



UNITED STATES
NUCLEAR REGULATORY COMMISSION

WASHINGTON, D. C. 20555

August 22, 1985

Docket Nos: 50-424
and 50-425

APPLICANT: Georgia Power Company

FACILITY: Vogtle, Units 1 and 2

SUBJECT: SUMMARY OF MEETING HELD JULY 31, 1985 ON TOXIC GAS EVALUATION
OF CHEMICALS

The staff met with the applicant and its representatives on July 31, 1985, to discuss Open Item 4, "Toxic gas evaluation of chemicals." The participants are listed in Enclosure 1.

The applicant described the location of its control building air intakes, the toxic gas (chlorine, hydrazine, and ammonia) stored onsite, and the intervening buildings. The intakes are located on Level 3 of the control building on either side of the northern end of the building. The closest chlorine is located approximately 615 feet southeast of the control building while the closest hydrazine is situated approximately 450 feet to the northeast. Drawings used by the applicant in its introductory presentation are included as Enclosure 2.

The applicant proceeded to describe a new analysis of the chlorine dispersion taking credit for the fact that chlorine is more than two times heavier than air and for the height differential between the ground and the intakes. In performing its calculation, the applicant used the Gaussian model of NUREG-0570. The applicant performed a similar analysis for hydrazine. Hydrazine is approximately 10% heavier than air. Both analyses showed that concentrations of gas at the outside air intakes would be essentially negligible. A similar calculation was not necessary for ammonia since both the applicant's and staff's earlier calculations indicated that it would not be a problem for the control room.

The staff indicated to the applicant that its analysis as presented did not appropriately account for wake effects from intervening buildings which may cause additional chlorine rise to the intakes than accounted for by the applicant or point source releases at ground level associated with neutral or unstable atmospheric diffusion conditions which could diffuse the chlorine gas up to the intakes. Consequently, the staff directed the applicant to perform two types of analyses for the two chemicals* as stated below.

*In a subsequent phone call on August 6, 1985, the staff told the applicant that a calculation for hydrazine was no longer necessary because the revised staff calculations indicated that it would not be a problem for the control room. Earlier staff calculations inadvertently included the assumption that part of the aqueous hydrazine would flash into vapor upon tank rupture. This is not possible since the boiling point of aqueous hydrazine is higher than ambient temperature.

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A PDR

- (1) Flat plain analysis -- assume a flat plain point source release with worst case stability and windspeed combinations which diffuses the chlorine to the intakes.
- (2) Building wake model -- assume stable low windspeed conditions taking into account the wake effects of intervening structures such as the containment building.

A telecon was established for 11:00 a.m. August 6, 1985, to discuss in detail the applicant's methodology for these calculations.

The staff and applicant also explored modeling differences for the hydrazine calculation. The applicant took credit for the structure surrounding the hydrazine container which would restrict its flow and therefore lower any release. The applicant also provided the staff with information regarding the evaporation of an aqueous solution of hydrazine. The excerpt in Enclosure 3 was provided by the applicant.

The staff and applicant also discussed infiltration and mixing in the control building. This information would prove helpful if the applicant's calculation showed that chlorine levels at the outside air intakes would be dangerous to the control room. The applicant has assumed 100% mixing in the spaces adjacent to the control room. Flow rates for the control building HVAC are shown in Enclosure 4. The applicant stated that the pressure in these spaces is less than a positive 1/16 inch water gauge and therefore it expects exfiltration from these areas. The staff indicated that wind effects can overcome this pressure and that pathways to the outside should be identified. The staff will follow up on this item depending on the outcome of the applicant's analysis and staff review.

The remaining portion of the open item concerning emergency procedures for the control room operator may not need to be addressed depending on the applicant's analysis results. The staff will follow-up as necessary.

Melanie A. Miller, Project Manager
Licensing Branch No. 4
Division of Licensing

Enclosures:
As stated

DESIGNATED ORIGINAL
Certified By Angela Henry

Mr. Donald Foster
Georgia Power Company

Vogtle Electric Generating Plant

cc:

Mr. L. T. Gucwa
Chief Nuclear Engineer
Georgia Power Company
P.O. Box 4545
Atlanta, Georgia 30302

Resident Inspector
Nuclear Regulatory Commission
P. O. Box 572
Waynesboro, Georgia 30830

Mr. Ruble A. Thomas
Vice President - Licensing
Vogtle Project
Georgia Power Company/
Southern Company Services, Inc.
P.O. Box 2625
Birmingham, Alabama 35202

Deppish Kirkland, III, Counsel
Office of the Consumers' Utility
Council
Suite 225
32 Peachtree Street, N.W.
Atlanta, Georgia 30303

Mr. R. E. Conway
Senior Vice President - Nuclear
Power
Georgia Power Company
P.O. Box 4545
Atlanta, Georgia 30302

James E. Joiner
Troutman, Sanders, Lockerman,
& Ashmore
Candler Building
127 Peachtree Street, N.E.
Atlanta, Georgia 30303

Mr. J. A. Bailey
Project Licensing Manager
Southern Company Services, Inc.
P.O. Box 2625
Birmingham, Alabama 35202

Douglas C. Teper
Georgians Against Nuclear Energy
1253 Lenox Circle
Atlanta, Georgia 30306

Ernest L. Blake, Jr.
Bruce W. Churchill, Esq.
Shaw, Pittman, Potts and Trowbridge
1800 M Street, N.W.
Washington, D. C. 20036

Laurie Fowler, Esq.
218 Flora Avenue, N.W.
Atlanta, Georgia 30307

Mr. G. Bockhold, Jr.
Vogtle Plant Manager
Georgia Power Company
Route 2, Box 299-A
Waynesboro, Georgia 30830

