LABORATORY TESTS AT ELEVATED TEMPERATURES FOR THE PREDICTION OF THE RATES
OF PRESSURE RISE IN HYDRAZINE TANKS AT NORMAL STORAGE TEMPERATURES

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ABSTRACT

Various types of laboratory equipment have been used to measure the rates of
gas evolution from liquid phase decomposition of hydrazine and from surface
decomposition at elevated temperatures. In general the rates were found to be
independent of time after the first few days on test and the surface rates
obeyed the Arrhenius relationship with respect to temperature, hence enabling
extrapolations to be made to normal storage temperatures. Good agreement was
obtained between the measured rate of pressure rise in a 32 litre, titanium
alloy tank at $70^{o}C$ and that predicted on the basis of samples tested in labora-
tory equipment at the same temperature. A procedure by which rates of pressure
rise can be converted to rates of hydrazine decomposition, taking into account
the solubilities of nitrogen and ammonia, is given.

1. INTRODUCTION

The internal volume of a hydrazine tank should be large enough to contain the
maximum load of propellant at the highest anticipated storage temperature
together with sufficient ullage to limit the pressure rise due to hydrazine
decomposition to an acceptable level throughout the storage life of the system.

Calculation of the minimum ullage, and from it the minimum size of tank,
requires a knowledge of the rates of decomposition of hydrazine both in the
liquid phase and in contact with the internal surface of the tank at the storage
temperatures of interest. In practise the rates of decomposition are often quite
slow and difficult to measure with accuracy at normal storage temperatures and
over short experimental times unless very careful control of test temperature is
maintained and sensitive pressure measuring devices are used. However, even

these slow rates can lead to considerable rises in ullage pressure over extended storage times, such as ten years, and methods for assessing the ullage requirements at the start of a project without recourse to sophisticated control and measuring equipment is desirable. The use of test temperatures in the range 60-90°C rather than the normal storage temperatures of 10-30°C produces rates of hydrazine decomposition that are typically 10 to 50 times higher. ·This data can then be extrapolated to the lower temperatures of interest providing that the rates of decomposition are not varying with respect to time and providing that they obey the normal Arrhenius relationship with respect to temperature (logarithm of rate proportional to reciprocal of absolute temperature). This enables relevant data to be obtained in much shorter times and reduces somewhat the need for very accurate control and measuring equipment.

Various types of laboratory test equipment that have been used to determine the rates of gas evolution from the liquid phase and from surfaces over a range of temperatures are described and examples of the data obtained are presented. Laboratory data obtained at 70°C is used to predict the rate of pressure rise in a 32 litre, titanium alloy tank and the measured rate at 70°C is compared with that predicted.

A procedure by which rates of pressure rise under given conditions can be converted into rates of hydrazine decomposition is given in an appendix. This makes allowance for the effects of the differing solubilities of nitrogen and ammonia in hydrazine and the effect of temperature on these solubilities is included. Data regarding the rate of pressure rise for a system with a known fraction of ullage can be converted into rates of pressure rise for any other fraction of ullage at that temperature.

2. TEST EQUIPMENT AND PROCEDURES

This section contains details of the different types of test equipment used at PERME to measure rates of gas evolution from hydrazine and includes cleaning procedures, calibration and filling procedures and methods of temperature control.

The hydrazine used in all the tests was purchased to conform with the US Military Specification MIL-P-26536C[1] and chemical analysis during the course of the tests confirmed this requirement. This specification requires the content of hydrazine to be above 98% w/w.

2.1 Pressure Measurement by Mercury Manometer (Equipment A)

The first type of equipment tested was made entirely from glass and had a ground joint which was greased connecting the tube containing hydrazine to the mercury manometer 'U' tube. Problems of sealing this joint at elevated temperatures resulted in a change to the equipment shown in Fig. 1 which employs a

screwed joint to squeeze a PTFE wrapped silicone rubber washer between the two glass surfaces. Figure 2 includes a section through this type of joint. The taps have PTFE keys to avoid the use of greases. The glass bulb and tap attached to the left-hand limb of the mercury manometer serves a dual purpose. The tap is closed during an experiment to isolate the mercury manometer from the effects of changing atmospheric pressure and the size of the bulb (30 cm^3 approx) is sufficient to ensure that movement of the mercury column due to gas generation makes virtually no difference to the volume and hence pressure of the air that is locked above the left-hand limb. The volume of ullage between the hydrazine and the right-hand limb (30 cm^3 approx at $70^{\circ}C$) is also sufficient to minimise changes on that side of the manometer.

The internal volume of the equipment to the right of the manometer was deter-mined by filling with water and weighing, the glassware then being cleaned by filling with concentrated nitric acid at $80^{\circ}C$ for at least one day, washed out with deionised water and then filled with anhydrous hydrazine and heated for several days at $70^{\circ}C$. After emptying this initial filling of hydrazine about 85 cm^3 of the hydrazine on test were placed in the tube and the exact quantity determined by weighing. The equipment was then placed in an oven controlled at
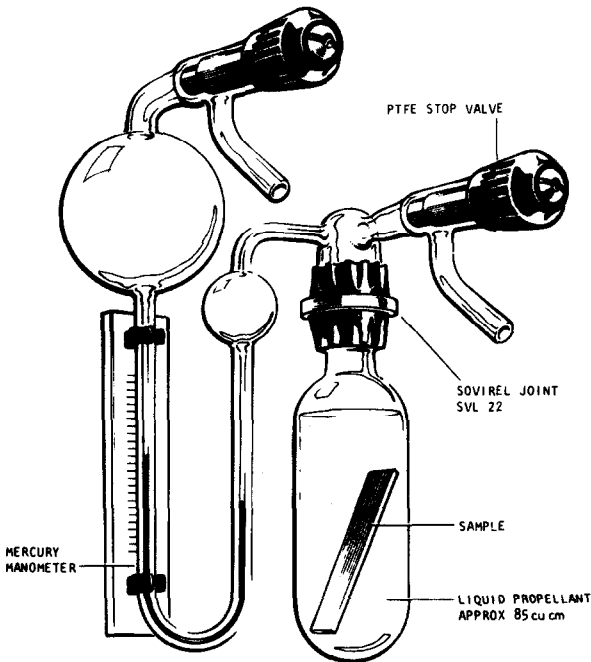

