

FLAMMABILITY AND EXPLOSIBILITY OF AMMONIA

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The flammability limits of oxygen/nitrogen/ammonia mixtures have been determined at ambient temperature, 300°C and 400°C. The explosibility characteristics of ammonia/air mixtures have also been measured.

Investigation of the flammability characteristics of ammonia/water vapour/air mixtures has shown that no aqueous solution of ammonia gives rise to flammable vapours when its temperature exceeds 49°C. It was also shown that solutions containing less than 5 mol. % ammonia in water do not produce flammable vapours at any temperatures.

INTRODUCTION

It is well known that vapours of hydrocarbons, hydroxylic compounds and even some chlorinated solvents can form flammable mixtures when mixed with air. The combustible nature of ammonia is much less well known, however, though explosions have occurred both with anhydrous ammonia/air mixtures and with the vapours from aqueous solutions of ammonia mixed with air.

Since ammonia is widely used in the gaseous form and also as an aqueous solution for the amination of organic compounds, reliable data is required on the flammability of both the anhydrous and aqueous material.

Some literature data exists on both systems. Coward and Jones (1) have reviewed the literature on the flammability of ammonia. White (2), Burgoyne and Neal (3), Frank and Doering (4) and Berl and Bausch (5) all obtained experimental data on the flammability of anhydrous ammonia/air mixtures under atmospheric and elevated pressures. There is inadequate information, however, on ammonia with oxygen deficient atmospheres and on flammability limits at high temperatures.

Even less literature data exist on the flammability of aqueous ammonia. Some German workers (6) carried out a limited amount of experimental work on this topic, but did not show how their results could be applied to practical situations.

The most comprehensive work on the flammability of both anhydrous and aqueous ammonia was carried out by DeCoursey et al (7). These workers carried out a more systematic examination of the flammability of ammonia. They did not, however, obtain any data at high temperatures or for oxygen deficient atmospheres. They also used a flat flame burner technique for their work rather than the more conventional open ended ignition tube.

The experimental work reported in the present paper was, therefore, carried out to provide more comprehensive data on the flammability of aqueous solutions of ammonia. Further information on the combustion properties of anhydrous ammonia at high temperatures and with oxygen deficient atmospheres was also obtained. A limited amount of work was also carried out on the ignition energy and explosibility of ammonia/air mixtures.

PART I:- FLAMMABILITY AND EXPLOSIBILITY OF ANHYDROUS AMMONIA1. EXPERIMENTAL

The apparatus used for the flammability measurements is shown in Fig (1). This is essentially a 50 mms. internal diameter pyrex glass tube connected in series with a glass solenoid operated circulating pump and a glass sampling vessel.

For measurements at ambient temperatures the system was evacuated to a pressure of less than

2 torr. and ammonia admitted to the required pressure. The solenoid pump was started and the desired premixed supporting atmosphere of oxygen and nitrogen let in until atmospheric pressure was reached. After 20 minutes circulation the pump was switched off and the sampling vessel removed for analysis. The ground glass plate at the base of the tube was removed and a 1.5 Joule inductance spark passed between the electrodes. The mixture under test was considered to be flammable if a flame travelled away from the electrodes for the full length of the tube.

A similar procedure was adopted for measurements at elevated temperatures except that the ammonia/oxygen/nitrogen mixtures were prepared in a heated 6 litre stainless steel bomb at above atmospheric pressure. The heated mixture was then analysed and admitted to the evacuated ignition tube. The ignition tube was surrounded by an electrically wound jacket and any passage of flame along the tube on sparking as observed through slits in the jacket.

A few experiments were carried out on the explosibility of ammonia mixtures. In this work the desired mixtures were prepared in the 6 litre bomb, ignited by a hot resistance wire at the centre of the bomb and the maximum explosion pressure and rates of pressure rise measured by a capacitance transducer sited in the vessel wall.

Check experiments were carried out in both the stainless steel bomb and the 50 mm. diameter glass tube to see if ammonia was lost by oxidation before the mixture could be ignited. In both cases a maximum of 4% of the ammonia was lost at the highest temperature used (400°C) and the longest residence time in the apparatus.

2. RESULTS

2.1 Flammability Limit Measurements

Flammability limit measurements were carried out at three temperatures - ambient, 300°C and 400°C with supporting atmospheres containing from 21% oxygen (air) down to 11.0% oxygen. All these experiments were carried out under atmospheric pressure. The results of this work are shown in Fig. (2), where vol. % ammonia in the mixture is plotted against vol. % oxygen in the supporting atmosphere.

