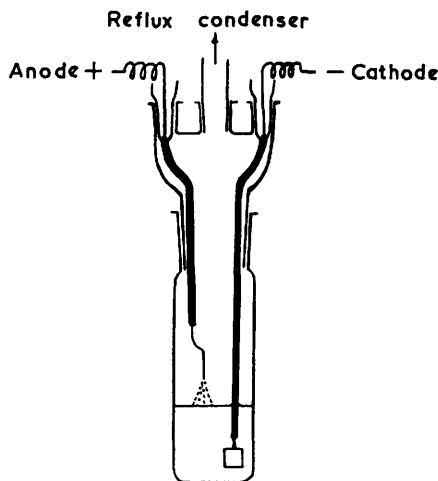


FIG. 1. Electrolytic cell.

The usual experimental procedure was to pass known quantities of electricity under different conditions and subsequently to analyse the solution and to express the yields of products in moles/faraday; the quantity of electricity passed was accurately measured by a hydrogen-oxygen voltameter of the Lingane type. Preliminary investigation³ showed that the main product in the liquid phase was hydrazine. This was identified by its reducing properties, precipitation as sulphate, reaction with salicylaldehyde, colour reaction with *p*-dimethylaminobenzaldehyde, and isolation by fractional distillation as a liquid of m. p. $1.0-1.5^{\circ}$, with vapour pressure of 10.5 mm. at 20° and n_D^{22} 1.4609. Other conceivable products such as azides, nitrites, hydroxylamine, and hydrogen peroxide (in the presence of water) were tested for but were not

normally found. The conditions for separation and exact estimation of the hydrazine were carefully worked out. It was found desirable to distil out the bulk of the ammonia slowly from the sample to be analysed, and to acidify the residue with sulphuric acid while a little ammonia remained. The resulting solution was diluted to a known volume and the hydrazine present estimated either volumetrically by the indirect iodate method, or colorimetrically with a Spekker absorptiometer and the *p*-dimethylaminobenzaldehyde reagent. Good agreement was given by the two methods.

RESULTS

Physical Features of the Discharge.—The discharge was a sharply defined yellow cone with the apex at the anode tip and the base in the liquid surface. Its physical characteristics were explored with the anode at various distances up to 1 cm. from the solution surface, with the pressure varied in the range 70 to 230 mm., and with currents of 0.006 to 0.1 A. The overall voltage between the anode and the solution increased linearly with rise of pressure and increase of anode distance, and it fell slightly with rise of current for electrode-solution distances greater than about 0.3 cm.; for smaller separations the negative voltage-current characteristic became positive. Over the whole range of conditions the total voltage across the discharge varied between a minimum of 470 and a maximum of 750 v. The potential distribution within the discharge was investigated by using a thin wire probe and valve voltmeter, and it was found that there was a potential difference of 390 v across a distance of 0.06 cm. from the liquid surface. In contrast to the total voltage, this cathode fall was largely independent of experimental variables such as current, electrode distance, and gas pressure, and it compares with a value of 415 v found for a similar cathode fall when aqueous solutions are used.¹

The area of the luminous spot in the liquid surface was also measured over a range of conditions. It increased with increasing anode distance and with decrease in gas pressure; it also increased with increasing current in such a way that the current density (c.d.) fell slightly. The latter is a parameter of importance since the concentration of any reactive species formed

in the reaction zone is likely to depend upon it. Under the standard experimental conditions the area of the glow spot was 0.13 sq. cm. and the c.d. in it was 0.19 A/sq. cm. It is noteworthy that over the whole range of conditions explored, the variation of c.d. was relatively small; its minimum value was 0.13 and its maximum value 0.38 A/sq. cm.

Chemical Effects of the Discharge.—Influence of general factors. (a) Quantity of electricity. The graph of yield of hydrazine in moles against quantity of electricity passed in faradays for a series of electrolyses under the standard conditions for various times has been previously shown.¹ The initial yield was approximately 2.5 moles of hydrazine/faraday of electricity passed, and this fell slightly as hydrazine accumulated in the electrolyte. It seems clear that two processes are occurring: initial formation of hydrazine in amount proportional to the quantity of electricity passed, and decomposition of hydrazine dependent upon its concentration in the solution. It is convenient for this reason to distinguish between the instantaneous or differential yield of hydrazine, as given by a tangent to the formation curve, and the integrated yield for the passage of a definite quantity of electricity; thus the differential yield at the beginning of electrolysis gives the rate of formation of hydrazine in moles/faraday before the decomposition reaction has any effect.