FIG.1 PRESSURE MEASUREMENT BY MERCURY MANOMETER — EQUIPMENT A

STAINLESS STEEL
TRANSDUCER
17/4 AND 17/7 PH

H30 ALUMINIUM
CONNECTOR

SOVIREL JOINT SVL 22

18/8 STAINLESS STEEL
HONE VALVE

PTFE WRAPPED SILICONE
RUBBER WASHER

SAMPLE

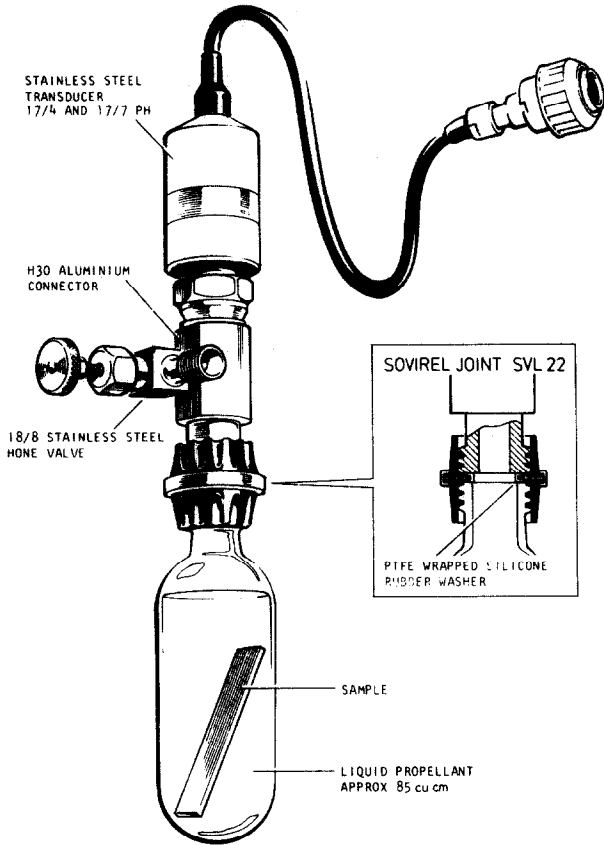LIQUID PROPELLANT
APPROX 85 cu cm

FIG.2 PRESSURE MEASUREMENT BY TRANSDUCER - EQUIPMENT B

the temperature required (usually 70, 80 or 90°C) and fitted with an "over-temperature" cut-out which was set 10°C above the test temperature for safety. The automatic control of the oven temperature was usually sufficient to reduce "drift" to about ±0.3°C, any movement outside this range being checked by use of the manual controls. During the time that the equipment was attaining the oven temperature the position of the mercury column was controlled by adding a little nitrogen to the left-hand side of the manometer the test being started with the mercury meniscus near the bottom of the attached scale that was 3 cm long and graduated in millimetres.

The position of the mercury meniscus was read twice daily until the mercury column (left-hand side) had risen to near the top of the scale, further runs could then be carried out by readjusting the position of the mercury column by means of the taps. When sufficient data had been obtained to enable a value for

the rate of pressure rise to be calculated, the test temperature could be changed and the procedure repeated.

This equipment can also be used to determine the rate of gas generation on the surface of samples added to the hydrazine when the rate of gas generation in the absence of the sample is subtracted from that with the sample added at the same temperature. Measurement of the rate of gas generation after removal of the sample indicates whether contamination of the hydrazine from the sample has occurred resulting in a change in decomposition rate. A typical type of sample would be a metal or plastic strip about 7.5 cm x 1.25 cm. Some details of the equipment are listed in Table 1.

TABLE 1   DETAILS OF TEST EQUIPMENT

Designation	Type	Internal Volume cm^3	Internal Surface Area cm^2	Weight of Hydrazine added g	% Ullage at Ambient Temperature, Approx
A	Mercury Manometer	120 approx (sample side of manometer)	170 approx	85 approx	30
B	Transducer	105 approx	150 approx	85 approx	20
C	Inverted Transducer	110 approx	160 approx	85 approx	23
D	Aluminium lined Vessel (without sample holder)	232	267	186	20
E	Titanium Alloy Vessel	1313	677	1238 413 159	10 (including manometer) 70 (" ") 88 (" ")
F	Stainless Steel Vessel	1294	672	1200 approx	10 (" ")
G	Titanium Alloy Tank	32 x 10^3	2400 (Ti6A14V) and 2400 (EPDM rubber)	24.05 x 10^3	25

2.2   Pressure Measurement by Transducer (Equipment B)

Equipment A has a number of disadvantages. It is fragile, it is difficult to control the position of the mercury column during "warm-up", it occupies consider-able space in the oven, the range of pressure measurement is limited, the mercury column tends to stick and hydrazine becomes trapped within the column producing gas bubbles and breaks within the column. For these reasons the use of pressure transducers was investigated and the first type of equipment developed is shown in Fig. 2 (details in Table 1). A stainless steel pressure transducer is mounted above an aluminium alloy connector which attaches to the screwed joint at the top of the sample tube. The connector is provided with a stainless steel relief

valve. The transducers were designed for use over the pressure range of 0-2 bar absolute and had a full scale output of 25 mv, they were calibrated against an accurate mercury manometer (vacuum type) before use and checked at intervals between tests. The transducers and other metal parts were given an initial cleaning in an ultrasonic bath containing an aqueous solution of a mild detergent, the glass tube was cleaned by the procedure outlined in Section 2.1. The internal volume of the equipment was determined before cleaning by filling with water and weighing.

About 85 g of hydrazine was weighed into the equipment and after placing in the oven at the set temperature the output of the transducer was monitored on a digital voltmeter twice daily until sufficient data had been obtained to define the rate of pressure rise or the pressure limit (2 bar) had been reached. Excess pressure could then be released through the valve and the process repeated or the experiment carried out at a different temperature.