Tim Johnson
Executive Director
Educational Campaign for
a Prosperous Georgia
175 Trinity Avenue, S.W.
Atlanta, Georgia 30303

Regional Administrator, Region II
U.S. Nuclear Regulatory Commission
101 Marietta Street, N.W., Suite 2900
Atlanta, Georgia 30323

PARTICIPANTS

NRC

M. Miller
T. Quay
K. Campe
K. Dempsey
A. Brauner
I. Spicker
J. Fairbent
W. LeFave

Bechtel

S. Cereghino
T. Luke
T. Mark
A. Cinar
Y. J. Lin

Southern Company Services

J. Bailey
R. Thomas
K. Kopecky
O. Batum

Georgia Power Company

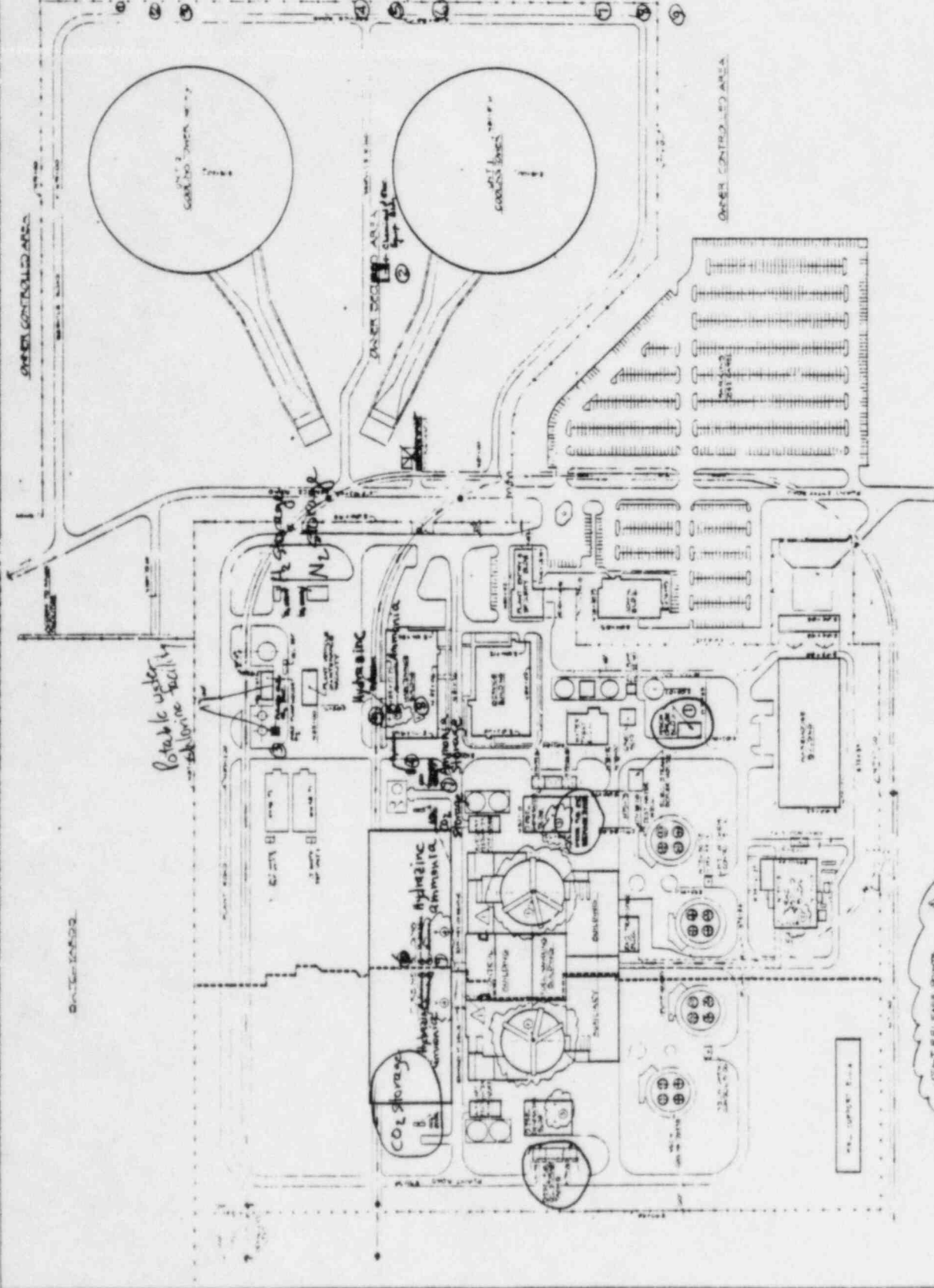
D. Hudson

Artemisia

1	12789 gal herb - 385'
2	250 gal herb - 740'
2	250 gal herbs - 195'
2	300 m ² herb - 155'