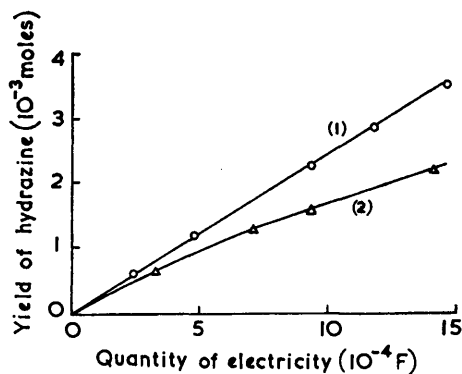


FIG. 2. Influence of current and quantity of electricity on yield of hydrazine.

(1) 0.025A; (2) 0.1A.

(b) Current. In Fig. 2 are shown the hydrazine yield curves for two series of experiments carried out at currents of 0.025 and 0.1 A, respectively. The initial differential yields are not very different, but for a definite quantity of electricity the integrated yield is less at the higher current. This is contrary to what might be expected if the hydrazine yield depended upon the electric power dissipated in the discharge since this is about four times that at the lower current. Since it has been found that the c.d. in the glow spot falls with increase in current, it appears that the hydrazine yield is favoured by a high c.d.

(c) Stirring. In the normal arrangement of the cell hydrogen gas was evolved at the immersed cathode and produced considerable stirring in the solution near the glow spot. To

TABLE 1.
Effect of stirring.

Duration of electrolysis (min.)	Quantity of electricity ($10^{-4}F$)	Yield of hydrazine (10^{-3} mole)	
		Unstirred	Stirred
15	2.33	0.55	0.61
30	4.65	1.23	1.21
60	9.30	2.38	2.27
120	18.6	4.27	4.32
240	37.2	7.25	8.0

ascertain whether this was beneficial the effect was tried of surrounding the cathode by a sheet of polyvinyl chloride which directed the gas to the side of the cell. Some of the results are listed in Table 1. Stirring has little effect upon the initial production of hydrazine, but increases it slightly as the hydrazine concentration increases.

Influence of factors affecting the discharge. (a) Electrode distance. Table 2 lists the yields of hydrazine obtained in experiments in which the distance of the anode from the liquid surface was varied from 0 to 1.1 cm.; each electrolysis was carried out under otherwise standard

conditions for 60 min. so that 9.3×10^{-4} F of electricity was passed. Except at small separations where the physical characteristics of the discharge change, the yield is almost independent of the anode-liquid separation.

(b) Pressure. Experiments were carried out under the above conditions, but with the standard distance of 0.5 cm. and with different pressures; the results are summarised in Table 3.

TABLE 2.

Effect of electrode distance.

Anode-surface distance (cm.)	1.1	0.5	0.3	0.2	0.15	0
Yield of hydrazine (10^{-3} mole) ...	2.27	2.27	2.05	1.94	1.80	1.58

TABLE 3.

Effect of pressure.

Pressure (mm.)	70	85	100	148	175
Yield of hydrazine (10^{-3} mole)	2.13	2.19	2.27	2.15	2.20

The yield is practically independent of gas pressure.

Influence of factors affecting the solution. (a) Temperature. Variation of temperature is limited by the freezing point of the solution on the one hand and by the boiling of the ammonia on the other. Under the usual conditions a solid carbon dioxide cooling bath at -78.5° was used and during an hour's electrolysis the temperature of the electrolyte rose to -75° . By raising the working pressure to 150 mm. it was possible to electrolyse with a chloroform-containing bath at -63.5° , the temperature of the electrolyte rising during the experiment to -59° . The yields obtained in the two experiments were 2.25 and 2.37×10^{-3} mole of hydrazine, respectively. Thus a rise of temperature of about 15° brings about a small increase in the hydrazine yield.

(b) Nature of electrolyte and its concentration. It is not easy to find suitable inert electrolytes which are reasonably soluble in liquid ammonia, but Table 4 summarises the results obtained with various salts at different concentrations in 60 min. electrolyses under otherwise standard conditions. It is clear that the formation of hydrazine is not critically dependent

TABLE 4.

Influence of electrolyte.