2.3 Pressure Measurement by Inverted Transducer (Equipment C)

The rates of gas generation measured in Equipment B were found to be about three or four times as high as those measured in Equipment A, presumably due to the decomposition of hydrazine on the metal surfaces of transducer, connector and valve. This would limit the use of Equipment B to the role of providing blanks for added samples and even here the size of the blanks would limit the accuracy with which the net rate due to the sample could be assessed. One possible solution is to replace the stainless steel transducer with one made from titanium alloy that joins directly to the screwed joint, pressure relief being provided by a glass/PTFE tap joined to the top of the sample tube below the joint. Titanium alloy is more compatible than stainless steel (see Section 3.4) but is considerably more expensive. An alternative approach is shown in Fig. 3 (details in Table 1) and this constitutes the present state of development of this type of equipment. The stainless steel transducer is now inverted and filled with mercury to prevent contact of hydrazine with the metal surface, pressure relief being from a glass/PTFE tap. Rates of gas generation with this type of equipment are similar to those found with Equipment A without the accompanying disadvantages. Procedures for measuring the internal volume, cleaning and for monitoring tests have been described previously. It is likely that this type of equipment or the modification of Equipment B using titanium alloy transducers will probably be used at PERME in the future for measuring either homogeneous or heterogeneous rate of decomposition.
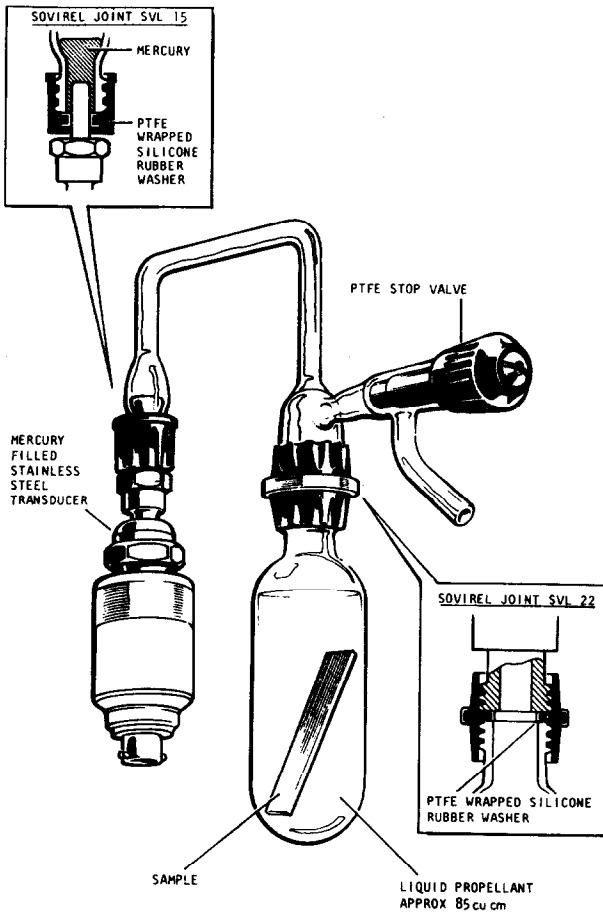
SOVIREL JOINT SVL 15
MERCURY
PTFE WRAPPED SILICONE RUBBER WASHER

PTFE STOP VALVE

MERCURY FILLED STAINLESS STEEL TRANSDUCER

SOVIREL JOINT SVL 22

PTFE WRAPPED SILICONE RUBBER WASHER

SAMPLE

LIQUID PROPELLANT APPROX 85 cu cm

FIG. 3 PRESSURE MEASUREMENT BY INVERTED TRANSDUCER — EQUIPMENT C

2.4 Aluminium Lined Pressure Container (Equipment D)

The rates of decomposition on some materials were sufficiently high to limit the useful experimental time available with the types of equipment described previously. The form of equipment shown in Fig. 4 (details in Table 1) was used for these materials. An aluminium (S1B) lined stainless steel pressure vessel was provided with a lid containing a stainless steel relief valve and a 0-10 bar stainless steel pressure gauge (Bourdon tube). A PTFE seal made the system pressure tight and a PTFE sample holder could be inserted into the container. The sample holder had room for two strip samples (15 cm x 1 cm) and prevented contact between the samples and the wall of the vessel.
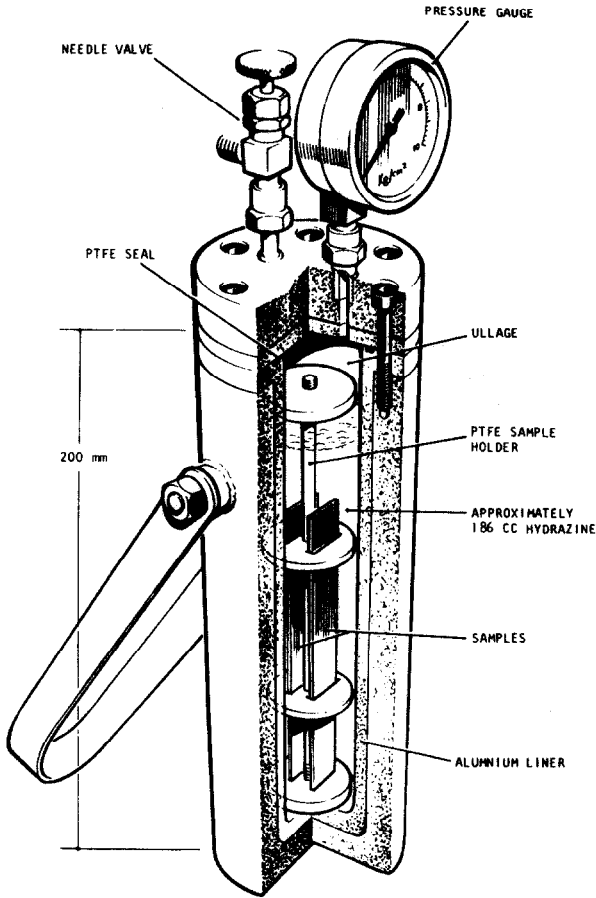
FIG.4 ALUMINIUM LINED PRESSURE CONTAINER – EQUIPMENT D

The container was cleaned by first degreasing with isopropyl alcohol, filling with 50% nitric acid for two hours at room temperature and then washing out with deionised water. The data from the first filling with hydrazine was rejected if the rate of pressure rise was abnormally high, the cleaning procedure then being repeated until the usual rate was obtained (0.10 to 0.15 bar/day at 70°C). The test procedure was similar to that described earlier, a blank rate first being obtained in the absence of the samples, the rate in the presence of the samples then being determined and finally a post blank rate being determined. The ullage space above the liquid was flushed free from air using argon gas when an analysis of the gases produced by decomposition was required.

