UNCLASSIFIED

AD NUMBER
AD908525
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to DoD and DoD contractors only; Foreign Government Information; AUG 1972. Other requests shall be referred to British Embassy, 3100 Massachusetts Avenue, NW, Washington, DC 20008.**
AUTHORITY
DSTL, AVIA 37/1344, 8 Dec 2008

THIS PAGE IS UNCLASSIFIED

ERDE
TR-113

BR33550

AD 908525



MINISTRY OF DEFENCE

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

TECHNICAL REPORT No 113

20080731 046

The Silica Gel Process: Small Scale Studies. Part 1: Comparison of Catalysts and Labelling Experiments

F A Armstrong
R T M Fraser

COUNTED IN

TECHNICAL LIBRARY
AMXBR-LB (Bldg. 305)
ABERDEEN PROVING GROUND, MD. 21005

PD 15585

FOR OVERSEAS RELEASE CONDITIONS SEE INSIDE COVER

WALTHAM ABBEY
ESSEX

August
1972

ERDE
TR-113

RELEASE CONDITIONS FOR OVERSEAS DISTRIBUTION

A

1. THIS INFORMATION IS RELEASED BY THE UK GOVERNMENT TO THE RECIPIENT GOVERNMENT FOR DEFENCE PURPOSES ONLY.
2. THIS INFORMATION MUST BE ACCORDED THE SAME DEGREE OF SECURITY PROTECTION AS THAT ACCORDED THERETO BY THE UK GOVERNMENT.
3. THIS INFORMATION MAY BE DISCLOSED ONLY WITHIN THE DEFENCE DEPARTMENTS OF THE RECIPIENT GOVERNMENT AND TO ITS DEFENCE CONTRACTORS WITHIN ITS OWN TERRITORY, EXCEPT AS OTHERWISE AUTHORISED BY THE DEFENCE RESEARCH INFORMATION CENTRE. SUCH RECIPIENTS SHALL BE REQUIRED TO ACCEPT THE INFORMATION ON THE SAME CONDITIONS AS THE RECIPIENT GOVERNMENT.
4. THIS INFORMATION MAY BE SUBJECT TO PRIVATELY-OWNED RIGHTS.

B

1. THIS INFORMATION IS RELEASED BY THE UK GOVERNMENT TO THE RECIPIENT GOVERNMENT FOR DEFENCE PURPOSES ONLY.
2. THIS INFORMATION MUST BE ACCORDED THE SAME DEGREE OF SECURITY PROTECTION AS THAT ACCORDED THERETO BY THE UK GOVERNMENT.
3. THIS INFORMATION MAY BE DISCLOSED ONLY WITHIN THE DEFENCE DEPARTMENTS OF THE RECIPIENT GOVERNMENT AND TO THOSE NOTED IN THE ATTACHED LIST, EXCEPT AS OTHERWISE AUTHORISED BY THE DEFENCE RESEARCH INFORMATION CENTRE. SUCH RECIPIENTS SHALL BE REQUIRED TO ACCEPT THE INFORMATION ON THE SAME CONDITIONS AS THE RECIPIENT GOVERNMENT.
4. THIS INFORMATION MAY BE SUBJECT TO PRIVATELY-OWNED RIGHTS.

C

1. THIS INFORMATION IS RELEASED BY THE UK GOVERNMENT TO THE RECIPIENT GOVERNMENT FOR DEFENCE PURPOSES ONLY.
2. THIS INFORMATION MUST BE ACCORDED THE SAME DEGREE OF SECURITY PROTECTION AS THAT ACCORDED THERETO BY THE UK GOVERNMENT.
3. THIS INFORMATION MAY BE DISCLOSED ONLY WITHIN THE DEFENCE DEPARTMENTS OF THE RECIPIENT GOVERNMENT, EXCEPT AS OTHERWISE AUTHORISED BY THE DEFENCE RESEARCH INFORMATION CENTRE.
4. THIS INFORMATION MAY BE SUBJECT TO PRIVATELY-OWNED RIGHTS.

D

5. THIS INFORMATION IS RELEASED FOR INFORMATION ONLY AND IS TO BE TREATED AS DISCLOSED IN CONFIDENCE. THE RECIPIENT GOVERNMENT SHALL USE ITS BEST ENDEAVOURS TO ENSURE THAT THIS INFORMATION IS NOT DEALT WITH IN ANY MANNER LIKELY TO PREJUDICE THE RIGHTS OF ANY OWNER THEREOF TO OBTAIN PATENT OR OTHER STATUTORY PROTECTION THEREFOR.
6. BEFORE ANY USE IS MADE OF THIS INFORMATION FOR THE PURPOSE OF MANUFACTURE, THE AUTHORISATION OF THE DEFENCE RESEARCH INFORMATION CENTRE. MUST BE OBTAINED.

MINISTRY OF DEFENCE

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

Technical Report No 113

August 1972

The Silica Gel Process: Small Scale Studies. Part 1: Comparison of Catalysts and Labelling Experiments

by

F A Armstrong
R T M Fraser

TECHNICAL LIBRARY
BLDG. 305
ABERDEEN PROVING GROUND, MD.
STEAP-TL

SUMMARY

Small scale experiments using silica gel, ammonium nitrate and urea show that formation of guanidine nitrate becomes erratic if insolubles build up on the catalyst surface. The rate of production of insolubles increases rapidly with temperature, so that a trade-off between low conversions at lower temperatures and insoluble formation at higher temperatures is possible. The yield/temperature relationship is a property of the silica gel used. Yields of guanidine nitrate can be higher than predicted, possibly because by-product water is removed in the form of ammonium silicates rather than ammonium carbamate. Experiments with ^{15}N and ^{18}O suggest that guanidine nitrate does not result from the direct combination of cyanamide and urea: oxygen (or hydroxyl groups) of the silica gel plays an important role. The rate of formation of guanidine nitrate is second order (first order in both urea and ammonium nitrate).

The phase diagram for the ternary system has been investigated.

Further copies of this technical report can be obtained from Defence Research Information Centre, Station Square House, St Mary Cray, Orpington, Kent. BR5 3RE

CONTENTS

		Page No
1	Introduction	1
2	Background	1
3	Analytical Methods	1
3 1	Urea	2
3 2	Total Nitrate	2
3 3	Guanidine Nitrate	2
4	Materials	2
4 1	Catalysts	3
5	Apparatus	3
6	Mass Spectrometry	3
7	Results	4
7 1	Formation of Guanidine Nitrate	4
7 2	Evidence for Intermediates	5
8	Labelling Experiments	5
8 1	^{15}N-ammonium Nitrate	5
8 2	^{18}O Experiments	6
9	Discussion	6
9 1	Labelling Experiments and the Reaction Mechanism	8
9 2	Gaseous Intermediates	11
10	Acknowledgements	11
11	References	12
	Appendix: The Phase Diagram for the System Ammonium Nitrate - Urea - Guanidine Nitrate	14
	Appendix: Solidus + Liquidus Equilibrium Temperatures	15 - 20
	Tables 1 to 26	23 - 48
	Figures 1 to 15	

Reference: WAC/220/011

1 INTRODUCTION

Because of current uncertainties in the continuing supply of dicyandiamide, interest has been shown again in the so-called silica gel process for guanidine nitrate manufacture. This Report deals with the results of small scale batch experiments carried out over extended periods of time; with a new catalyst; and with newer methods of analysis for the various reactants and products involved.

2 BACKGROUND

The use of silica gel as a catalyst for the manufacture of guanidine nitrate from urea and ammonium nitrate was first reported in 1955.[1] To a first approximation, two moles of urea react with one of ammonium nitrate, forming one mole of guanidine nitrate and one of ammonium carbamate:

$$2\ NH_2CO.NH_2 + NH_4NO_3 = (NH_2)_2C{=}NH_2.NO_3 + NH_4CO_2NH_2$$

Later work[2,3] showed that at least on the small scale the optimum ratio of reactants lies between 2:2:1 and 2:2:1.8 (urea:ammonium nitrate:silica gel). Although several mechanisms have been postulated[3] for the reaction, nothing has been done until now to distinguish between them - in fact, very few studies of the reaction beyond the first four hours have been made. Within these limitations, several patents covering various aspects of the process have been granted,[4-7] and more recently a number of papers have appeared in the open literature dealing with the thermolysis of urea (both with[8-10] and without[11,12] ammonium nitrate, and with and without[8] silica gel as catalyst), culminating in the description[13] of a continuous process using a small column.