BECHTEL
LOS ANGELES

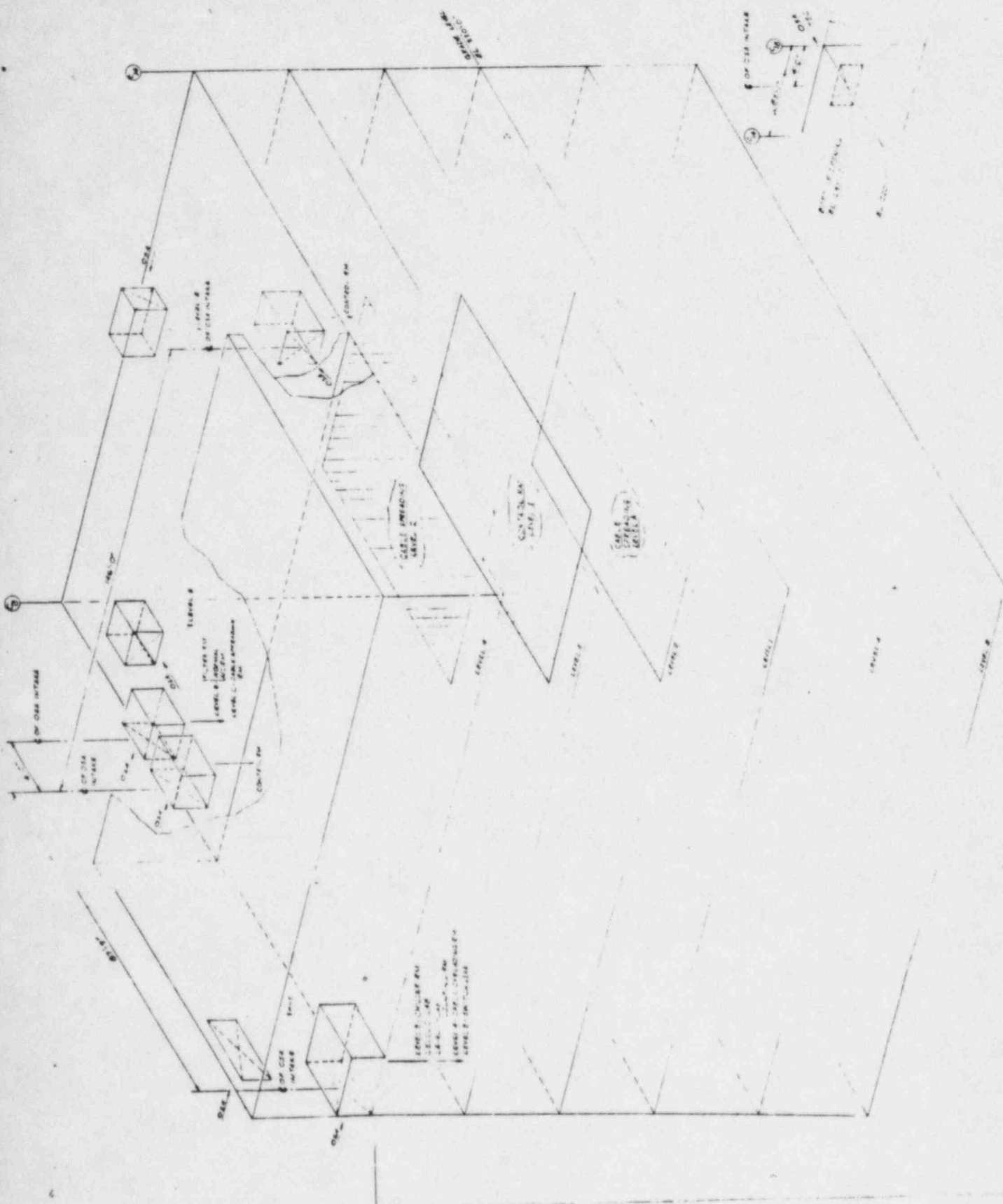
GEORGIA POWER COMPANY
ELVIN W. VOGTLE NUCLEAR PLANT



PRINT RE-EACH MONTH Δ

① JANUARY 1987 \$1.45
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Date		Time		Location		Weather		Wind		Sea		Visibility		Temperature		Humidity		Pressure		Remarks	
Day	Month	Hour	Minute	Lat	Long	Clouds	Temp	Dir	Force	Height	Direction	Force	Distance	Air	Sea	Bar	Rel	Bar	Rel	Remarks	
1	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
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5	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
6	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
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8	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
9	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
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11	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
12	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
13	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
14	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
15	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
16	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
17	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
18	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	
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20	1	12	00	10° 00' N	105° 00' E	100	28.0	000	0	10	000	0	10	28.0	0	1010	80	1010	80	Clear	



CONSTRUCTION
 DETAILS

THE Chemistry of Hydrazine

L. F. AUDRIETH

*Professor of Chemistry
University of Illinois*

BETTY ACKERSON OGC

*Research Associate
University of Illinois*

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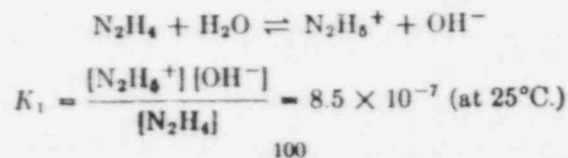
Properties of Aqueous Solutions of Hydrazine

Solutions of hydrazine in water are available commercially in several concentrations containing 40, 85, and 100 per cent hydrazine hydrate, respectively. Although it is doubtful if hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) as such exists in aqueous solution or as a pure liquid compound, this convention has long been used to specify the strength of solutions of hydrazine containing less than 50 mole per cent hydrazine. Hydrazine hydrate in the indicated concentrations is useful directly for a variety of chemical reactions, such as those involved in the synthesis of azides by reaction with nitrous acid and nitrites, and for solvolytic reactions in which the ester group or an active halogen in an organic compound is replaced by the hydrazide radical:



GENERAL CHEMICAL PROPERTIES

Solutions of hydrazine in water are basic. Reaction between hydrazine and water is represented by the following equilibrium for which the dissociation constant of hydrazine as a base has been calculated:¹



Hydrazine is a weaker base than ammonia, which might be anticipated from the fact that hydrazine may be regarded as an ammonia derivative in which one of the hydrogen atoms has been replaced by the more negative NH_2 group. The second ionization constant for hydrazine in aqueous solution has a value of about 10^{-16} . In aqueous solution hydrazine resembles ammonia, however, more than it does the organic diamines. It is primarily a monobasic base, although a goodly number of salts containing two moles of HX per mole of hydrazine have been prepared. These, however, are stable only in the solid state. Many salts of hydrazine have been isolated and characterized and will be discussed in more detail in Chapter 8.