2.5 Titanium Alloy Vessel (Equipment E)

The rate of decomposition on strip samples of titanium alloy (Ti6A14V) was too low to measure with confidence using Equipment A or C and it was therefore decided to fabricate a small vessel from this alloy to facilitate measurements. The vessel was in the form of a cylinder (11.45 cm diameter x 17.3 cm) with a wall thickness of about 0.64 cm. A circumferential weld was located near the top of the vessel and a tube (0.63 cm OD) of Ti6A14V was welded to the centre of the flat top of the vessel and protruded about 15 cm above it. The capacity of the vessel was determined by accurate measurement and confirmed by filling with water. Some details of the vessel are given in Table 1. Polythene tubing was used to connect the top of the vessel to a mercury manometer, the vessel being mounted vertically and completely immersed in a water bath at 70°C whilst on test. A total of 1238 g of hydrazine was accurately added to the vessel and the ullage space was filled with argon. The rate of gas evolution was measured with the manometer over a period of about ten days, the excess gas vented through a two-way tap on top of the manometer, and the procedure repeated seven times. A sample of the gas was taken for analysis by chromatography. The amount of hydrazine in the vessel was then reduced to 413 g and the rate of gas evolution re-measured (average of six determinations). Finally the amount of hydrazine was reduced to 159 g and the procedure repeated.

2.6 Stainless Steel Vessel (Equipment F)

An almost identical vessel to the one made in titanium alloy (Equipment E) was made from stainless steel (S 130). Details are given in Table 1. Experimental procedures were similar to those described above except that 1200 g of hydrazine was added and experiments were carried out at temperatures of 30, 40, 50, 60 and 70°C.

2.7 Titanium Alloy Tank (Equipment G)

A 32 litre spherical titanium alloy tank (Ti6A14V) was manufactured as part of an ESRO programme[2] and was available for compatibility tests. The tank was designed for positive expulsion and had a hemispherical, elastomeric diaphragm made from a modified EPDM rubber (a terpolymer of ethylene/propylene/diene monomer). Details are given in Table 1.

The tank was evacuated, about 24 kg of hydrazine was weighed into the tank and then nitrogen gas at atmospheric pressure was introduced on the gas side of the diaphragm which was connected to a mercury manometer. The tank was immersed in a water bath maintained at 70°C and the rate of pressure rise was monitored over a period of 28 days. A sample of hydrazine taken from the tank at the end of the test period was checked for gas evolution rate in Equipment A and a sample of ullage gas was checked for hydrogen content.

3. RESULTS AND DISCUSSION

3.1 Presentation of Data

Many different units have been used to tabulate data obtained by various workers for rates of gas evolution, rates of pressure rise or rates of hydrazine decomposition and there are arguments both for and against any particular system adopted depending on the context of the work and the use to which the data is to be applied. There is no doubt that the most fundamental units are those that refer to the rate of hydrazine decomposition (e.g. mg of hydrazine decomposed per unit time) but units that refer to rates of pressure rise or rates of gas evolution are of more immediate value to the designer who is concerned with the amount of ullage to leave in a tank. Because the present work is intended to be used in this context rather than that of the chemical kineticist the data is presented in terms of rates of gas evolution. In some instances the rate of gas evolution was measured directly (Equipment E and F) whilst in others it was calculated from a knowledge of the rate of pressure rise and the volume of the ullage (Equipment A, B, C and D). The rate of gas evolution is expressed in standard cubic centimetres (SCC) per unit time, which is the volume of gas reduced to standard conditions of $0^{\circ}C$ and 1 atmosphere pressure. This rate is divided by the weight of hydrazine in the case of gas evolution from the liquid phase or by the surface area involved in the case of heterogeneous decomposition. The tabulated rates of gas evolution at a particular temperature can be used to calculate rates of pressure rise for systems having ullages that occupy between 10 and 40 per cent of the tank volumes and at temperatures up to $90^{\circ}C$ without introducing errors greater than 10 per cent into the calculation. However for ullages smaller than 10% the increasing fraction of nitrogen that remains dissolved in the hydrazine and for ullages over 40% the increasing fraction of ammonia that is released to the ullage introduce progressively greater errors into the calculation. A method by which account can be taken of the solubilities of nitrogen and ammonia is given in the Appendix which relates rates of gas evolution to the more fundamental units of rates of hydrazine decomposition. Gas analysis of the products of decomposition of the liquid phase and of the decomposition on stainless steel or titanium alloy have shown that only small quantities of hydrogen are produced (typically 1%) and the stoichiometry of decomposition at temperatures up to $90^{\circ}C$ can be represented by

$$3N_2H_4 \;=\; N_2 + 4NH_3$$
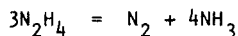
2.24×10^4 scc of nitrogen are therefore produced by the decomposition of 96 g of hydrazine.

3.2 Processes Contributing to Hydrazine Decomposition

Hydrazine may decompose homogeneously in the liquid phase and the vapour phase or heterogeneously on surfaces both below and above the liquid level. However the rate of homogeneous vapour phase decomposition at the temperatures of interest can be shown to be negligible by extrapolation of data obtained at high temperatures[3]. One question that the present work was designed to answer was the relative contributions of the surface decomposition above and below the liquid level and the tests with Equipment E were planned to give an answer to that question.

3.3 Liquid Phase Decomposition (Equipment A)

Decomposition of hydrazine in the liquid phase is not easy to measure due to the fact that most container surfaces contribute to the overall rate of gas generation. The Equipment A was designed to minimise surface decomposition but it was necessary to demonstrate that the surface contribution was indeed small. This was done in two ways. The rate of gas generation from a sample of hydrazine in the Equipment A was first measured at $70^{\circ}C$ and then a large number of glass rods of small diameter were introduced and the rate was remeasured. Although the surface area of glass had been increased by a factor of four the rate of gas generation was almost unchanged. In a second series of experiments the amount of hydrazine in the tube of Equipment A was reduced in stages and the rate of gas generation (corrected for gas solubility) was calculated for each stage. It was found that the rate of gas generation per unit weight of hydrazine was approximately constant. These two sets of measurements confirm that the contribution of the glass, PTFE and mercury surfaces in Equipment A can be neglected. Other workers[4,5,6] who have used mercury manometers have not noticed any signs of incompatibility with hydrazine.