The data in Fig. (2) show that ammonia behaves in a similar manner to hydrocarbon vapours and the flammability limits widen as temperature increases. Thus the limits for ammonia in air increase from 16.6-27.2% ammonia in the mixture at ambient temperatures to 13.1-34.3% at 300°C and 11.2-37.1% at 400°C.

Compilations of data such as Coward and Jones (1) and Zabetakis (8) give lower limits for ammonia and air at ambient temperatures between 15.0 and 17.1 vol % and upper limits between 26.4 and 28.0 vol %. None of these measurements were carried out with an open ended tube (i.e. at constant pressure), which is the preferred method. The influence of temperature on the flammability limit has been measured by White (2) and more recently by Rolingson (9). Their results show the same increase in the flammable range with temperature increase as found in the present work. All these higher temperature flammability limit data are plotted in Fig. (3) together with the more recent literature data of De Coursey et al (7) obtained at ambient temperature using a flat flame burner technique.

The value of the lower flammability limit at ambient temperature found in the present work agrees well with the flat flame burner determinations (7) and with other literature data. Agreement is not as good for the upper limit. This limit is always practically more difficult to measure than the lower limit and both limits are influenced to some extent by the strength of the ignition source. In the experience of the authors powerful ignition sources e.g. gun cotton tend to give an unrealistic widening of the limits, particularly if they are measured in a closed vessel.

One further parameter shown in Fig.(2) is of importance for application to chemical plant design. This is the minimum oxygen concentration in the supporting atmosphere, below which no ammonia containing mixture will burn. Examination of Fig. (2) shows that this decreases from 17 vol. % oxygen at ambient temperature to 12.8% at 300°C and 11.0% at 400°C. These minimum oxygen concentrations are plotted against temperature in Fig. (4) together with similar data obtained under elevated pressure by Buckley and Husa (10). As can be seen all the data lie on a good straight line enabling extrapolation to temperatures of 500-600°C (where experimental work is difficult to be carried out with reasonable accuracy).

2.2 Explosibility Measurements

The measurements of the explosibility of ammonia were carried out in a 6 litre stainless steel bomb with ammonia containing mixtures initially under atmospheric pressure. Explosion pressures were measured at the three temperatures - ambient, 300°C and 400°C used in the flammability limit work, but the only supporting atmosphere investigated was air.

The results showed the same characteristics as measurements made with hydrocarbon/air mixtures. Both the maximum explosion pressure and rates of pressure rise gave a maximum value for an ammonia/air mixture with a composition close to the stoichiometric. Table (1) shows the maximum values of these 3 parameters together with the maximum explosion pressure and rates of pressure rise for the most explosive mixture of a typical hydrocarbon (pentane) in the same 6 litre bomb.

TABLE (1):- Explosibility of Ammonia
(most explosive ammonia/air mixture)

Temperature (°C)	Max. Explosion Press (bars)	Av. Rate Press Rise (bars/sec.)	Max. Rate Press Rise (bars/sec.)
Ambient	5.93	9.65	17.92
300	3.45	28.95	66.17
400	2.76	40.67	84.78
3.0 mol % Pentane in air			
Ambient	8.13	189.5	448.0

These results show that explosion pressure decreases with increase in temperature as would be expected for explosions in a vessel with a constant volume. This temperature effect has already been seen in the work of Crouch et al (11). The maximum explosion pressure for ammonia is also appreciably less than for a typical hydrocarbon - pentane.

The rates of pressure rise both increase with increase in temperature and, in line with the reduced maximum explosion pressure, the rates of pressure rise are considerably less than those for pentane at ambient temperature.

This rexplosibility data indicated that when ammonia/air mixtures are ignited they burn much more slowly than hydrocarbon/air mixtures. It was of interest to see whether ammonia containing mixtures were also less easy to ignite than hydrocarbon mixtures.

2.3 Ease of Ignition of Ammonia

Measurement of ignition energy presents considerable practical difficulties - nature of spark (capacitance or inductance), geometry of electrodes, electrode gap etc. The limited amount of literature on this subject Buckley and Husa (10) and Magison (12) show considerable discrepancies in the measured values of ammonia ignition energies, probably because of the practical difficulties listed above.