A brief summary of production cost factors relative to those for other methods has been made.[14]

3 ANALYTICAL METHODS

A number of methods for analysing for urea, ammonium nitrate, and guanidine nitrate are reported in the literature. Several of these have been used for the analysis of fertilisers, that is, for systems fairly similar to those encountered in the melt from the silica gel process. Thus, urea can be determined using urease,[15-17] colorimetrically with diacetyl monoxime and thiosemicarbazide,[18] or (if interferences from ammonium nitrate can be removed) spectrophotometrically in the ultraviolet.[19,20] Ammonium nitrate in the presence of guanidine is probably determined most accurately by micro-diffusion.[21] Biuret can be estimated colorimetrically,[22,23] spectrophotometrically,[24] or polarographically.[25,26]

Methods are also available for melamine, cyanuric acid, ammeline, and ammelide.[27-30]

For the purposes of this investigation however, it was decided to determine urea colorimetrically by treatment with p-(N,N-dimethylamino)benzaldehyde,[31] total nitrate spectrophotometrically,[32] and guanidine nitrate by precipitation with magnesium dipicrylaminate.[33] Ammonium nitrate concentrations were taken as the differences between the total nitrate values found and the corresponding guanidine nitrate figures.

3 1 Urea

An aliquot (10 ml) of the solution was treated with 10 ml of the reagent (prepared from 2.0 g of p-(N,N-dimethyl)aminobenzaldehyde dissolved in 100 ml of 95% ethanol and 10 ml of concentrated hydrochloric acid), made up to 25 ml in a volumetric flask and allowed to stand for ten minutes.[31] The absorbance of a typical solution, measured against a blank prepared from 10 ml of the reagent and 10 ml of distilled water is shown in Figure 1(a): concentration can be determined from the optical density at 425 nm, and Beer's law is followed up to 10^{-2} M. The extinction coefficient depends on the temperature of the solutions, so thermostatting is necessary.

3 2 Total Nitrate

The optical density of the solution at 302 nm (Figure 1(b)) is a measure of the nitrate ion concentration, although the extinction coefficient is relatively small (≈ 7 l mole^{-1} cm^{-1}). Sodium nitrate can be used for calibration, and temperature has relatively little effect on the extinction coefficient (-0.1% per degree Celsius).[32]

3 3 Guanidine Nitrate

Dipicrylamine (hexanitrodiphenylamine) has been found preferable to picrate for the precipitation of guanidine.[33] Thus, dipicrylamine (12 g) and magnesium oxide (1.5 g) were stirred together in 400 ml of water for 12 h, allowed to stand overnight and the solution filtered. Aliquots of the guanidine nitrate solutions (adjusted to pH 8) were treated with a 20% excess of the reagent and allowed to stand for two hours at room temperature, followed by thirty minutes at 0°C. The precipitate formed was filtered off as quickly as possible, washed with 5 ml of a solution of guanidine dipicrylaminate (saturated at 0°) and dried at 110°C.

Ammonium nitrate, but not urea, interferes. This was removed by treatment with 20% formaldehyde solution followed by sufficient sodium hydroxide to bring the pH back to 8.

4 MATERIALS

Ammonium nitrate and urea were both Analar grade (≥99.5%). They were dried overnight in an oven and stored in desiccators.

Urea labelled with ^{18}O was prepared from $H_2{}^{18}O$ (Prochem Ltd, 19.2% ^{18}O) and cyanamide.[34]

Ammonium nitrate labelled with ^{15}N was used as received (Prochem Ltd, 95% $^{15}NH_4NO_3$).

4 1 Catalysts

4 1 1 Silica Gel

Commercial silica gel (BDH; Crossfield Intermediate Density; Crosfield U30; Houdry HSC 532) and silica gel free from sodium ion, prepared[35] by treating tetraethyl silicate with hydrochloric acid were used: the normal drying was overnight in an oven at 110°C.

"Dried" or "dehydrated" silica gel was obtained by heating BDH material to 600°C for 8 h. The product was cooled and stored in a vacuum desiccator and should have had a water content of less than 2% (Table 1).[36]

"Esterified" silica gel resulted when silica gel was refluxed with n-octanol for 4 h, and then washed with ethanol and ether, filtered and stored in an evacuated desiccator.

"Modified" silica gel, described in two Roumanian patents,[37,38] was prepared by refluxing silica gel with silicon tetrachloride, evaporating off excess reagent and treating the dry solid left with dry gaseous ammonia. The product was sieved to remove as much of the ammonium chloride produced as possible.

4 1 2 Miscellaneous

Aluminium oxide, chromium oxide, and titanium dioxide were all commercial materials used as received, after drying at 110°C. Two samples of molecular sieve (Union Carbide 4A and 13X) and an aluminosilicate catalyst (Crosfield Synclyst 3A) were treated similarly.

5 APPARATUS

Most reactions were carried out in boiling tubes, as described previously.[2] The small scale labelling experiments were carried out with the apparatus shown in Figure 2 so that nitrous oxide, formed at higher temperatures, could be trapped in a nitrometer filled with concentrated potassium hydroxide solution and connected to the exit arm.

A Wood's metal bath was used for heating the tubes. The temperatures of the bath and tube contents were monitored and controlled either manually or by the use of a Therm-o-Watch controller.

6 MASS SPECTROMETRY

Initial experiments searching for gaseous intermediates were carried out at the University of Essex using a quadrupole mass spectrometer. Measurements of ^{15}N and ^{18}O abundances were made on an MS 30 double beam spectrometer.

The most satisfactory method found for introducing ammonium carbamate was through a gas inlet (the compound is very volatile, dissociating into ammonia and carbon dioxide); this avoided contamination of the spectrum by traces of urea vaporised and carried over in the gas stream with ammonium carbamate during collection. Guanidine nitrate and urea itself were examined as solids introduced on the direct insertion probe.

7 RESULTS

7 1 Formation of Guanidine Nitrate

High yields of guanidine nitrate can be obtained if the silica gel used is thoroughly dry: Figure 3 shows (dotted lines) the variation in products and reactants for 12 g urea, 16 g ammonium nitrate and 6 g of the dehydrated silica gel (2:2:1) at 180°C. Exposure of the catalyst to the air for one day is sufficient to reduce the amount of guanidine nitrate formed by 50% at 7 h (the solid lines refer to individual tubes, each containing initially 2 g urea, 2.7 g ammonium nitrate and 1 g of silica gel). However, it should be noted that these results are for a single experiment (that is, for one batch), and the activity of the catalyst can vary with time: Table 2 shows the results for Houdry catalyst at 180°C, where mixtures of 12 g urea and 16 g ammonium nitrate were added to 6 g of catalyst, heated for 1½ h, the melt poured off and analysed - the same catalyst sample being used throughout the eight runs.

Finely divided catalysts (U 30, Synclyst 3A) tend to show a more vigorous reaction initially, but less conversion over an extended period: thus the yield of guanidine nitrate formed by U 30 under the conditions of Table 2 decreased by a factor of 2 over the first three batches.

Somewhat different results are obtained when each batch is heated for up to 4 h, and when the experiment is continued over a period of two days. Tables 2 - 17 show results obtained for silica gel prepared from tetraethyl silicate, commercial silica gel, and Houdry catalyst. In general, weight losses (volatiles) decrease steadily with time, but the formation of guanidine nitrate after the first three or four batches becomes irregular. This can best be seen in Figures 4 and 5, along with the corresponding variations found for the insolubles contained in the decanted melts (see Figure 6). However, these must be treated cautiously since Table 18 shows that a considerable quantity of the insolubles found is actually silica gel fines, not additional insoluble material (ammelide) formed during the reaction as is the case for the Houdry catalyst.