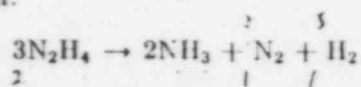
Related to this tendency on the part of hydrazine to coordinate the hydrogen ion to form the corresponding onium ion, $\text{N}_2\text{H}_4 \cdot \text{H}^+$, is its ability to act as an electron pair donor in the formation of metallic ion complexes. In forming such hydrazinates it behaves very largely as a bidentate molecule. Most of the coordination compounds contain only half as many molecules of hydrazine as required for the coordination number of the metallic ion. Many hydrazinates have been isolated and characterized and are discussed in Chapter 9.

One of the very characteristic reactions of hydrazine in aqueous solution is its ability to act as a reducing agent. Aqueous solutions of hydrazine have been employed to effect reduction of various metallic ions to the metallic state, as for instance in the case of copper, silver, gold, and the platinum metals. Hydrazine also brings about the reduction of strong oxidizing agents such as permanganate, iodate, hypiodite, iodine, cerate, and the like. Many of these reactions have been used for the quantitative determination of hydrazine, but only under very special conditions. Oxidation of hydrazine does not always proceed directly to nitrogen but may give a variety of products, including nitrogen as well as ammonia and, in some instances, hydrazoic acid. Formation of hydrazoic acid takes place most readily in strongly acid solutions containing the hydrazonium ion when such oxidizing agents as hydrogen peroxide and peroxydisulfate are employed.

Aqueous solutions of hydrazine undergo autoxidation quite rapidly to yield some hydrogen peroxide as an initial product of the reaction. Dilute solutions of hydrazine, therefore, undergo rapid deterioration on contact with the atmosphere. This fact

must be kept in mind when aqueous solutions of hydrazine are employed in synthetic reactions and when hydrazine is to be determined quantitatively as a base by titration with standard acid. Deterioration can be prevented only by keeping such solutions under an atmosphere of nitrogen. The oxidation of hydrazine is an intriguing subject and is discussed in some detail in Chapter 6.

Reference has already been made to the fact that the anhydrous base is a thermodynamically unstable compound. Hydrazine tends to undergo decomposition even in aqueous solution, especially in the presence of catalytically active metals. The exact nature of the products obtained is dependent upon the pH of the solution. Dilute solutions of hydrazine in water decompose in accordance with the equation:



As the hydroxyl ion concentration is increased, more and more nitrogen and hydrogen are obtained in proportion to the quantity of ammonia. At a high pH, the catalytic decomposition of hydrazine in dilute aqueous solution approaches complete decomposition into nitrogen and hydrogen as the limiting reaction. This subject is also taken up in Chapter 6.

The instability of aqueous solutions of hydrazine has developed into a problem of some importance. Not only must care be taken to avoid contact with the atmosphere because of reaction with oxygen and absorption of carbon dioxide, but many other impurities also cause rapid deterioration. Decomposition is brought about by contact of aqueous solutions of hydrazine with metallic oxides and such metals as copper, iron, and steels. Statements are also recorded in the literature that hydrazine solutions are susceptible to decomposition in glass containers. If, however, the glass (especially Pyrex glass) is carefully cleaned, 85 per cent hydrazine hydrate will undergo no decomposition over periods as long as 6 months.² It is quite probable that such decomposition as may have been noted is due to the fact that care was not taken to insure clean glass surfaces. Since hydrazine attacks rubber, cork, and organic materials in general, such substances must be avoided when hydrazine is subjected to storage.

PHYSIOLOGICAL EFFECTS *

Precautionary measures must be taken in both the manufacture and the use of hydrazine and its salts. Hydrazine vapor attacks the nose and throat upon inhalation. During the early operation of the German Gersthofen plant, it was reported that workmen exposed to the vapors of hydrazine hydrate were likely to suffer from a delayed action on the eyes. No effects were felt for a period of perhaps 10 hours, after which the eyes became inflamed and swollen, and discharged pus. Temporary blindness for about 3 days often followed. Patients usually recovered fully in about a week. Precautions were taken to prevent the escape of the vapor into the air; workers unavoidably exposed were required to wear gas masks identical with those used for ammonia.³ Contact of the liquid hydrazine on the skin has also been found to cause varying conditions of dermatitis, depending upon the individual's sensitivity to the chemical.

Since hydrazine reacts with compounds containing a carbonyl group, it might have been expected to have some action on organisms. Loew⁴ found that seedlings, algae, fission organisms, mollusks, and lower water organisms are destroyed rapidly by a dilute solution of hydrazine sulfate, but Raciborski⁵ claimed that the salts are not invariably poisonous; some fungi actually assimilate them.

Physiologists and biochemists have investigated the toxicity of hydrazine administered internally to animals and have attempted to explain its action. Loew⁴ found that a dose of 0.1 g. of hydrazine sulfate neutralized with sodium carbonate and administered subcutaneously to a guinea pig caused death in 2¼ hours; a dose of 0.5 g. administered to a puppy in a similar manner caused death in 2½ hours. When small doses (0.05 g. per kilo body weight) were injected subcutaneously into dogs, a slight stimulation was produced; in large doses (0.1 g. per kilo) the stage of stimulation was more intense and was followed by depression, ending in coma and death within 2 days. Given by mouth, it produced salivation and sickness. The heart beat was more rapid at first, then slowed gradually and became irregular; body tem-

* The authors desire to express their appreciation to Dr. V. Thomas Austin of the Carle Memorial Clinic, Urbana, Illinois, for his assistance in reviewing the material on the physiological properties of hydrazine.

perature decreased. The respiratory movements were observed to be similar to those caused by asthma.