A few measurements were, however, carried out using first an inductive spark and then a capacitance spark. The results obtained with these two sparks for the most explosive ammonia/air mixture are given in Table (2) together with the literature data.

TABLE (2):- Minimum Ignition Energies of Ammonia

Source of Data	Explosive Mixture	Type of Igniting Circuit	Voltage (Volts)	Current (amps)	Inductance (Henrys)	Minimum Ignition Energy (mJ)
This Work	Ammonia/Air	Inductive	350	0.11	15	< 90
"	"	Capacitive	10,000	-	-	170
Magison	"	Inductive	24	1.13	0.095	60
Magison	"	Inductive	24	0.25	1.1	40
Buckley and Husa	"	Capacitive	Variable	-	-	680
Magison	Pentane/Air	Inductive	24	0.16	0.095	1.2
Magison	Pentane/Air	Inductive	24	0.045	1.1	1.0

Examination of Table (2) shows that the data obtained with inductance sparks agrees reasonably well with that of Magison, but the measured ignition energy was higher with the capacitance spark. The ignition energies given by Magison and those obtained in the present work are considerably lower than the data of Buckley and Husa. The most important conclusion from the data in Table (2) is that mixtures of ammonia and air are appreciably more difficult to ignite than those of a typical hydrocarbon, pentane, and air (40-170 mJ vs 1.0-1.2 mJ).

3. CONCLUSIONS

The flammability data for anhydrous ammonia/oxygen/nitrogen mixtures obtained in the present work provides adequate information for plant design purposes for a range of supporting atmospheres and temperatures up to 400°C.

Agreement with other published data is good, at least for the lower flammability limit. Some doubt still exists about the upper flammability limit, but the data presented are from experiments in an open tube using a realistic source of ignition (high energy spark), where flames were seen to travel an appreciable distance from the source of ignition.

Explosibility measurements show that ammonia/air mixtures are significantly less explosive than a typical hydrocarbon, pentane, mixed with air. A few measurements on ease of ignition showed that the most explosive mixture of ammonia and air was much more difficult to ignite than the corresponding pentane/air mixture.

PART (2):- FLAMMABILITY OF AQUEOUS AMMONIA

1. EXPERIMENTAL

The flammability limits of ammonia/air/water vapour mixtures were determined in the apparatus used for the work on anhydrous ammonia (see Fig. (1)). The equipment was again evacuated to less than 2 torr. and the required amounts of ammonia and water vapour admitted in turn. Air was then admitted until the pressure reached atmospheric and the ammonia, water vapour and air mixed by means of the solenoid pump.

In each experiment a sample of the mixture under test was taken and analysed for ammonia and water vapour content. A 1.5 Joule inductance spark was again used to ignite the mixture and the ground glass plate at the base of the ignition tube was removed before ignition.

All the experiments on ammonia/water vapour/air mixtures were carried out at one temperature, 80°C, to prevent condensation of water vapour inside the equipment. For this purpose all the equipment, solenoid pump and sample tube included was enclosed in an oven.

2. RESULTS

The results of these experiments are shown in Fig.(5), where vol. % oxygen in the mixture under test is plotted against vol. % ammonia in the same mixture. For comparison purposes the flammability limits of anhydrous ammonia/air at the same temperature, 80°C, are plotted on the graph.

Examination of this figure shows that a minimum oxygen content of 14.5% in the total gases (at 80°C) is required to support combustion where water vapour is present, but mixtures containing as little as 13.0 vol. % oxygen in the total gases will burn for anhydrous ammonia/air mixtures. Thus water vapour is a more efficient quenching agent than nitrogen, as would be expected from its higher molar heat capacity.

Comparison of the results of this work with the limited amount of literature data (6), (7) is difficult because of the different experimental conditions employed by the various sets of workers. The data of Schliephake (6) is taken from some old German work, which was carried out in a closed vessel at 44°C, while DeCoursey et al (7) made their measurements at 65°C using a flat flame burner technique at various linear velocities.

To give an approximate comparison the minimum water level (vol %) in the total gases to completely suppress combustion was calculated for each set of data. These figures are shown in Table (3).

TABLE (3):- Minimum Water Content to Suppress Combustion (vol %)

Present Work Open Tube 80°C	De Coursey et al Flat Flame Burner 65°C	Schliephake et al Closed Vessel 44°C
11.0	10.8	7.2

Considering the wide variation in experimental techniques these results are reasonably consistent with the expected decrease in the amount of water required to suppress flame as mixture temperature decreases.