Tables 19 - 22 give urea conversions and guanidine nitrate yields,* where

$$\text{urea conversion} = \frac{\text{(moles of urea consumed)}}{\text{(moles of urea added)}}$$

*The efficiency of the reaction is given by the product of the conversion and yield:

$$\text{efficiency} = \frac{2\ \text{(moles of guanidine nitrate formed)}}{\text{(moles of urea added)}}$$

$$\text{guanidine nitrate yield} = \frac{2(\text{moles of guanidine nitrate formed})}{(\text{moles of urea consumed})}$$

In general, yields tend to increase with time, although the actual values depend on the temperature of the experiment, and at least in the case of Houdry catalyst, show a maximum at 180°C (2:2:1 composition). Overall the extent of conversion tends to decrease with time, markedly for Houdry catalyst, less so for silica gel. There are some exceptions: for example, conversions at 170°C using silica gel increase. At lower temperatures, at least some of the low conversion is due to the formation of biuret as an intermediate (compare Table 19; Figure 7).

The apparent conversions greater than 1.00 are not due to experimental errors: at longer times the amount of ammonium carbamate formed decreases (Tables 23, 24; Figure 8).

The weight of insolubles found in the melt increases rapidly with temperature; Figure 9 shows the variation found for the same weights of guanidine nitrate formed. Almost no precipitate is produced at 160°C, although the Houdry catalyst itself shows an increase in weight (Tables 3, 18).

Commercial (U30) silica gel is not as effective as silica gel prepared from tetraethyl silicate (Tables 10, 11, 20, 22).

7 2 Evidence for Intermediates

Silica gel (BDH, 200 - 300 mesh; 2 g), urea (2 g), and ammonium nitrate (2.7 g) were heated together at 180°C for 5 min, and as much of the melt as possible poured off. The residue was allowed to cool and then crushed: small quantities were used to fill capillary glass tubes. These in turn were introduced directly into the source of a quadrupole mass spectrometer and heated. Spectra were recorded once every two minutes: measurements were made either as a function of time and temperature, or of time alone. Figure 10 shows typical variations found for a number of peaks in relation to their initial heights. A comparison of the mass spectrum of the reaction mixture at 120°C with that at 180°C (Figure 11) shows close similarities except at m/e 30 and m/e 46, peaks arising from the nitrate group of the ammonium nitrate.

8 LABELLING EXPERIMENTS

8 1 ^{15}N-ammonium Nitrate

Since at least one mechanism suggested[3] for the silica gel reaction involves formation of ammonia from the reacting ammonium nitrate, the role of the various nitrogen atoms has been investigated using ammonium nitrate labelled in the ammonium ion with 95 atom per cent ^{15}N. Figure 12 shows part of the high resolution mass spectrum of the ammonium carbamate collected after 3 h from urea (0.2992 g : 2 moles), ammonium nitrate (0.3995 g ; 2 moles), and BDH silica gel (0.2572 g ; 1.7 moles). Whereas the background contains peaks at 16.000 (O^+), 17.0081 (HO^+), 18.0163 (H_2O^+), and 19.0224 (H_3O^+), the ammonium carbamate spectrum shows peaks as well at

16.0238 (NH_2^+)	16.0130 ($^{15}NH^+$)
17.0319 (NH_3^+)	17.0211 ($^{15}NH_2^+$)
18.0401 (NH_4^+)	18.0293 ($^{15}NH_3^+$)
	19.0374 ($^{15}NH_4^+$)

A comparison of peak heights for corresponding species (for example, NH_2^+ and $^{15}NH_2^+$) gave $^{15}N/^{14}N$ as $1/(2.08 \pm 0.1)$. A second experiment, using the same quantities as above, but heated for only thirty minutes instead of three hours, gave ammonium carbamate with the $^{15}N/^{14}N$ ratio of $1/(1.91 \pm 0.1)$.

The residue from the first experiment was dissolved in a small amount of hot water, filtered, and the filtrate reduced to half volume before cooling. Guanidine nitrate precipitated and was washed with a small amount of ethanol and then dried. The remaining solution was evaporated to dryness to yield ammonium nitrate. The mass spectrum of guanidine nitrate has been reported in the literature:[39] the base peak is m/e 59. Figure 13 shows the mass spectrum for unlabelled guanidine nitrate, together with that obtained for the guanidine nitrate from the labelling experiment. It is clear that m/e 60 and 61 have replaced m/e 59, and the ratio found for m/e 61:m/e 60 is 4:5.

The ammonium nitrate recovered was boiled with a small amount of water to form nitrous oxide. The m/e 44 and 45 peaks in the mass spectrum of this gave a $^{14}N/^{15}N$ ratio of 93.6/6.4.

A third labelling experiment was carried out: the mixture, containing ammonium nitrate (9.9 atom per cent ^{15}N) was swept with carbon dioxide and the resulting gases passed through a nitrometer. The temperature used for the experiment was 200°C so as to produce a reasonable amount of gas. Three samples were collected; the first, from the first fifty minutes, showed a ^{15}N content of 2.79 atom per cent; the second (up to seventy-five minutes), 2.82 atom per cemt; and the third, 2.86 ^{15}N atom per cent. The value for complete randomisation would have been 3.26 per cent.

8 2 ^{18}O Experiments

The small scale heating experiments of the last section were repeated using urea containing 14.8 atom per cent of oxygen-18. The relative heights of the m/e 44 and 46 peaks found for ammonium carbamate in the mass spectrometer were 100:21.4 (the calculated values, assuming no ^{18}O losses, are 100:34.7), so that only two-thirds of the labelling expected was found. On the other hand, repeating the experiment using the same sample of silica gel but fresh (unlabelled) urea and ammonium nitrate produced ammonium carbamate containing 2.3 atom per cent of ^{18}O.

9 DISCUSSION

The experiments have been designed to lead on directly from the earlier work of Roberts,[2,3] and this has both advantages and disadvantages. It does mean that a number of the early conclusions can be applied to the present work,

and on the other hand some of the conclusions reached here serve to clarify earlier points. While the results from the extended runs may not have a direct bearing on factors involved in the continuous process, they do serve to show some of the points that must be considered in choosing a catalyst. Single runs of 1 h or even 4 h do not necessarily give a good indication of relative catalytic activity, and this can be seen from a comparison of Table 2 and Table 7.

Batch-to-batch variation is another factor which may be important, although more difficult to deal with. In the present study, one batch of Houdry beads has been compared mostly with silica gel prepared from tetraethyl silicate and hydrochloric acid. Such material contains almost no impurities beyond a trace of iron (0.046% Fe: overall purity, 99.936%),[40] it can be obtained in relatively large pieces (> 8 mesh), and its properties are generally reproducible. It is thus a good standard material, unlike commercial silica gel which may have been prepared by different (although unknown) methods and where the activity varies from one batch to the next. Where experiments were carried out with commercial (BDH, Crosfield) silica, this has been indicated in the tables.

Some studies of the effect of catalyst particle size on the reaction rate have already been made.[3] Although finer material may speed up the conversion to guanidine nitrate, mechanical losses tend to be much greater during decanting of the melt: an extreme case of this was found with Porasil A (Pechiney-St Gobain: 100 - 150 mesh) and porous glass (Applied Science Laboratories: 60 - 80 mesh): the results of several experiments are shown in Table 25. While the amount of guanidine nitrate formed by the Porasil was much greater, the catalyst tended to form a gel with the melt and after the second run it was impossible to separate the two. This did not happen with the porous glass. Temperature also plays a part in catalyst losses; higher temperatures reduce particle size much more rapidly, with the result that significant quantities of catalyst fines may be found in the melt. Table 12 shows that this can happen for the Houdry catalyst as well.

A number of points arise from the results listed in Tables 2 - 17: it is clear for example that the amount of insoluble material (ammelide) increases rapidly with temperature. In the case of the Houdry catalyst, part of the insolubles are formed at the expense of guanidine nitrate so that although the time of heating at 190°C was reduced so as to give approximately the same degree of urea conversion as at 180°C (Table 8), the guanidine nitrate yields were reduced by 15%. A comparison of Tables 19 and 20 shows the differences between silica gel and the Houdry beads: temperature for temperature, conversions are generally higher for the Houdry catalyst (except at 190°C). The fluctuations in guanidine nitrate formation and the accompanying variations in the amount of insolubles formed have already been noted and are shown in Figures 4 - 6: in the case of the Houdry catalyst there appears to be a shell of insoluble material building up around the beads. From time to time pieces of this crack off, but even so, such a formation preventing easy access of reagents could account for the decrease in conversion noted. Low conversions at low temperatures result partly from the deammoniation of urea to biuret: in a batch reaction this leads to a non-productive consumption of urea (in a continuous process with recycle, the

biuret provides a further source of guanidine nitrate).