Samples of hydrazine conforming to MIL-P-26536C but taken from five different drums were tested at temperatures of 70, 80 and $90^{\circ}C$ in Equipment A. The rates of gas evolution were found to be steady after the first few days and are shown in Fig. 5 where it is seen that there is considerable sample to sample variation between different drums and that even from one drum successive samples also show considerable scatter. One reason for this scatter is probably contamination from the atmosphere during transfer because it was not appreciated at the time that these experiments were carried out that traces of carbon dioxide, for example, can cause changes in the rate of decomposition. Future work will employ glove box procedures for filling sample tubes. The data has been treated as a single set for the pruposes of extrapolation to lower temperatures and the assumption made that the Arrhenium relationship can be applied. Further work over a wider range of temperature is required to confirm this assumption. The slope of the
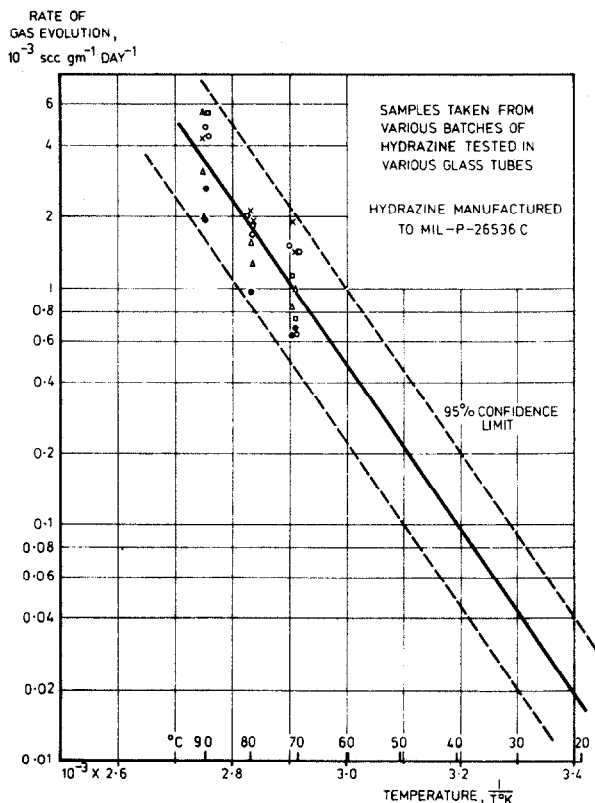
FIG.5 RATE OF HOMOGENEOUS DECOMPOSITION OF HYDRAZINE IN GLASS — EQUIPMENT A

line yields an activation energy of 66.3 kJ mole^{-1} (15.8 kcal mole^{-1}). It
should be emphasised that hydrazine manufactured to a different specification
will probably yield different rates of gas evolution and different values for
the activation energy. The present work indicates that decomposition in the
liquid phase is catalysed by impurities and that the true homogeneous rate of
pure hydrazine may be considerably lower than those measured here.

3.4 Decomposition on Surfaces

  3.4.1 Aluminium lined pressure vessel (equipment D)

  The aluminium lined pressure vessels (Fig. 4) minus the PTFE sample holder
were used to determine the rate of gas evolution from 99.5% aluminium (S1B). A
total of nine vessels was used at temperatures up to 90°C and the results are
shown in Fig. 6. A sample of hydrazine taken from one of these containers and
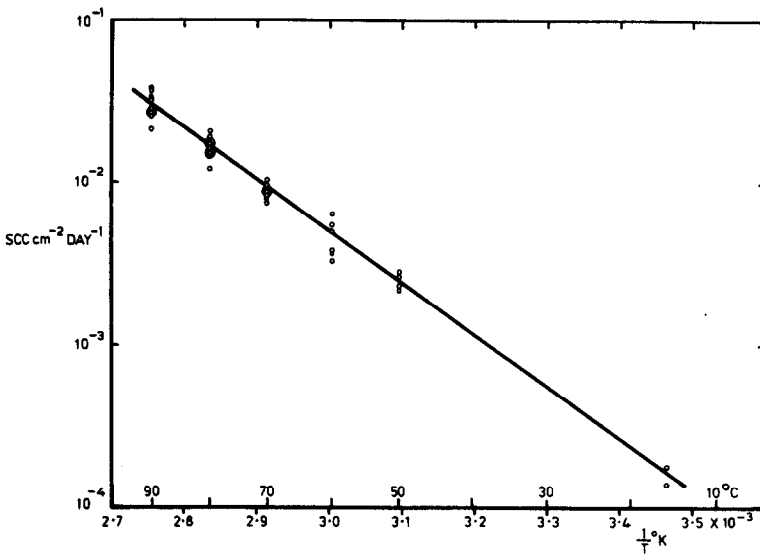
FIG. 6 GAS EVOLUTION RATE FROM ALUMINIUM LINED VESSEL – EQUIPMENT D

tested in Equipment A confirmed that less than 5% of the gas evolved came from the liquid phase. The rate of gas evolution has been divided by the total internal surface area of aluminium to yield a rate per unit area rather than by the area beneath the liquid surface. The reason for this will be explained in the next section. The data in Fig. 6 show that there is considerable variation from vessel to vessel but the data has been treated as a single set and obeys the Arrhenius expression. The activation energy is 61.1 kJ mole^{-1} (14.6 kcal mole^{-1}) The reason for the variation from vessel to vessel is not known but may be associated with differences in surface finish (true surface area), differences in the hydrazine purity (a glove box was not used for filling) or variable contribution to the gas generation rate from the stainless steel pressure gauge and relief valve. Average data is also presented in Table 2.

3.4.2 Titanium alloy vessel (equipment E)

The rate of gas evolution for three different quantities of hydrazine was measured at 70°C and using the method given in the Appendix was converted to a rate of nitrogen formation. Analysis of a sample of gas from this vessel had shown only traces of hydrogen and the assumption regarding the stoichiometry of the reaction made in the Appendix was therefore valid. The data is shown in Fig. 7 and it is seen that there appears to be a linear increase in rate with the quantity of hydrazine present and that extrapolation of the data to zero quantity of hydrazine yields a positive intercept for the rate of formation of nitrogen.