3. APPLICATION OF RESULTS TO PLANT DESIGN

Much the most important aspect of this work on the flammability of aqueous ammonia is the way in which it can be applied to problems of plant design.

If an aqueous solution of ammonia of known strength is being handled it is possible to calculate the composition of the vapour phase above the solution from vapour/liquid equilibrium data. Suitable data for aqueous ammonia is given in Perry (13). Using this data the vol. % oxygen and ammonia in the gas phase above aqueous ammonia solutions with strengths of 5-25% were calculated for a series of temperatures. The results of these calculations are shown along with the flammability limit measurements made at 80°C in Fig. (6).

Examination of this figure shows that the vapour phase above solutions containing 5% or less ammonia (by vol.) are non-flammable up to 80°C (temperature at which limits determined). More concentrated solutions of ammonia give flammable vapours when the solution is between certain temperatures. A few solution temperatures are shown in Fig. (6) to illustrate this point.

Fig. (7) shows the above data plotted in a different way. Here the vapour phase composition, at a given solution temperature, for all the aqueous ammonia solutions are shown to lie on straight lines. Again the flammability limits (80°C) are plotted on the graph.

From this figure it can be seen that the vapour phase above any ammonia solution will be non-flammable if the temperature of the solution is above 49°C.

4. CONCLUSIONS

The experimental data on the flammability of aqueous ammonia/air vapour mixtures can readily be applied to the hazards of handling aqueous solutions of ammonia.

Two important points emerge from this work (a) the vapour above solutions containing 5% or less ammonia are non flammable at any solution temperature (b) no aqueous solution of ammonia will give flammable vapour when its temperature is above 49°C.

These conclusions apply only to solutions of ammonia in open vessels, but similar calculations based on vapour/liquid equilibrium data can be made for ammonia solutions in sealed vessels.

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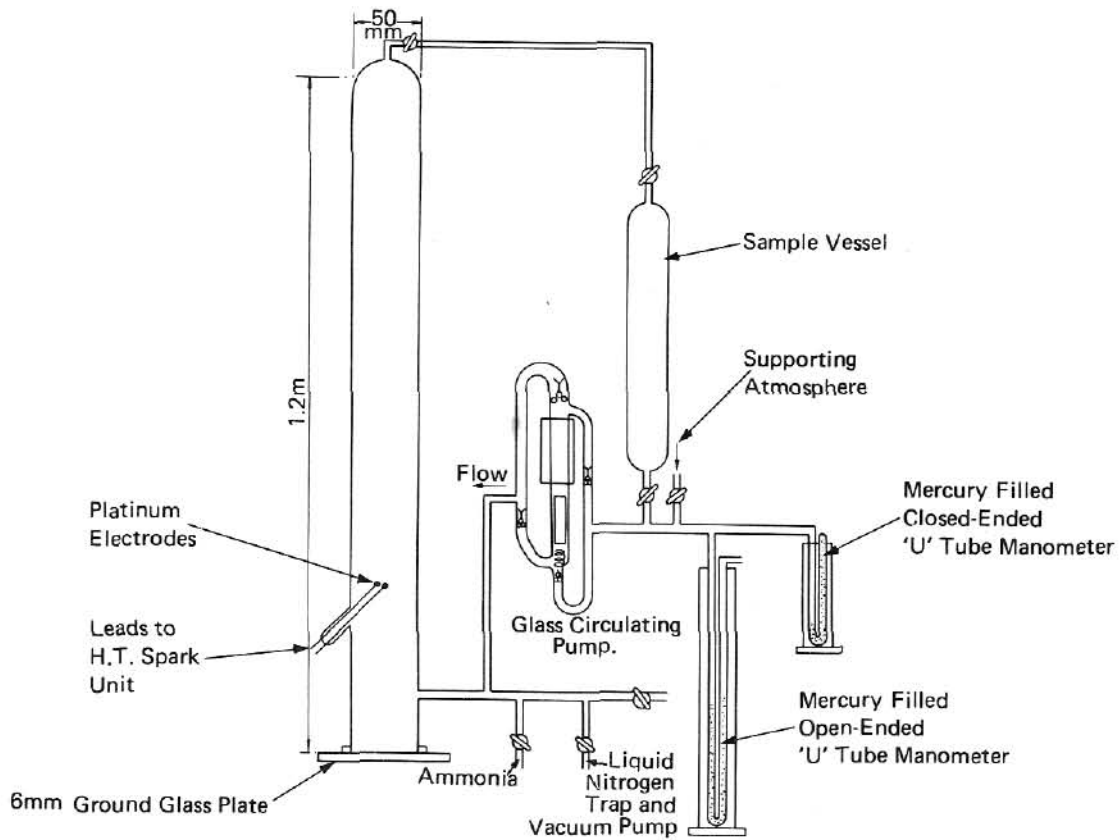