Electrolyte (M)	Yield of hydrazine (10^{-3} mole)	Electrolyte (M)	Yield of hydrazine (10^{-3} mole)
NH_4NO_3	0.005	$\text{CH}_3\text{-CO}_2\text{NH}_4$...	0.01
	0.01	KNO_3	0.01
	0.025	NH_4SCN	0.1
	0.05	$\text{NH}_4\text{NO}_3\text{-KNO}_3$	0.01-0.09
	0.075	$\text{NH}_4\text{NO}_3\text{-KNO}_3$	0.01-Satd.
	0.1		
	2.39		2.31
	2.27		2.07
	2.09		1.60
	1.95		1.82
	1.69		1.45
	1.59		

upon the nature or concentration of the electrolyte, but in general the highest yields are obtained in very dilute solution. Potassium nitrate seems less favourable than ammonium salts, and this may be connected with the formation of an electron solution at the cathode which exerts a scavenging action on radical precursors of the hydrazine.

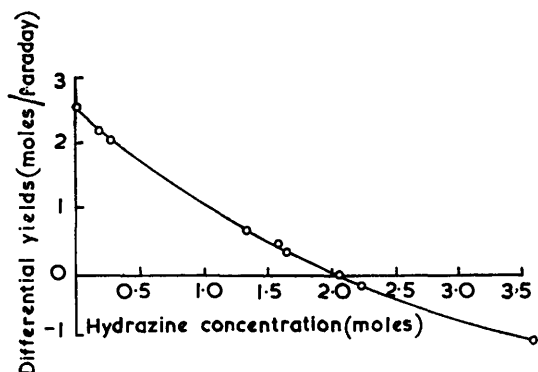
(c) Poisons and catalysts. The effect of coating the cell walls with paraffin wax was investigated, and also in different experiments the cathode was platinised and poisoned by electrodepositing arsenic on it. None of these treatments affected the yield of hydrazine appreciably, indicating that it is not produced by a wall reaction and that the cathode is not involved in its production or decomposition.

The Stationary Concentration of Hydrazine.—The graph showing the variation of yield of hydrazine with quantity of electricity passed (Fig. 2) indicates that the differential yield decreases as the hydrazine accumulates in the electrolyte. To explore this further, experiments were carried out with solutions to which known amounts of pure hydrazine had been added; these were electrolysed for short times and the change in the amount of hydrazine with quantity of electricity passed was measured. The results are shown in Fig. 3 by plotting $d(\text{N}_2\text{H}_4)/dF$ against average hydrazine concentration. The graph is a shallow curve which cuts

the axis at a hydrazine concentration of 2.04M, and this is the limiting stationary concentration which can be reached by glow-discharge electrolysis. Check experiments showed that this value was independent of the volume of the electrolyte and the gas pressure; it was raised slightly by increase of temperature.

Analysis of Gaseous Products and the Material Balance.—In order to examine the gaseous products formed, the apparatus was modified by decreasing the dead space and connecting the cell through a cold trap to a Sprengel pump and a gas-measuring and -sampling system. A considerable volume of gas was obtained which on analysis was found to contain only nitrogen and hydrogen, the latter being in excess of the amount to be expected from the complete dissociation of ammonia. On subtracting the volume of hydrogen corresponding to the hydrazine formed in the solution, the ratio $H_2:N_2$ in the remaining gas was found to be 3.06 which indicates that a satisfactory material balance of nitrogen, hydrogen, and hydrazine exists. The volume of the gas obtained suggested that about 3 molecules of ammonia decompose into nitrogen and hydrogen for each molecule decomposing to give hydrazine under

FIG. 3. Influence of hydrazine concentration on differential yield.



the particular conditions adopted. However, the decomposition of ammonia into nitrogen and hydrogen appeared to arise mainly from the electric discharge in the gas phase since similar amounts could be produced by passing a discharge between two metal electrodes in the ammonia vapour. No hydrazine could be detected under these conditions, however, indicating that the hydrazine arises exclusively in the present work by reaction in the liquid phase.

Glow-discharge Electrolysis with Alternating Current.—By supplying high voltage a.c. to the electrolytic cell it was possible to carry out glow-discharge electrolysis with alternating current; in these circumstances much heat is dissipated at the metal electrode in the gas phase, and the thin wire normally used had to be replaced by a massive platinum electrode. Except at low currents, where some rectification took place, the discharge struck in each half cycle so that the electrode in the gas phase was alternately anodic and cathodic. Hydrazine formation occurred in the liquid in the usual way, but the initial yield was only 1.32 moles/faraday. This is only slightly greater than half the normal yield and it suggests that the major portion of the hydrazine is formed when the gas phase electrode is anodic and the solution surface cathodic. This was confirmed by carrying out a d.c. glow-discharge electrolysis with the gas-phase electrode as a cathode; hydrazine was formed but in relatively small amount. This result is to be expected since it is only when the liquid surface is cathodic that a considerable fall of potential occurs at its surface.