While conversions are lower for the silica gel prepared from tetraethyl silicate when compared with the Houdry catalyst, they are a little better than those from commercial silica gel (U 30) and so are the yields. It should be pointed out here that the first values given in each column for yield and conversion have little significance since they are based only on the amount of material actually decanted from the catalyst: this may be small compared with the quantities subsequently recovered - hence the reason for the parentheses shown (see the discussion later on the effect this retention of melt has on the average reaction time). However, Tables 19 - 21 do suggest that the reaction is more sensitive to relative proportions of reactants and catalyst when silica gel is used, showing in the conversions obtained.

Section 9 1 notwithstanding, the relationship between amount of catalyst (that is, the weight added) and yield of guanidine nitrate is not simple when the catalyst is retained for more than one batch. Tables 20 and 21 show that as long as there is little loss of silica gel, the yield increases with time, particularly at the lower catalyst:reactants ratios. This increase helps offset any decrease resulting from mechanical losses of the catalyst in decanting the melts (as for example in the experiments of Table 16). Further levelling is due to the fact that mixtures which are subject to high catalyst losses (either because of high catalyst levels or finely divided material), are just those where a significant quantity of the melt is retained on the catalyst each time. The system of Table 10 (U 30 silica gel) is one: others can be recognised easily since the amount of melt recovered from the first stage is very much less than from the succeeding. Even where the hold-back is moderate, as with silica gel prepared from tetraethyl silicate, the average residence time of the reactants may be quite large. Figure 14 shows the distribution found for a 2:2:1.7 system with each batch heated for $3\frac{3}{4}$ hours at 180°C. Here approximately one-third of the melt is retained by the catalyst: assuming uniform mixing over the heating period, this leads to an average residence time of 5.45 h. After the fifth batch, one-third of the components in the melt recovered have been heated for $7\frac{1}{2}$ hours, and one tenth have been heated for $11\frac{1}{4}$ hours (the actual fractions vary slightly depending on the weight of melt decanted).

The simple mechanism deduced later suggests that there should be a linear relation between the number of active sites provided by the catalyst and the rate of reaction. This does not mean a linear relationship between the amount of guanidine nitrate formed in a given time and the amount of catalyst in the system. Yields may be high, even greater than 1.0 (Tables 13, 21), at very low catalyst levels because of the relative importance of the uncatalysed path. Efficiencies, however, remain low unless the amount of catalyst is increased.

9 1 Labelling Experiments and the Reaction Mechanism

Analysis of the ammonium carbamate from the ^{15}N labelling experiments suggests that considerable mixing of the nitrogens (other than that of the nitrate group) takes place. It seems unlikely that this arises from direct

interchange between gaseous ammonia and ammonium nitrate,

$$NH_3 + {}^{15}NH_4NO_3 \rightleftharpoons {}^{15}NH_3 + NH_4NO_3$$

since there is little difference in the $^{15}N/^{14}N$ ratios found at 30 min and 2 h. On the other hand, direct exchange between ammonium nitrate and urea is also slow.[41] Randomisation is not a general phenomenon in the system, for the mass spectrum of the guanidine nitrate formed shows peaks at m/e 60 and 61, corresponding to the molecular ions of species containing one and two ^{15}N atoms respectively (randomisation, starting from equimolar amounts of urea and 95 atom per cent ^{15}N ammonium nitrate would lead to a mixture of guanidine nitrates containing zero, one, two, and three ^{15}N atoms in the proportions of 0.0328:0.2089:0.4439:0.3144): no m/e 62 is found. The overall isotopic content is considerably higher than in the ammonium carbamate (51.8 atom percent as against 32.5). An approximate calculation to balance the isotope content of reactants and products confirms that the ^{15}N content of the ammonium nitrate left after reaction should be low (compare the nitrous oxide value in the Results section). The mechanism outlined below can go a long way in explaining the earlier[3] results, where only the reaction of dimethyl urea with ammonium nitrate gave rise to methylguanidine nitrate, and the reaction of methyl urea and ammonium nitrate formed guanidine nitrate, together with a sublimate smelling of both ammonia and methylamine.

It has been shown[3,8] that urea, heated alone or with silica gel gives rise to some guanidine (in the form of the cyanate or carbonate), but not very much. On the other hand, heating a mixture of ammonium nitrate and urea with esterified silica gel produces only traces of guanidine nitrate. This suggests that both hydroxyl groups and ammonium ions are necessary for good yields. Water present in the silica gel or reactants can reduce the yield, due to loss of urea as ammonium carbamate (but see below), and removal of water (either by heating the silica gel to a high temperature - but below 800°C - or by reaction with silicon tetrachloride and ammonia[37]) can improve the yield as shown in Figure 3. But this is only a temporary improvement, and the silica gel probably reaches an equilibrium with water produced during the course of the reaction.[3] On the other hand, the results of Figure 8 and Tables 19, 20 and 21 show that at least when the reaction is carried out in a boiling tube the ratio of guanidine nitrate/ammonium carbamate rises above the value of 1.00 predicted by the simple hypothesis of two moles of urea reacting with one of ammonium nitrate to give one mole of guanidine nitrate and one of ammonium carbamate. A possible explanation for this lies in the observations made at 180°C.

Using silica gel (2:2:1 composition), the melts obtained were clear both when decanted from the catalyst and while they were liquid, and they produced insolubles only when diluted with water. The weight losses recorded during the course of the experiments show that these insolubles are silica gel, not ammelide produced during the reaction itself. The most likely explanation is that melt-soluble ammonium silicates form:

$$SiO_2 + 2NH_3 + H_2O = (NH_4)_2SiO_3$$

$$SiO_2 + 4NH_3 + 2H_2O = (NH_4)_4SiO_4$$

Such salts are unknown in aqueous solution because they undergo spontaneous hydrolysis:

$$(NH_4)_2SiO_3 + 2H_2O = 2NH_4OH + SiO_2.H_2O$$

Their formation however, by providing an additional path for water removal, would promote the conversion of additional urea to guanidine nitrate and thus account for the higher yields observed.

The ^{18}O experiments, where only two-thirds of the oxygen expected is recovered in the ammonium carbamate, show that the hydroxyl groups (or at least the surface oxygens) of the silica gel participate in an exchange reaction with the oxygen of the urea C=O group, and this can be accounted for in the reaction scheme:

$$\left.\begin{array}{l} NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \\ NH_4NO_3 \rightleftharpoons NH_4^+ + NO_3^- \end{array}\right\} K$$

or

$$NH_2C{=}O.NH_2 \rightleftharpoons NH_3 + HOCN \qquad (1)$$

$$HO\text{-}Si^+ + NH_2C{=}O.NH_2 \rightleftharpoons HO\text{-}Si^+ - O\text{-}C(NH_2)_2 \qquad (2)$$

$$HO\text{-}Si^+ - O\text{-}C(NH_2)_2 + NH_3 \rightarrow HO\text{-}Si\text{-}OH + C(NH_2)_3^+ \qquad (3)$$

$$HO\text{-}Si\text{-}OH + NCOH \rightarrow HO\text{-}Si - O\text{-}C{\equiv}N + H_2O \qquad (4)$$

$$HO\text{-}Si - O\text{-}C{\equiv}N + NH_4^+ \rightarrow HO\text{-}Si^+ - O\text{-}C(NH_2)_2 \qquad (5)$$

$$HO\text{-}Si\text{-}O\text{-}C{\equiv}N + H_2O \rightarrow HO\text{-}Si\text{-}OCONH_2 \qquad (6)$$

$$HO\text{-}Si\text{-}OCONH_2 \rightarrow HO\text{-}Si^+ + NH_2CO_2^- \qquad (7)$$

$$NH_2CO_2^- + NH_4^+ \rightarrow 2\,NH_3 + CO_2 \qquad (8)$$

This is coupled with a secondary path involving the formation of biuret:

$$NH_2C{=}O.NH_2 \rightleftharpoons NH_3 + HOCN \qquad (1)$$

$$HOCN + NH_2C{=}O.NH_2 \rightarrow NH_2C{=}O.NH.C{=}O.NH_2 \qquad (9)$$

Evidence for reaction (1) has been presented previously;[3] a mixture of ammonium nitrate and potassium cyanate can be used in place of ammonium nitrate and urea.