FIG. 1 VERTICAL TUBE FOR ROOM TEMPERATURE WORK

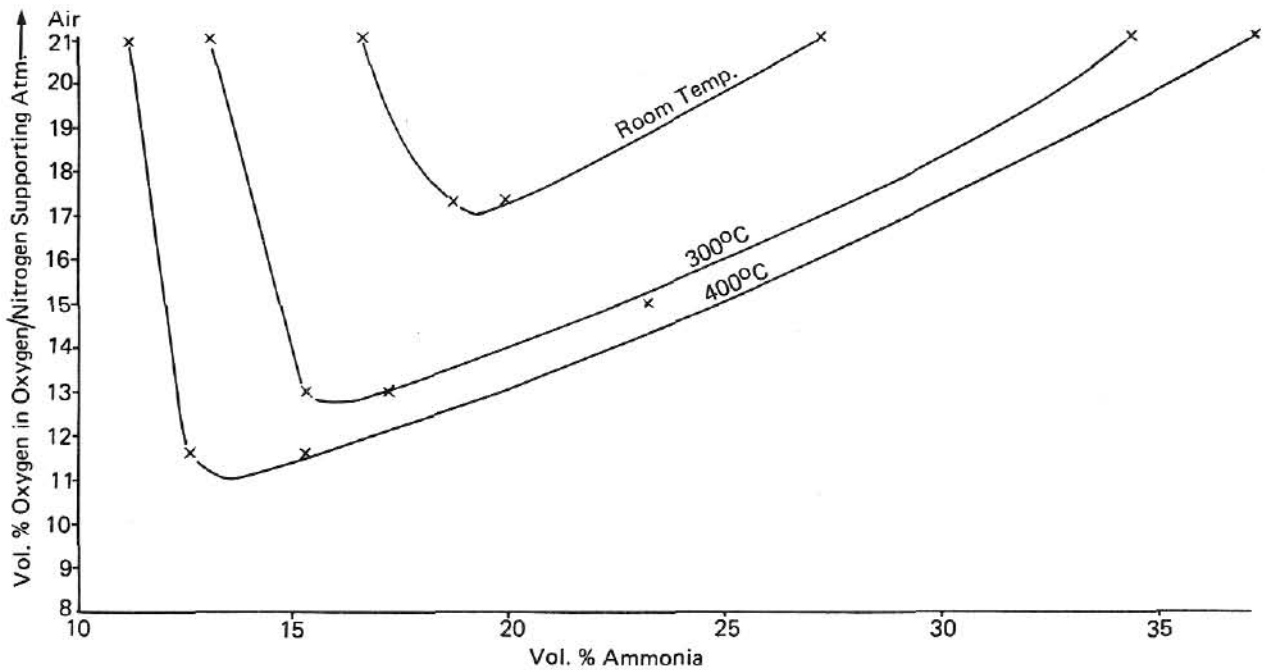


FIG. 2 FLAMMABLE LIMITS AMMONIA - AIR - NITROGEN MIXTURES : AMMONIA VS OXYGEN CONTENT OF SUPPORTING ATMOSPHERE

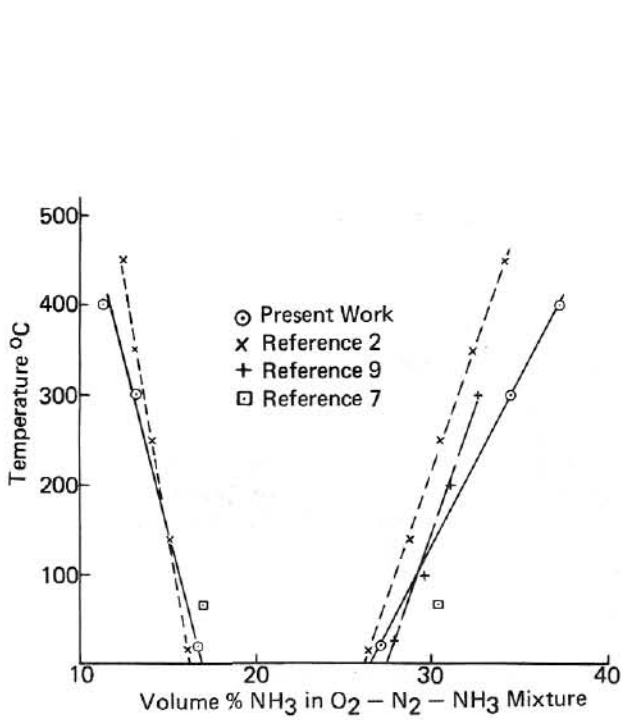