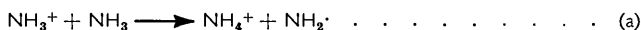
Conventional Electrolysis of Liquid Ammonia Solutions.—In the conventional electrolysis of liquid ammonia solutions with immersed electrodes it might be expected that NH_2^- ions would discharge at the anode and that hydrazine might be formed to some extent, and this has in fact been claimed.⁴ To clarify the position, electrolyses have been carried out with platinum, nickel, gold, and carbon anodes in ammonium nitrate solutions in liquid ammonia of various concentrations from 0.01 to 1.0M, and with a saturated solution of potassium amide, with c.d.'s varying from 0.05 to 1.0 A/sq. cm. In no case was hydrazine detected in the solution, and it seems that it does not arise in conventional electrolysis at all.

⁴ Gessler and Pleskov, *J. Phys. Chem. U.S.S.R.*, 1950, **24**, 445.

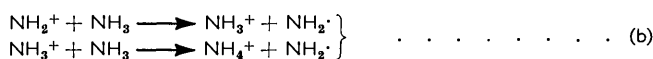
DISCUSSION

The experimental results indicate clearly that the hydrazine is produced in the liquid and that the yield is closely related to the quantity of electricity passed; it is largely independent of other variables and in particular of the electric power dissipated in the discharge in the gaseous phase. The results are closely analogous to what has been observed¹ with aqueous systems and they agree with the view that the reaction is brought about by positive gaseous ions accelerated in the cathode fall and driven into the liquid. These might be expected to bring about reaction both by charge- and energy-transfer and since the yield of hydrazine is much greater than 1 equivalent/faraday it is apparent that the latter process is of importance.

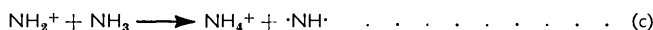
Mass-spectrometer experiments suggest⁵ that the main species present in ionised ammonia at low pressures are NH_3^+ and NH_2^+ . The former reacts with ammonia to yield amino-radicals⁶



while the latter may react to give either amino-radicals

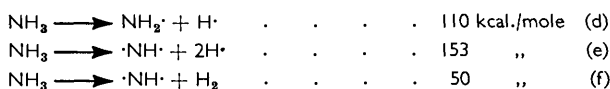


or imino-radicals



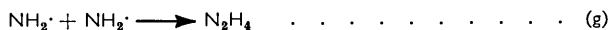
Reaction (c) is energetically favourable but it involves considerable bond rearrangement, so that (b) is the most likely fate of NH_2^+ entering the liquid.

The energies of the gaseous ions on entering the liquid are not accurately known. The upper limit would be 390 ev if they passed through the cathode fall without undergoing retarding collisions. If it were possible to calculate the mean free path of the ions under the experimental conditions a precise estimate could probably be made⁷ although experimental measurements⁸ in gas discharges have suggested that the energies are probably greater than those expected for acceleration through one mean free path. The cathode fall in the present case is only slightly less than that in aqueous systems where an average energy of about 100 ev seems to fit the experimental results and thus it may be tentatively assumed that in the ammonia system the energies of the gaseous ions are of this order of magnitude. This is amply sufficient to bring about dissociation of ammonia molecules, either homolytically or *via* ionisation, since the energies required are



Reaction (f) is the most favourable reaction energetically, but it seems doubtful whether the formation of the hydrogen molecule could occur readily on spatial grounds; and, if this is so, (d) would be the preferred reaction.

Thus it seems likely that both charge-transfer and energy-transfer reactions will give amino-radicals as primary products, although the formation of imino-radicals cannot be completely excluded. Hydrazine might then be expected to arise by a dimerisation process



although the recombination reaction



⁵ Mann, Hustrulid, and Tate, *Phys. Rev.*, 1940, **58**, 346.

⁶ Dorfman and Noble, *J. Phys. Chem.*, 1959, **63**, 980.

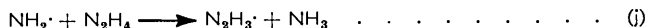
⁷ Compton and Morse, *Phys. Rev.*, 1927, **30**, 305.

⁸ Choudrhi and Oliphant, *Proc. Roy. Soc.*, 1933, *A*, **87**, 662.