By assuming steady state conditions for reactions (1) to (3) the rate of formation of guanidine nitrate is given by

$$\frac{d(\text{guanidine nitrate})}{dt} = \frac{k_2(S)(\text{urea})(\text{ammonium nitrate})}{k_3(\text{ammonium nitrate}) + k_{-2}}$$

where (S) is the concentration of free active sites on the silica gel. Since ammonium nitrate is generally in excess so that its concentration changes only slowly, the formation of guanidine nitrate is approximately second order, first in both ammonium nitrate and urea. Table 26 lists data from Figure 7 for guanidine nitrate, ammonium nitrate, and urea concentrations at different times, and the comparison between guanidine nitrate values calculated from a second order rate law by graphical integration and the actual values is shown in Figure 15. Reactions (5) and (3) in the mechanism account for the occurrence of two labelled nitrogens in guanidine nitrate from the labelling experiments: a second path for the exchange might involve urea-ammonium cyanate-ammonium nitrate, but this should show a greater time dependence than is found. The steady state approximation can be extended to cover all steps (1) to (8), but the treatment still shows that formation of guanidine nitrate is approximately second order.

9 2 Gaseous Intermediates

Other workers[8] have claimed that decomposition of urea by itself involves the simultaneous dehydration and deammoniation of the $NH_2C{=}O.NH_2$ molecule (the two primary reactions) to give on the one hand cyanamide and on the other cyanic acid. In spite of this, chemical tests have failed to detect any cyanamide, and the concentration of cyanic acid in the melts has been estimated at less than 0.005%. It was hoped that the quadrupole mass spectrometer might produce a tool for examining the point further for the urea - ammonium nitrate nitrate mixtures, but the experiments were inconclusive.

10 ACKNOWLEDGEMENTS

The quadrupole mass spectra run at the University of Essex were arranged by Dr J R Gilbert. High resolution spectra were measured by N C Paul. C Manning assisted in the experimental work and analysis.

11 REFERENCES

1		Final and Summary Report. Pittsburgh Coke and Chemical Company, September 1955
2	Martin T, Roberts E	ERDE XR 441/177, May 1956
3	Martin T, Roberts E	ERDE XR 441/178, June 1958
4	Boatright L G, Mackay J S	USP 2,783,276 (1957)
5	Mackay J S	USP 2,949,484 (1960)
6		Ger. P 1,131,656 (1962) Chemisches Werke LOWI GmbH.
7	Roberts E, Martin T	USP 3,043,878 (1962)
8	Ostrogovich G, Bacaloglu R	Rev. roum Chim., 10, 1115 (1965)
9	Kazarnovskii S N, Spasskaya R I	Zhur. priklad. Khim., 34, 2079 (1961)
10	Spasskaya R I, Kazarnovskii S N	Zhur. priklad. Khim., 35, 1842 (1962)
11	Malkina N I, Kazarnovskii S N	Zhur. priklad. Khim., 34, 1583 (1961)
12	Baranski A	Chem Stosowana., Ser. A 7(A), 567 (1963)
13	Spasskaya R I, Kazarnovskii S N	Khim. Prom., 498 (1963)
14	Batty W E	ERDE TN 35, September 1971
15	Fox E J, Geldard W J	Ind Eng Chem., 15, 743 (1923)
16	Smith J A, Dock D G, Rich R W	J. agric Fd. Chem., 6, 587 (1958)
17	Wilson B W	Clinica Chem., 12, 360 (1966)
18	Coulcombe J J, Favrean L	Clinica Chem., 9, 102 (1963)
19	Mushkin Yu I	Tr. po Khim. i Khim. Tekhnol., 404 (1962)
20	Babkin E E	Akad. Nauk. SSR, Otd. Biokhim., Biofiz. Khim. Fiziol. Aktiv. Soedin, 353 (1966)
21	Takimoto M, Tawara M	Kogyo-kwaguku Zasshi, 63, 2059 (1960)
22	Ellis G G, Formaini R L	J. agric Fd. Chem., 3, 6158 (1955)
23	Guerts J J, van Stelle J E, Brinkman E G	Analyt Chim. Acta, 41, 113 (1968)

24	Sanyal R M, Pal P K, Banerji K C	Technology, 2, 172 (1965)
25	Curti R, Riganti V, Locchi S	Chim. Ind., 43, 782 (1961)
26	Mishra M B, Banerjee B K	Technology, 6, 35 (1969)
27	Kazarnovskii S N, Lebedev O I	Trudy Gor'kovsk. Politekh. Inst. khim-technol Silik Fak, 11, 52 (1955)
28	Kazarnovskii S N, Malkina N I	Trudy Gor'kovsk. Politekh. Inst. khim-technol Silik Fak, 11, 56 (1955)
29	Ostrogovich G, Nemes A	Baza cercetari stii. Timisoara Studii cercetari stii., Ser. Stii. chim., 7, 285 (1960)
30	Marek R W	USP 2,986,452 (1961)
31	Watt G W, Chrisp J D	Analyt. Chem., 26, 452 (1954)
32	Strickler S J	Tech. Rep. 4, Project NR-019-134 ONR (1961)
33	Ghosh P, Sarkar J M	Technology, 5, 7 (1968)
34	Laulicht I, Pinchas S, Petreanu E, Samuel D	Spectrochim Acta, 21, 1487 (1965)
35	Peri J B	J. Phys. Chem., 70, 2937 (1966)
36	Gregg S J	in "Chemisorption", W E Garner, ed., Butterworths London, 1957, p 68
37	Bacaloglu R, Ostrogovich G	Rom. P 51080 (1969)
38	Bacaloglu R, Ostrogovich G	Rom. P 51083 (1969)
39	Beynon J H, Hopkinson J A, Williams A E	Org. Mass Spectrometry, 1, 169 (1968)
40	Peri J B, Hensley A L	J. Phys. Chem., 72, 2926 (1968)
41	Schaedel E, Huebner H	Kernenergie, 5, 347 (1962)

APPENDIX

THE PHASE DIAGRAM FOR THE SYSTEM AMMONIUM NITRATE - UREA - GUANIDINE NITRATE

The solidus + liquidus equilibrium temperatures were determined for mixtures of ammonium nitrate with urea and with guanidine nitrate, of guanidine nitrate with urea, and of guanidine nitrate, urea, and ammonium nitrate together, by recording cooling curves with an accuracy of $\pm$ 0.5°C. The samples generally contained 10 - 30 g of the components, and the composition was determined from the weights of the solids taken. To avoid decomposition at elevated temperatures, no sample was raised to a temperature more than 25°C above the melting point. At the same time, the sample was kept homogeneous by efficient stirring. Approximately 150 equilibrium temperatures were measured, and these are listed in the table. The temperature projection on the basal plane (constant pressure assumed) is shown in the figure. The ternary eutectic point occurs at guanidine nitrate, 5%; ammonium nitrate, 50%; urea, 45% (all by weight), giving a minimum temperature of 42.0°C for the system.

APPENDIX

SOLIDUS + LIQUIDUS EQUILIBRIUM TEMPERATURES

Guanidine Nitrate (weight percentage)	Ammonium Nitrate (weight percentage)	Urea (weight percentage)	Temperature, °C
5	50	45	42
7	49	44	43
7	47	46	43
5	51	43	43
4	50	46	43
3	52	45	43
2	53	45	44
-	52½	47½	44½
3	50	47	45
1	52	47	45
-	55	45	46
8½	48	43½	47
5	52	43	47
5	47½	47½	48
9	46	45	49
-	57	43	49
7	52	41	50
10	43	47	51
9	50	41	51
2	55	43	51
8	43	49	52
7	44	49	52
9	51	40	53
5	45	50	53
3	55	42	53
10	45	45	53
10	40	50	54
10	50	44	56
5	55	40	57
-	47	53	57½

APPENDIX

Guanidine Nitrate (weight percentage)	Ammonium Nitrate (weight percentage)	Urea (weight percentage)	Temperature, °C
7	55	38	59
13	37	50	60
11	50	39	60
7	40	53	60
3	58	39	60
12	35	53	61
10	54	36	61
10	37	53	61
12	44	44	62
10	55	35	62
-	61½	38½	62
11	53	36	63
6	57	37	64
10	35	55	65
15	32	53	66
5	37½	57½	68
18	27	55	70
15	40	45	70
13	56	31	70
10	33	57	70
19	27	54	71
18	29	53	71
17	33	50	71
7	60	33	71
20	25	55	72
14	46	40	72
20	24	56	74
-	66	34	76
16½	43	40½	77
14½	57	28½	77
5	33	62	77