TABLE 2   RATE OF GAS EVOLUTION FROM DECOMPOSITION OF HYDRAZINE ON SURFACES

Material	Measured rate of gas evolution, 10^{-3} scc cm^{-2} day^{-1}								Equipment Used (see Table 1)
	90°C	80°C	70°C	60°C	50°C	40°C	30°C	20°C	
Titanium Alloy (6A1.4V)			0.7 (from Fig 7)						E
Aluminium Alloy DTD 5080			<3						D
Aluminium, S1B	31	17	9.6	4.9	2.5	1.2	0.55	0.24	D
Stainless Steel (Niobium stabilised) S527, S130			6.8, 9.6	4.1	2.4	1.3	0.7		F, D
Stainless Steel (Titanium stabilised) S526			68 → 130						D
Inconel 600		66	45						D
Radiometal 50 (50% Fe, 50% Ni)		160	93						D
Tungsten Carbide (polished) (94% WC, 4% Co)			120						D
Butyl Rubber (Carbon filler)			40						A
Butyl Rubber (Silica filler)			5						A
Ethylene/Propylene Rubber (Carbon filler)			88						A
Ethylene/Propylene Rubber (Silica filler)			3						A
Modified EPDM Rubber (Silica filler)			0.15						A

RATE OF FORMATION OF NITROGEN (EVOLVED + DISSOLVED) IN SCC DAY^{-1}

SURFACE RATE AT 70°C
INTERNAL SURFACE AREA OF Ti 6Al 4V = 677 cm^2
RATE $= \dfrac{0.45}{677} = 6.65 \times 10^{-4}$ SCC cm^{-2} DAY^{-1} OF N$_2$

LIQUID PHASE RATE AT 70°C
WEIGHT OF HYDRAZINE TO FILL AT 70°C = 1264 g
RATE $= \dfrac{1.61-0.45}{1264} = 9.18 \times 10^{-4}$ SCC g^{-1} DAY^{-1} OF N$_2$

TWO SAMPLES TAKEN FROM VESSEL AND TESTED IN EQUIPMENT A
GAVE A MEAN RATE OF 9.8×10^{-4} SCC g^{-1} DAY^{-1} OF N$_2$
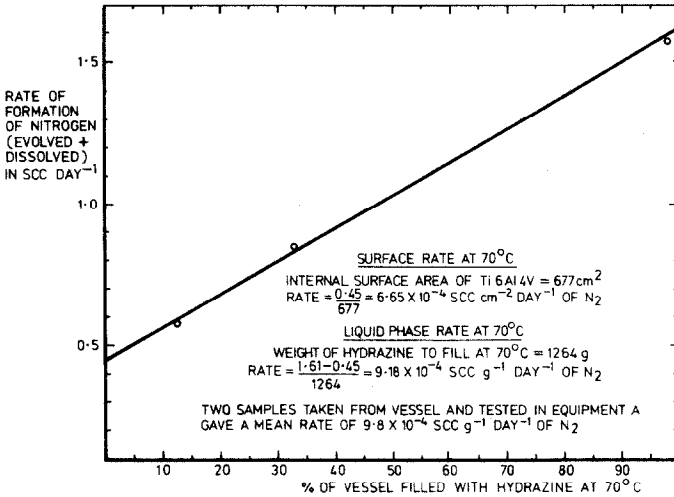
% OF VESSEL FILLED WITH HYDRAZINE AT 70°C

FIG.7   DATA FROM TITANIUM ALLOY VESSEL — EQUIPMENT E

A sample of hydrazine was taken from the vessel when the ullage was being increased from 10 to 70% and a further sample when the ullage was increased from 70 to 88% at room temperature.   These two samples were tested in Equipment A and gave a mean value for the rate of nitrogen formation due to homogeneous decomposition of 9.8×10^{-4} scc g^{-1} day^{-1} at 70°C.   This value accounts for the

whole of the increase in rate of nitrogen formation that was measured with respect
to the fraction of the vessel filled with liquid. Indeed if one assumes that the
whole of this increase is due to homogeneous decomposition it yields a calculated
rate of 9.2×10^{-4} scc g^{-1} day^{-1} at $70^{\circ}C$ (Fig. 7). The rate extrapolated to 0%
filled must be due to surface decomposition and the fact that the total rate at
100% filled can be interpreted as the sum of the rate at 0% filled and that due
to homogeneous decomposition suggests that within experimental error the surface
rate is independent of the position of the liquid level. This implies that the
rate on the titanium surface above the liquid is the same as that below and this
conclusion is not unreasonable when it is recognised that condensation of hydra-
zine vapour due to minor variations in temperature may be regularly wetting the
surface.

The calculated rate for nitrogen formation on the titanium alloy surface is
shown on Fig. 7 and Table 2 and is the lowest value found for a metallic surface.

3.4.3 Stainless steel vessel (equipment F)

The total amount of gas evolved per day from the stainless steel (S 130) vessel
is plotted on Fig. 8 against temperature which ranges from $30^{\circ}C$ to $70^{\circ}C$. The
Arrhenius relationship is obeyed and the activation energy is 50.6 kJ $mole^{-1}$
(12.1 kcal $mole^{-1}$). These rates were divided by the total internal surface area
of steel to give the data presented in Table 2. The rates presented in Table 2
may be 10 to 15% too high due to the contribution from liquid phase decomposition
which was not separately measured in Equipment A at the time of these tests.

scc DAY^{-1}
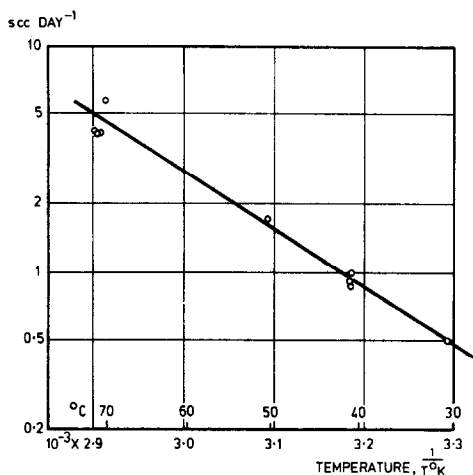
TEMPERATURE, $\frac{1}{T^{\circ}K}$

TOTAL INTERNAL SURFACE AREA OF STAINLESS STEEL
VESSEL = 672 cm^2

WEIGHT OF HYDRAZINE ADDED = ~1200 g

FIG. 8 PLOT OF GAS GENERATION RATE
AGAINST TEMPERATURE FOR STAINLESS
STEEL VESSEL — EQUIPMENT F

3.4.4 Various surfaces

Samples of various types of metal in the form of strips were tested in Equipment D whilst samples of rubbers were tested in Equipment A. The results are given in Table 2 and it is seen that rates of gas evolution vary considerably with the material on test. In general it was found that austenitic stainless steels containing titanium as an additive (e.g. S 526) gave higher rates than those containing niobium (e.g. S 527 or S 130) and furthermore the rate on a sample of S 526 increased during the first 20 days on test and then maintained its higher value during the next 40 days. Exposure of stainless steel samples to the atmosphere whilst wet with hydrazine caused marked increases in the rate of decomposition on subsequent immersion (rates as high as 1 scc cm^{-2} day^{-1}) and this was probably due to the absorption of carbon dioxide and the formation of carbazic acid[7]. The effect of carbazic acid on the decomposition of hydrazine on a steel surface has been noted[8] at Jet Propulsions Laboratory, Pasadena. It is therefore apparent that contact with the atmosphere must be avoided when materials are wet with hydrazine especially in the case of steels.