Hydrazine salts cause hyperglycemia and reduce hepatic glycogen, which is not due to a transference of glycogen to the muscles since here too the glycogen is reduced.⁷ Since the glyoxalase activity of the liver is not markedly altered, however, by the action of the hydrazine, the explanation must lie elsewhere.⁸ The respiratory quotient of hydrazinized dogs indicates that the hyperglycemia and loss of glycogen might be due to an increased combustion of carbohydrate.⁹

The most deep-seated changes occur in the liver, where hyperemia is observed to take place.⁸ According to Wells,¹⁰ the cytoplasm of the liver cells undergoes a profound metamorphosis after the subcutaneous injection of hydrazine into dogs. Hydrazine seems to have little effect on other than the hepatic cells and does not cause any appreciable destruction of red corpuscles; slight hemorrhages are occasionally produced, but much less than by other liver poisons. It attacks only the cytoplasm of the liver, never affecting the nucleus primarily, and causes profound fatty degeneration. In this respect, it resembles phosphorus, but differs in two important particulars. Hydrazine attacks first the cells in the center of the lobules, whereas phosphorus shows its first and most marked effects upon the peripheral cells; second, phosphorus usually causes marked fatty changes throughout the body, whereas the effect of hydrazine is limited largely to the liver. The presence of adrenaline can also still be demonstrated in the adrenals in the case of hydrazine poisoning.

Hydrazine in dogs causes an increase in the blood concentration (anhydremia), which is ascribed to fluid loss and failure of fluid retention. It is probable that concentration of the blood may be a prominent factor contributing to the usual fatal outcome of this intoxication. There is no necessary relationship between the degree of blood concentration and the extent of hyperglycemia, although generally blood concentration is at its maximum when hyperglycemia is most marked. Previous to the decrease in blood sugar content, a transient condition of hyperglycemia prevails without any evidence of kidney lesion or appearance of sugar in the urine.¹¹ After the disappearance of the anhydremia, a slight reduction in the blood cell count may occur,¹² and it has been stated that both oxyhemoglobin and methemoglobin are changed by the hydrazine

in some way.¹³ It has also been noticed, after the administration of hydrazine to dogs, that fat in the blood is markedly increased, the maximum being coincident with the hyperglycemia condition.¹⁴

It is interesting to note that phenylhydrazine causes hemolysis of mature red cells and has been used extensively in the treatment of polycythemia vera; yet this effect is apparently a specific one and is not shared by hydrazine itself.

PHYSICAL PROPERTIES OF THE HYDRAZINE-WATER SYSTEM

Reference was made in Chapter 4 to the fact that hydrazine is an associated liquid. Water is also highly associated. In interpreting the behavior of any but the very dilute solutions of hydrazine in water consideration must be given to the fact that both hydrazine and water are associated liquids and that some reaction between the two components does occur at all concentrations involving (1) limited formation of ionic species that can be only hydrazonium and hydroxyl ions and (2) hydrogen bonding between simple and polymerized molecular species of both hydrazine and water.

Considerable hydrogen bonding does take place in a liquid solution of hydrazine and water as indicated by several outstanding properties of the hydrazine-water system. Hydrazine and water form a constant boiling mixture with a maximum boiling point at 120.5°C. (771 mm. pressure), corresponding to a mixture containing 58.5 mole per cent hydrazine. This indicates that vapor pressures of hydrazine-water mixtures exhibit a negative deviation from Raoult's law and that these vapor pressures, or the partial pressures of each of the constituents, are therefore less than might be calculated from the mole fractions of each. The data given in Tables 1 and 2 represent the only published information on the vapor-liquid equilibria in the binary system at approximately atmospheric pressure. The older data accumulated by Lobry deBruyn and Dito¹⁵ give the boiling points of various mixtures up to 76 mole per cent hydrazine. The more recent information presented by Björkman¹⁶ does not extend beyond 48 mole per cent hydrazine. It is apparent that ordinary fractional distillation of dilute solutions will make impossible concentration of a residual liquor beyond the composition of the constant boiling mixture.

Inspection of the density-composition data also demonstrates that the binary system is far from ideal in its behavior. Maximum densities correspond to mixtures approaching the composition of a monohydrate. The older data by Dito¹⁷ and values determined by Semishin¹⁸ at 0°, 25°, and 50°C. are given in Table 3.

TABLE 1

BOILING POINTS OF THE $N_2H_4-H_2O$ SYSTEM(According to Lobry de Bruyn and Dito¹⁷)

Temperature, °C.	Pressure, mm.	Mole per cent N_2H_4	
		Liquid	Vapor
102.2	9.4	0.18
104.5	755.5	14.2
106.5	755.5	1.6
107.15	755.5	19.5	2.7
109.15	755.5	3.9
111.0	755.5	6.2
114.05	755.5	34.0	13.8
117.05	755.5	41.7	25.0
118.5	768.0	42.9	30.3
119.2	768.0	45.2	34.9
119.5	768.0	50.3	41.7
120.2	770.8	51.8	44.6
120.45	770.8	53.3	48.75
120.15	770.8	54.8	52.8
120.5	770.8	56.0	53.0
120.5	58.5	58.5
120.45	771.1	62.5
120.25	771.1	65.8	72.0
119.9	771.1	68.3	75.5
119.5	771.1	72.7	81.0
119.25	771.1	73.6	83.7
118.8	771.1	76.0