APPENDIX

Guanidine Nitrate (weight percentage)	Ammonium Nitrate (weight percentage)	Urea (weight percentage)	Temperature, °C
15	25	60	78
5	63	32	78
25	19	56	79
24	17	59	79
20	30	50	79
10	28	62	79
9	62	29	79
20	20	60	80
26	15	59	80
20	34	46	81
27	16	57	82
24	23	53	82
16	52½	31½	82
27	13	60	83
18	47	35	83
30	12	58	84
30	10	60	86
15½	61½	23	88
10	23	67	88
34	8	58	89
28	20	52	89
24	12	64	89
22	38	40	89
-	30	70	89
25	30	45	90
4	69	27	90
17	62	21	91
16	63	21	91
37½	-	62½	91½
40	-	60	92
20	50	30	93
-	73	27	94½

APPENDIX

Guanidine Nitrate (weight percentage)	Ammonium Nitrate (weight percentage)	Urea (weight percentage)	Temperature, °C
33½	-	66½	95½
20	10	70	97
-	21½	78½	99
32	21	47	100
26	39	35	100
10	15	75	100
17	66½	16½	101
10	70	20	101
-	77	23	105
25	-	75	105½
25	50	25	106
40	10	50	108
10	74	16	109
24	58	18	110
7	10	83	111
20	70	10	111
30	40	30	112
24	64	12	112
-	12	88	114
-	82	18	114½
50	-	50	118
40	20	40	119
24	71	5	119
25	70	5	119
29	57	14	120
15	-	85	120
10	79	11	120
47½	5	47½	121
45½	10	44½	121
25	71	4	121
5	5	90	121
45½	9	45½	122

APPENDIX

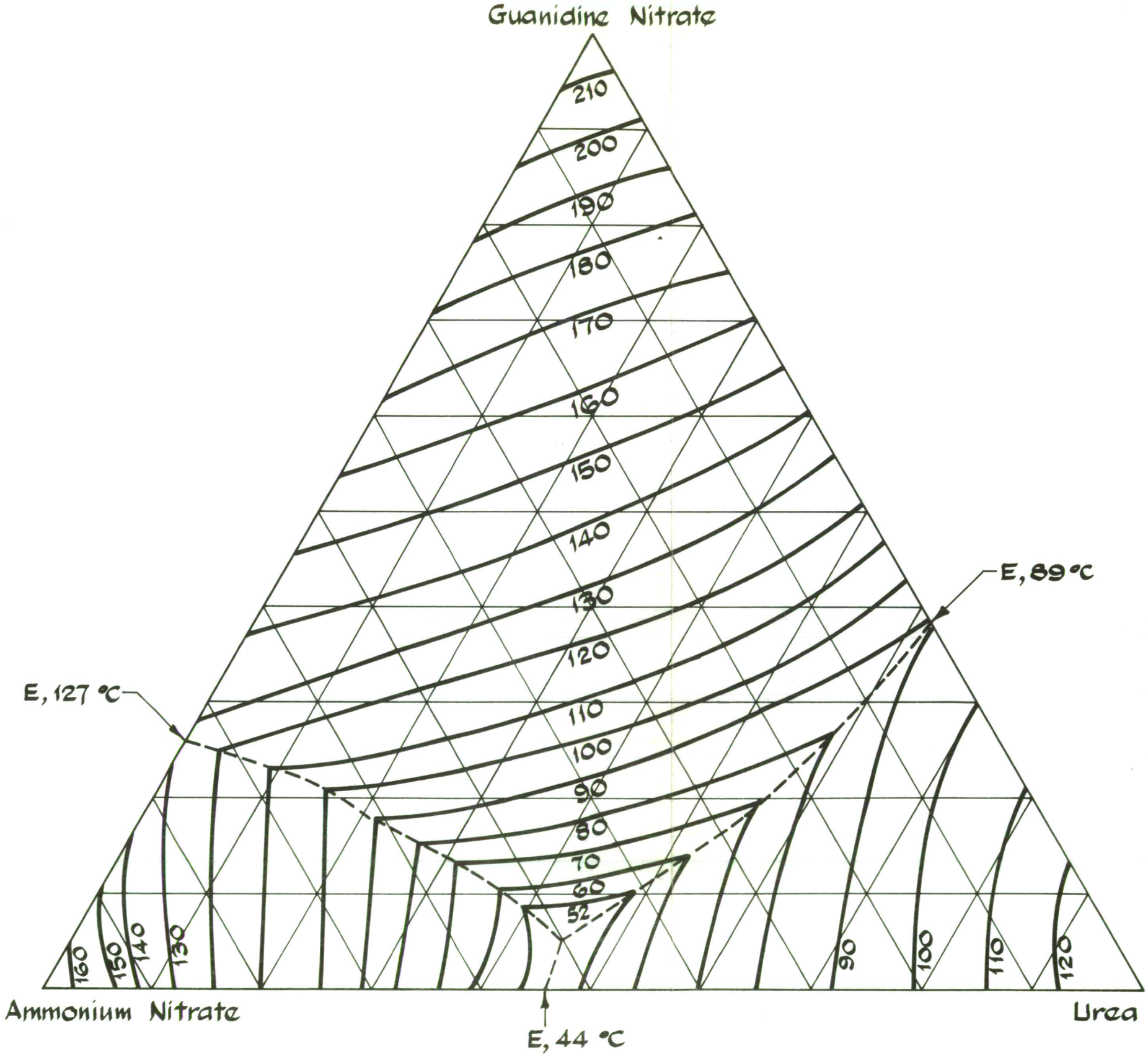
Guanidine Nitrate (weight percentage)	Ammonium Nitrate (weight percentage)	Urea (weight percentage)	Temperature, °C
25	72	3	122
15	78	7	123
32	53	15	125
30	60	10	125
28	65	7	125
-	87	13	125½
30	70	-	128
50	10	40	129
42	27	31	129
35	50	15	129
31	64	5	130
10	84	6	130
39	42	19	131
33	59	8	132
-	-	100	132
-	90	10	132½
37½	50	12½	133
40	40	20	134
33	67	-	136
20	80	-	137½
46½	30½	23	138
5	90	5	141
43	57	-	148
-	92	8	148
65	-	35	149½
61	10	29	150
47½	47½	5	151
10	90	-	152
-	97	3	160
60	30	10	163
75	-	25	169
60	40	-	169

TECHNICAL LIBRARY
BLDG. 305
ABERDEEN PROVING GROUND, MD.
STEAP-TL

APPENDIX

Guanidine Nitrate (weight percentage)	Ammonium Nitrate (weight percentage)	Urea	Temperature, °C
-	100	-	169½
70	20	10	172
90	-	10	184½
70	30	-	185
100	-	-	217

APPENDIX



BASAL PROJECTION

TABLE 1

WATER CONTENTS OF A TYPICAL SILICA GEL[36]

Temp, °C	200	400	600	800	900
Specific surface	715[a]	639	546	397	237
Water	65[b]	40	17.5	5.5	2
Surface coverage	0.46[c]	0.32	0.16	0.07	0.04

[a] $m^2\ g^{-1}$ of anhydrous solid

[b] mg g^{-1} of anhydrous solid

[c] fraction of surface covered by OH groups

TABLE 2

BATCH RUNS (90 min at 180°C), USING AMMONIUM NITRATE, UREA, HOUDRY CATALYST (2:2:1)

Run	Weight loss[a]	Weight of melt[a]	Insolubles from melt[a]	Melt	
				Guanidine Nitrate[b]	Urea[b]
1	4.3	16.6	-	0.152	0.743
2	2.7	25.1	0.028	.278	1.170
3	2.9	24.8	0.051	.429	1.160
4	2.6	25.4	0.049	.452	1.217
5	2.6	25.3	0.042	.439	1.073
	catalyst then stored in desiccator for five days				
6	1.8	26.0	-	.272	1.420
7	2.4	25.3	0.021	.361	1.268
8	2.0	26.5	0.039	.431	1.225

[a]Gram per 12 g (2 moles) urea

[b]Moles per 12 g (2 moles) urea

TABLE 3

BATCH RUNS (4 h at 160°C) USING AMMONIUM NITRATE, UREA, HOUDRY CATALYST (2:2:1.7)