FIG. 3 FLAMMABILITY OF AMMONIA - AIR MIXTURES AT ELEVATED TEMPERATURES

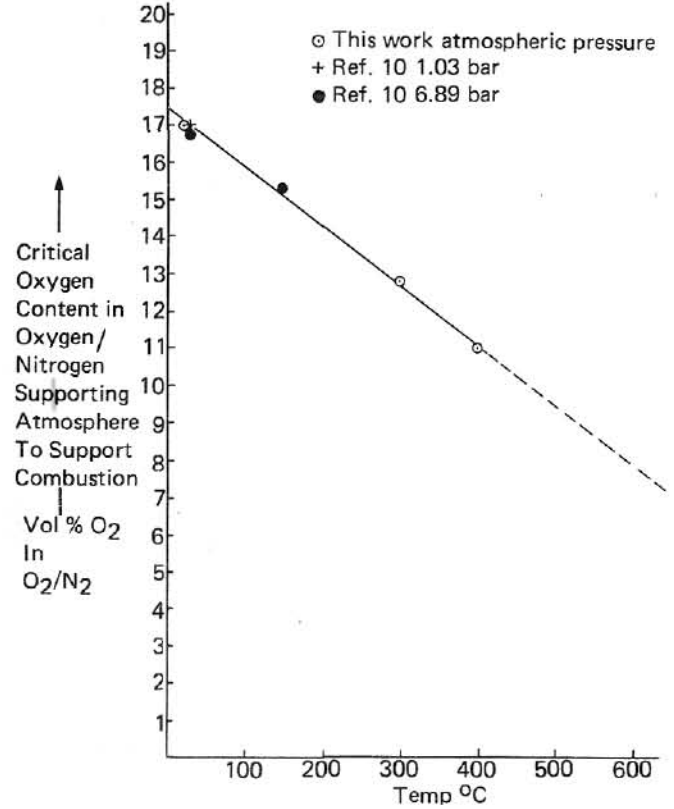


FIG. 4 OXYGEN CONTENT OF SUPPORTING ATMOSPHERE TO SUPPORT COMBUSTION AT VARIOUS TEMPERATURES