Data for the refractive indexes of hydrazine-water mixtures may also be expected to exhibit some deviation from a linear relationship. Most marked, however, are the deviations from ideal behavior in the viscosities of mixtures of hydrazine and water. Values go through a maximum, and this maximum becomes more pronounced the lower the temperature.¹⁸

Measurement of surface tension¹⁹ of hydrazine-water mixtures at 25°C. reveals the existence of a maximum at a concentration of 30 to 35 mole per cent hydrazine. This is the only exception to

the general observation that physical properties of the binary system show a maximum or minimum value in the region of 50 mole per cent corresponding to $N_2H_4 \cdot H_2O$. The existence of a maximum for a composition containing 33 mole per cent hydrazine might lead to the assumption that a 2-hydrate, $N_2H_4 \cdot 2H_2O$, should form (and indeed, such a compound was assumed to exist

TABLE 2

LIQUID-VAPOR EQUILIBRIA FOR THE $N_2H_4-H_2O$ SYSTEM

(At 760 mm.)

(According to Björkman¹⁸)

Weight per cent N_2H_4		Mole per cent N_2H_4		Temperature, °C.
Liquid	Vapor	Liquid	Vapor	
4.50	0.14	2.6	0.1
18.2	2.45	11.1	1.4	104.9
19.73	2.62	11.9	1.5	106.2
28.5	6.91	18.3	4.0	107.8
38.9	16.5	26.4	10.0	111.2
45.2	24.7	31.7	15.5	116.1
46.2	26.4	32.6	16.8	116.8
46.7	28.0	33.2	18.4	116.8
50.8	31.2	36.7	22.6	118.9
55.4	44.3	41.1	30.9
59.3	52.9	45.0	38.7	119.7
62.0	56.2	47.9	41.9	120.2
62.1	56.8	48.0	42.5	121.7

by Curtius), but the melting point diagram reveals no evidence for the existence of such a molecular species.

The parachor values calculated from surface tension and the density data of Semishin¹⁸ do pass through a minimum at approximately 50 mole per cent hydrazine. Values are given in Table 4.¹⁹

It might be well to consider the question of the existence of hydrazine hydrate in this connection. The maximum boiling composition is close to that required for a 1:1 compound of hydrazine and water. Maximum deviations in the physical properties (with the exception of surface tension) of hydrazine-water mixtures in the liquid state also lie in the range of ± 10 per cent of those corresponding to a composition containing equimolar proportions of the two constituents. The lower the temperature, the more definitely does the locus of the maximum deviation approximate a

5.1 8.21 10.4 7.59 10.5

TABLE 3

DENSITIES OF $N_2H_4 \cdot H_2O$ MIXTURES(According to Dito ¹⁷)

Weight per cent N_2H_4	d_4^{15}	Weight per cent N_2H_4	d_4^{15}
14.0	1.0142	67.4	1.0164
26.4	1.0272	72.0	1.0440
31.2	1.0340	74.9	1.0421
40.8	1.0339	78.5	1.0400
46.1	1.0125	80.0	1.0379
55.3	1.0161	84.0	1.0358
59.9	1.0164	90.8	1.0300
64.1	1.0170	100.0	1.0114

(According to Semishin ¹⁸)

Mole per cent N_2H_4	d_4^{25}	d_4^{25}	d_4^{50}
100.0	1.0231	1.0024	0.9801
89.0	1.0307	1.0094	0.9888
83.1	1.0351	1.0161	0.9960
77.8	1.0405	1.0205	1.0005
71.8	1.0443	1.0248	1.0056
69.0	1.0461	1.0268	1.0074
63.0	1.0473	1.0298	1.0119
60.0	1.0479	1.0314	1.0126
56.7	1.0480	1.0318	1.0133
51.0	1.0481	1.0322	1.0136
49.0	1.0477	1.0319	1.0137
47.2	1.0473	1.0313	1.0135
43.0	1.0466	1.0305	1.0133
40.0	1.0454	1.0293	1.0128
36.0	1.0440	1.0278	1.0120
31.0	1.0420	1.0264	1.0116
31.1	1.0401	1.0257	1.0108
28.7	1.0382	1.0246	1.0095
26.0	1.0361	1.0231	1.0084
21.0	1.0308	1.0192	1.0042
16.0	1.0250	1.0152	1.0022
13.0	1.0207	1.0121	1.0000
9.1	1.0150	1.0082	0.9972
7.0	1.0119	1.0061	0.9952
1.0	1.0025	0.9995	0.9903
0.0	0.9999	0.9971	0.9881

1:1 combination. It is probable, however, that a compound of hydrazine and water in a 1:1 ratio exists only in the solid state, as determined from the melting point diagram of the system. This does not rule out the existence in the liquid state of an equilibrium



which is displaced to the right with rise in temperature.

TABLE 4

SURFACE TENSION AND PARACHOR OF AQUEOUS HYDRAZINE SOLUTION AT 25°C

Mole per cent N_2H_4	d_4^{25} *	γ	Parachor of Solution	Parachor of Hydrazine
0.0	0.9971	71.90	52.6
6.7	1.0046	73.11	55.1	91.1
10.5	1.0087	73.68	56.6	90.5
20.5	1.0184	75.10	60.3	90.4
26.5	1.0228	75.41	62.5	90.4
28.7	1.0241	75.47	63.3	90.0
33.9	1.0274	75.47	65.3	90.2
40.1	1.0294	75.28	67.7	90.3
48.8	1.0317	74.18	70.6	89.5
49.1	1.0318	74.24	70.8	90.2
63.0	1.0298	72.38	76.3	90.0
69.7	1.0267	71.88	78.8	90.3
83.1	1.0161	69.97	84.5	91.0
84.9	1.0146	69.81	85.3	91.3
96.9	1.0051	67.57	90.2	91.4
100.0	1.0024	66.67	91.5	91.5