Run	Weight loss[a]	Weight of melt[a]	Insolubles	Guanidine Nitrate[b]	Melt	
					Ammonium Nitrate[b]	Urea[b]
1	4.9	8.6	no insolubles	0.169	0.486	0.336
2	2.9	24.9		.108	1.801	1.274
3	1.9	25.2		.156	1.823	1.478
4	2.8	26.9		.146	1.994	1.486
5	2.5	25.2		.236	1.711	1.486
6	2.6	26.0		.137	1.902	1.470
7	2.1	26.0		.159	1.822	1.402
8	2.6	25.0		.176	1.742	1.280
9	3.0	25.4		.186	1.849	1.376
10	2.1	25.6		.326	1.543	1.446
11	3.8	24.5		.241	1.725	1.208

[a]Grams for 10.2 g catalyst treated with 12 g urea, 16 g ammonium nitrate

[b]Moles per 2 moles (12 g) urea

TABLE 4

BATCH RUNS (4 h at 160°C), USING AMMONIUM NITRATE, UREA, SILICA GEL (2:2:1.7)

Run	Weight loss[a]	Weight of melt[a]	Insolubles	Melt		
				Guanidine Nitrate[b]	Ammonium Nitrate[b]	Urea[b]
1	5.6	13.4	no insolubles	0.050	1.029	0.688
2	1.4	24.7		.120	1.774	1.406
3	1.6	25.0		.145	1.765	1.244
4	1.6	26.4		.166	1.881	1.470
5	1.8	24.9		.155	1.682	1.528
6	1.8	28.6		.168	2.005	1.642
7	1.6	29.0		.185	2.120	1.782
8	2.0	22.7		.157	1.593	1.262
9	2.2	28.0		.150	2.010	1.506
10	1.7	27.5		.194	1.943	1.434
11	3.1	23.1		.194	1.664	1.094

[a]Grams for 10.2 g silica gel treated with 12 g urea, 16 g ammonium nitrate

[b]Moles per 2 moles (12 g) urea

TABLE 5

BATCH RUNS (4 h at 170°C) USING AMMONIUM NITRATE, UREA, HOUDRY CATALYST (2:2:1.7)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt		
				Guanidine Nitrate[b]	Ammonium Nitrate[b]	Urea[b]
1	5.8	8.3	0.010	0.153	0.503	0.240
2	4.0	23.8	.069	.450	1.611	.948
3	5.5	22.6	.132	.559	1.410	.783
4	3.9	24.2	.126	.641	1.393	.940
5	4.2	23.7	.107	.548	1.442	.965
6	4.0	25.3	.118	.176	1.082	.768
7	5.6	22.6	.160	.531	1.363	.773
8	4.6	23.5	.151	.448	1.479	.883
9	3.9	24.1	.104	.436	1.482	.963
10	3.7	22.5	.082	.369	1.241	.935
11	4.2	25.6	.128	.532	1.212	1.060
12	4.1	22.4	.113	.581	1.290	.875
13	3.5	25.4	.090	.448	1.621	1.012

[a]Weight (g) from 12 g urea, 16 g ammonium nitrate

[b]Moles per 2 moles (12 g) urea

UNCLASSIFIED

UNCLASSIFIED

TABLE 6

BATCH RUNS (4 h at 170°C) USING AMMONIUM NITRATE, UREA, SILICA GEL (2:2:1.7)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt		
				Guanidine Nitrate[b]	Ammonium Nitrate[b]	Urea[b]
1	7.3	11.5	-	0.174	0.873	0.381
2	3.1	24.5	-	.330	1.743	1.073
3	3.2	24.9	-	.455	1.582	1.178
4	2.9	26.0	-	.702	1.363	1.250
5	3.4	23.2	-	.424	1.428	1.061
6	3.1	27.0	.057	.277	1.608	1.295
7	3.3	23.1	.046	.033	.404	1.071
8	3.7	25.0	.014	.249	1.495	1.051
9	3.1	25.0	.049	.295	1.615	1.100
10	4.0	24.4	.109	.422	1.044	.988
11	3.3	22.4	.093	.416	1.332	.913
12	3.3	25.4	.108	.514	1.351	1.088
13	3.3	24.3	.047	.352	1.206	1.427

[a]Weight (g) from 10.2 g silica gel with increments of 12 g urea, 16 g ammonium nitrate

[b]Moles per 2 moles urea (12 g) added

TABLE 7

BATCH RUNS (3.75 h at 180°C) USING AMMONIUM NITRATE, UREA, HOUDRY CATALYST (2:2:1)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt		
				Guanidine Nitrate[b]	Ammonium Nitrate[b]	Urea[b]
1a	6.8	13.3	0.037	0.435	-	-
2a	6.1	22.6	0.119	0.67	1.32	-
3a	5.5	21.6	0.294	0.78	1.20	-
1b	6.8	13.0	0.092	0.577	0.52	0.285
2b	5.0	21.4	0.192	0.573	1.25	0.668
3b	5.0	22.7	0.209	0.614	1.29	0.664
4b	5.5	22.0	0.241	0.613	1.29	0.600
5b	4.8	23.9	0.216	0.627	1.33	0.709
6b	6.0	23.0	0.208	0.729	1.21	0.664
7b	6.0	22.3	0.505	0.979	0.93	0.390
8b	5.1	22.9	0.272	1.050	0.83	0.537
9b	4.9	24.4	0.240	0.943	1.05	0.685
10b	4.7	23.1	0.191	0.656	1.27	0.634
11b	4.8	24.0	0.209	0.940	1.02	0.667
12b	3.8	24.0	0.137	0.409	1.48	0.882
13b	3.7	25.0	0.126	0.558	1.48	0.937

[a]Weight (g) from 6 g Houdry catalyst with increments of 12 g urea, 16 g ammonium nitrate

[b]Moles per 2 moles urea (12 g) added

UNCLASSIFIED

UNCLASSIFIED

TABLE 8

BATCH RUNS (3.75 h at 180°C) USING AMMONIUM NITRATE, UREA, HOUDRY CATALYST (2:2:½)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt	
				Guanidine Nitrate[b]	Ammonium Nitrate[b]
1	4.9	9.8	0.475	0.32	0.56
2	5.7	21.9	1.10	0.731	1.24
3	2.9	26.3	0.73	0.49	1.40
4	3.1	24.9	0.40	0.268	1.70
5	2.9	24.4	0.314	0.210	1.68
6	3.1	26.7	0.685	0.459	1.50
7	2.8	24.7	0.625	0.420	1.46

[a]grams for 12 g urea, 16 g ammonium nitrate, 3 g Houdry catalyst

[b]Moles per 2 moles of urea

TABLE 9

BATCH RUNS (3.75 h at 180°C) USING SILICA GEL, AMMONIUM NITRATE, AND UREA (1.7:2:2)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt		
				Ammonium Nitrate[b]	Guanidine Nitrate[b]	Urea[b]
1	10.2	4.8	0.019	0.351	0.136	0.038
2	7.2	18.8	.224	1.297	.560	.256
3	6.5	22.9	.163	1.677	.676	.391
4	7.0	22.2	.996	1.416	.630	.468
5	6.2	22.4	.265	1.488	.584	.541
6	5.7	22.2	.194	1.565	.496	.611
7	5.1	20.4	.236	1.417	.428	.599
8	6.5	21.5	.202	1.620	.432	.610
9	6.8	21.8	.242	1.537	.557	.489
10	6.5	21.8	.177	1.511	.594	.509
11	6.7	21.8	.117	1.488	.576	.519
12	5.6	21.9	.161	1.414	.530	.596
13	7.0	17.7	.210	1.224	.417	.391
14	5.8	23.8	.357	1.815	.358	.506
15	4.7	23.5	.402	1.465	.510	.561