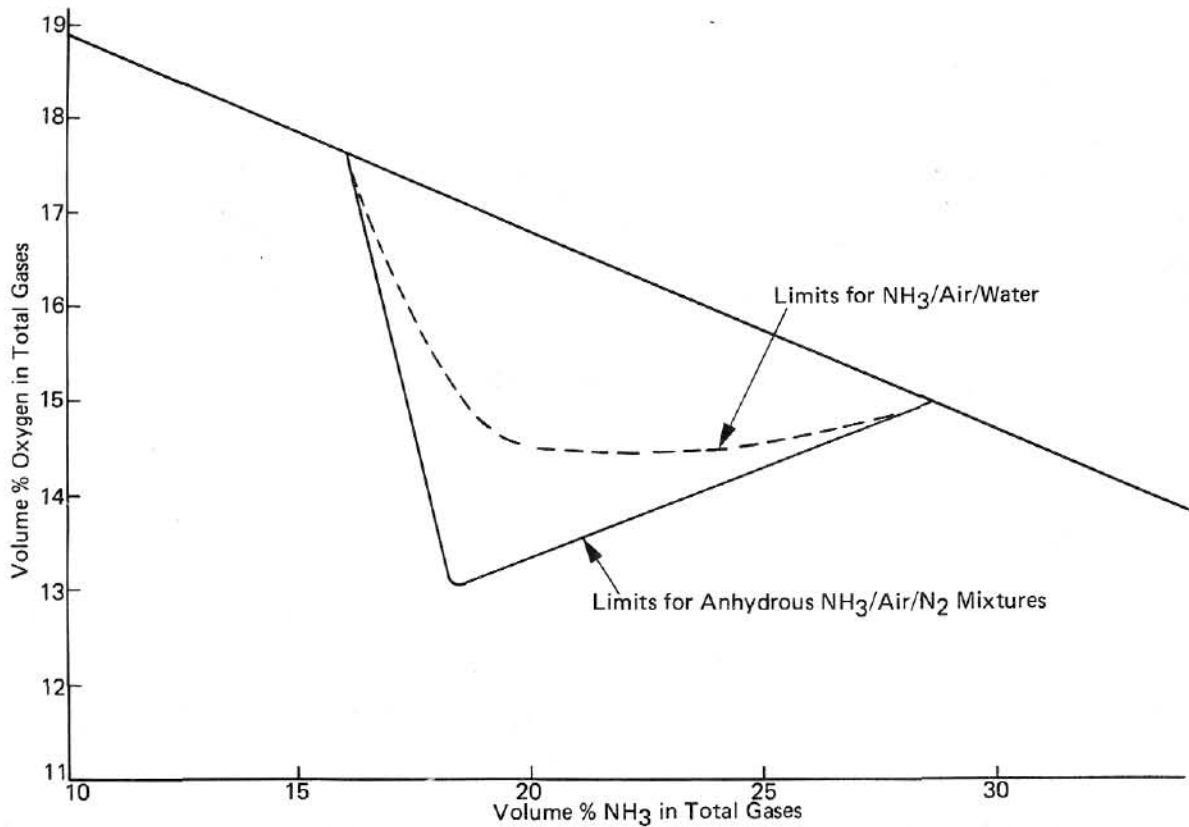


FIG. 5 FLAMMABILITY LIMITS OF AMMONIA SYSTEMS AT 80°C AND ATMOSPHERIC PRESSURE

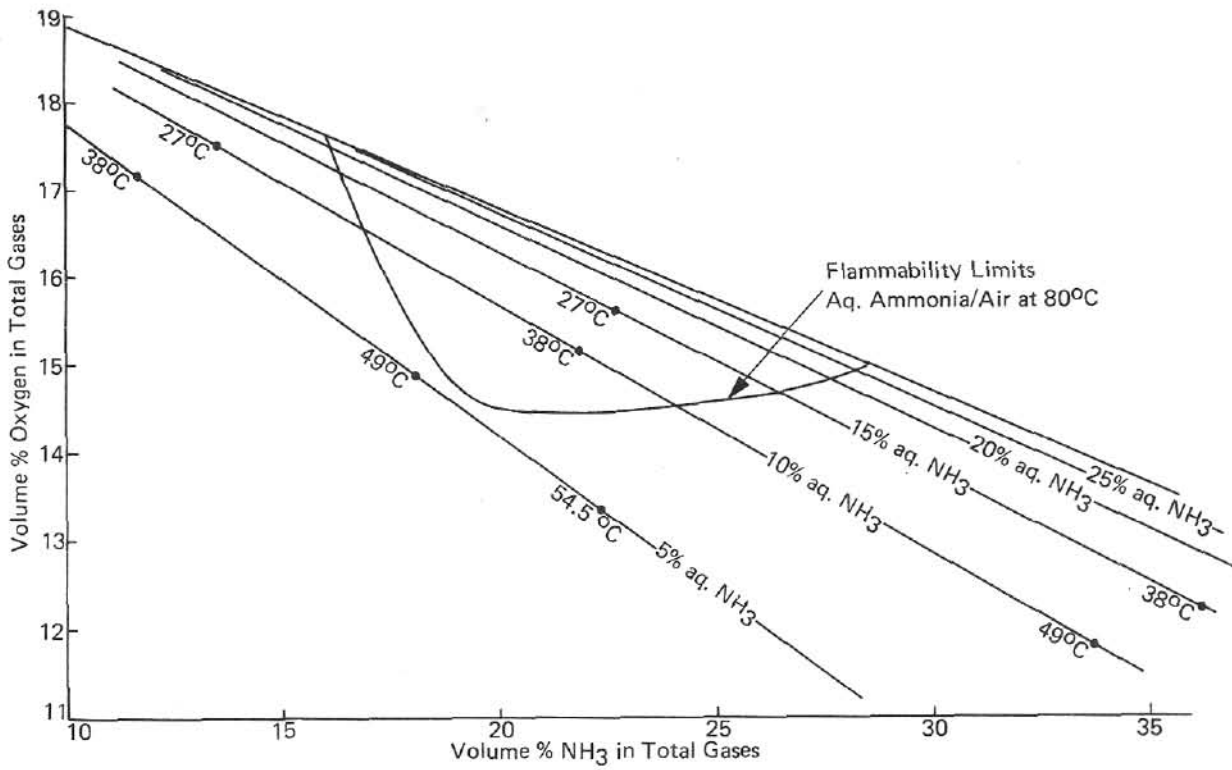


FIG. 6 FLAMMABILITY OF AMMONIA - WATER VAPOUR - AIR SHOWING VAPOUR