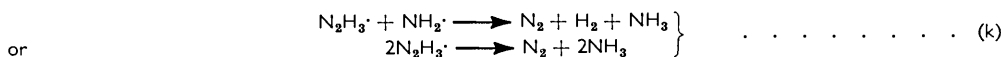
will be a possible competitor. Hydrogen atoms may also be removed by combination to give molecules



The glow-discharge results suggest that hydrazine when it builds up to a sufficient concentration is decomposed by the very species which leads to its formation, and in photochemical and gas-discharge studies the reaction



has often been postulated. This may then be followed by further decomposition such as



Thus the primary reactions in glow-discharge electrolysis of liquid ammonia are probably (a), (b), and (d) leading to NH_2 radicals as the precursors of the hydrazine subsequently formed. In this connection it is noteworthy that in some experiments on the glow-discharge electrolysis of liquid ammonia containing benzoic acid as a solute aminobenzoic acids could be detected among the products and the *o*-, *m*-, and *p*-aminobenzoic acid were separately recognisable by paper chromatography. After the primary act the immediate interaction of the active products is probably largely governed by spatial considerations, but once these species have diffused sufficiently far apart it seems likely that the reactions may be treated as homogeneous chemical reactions and that it is their competition which determines the yield of ultimate products obtained. Therefore it is proposed that the yield of NH_2 radicals/faraday remains constant throughout the electrolysis in the standard case, and that it is the velocity of the secondary reactions (g), (h), and (j) that governs the variation of the differential yield with hydrazine concentration. Thus if n equivalents of $\text{NH}_2\cdot$ are formed per faraday, and if v_1 , v_2 , and v_3 are the velocities of reactions (h), (g), and (j) in the stationary state, then the differential hydrazine yield, G , in moles/faraday * at any time in the electrolysis will be given by

$$G = \frac{n}{2} \frac{(v_2 - v_3)}{v_1 + v_2 + v_3} \quad (1)$$

If the velocities are expressed in terms of the concentrations of the reacting species this becomes

$$G = \frac{n}{2} \frac{k_2[\text{NH}_2]^2 - k_3[\text{NH}_2][\text{N}_2\text{H}_4]}{k_1[\text{H}][\text{NH}_2] + k_2[\text{NH}_2]^2 + k_3[\text{NH}_2][\text{N}_2\text{H}_4]}, \quad (2)$$

which simplifies to

$$G = \frac{n}{2} \frac{\frac{k_2}{k_3} [\text{NH}_2] - [\text{N}_2\text{H}_4]}{\frac{k_1}{k_3} [\text{H}] + \frac{k_2}{k_3} [\text{NH}_2] + [\text{N}_2\text{H}_4]} \quad (3)$$

If it is assumed as an approximation that under a given set of experimental conditions the stationary concentrations of NH_2 radicals and hydrogen atoms are substantially constant, this may be written

$$G = \frac{n}{2} \frac{A - [\text{N}_2\text{H}_4]}{A + B + [\text{N}_2\text{H}_4]} \quad (4)$$

where $A = k_2[\text{NH}_2]/k_3$ and $B = k_1[\text{H}]/k_3$. This equation indicates that at the start of

* G , as used here, is not the same as that employed in radiation chemistry where the yield is expressed in molecules/100 ev. If, however, the average energy of the positively charged gaseous ions initiating the reactions were 100 ev it would be identical.

electrolysis the differential yield will be given by $G_0 = nA/2(A + B)$. It will decrease as the hydrazine concentration increases and becomes zero when $[N_2H_4] = A$. Furthermore, if $[N_2H_3]$ exceeds A initially, then on glow-discharge electrolysis G will be negative and the concentration of hydrazine will decrease until the stationary concentration is reached. This is qualitatively what is found in practice.

The various parameters may be elucidated from the experimental results as follows. A is found directly from the stationary concentration of hydrazine. B and n may be calculated by taking experimental values of G at different hydrazine concentrations and setting up a system of simultaneous equations. When this was done for the standard case, A was found to be 2.04 and the average values of n and B were 12.5 and 2.96, respectively. Thus the differential yield should be approximately given by

$$G = 6.25 \frac{2 - N_2H_4}{5 + N_2H_4} \quad (5)$$

This relation has been tested by calculating G for different hydrazine concentrations and in Table 5 these calculated values are compared with those found experimentally.

TABLE 5.

Experimental and calculated hydrazine yields.