Another significant result of the tests is that rubbers which have a silica filler are much more compatible than those containing the more usual carbon filler.

3.4.5 Titanium alloy tank (equipment G)

The rate of pressure rise in the ullage of the tank when on test at $70^{o}C$ was compared with that predicted on the basis of tests in laboratory equipment. Table 3 contains details of this comparison. Analysis of a sample of ullage gas at the end of the test showed only a trace of hydrogen which confirms checks made from laboratory equipment.

The predicted contributions of liquid phase, titanium alloy surface and rubber diaphragm surface are listed in Table 3, the sum of these leading to a predicted rate of pressure rise that is close to the one actually measured. It is seen that for this size of tank (32 litre) made from the most compatible materials tested (Table 2) the majority of the gas evolved results from liquid phase decomposition. However for much smaller tanks (e.g. 1-5 litres) with higher ratios of surface to volume and especially if constructed from somewhat less compatible materials (e.g. stainless steel) then the surface rates of decomposition may predominate.

TABLE 3   MEASURED AND CALCULATED RATES OF PRESSURE RISE IN THE TITANIUM ALLOY
TANK (G) AT 70°C

Tank Data

Weight of hydrazine		=	24.05×10^3 g
Volume of ullage at 70°C		=	7.03×10^3 cm^3
Surface area of titanium alloy exposed to hydrazine	=	2.4×10^3 cm^2
Surface area of EPDM rubber exposed to hydrazine	=	2.4×10^3 cm^2

Test Data

Measured rate of gas evolution from liquid
  phase sample at 70°C (equipment A)   = 1.41×10^{-3} scc g^{-1} day^{-1}

Therefore calculated rate from 24.05×10^3 g   = 34.0 scc day^{-1}

Measured rate of gas evolution from titanium
  alloy at 70°C (equipment E)   = 0.67×10^{-3} scc cm^{-2} day^{-1}

Therefore calculated rate from 2.4×10^3 cm^2 = 1.6 scc day^{-1}

Measured rate of gas evolution from EPDM
  rubber at 70°C (equipment A)   = 0.15×10^{-3} scc cm^{-2} day^{-1}

Therefore calculated rate from 2.4×10^3 cm^2 = 0.4 scc day^{-1}

      Total calculated rate of gas evolution   = 36.0 scc day^{-1}

Calculated rate of pressure rise in ullage of
  7030 cm^3 at 70°C = $\frac{36}{7030} \times \frac{343}{273} \times 1.013$ = 6.52×10^{-3} bar day^{-1}

Observed rate of pressure rise at 70°C   = 6.71×10^{-3} bar day^{-1}

4. SUMMARY AND CONCLUSIONS

Various types of laboratory equipment have been used to measure the rates of
gas evolution from liquid phase decomposition of hydrazine and from surface
decomposition at elevated temperatures. In general after the first few days on
test the rates of gas evolution were found to be independent of time and the
surface rates varied with respect to temperature in accordance with the Arrhenius
relationship. This gives confidence that the surface rates determined at
elevated temperatures can be extrapolated to normal storage temperatures and used
to predict rates of pressure rise in hydrazine systems over extended periods of

storage. Further work is required before the homogeneous rates can be extrapo-
lated with confidence. The rate of pressure rise in a titanium alloy tank at
$70^{\circ}C$ was predicted on the basis of laboratory tests on the hydrazine, the
titanium alloy and the rubber diaphragm, good agreement being obtained with the
rate found whilst the tank was on test.

Tests in a titanium alloy vessel at $70^{\circ}C$ and containing various quantities of
hydrazine indicate that the rates of gas evolution from the surface above the
liquid level is the same as that below. This implies that when predictions are
made regarding the rate of pressure rise in closed systems the whole internal
surface of the system must be considered and not just that part below the liquid
surface.

The importance of avoiding contamination with carbon dioxide is apparent from
tests with stainless steel samples and the superior compatibility of rubbers
having a silica filler rather than a carbon filler was noted.

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APPENDIX   CALCULATION OF RATES OF HYDRAZINE DECOMPOSITION
FROM RATES OF PRESSURE RISE

A1. INTRODUCTION

At normal storage temperatures and at the elevated temperatures (e.g. up to
$100^{\circ}C$) used to accelerate compatibility/stability tests liquid anhydrous hydra-
zine decomposes either homogeneously or heterogeneously to yield mainly nitrogen
and ammonia as products. Nitrogen gas is only sparingly soluble in the liquid

phase but ammonia is appreciably soluble and in order to relate the rates of pressure rise in the ullages of the closed systems under test to rates of hydrazine decomposition in a quantitative manner it is necessary to take account of the solubilities of these two gases. The fraction of the gas produced by decomposition that is released to the ullage is a function of the relative size of the ullage and liquid phases as well as a function of the solubility of the gas which itself varies with temperature.

In the first part of the Appendix an expression is derived which enables the fraction of the gas released to the ullage to be calculated and data for nitrogen and ammonia at ullages of 0-100% and temperatures of 20, 40, 60, 70 and 80°C are tabulated. In the second part the way in which this data can be used to calculate rates of hydrazine decomposition from rates of pressure rise is illustrated.

A2. PARTITION OF GAS BETWEEN ULLAGE AND LIQUID HYDRAZINE

Let W = weight in g of gas dissolved in hydrazine

M = molecular weight of the gas

T = temperature in °K

At this temperature T

Let V_H = volume of hydrazine in cm^3

V_U = volume of ullage in cm^3

D = density of hydrazine in g cm^{-3}

K = mole fraction of dissolved gas in liquid hydrazine in equilibrium with a partial pressure of 1 atmosphere of the gas

Now moles of gas dissolved in hydrazine $= W/M$

and moles of hydrazine (mol.wt.32) $= V_H D/32$

Therefore mole fraction of dissolved gas $= \dfrac{W/M}{V_H D/32 + W/M} = K$

for partial pressure of 1 atmosphere.