* Densities taken from Semishin.¹⁸

Study of the spectrum of hydrazine hydrate in the near infrared gives rather definite evidence for the existence of $N-H-O$ bonds.²⁰ It may thus be assumed with certainty that appreciable hydrogen bonding with formation of $N-H-N$, $N-H-O$, and $O-H-O$ bonds does take place in the liquid system. The situation is still somewhat confused with respect to the nature of the vapor over hydrazine-water mixtures. Older vapor density data led to the conclusion that hydrazine hydrate is dissociated into water and hydrazine to the extent of 58 per cent at 100°C. and completely at 140°C.²¹ But hydrogen bonds are usually destroyed in the vapor state. It has furthermore been observed that the absorption spectrum of hydrazine hydrate in the vapor phase

consists of the superposition of the spectra of hydrazine and of water.²² Until a more definitive investigation is made, it may be assumed that no association occurs in the vapor state.

TABLE 5
FREEZING POINTS OF THE N_2H_4 - H_2O SYSTEM

Weight per cent N_2H_4	Mole per cent N_2H_4	Freezing Point, °C.	Weight per cent N_2H_4	Mole per cent N_2H_4	Freezing Point, °C.
5.40	3.11	-3.80	57.4	43.0	-53.7
6.40	3.71	-4.30	58.1	43.9	-53.4
7.60	3.43	-5.30	59.9	45.8	-52.6
7.70	4.49	-5.40	60.6	46.5	-52.2
8.70	5.10	-6.40	63.1	49.1	-51.7
11.9	7.06	-9.80	64.2	50.2	-51.7
12.6	7.51	-10.3	64.7	50.8	-52.0
13.9	8.32	-12.8	66.5	52.8	-52.2
14.3	8.58	-12.7	66.6	52.9	-52.7
18.4	11.2	-19.1	67.6	54.0	-52.6
19.0	11.6	-20.4	69.2	55.8	-50.3
19.7	12.1	-22.0	69.6	56.2	-52.8
19.9	12.2	-22.2	70.3	57.1	-46.8
20.3	12.5	-22.3	70.4	57.1	-46.2
21.4	13.3	-24.7	70.7	57.6	-44.2
22.2	13.8	-25.3	72.0	59.1	-40.2
23.4	14.7	-30.3	72.6	59.8	-40.2
24.1	15.2	-30.8	74.8	62.5	-34.1
24.8	15.6	-33.3	75.0	62.8	-32.7
26.0	16.5	-37.3	81.0	70.5	-20.4
26.2	16.6	-34.9	84.1	74.9	-15.6
27.5	17.6	-41.6	85.1	76.2	-14.8
28.4	18.2	-44.3	90.1	83.6	-8.7
29.6	19.2	-46.3	97.9	96.4	-0.10
35.6	23.7	-65.9	98.4	97.1	0.20
45.0	31.4	-75.8	99.0	98.2	0.90
49.3	35.4	-81.7	99.6	99.3	1.60

Freezing point data for the hydrazine-water system²² reveal the existence of a hydrate as a solid phase, melting at -51.7°C . Two eutectic compositions consisting of N_2H_4 - N_2H_4 - H_2O and H_2O - N_2H_4 - H_2O also form. The hydrazine-rich eutectic has a

melting point of -54°C ., corresponding to a mixture containing 69 per cent hydrazine by weight (56 mole per cent). The exact composition of the water-rich eutectic could not be determined because of the viscous nature of solutions containing 35 to 49 per cent hydrazine by weight. Data given in Table 5 and depicted in Figure 1 represent the most recent determinations.²² Values for hydrazine-rich mixtures agree with those previously determined

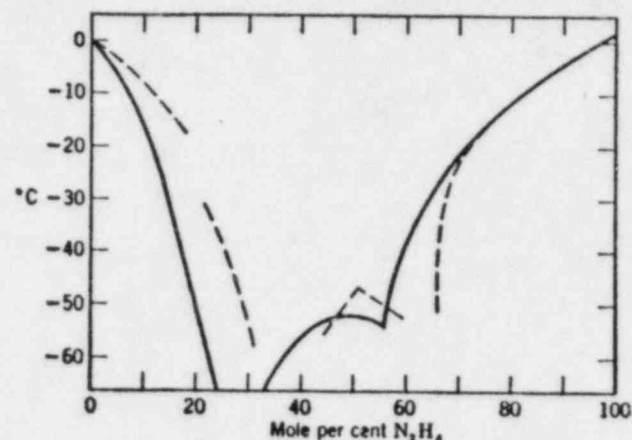


FIGURE 1. Melting-point diagram for the hydrazine-water system. --, data by Semishin;¹⁸ —, data by Mohr and Audrieth.²²

by Semishin;¹⁸ marked differences are to be noted, however, in the water-rich range of mixtures.

TERNARY SYSTEMS

Addition of sodium hydroxide to certain hydrazine-water mixtures results in the formation of two liquid phases at temperatures above 60°C . The upper hydrazine-rich phase can easily be separated from the heavier solution containing the greater part of the water and added alkali, thus affording a simple procedure for the concentration of hydrazine.²³ (See page 50.) The summary of plait points and limiting compositions of the conjugate liquid phases is given in Table 6.

Data for the ternary system at 100°C . are depicted graphically in Figure 2. One important reason for undertaking a study of the ternary system, N_2H_4 - H_2O - $NaOH$, was to determine if concentra-

hydrazine, that is, those in which hydrazine acts as the solvent and water as the solute. Since hydrazine is a strongly basic solvent, we might expect under the circumstances that water would behave as a weak acid in anhydrous hydrazine, especially since the hydrazonium ion is the bearer of acidity in solutions of anhydrous hydrazine. This fact should be borne in mind if and when any extensive work is undertaken to determine the exact nature and behavior of solutions that contain an excess of hydrazine.