$[N_2H_4]$ (M)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
G , expt.	2.19	1.88	1.61	1.35	1.09	0.85	0.62	0.41	0.22	0.04	-0.14
G , calcd.	2.21	1.90	1.61	1.34	1.08	0.85	0.63	0.42	0.22	0.04	-0.14

The agreement is very good, and while not too much importance should be attached to this since the method of calculating the parameters automatically ensures that certain experimental and calculated figures coincide, it does indicate that the form of the equation is correct. Equation (4) can be integrated to give the concentration of hydrazine which will exist after the passage of a quantity of electricity, Q faradays, starting with no hydrazine initially present. The integrated equation is

$$\frac{nQ}{2V} = (2A + B) \log_e \frac{A}{A - [N_2H_4]} - [N_2H_4] \quad (6)$$

where V is the volume of the solution; and this equation also fits the experimental results satisfactorily.

The quantitative treatment given above, although it seems fairly successful, is certainly oversimplified. Thus in the conventional radiation chemistry of liquids it seems clear that the initial juxtaposition of radicals causes a proportion of them to combine regardless of competing reactions, and it is probable therefore that in the present case there is a molecular yield of hydrazine arising from the primary act which forms part of the total yield. Furthermore, local concentrations in the reaction zone are not necessarily the same as in the bulk liquid. In a more sophisticated treatment some allowance for these factors would have to be attempted, but as a first, rather crude approximation the present treatment seems adequate.

The influence of the main factors—quantity of electricity and hydrazine concentration—on the hydrazine yield can thus be reasonably interpreted on the mechanism proposed. Some light on the influence of secondary factors can be shed by considering the likely effect of c.d. in the reaction zone. It seems likely that the stationary radical and atom concentrations will be proportional to c.d. and, if this is so, the parameters A and B will be proportional also. It is then clear that the initial differential hydrazine yield, $G_0 = nA/2(A + B)$, will be independent of c.d., but the yield at a definite hydrazine

concentration (equation 4) will be higher the greater the c.d. This is qualitatively in agreement with what has been found for the variation of current; however, c.d. increases with rise of gas pressure but the effect on the hydrazine yield is slight.

The glow-discharge electrolysis of liquid ammonia has many features similar to those observed in aqueous systems.¹ Thus the product hydrazine is analogous to hydrogen peroxide which is formed in aqueous solutions when no oxidisable substrate is present, and the cathode fall of 390 v is similar to that of 415 v observed with water and occurs over practically the same distance. Moreover, the main phenomena can be accounted for by similar reaction schemes. The average n value for ammonia of 12.5 is, however, substantially higher than that of 7.7 for water, although in view of the smaller dissociation energy of the H-NH₂ bond than of the H-OH bond a change in this direction is to be expected.

There is usually a striking parallelism between the results of glow-discharge electrolysis and the effect of ionising radiations, and in fact the gaseous ions postulated in the present work should be analogous in their action to a very intense beam of very low-energy α -particles. Until recently, little work had been reported on the radiolysis of liquid ammonia, but Dorfman⁹ has now shown that electron radiolysis leads to substantial conversion into hydrazine, and Collinson, Cleaver, and Dainton¹⁰ have made a very thorough and comprehensive study of the effect of X- and γ -radiolysis. They have shown that considerable hydrazine is produced and subsequently undergoes decomposition as its concentration increases in the liquid, and by using radical scavengers they have established that the NH₂ radical is involved in both processes. Thus as regards qualitative results and mechanism there is a striking measure of agreement between the two systems, but when the yield per unit of energy is considered the glow-discharge electrolysis appears to be a more efficient process for hydrazine production. Thus, if all the NH₂ radicals form hydrazine in the radiolysis the maximum yield appears to be about 1 mole per 100 ev, while the actual yield in glow-discharge can be as high as 2.5. The difference probably originates in the very different dose rates employed. In the radiolysis work the dose rate was of the order 5×10^{18} ev l.⁻¹ sec.⁻¹. In the glow-discharge the dose rate is about 2×10^{19} ev l.⁻¹ sec.⁻¹ and this is confined to a minute volume of solution immediately below the glow spot; the gaseous ions are unlikely to penetrate very far into the liquid and the volume might well be of the order of 10^{-5} ml., which would correspond to a dose rate per l. of about 10^{27} ev sec.⁻¹.

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DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
THE UNIVERSITY, LIVERPOOL.

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⁹ Dorfman, A 1021, 17th International Congress for Pure and Applied Chemistry, 1960.

¹⁰ Cleaver, Collinson, and Dainton, *Trans. Faraday Soc.*, 1960, **56**, 1640.