Therefore for this condition, moles of dissolved gas, $W/M = \dfrac{KV_H D}{32(1-k)}$ ... A

Also for this condition, moles of gas in ullage $= \dfrac{V_u}{22,400} \times \dfrac{273}{T}$ ..... B

Therefore the fraction of the gas in the ullage (i.e. $\dfrac{B}{B+A}$)

$$= \frac{\dfrac{273\, V_u}{22,400T}}{\dfrac{273\, V_u}{22,400T} + \dfrac{KV_H D}{32(1-K)}}$$

$$= \frac{V_u}{V_u + \dfrac{2.564\ KV_HDT}{(1-K)}}$$

In the above equation the actual values of V_H and V_u can be substituted by % hydrazine and % ullage without changing the numerical value obtained for the fraction of gas in the ullage.

A2.1 Data for Nitrogen

Values of K for nitrogen from Journal of Physical Chemistry Vol. 72, No. 2 p.638, February 1968:

Extrapolation of values to higher temperatures tabulated below.

Temperature $^\circ$C	Temperature T $^\circ$K	$\log_{10}K$	K	D	$\dfrac{2.564K\ \ DT}{1-K}$
20	293	-5.161	6.902×10^{-6}	1.008	5.227×10^{-3}
40	313	-5.055	8.810×10^{-6}	0.990	7.000×10^{-3}
60	333	-4.958	1.102×10^{-5}	0.972	9.146×10^{-3}
70	343	-4.921	1.225×10^{-5}	0.963	1.038×10^{-2}
80	353	-4.870	1.349×10^{-5}	0.953	1.164×10^{-2}

% Hydrazine	% Ullage	Fraction of gas in ullage $= \dfrac{V_u}{V_u + \dfrac{2.564\ KV_HDT}{1-K}}$				
		20°C	40°C	60°C	70°C	80°C
99	1	0.659	0.591	0.525	0.493	0.465
98	2	0.796	0.745	0.691	0.663	0.637
97	3	0.855	0.815	0.772	0.749	0.727
95	5	0.910	0.883	0.852	0.835	0.819
90	10	0.955	0.941	0.924	0.915	0.905
80	20	0.980	0.973	0.965	0.960	0.956
60	40	0.992	0.990	0.986	0.985	0.983

A2.2 Data for Ammonia

Values of K for ammonia taken from RPE Tech Memo 611, PERME, Westcott, UK, and extrapolated to higher temperatures below.

Temperature $^\circ$C	Temperature T $^\circ$K	$\log_{10}K$	K	D	$\dfrac{2.564K}{1-K}$ DT
20	293	-0.958	1.102×10^{-1}	1.008	93.79
40	313	-1.208	6.194×10^{-2}	0.990	52.46
60	333	-1.426	3.750×10^{-2}	0.972	32.33
70	343	-1.524	2.992×10^{-2}	0.963	26.12
80	353	-1.619	2.404×10^{-2}	0.953	21.25

% Hydrazine	% Ullage	Fraction of gas in ullage $= \dfrac{V_u}{V_u + \dfrac{2.564\,KV_HDT}{1-K}}$				
		20°C	40°C	60°C	70°C	80°C
80	20	0.0027	0.0047	0.0077	0.0095	0.0116
60	40	0.0071	0.0125	0.0202	0.0249	0.0304
40	60	0.0158	0.0278	0.0443	0.0543	0.0659
20	80	0.0410	0.0709	0.110	0.133	0.158
10	90	0.0877	0.146	0.218	0.256	0.298
5	95	0.168	0.266	0.370	0.421	0.472
3	97	0.257	0.381	0.500	0.553	0.603
2	98	0.344	0.483	0.602	0.652	0.698
1	99	0.514	0.654	0.754	0.791	0.823

A3. CALCULATION OF RATES OF HYDRAZINE DECOMPOSITION FROM RATES OF PRESSURE RISE

It is assumed that the rate of pressure rise in atmospheres per unit time $\dfrac{dp}{dt}$ at a given temperature T ($^\circ$K) and the volume of the ullage V_u (cm^3) at that temperature are known. Also the total volume of the system is known. The rate of pressure rise is first converted to a rate of gas generation in standard cubic centimetres (scc) per unit time.

$$\text{Rate of gas generation} = V_u \times \frac{dp}{dt} \times \frac{273}{T} \text{ scc/unit time.}$$

It is next assumed that the decomposition proceeds according to

$$3N_2H_4 \longrightarrow 4NH_3 + N_2$$

$$(96 \text{ g}) \qquad (4 \times 22.4 \times 10^3 \text{ scc}) \quad (1 \times 22.4 \times 10^3 \text{ scc})$$
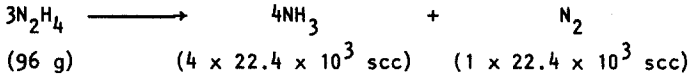
Let us assume that b (scc) of nitrogen are being generated per unit time.

By use of the tabulated data (for temperature T) the fraction of this nitrogen that is released to the ullage (for the % ullage of the system at temperature T) can be estimated.

Let this fraction be f_{N_2} .

Similarly the volume of ammonia being generated per unit time is 4b (from chemical equation above) and the fraction released to the ullage if f_{NH_3}, therefore

$$4b \ f_{NH_3} + b f_{N_2} = \frac{273 \ V_u}{T} \times \frac{dp}{dt}$$

from which the value of b can be calculated.

This can then be converted to weight of hydrazine decomposed per unit time since 96 g (N_2H_4) yields 22,400 scc (N_2).

APPENDIX

80°C
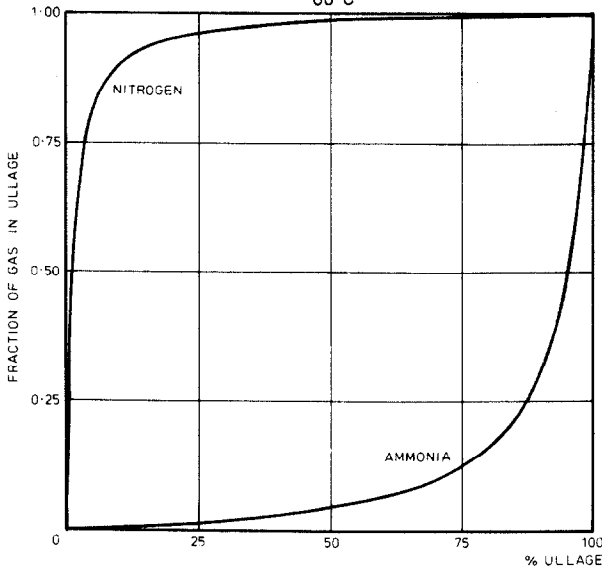
ANHYDROUS HYDRAZINE – PARTITION OF GAS
BETWEEN LIQUID PHASE AND ULLAGE