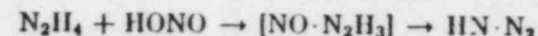
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CHAPTER 6

Oxidation of Hydrazine; Catalytic Decomposition

The ability of hydrazine to act as a powerful reducing agent has always been recognized as one of its outstanding chemical properties. Early workers paid little attention, however, to the fate of hydrazine, that is, to the oxidation products resulting from such reductions. When Curtius^{1,2} discovered that hydrazoic acid could be obtained by the action of nitrous acid upon hydrazine,

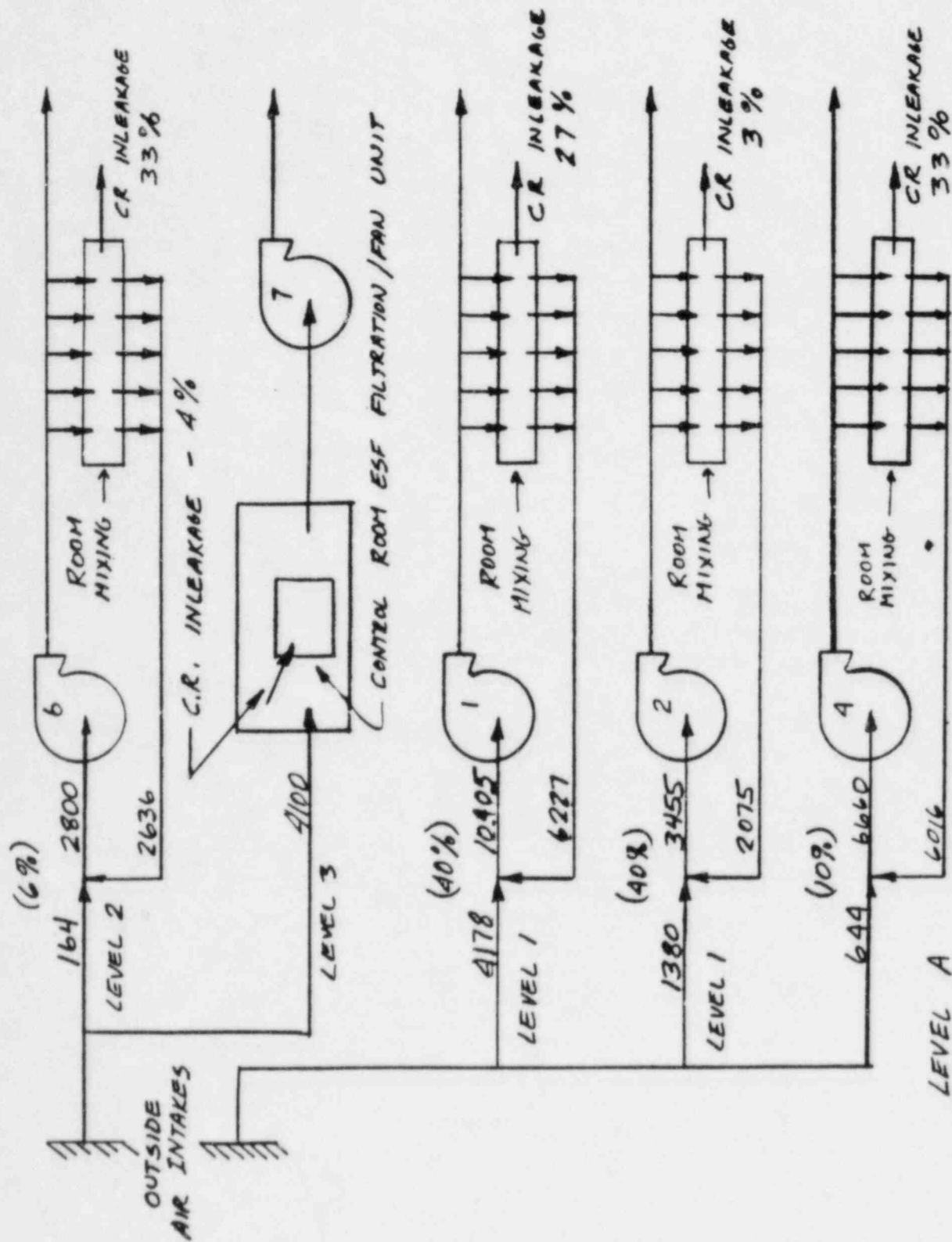


investigators studied such presumed oxidation reactions to determine if other nitrogen-containing oxidants might be employed for synthesizing hydrazoic acid from hydrazine. It was taken for granted that a nitrogen-containing compound was necessary. This hypothesis seemed well established after it had been found that azide could be obtained by the decomposition of hydrazine nitrate³ and of hydrazine sulfate in the presence of strong nitric acid⁴ and by interaction of nitrogen trichloride⁵ with hydrazine.

In 1905 A. W. Browne⁶ found that hydrogen peroxide could also be made to react with hydrazine in acid solution to give hydrogen azide. Browne and Shetterly^{4,7} subsequently studied the action of many other nonnitrogen-containing oxidizing agents upon hydrazine, generally in acid solution, in an effort to determine what sort of mechanism might be devised to account for the formation of this product. Only a limited number were found to give hydrogen azide; nitrogen and ammonia were generally obtained. In only a few cases was nitrogen found to be the sole oxidation product.

To gain a clearer insight into the mechanism of the oxidation of hydrazine, it is desirable to consider a number of related factors

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