COMPOSITION ABOVE AQUEOUS AMMONIA SOLUTIONS AT VARIOUS TEMPS.

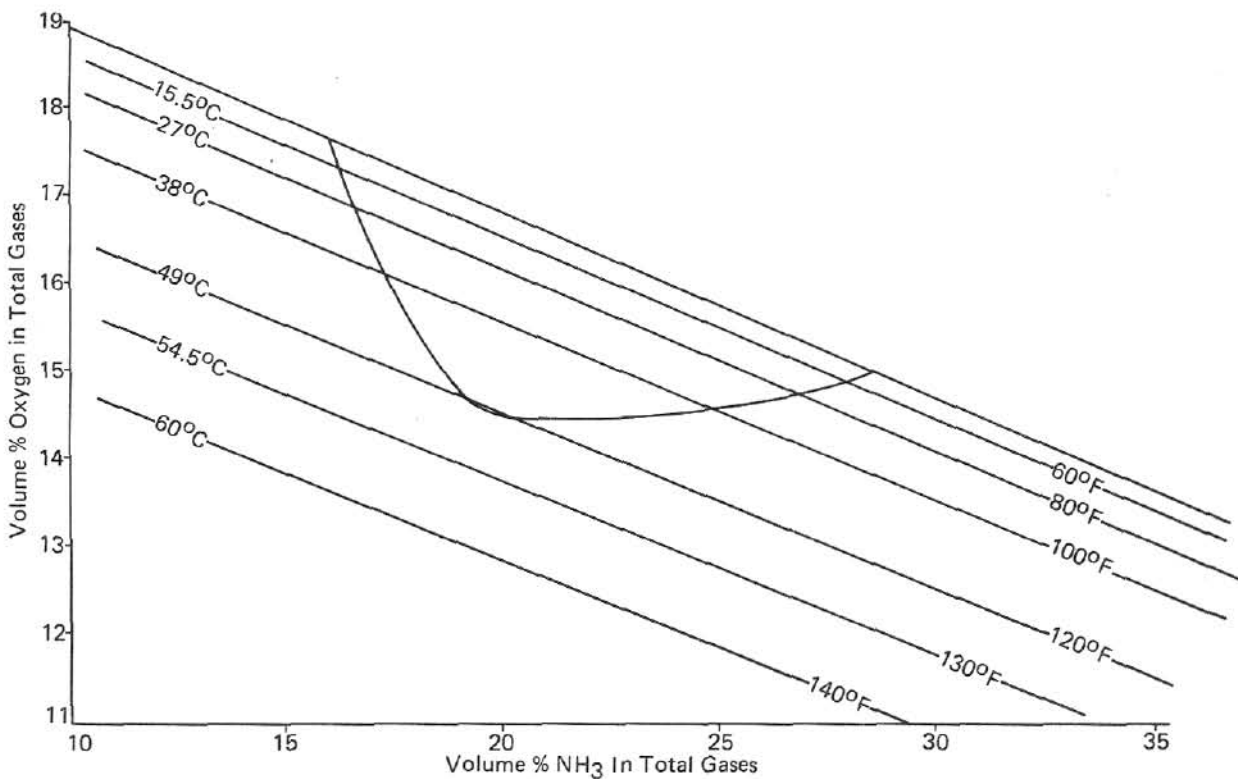


FIG. 7 FLAMMABILITY OF AMMONIA - WATER VAPOUR - AIR WITH ISOTHERMS SHOWING COMPOSITION OF VAPOUR OVER AQUEOUS AMMONIA SOLUTIONS