[a]grams for 12 g urea, 16 g ammonium nitrate, 10.2 g silica gel

[b]Moles per two moles (12 g) of urea

Catalyst left in tube at end of experiment: 8.155 g

UNCLASSIFIED

UNCLASSIFIED

TABLE 10

BATCH RUNS (3.75 h at 180°C) USING AMMONIUM NITRATE, UREA, SILICA GEL (2:2:1)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt	
				Guanidine Nitrate[b]	Urea[b]
1	6.6	12.5	-	0.264	0.326
2	3.7	23.8	.130	.449	.838
3	4.2	23.8	.110	.448	.738
4	4.2	23.9	.113	.463	.807
5	4.4	23.6	.171	.492	.805
6	4.2	23.0	.233	.414	.802
7	3.5	26.7	.072	.628	1.065
8	3.9	22.4	.121	.357	.843
9	3.7	25.6	.104	.474	.899
10	3.8	23.6	.151	.515	.915
11	3.0	25.6	.153	.304	1.056
12	4.3	24.4	.176	.505	.939

[a]Weight (g) from 12 g urea

[b]Moles per 2 moles (12 g) of urea

TABLE 11

BATCH RUNS (3.75 h at 180°C) USING AMMONIUM NITRATE, UREA, U 30 SILICA GEL[a] (2:2:1)

Run	Weight loss[b]	Weight of melt[b]	Insolubles[b]	Melt	
				Guanidine Nitrate[c]	Urea[c]
1	7.3	9.6	0.053	0.282	0.126
2	4.5	22.4	.346	.552	.582
3	2.7	27.5	.192	.481	1.090
4	2.8	25.4	.213	.302	.987
5	2.6	25.8	.098	.267	1.004
6	2.9	25.2	.180	.298	.963
7	2.6	26.8	.386	.274	1.089
8	2.2	25.9	.112	.361	1.088
9	2.9	25.9	.208	.366	1.041
10	1.8	26.6	.135	.286	1.329
11	2.6	25.6	.141	.355	1.170
12	2.6	26.5	.172	.294	1.098

[a]Crosfield catalyst

[b]Weight (g) from 12 g urea

[c]Moles per 2 moles (12 g) urea

TABLE 12

BATCH RUNS (100 min at 190°C) USING AMMONIUM NITRATE, UREA, HOUDRY CATALYST (2:2:1.7)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt	
				Guanidine Nitrate[b]	Urea[b]
1	8.4	7.0	0.060	0.137	0.176
2	5.3	22.5	.185	.385	.200
3	5.3	22.1	.187	.397	.361
4	5.6	22.2	.239	.383	.403
5	5.6	20.4	.211	.336	.397
6	4.5	23.9	.413	.442	.434
7	6.8	18.8	.314	.309	.380
8	5.1	25.1	.437	.411	.450
9	6.1	22.6	.384	.416	.458
10	6.3	21.0	.433	.340	.444
11	6.4	21.9	.415	.332	.448
12	5.1	23.0	.714	.359	.456

[a]Weight (g) from 12 g of urea

[b]Moles per 2 moles (12 g) of urea

Weight of catalyst at end of series: 9.527 g

TABLE 13

BATCH RUNS (100 min at 190°C) USING AMMONIUM NITRATE, UREA AND SILICA GEL (2:2:0.25)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt	
				Guanidine Nitrate[b]	Urea[b]
1	2.3	22.9	0.058	0.195	0.097
2	1.8	26.4	.087	.234	1.220
3	1.8	26.0	.102	.357	1.279
4	1.7	26.0	-	1.312	1.329
5	1.7	26.5	.035	.285	1.310
6	1.8	26.5	.021	.078	1.353
7	1.9	26.2	.016	.316	1.315
8	1.7	26.6	.025	.085	1.329
9	2.0	25.8	.365	.319	1.287
10	2.0	25.4	.063	.381	1.257
11	1.6	25.6	.101	.018	1.245
12	1.7	25.7	.072	.318	1.235
13	2.0	25.8	.116	.125	1.160
14	2.0	26.1	.129	.300	1.345
15	1.9	26.2	.105	.294	1.293

[a]Weight (g) from 12 g urea

[b]Moles per 2 moles (12 g) of urea

Weight of catalyst at end of series: 1.055 g

UNCLASSIFIED

UNCLASSIFIED

TABLE 14

BATCH RUNS (100 min at 190°C) USING AMMONIUM NITRATE, UREA AND SILICA GEL (2:2:0.5)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt	
				Guanidine Nitrate[b]	Urea[b]
1	3.1	20.9	0.028	0.2235	0.935
2	2.3	25.6	.017	.2076	1.197
3	2.3	27.9	.021	.2937	1.206
4	2.4	27.0	.123	.2745	1.284
5	2.3	24.9	.103	.1708	1.174
6	2.3	25.2	.082	.2142	1.173
7	2.5	25.8	.179	.2888	1.213
8	2.3	25.0	.121	.2685	1.213
9	2.2	25.7	.092	.2653	1.214
10	2.2	25.7	.118	.2859	1.219
11	2.4	25.1	.119	.2610	1.145
12	2.3	26.0	.139	.2587	1.288
13	2.6	26.0	.184	.2882	1.203
14	2.4	25.6	.188	.2947	1.130
15	2.6	25.2	.173	.2073	0.938

[a]Weight (g) per 12 g urea

[b]Moles per 2 moles (12 g) urea

Weight of silica gel at end of series: 2.654 g

TABLE 15

BATCH RUNS (100 min at 190°C) USING AMMONIUM NITRATE, UREA, SILICA GEL (2:2:1.7)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt	
				Guanidine Nitrate[b]	Urea[b]
1	8.1	14.8	0.181	0.231	0.260
2	4.8	19.6	.284	.367	.428
3	2.5	26.1	.269	.532	.614
4	8.3	17.9	.299	.296	.502
5	4.6	22.5	.382	.381	.564
6	5.2	18.6	.474	.371	.500
7	5.5	25.1	.490	.351	.552
8	5.6	22.5	.754	.407	.550
9	4.5	24.5	.385	.444	.572
10	5.0	22.7	.433	.475	.556
11	5.0	22.4	.611	.361	.552
12	8.2	20.1	.804	.255	.518
13	5.3	20.6	.481	.248	.518

[a]Weight (g) from 12 g urea

[b]Moles per 2 moles of urea (12 g urea)

Weight of catalyst at end of series: 6.982 g

TABLE 16

BATCH RUNS (100 min at 190°C) USING AMMONIUM NITRATE, UREA, U 30 SILICA GEL CATALYST (2:2:1.7)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt		
				Ammonium Nitrate[b]	Guanidine Nitrate[b]	Urea[b]
1	8.4	-[c]	-	-	-	-
2	6.7	18.6	1.142	1.241	0.490	0.175
3	6.1	23.8	1.094	1.768	.509	.384
4	5.6	27.3	2.082	1.739	.666	.605
5	6.0	23.9	0.494	1.629	.575	.592
6	3.4	27.8	1.364	1.793	.520	.912
7	4.6	24.7	0.447	1.737	.443	.815
8	5.4	23.4	0.788	1.618	.413	.716
9	4.7	23.8	0.367	1.720	.439	.793
10	5.0	25.2	0.680	1.874	.474	.806
11	4.3	24.5	0.299	1.740	.396	.888
12	4.6	21.8	0.247	1.614	.282	.795
13	3.5	25.5	0.441	1.781	.378	.989
14	4.6	22.2	0.355	1.544	.346	.814
15	4.0	25.8	0.561	1.692	.411	.956

[a]Weight (g) from 12 g urea

[b]Moles per two moles (12 g) urea

[c]No melt recovered

Catalyst left in tube at end of experiment: 3.576 g

TABLE 17

BATCH RUNS (100 min at 190°C) USING AMMONIUM NITRATE, INTERMEDIATE DENSITY SILICA GEL, UREA (2:1.7:2)

Run	Weight loss[a]	Weight of melt[a]	Insolubles[a]	Melt		
				Ammonium Nitrate[b]	Guanidine Nitrate[b]	Urea[b]
1	7.4	-[c]	-	-	-	-
2	7.8	13.3	1.142	0.739	0.364	0.114
3	6.2	25.6	1.094	1.907	.541	.399
4	5.7	31.2	2.082	2.197	.689	.624
5	5.3	22.9	0.494	1.576	.552	.594
6	4.8	34.7	1.364	2.444	.625	1.029
7	3.2	24.7	0.447	1.750	.329	0.982
8	3.2	25.7	0.788	1.786	.267	1.034
9	3.4	25.5	0.367	1.893	.252	1.049
10	2.9	25.4	0.680	1.913	.235	1.033
11	3.2	25.5	0.299	2.071	.249	1.128
12	1.7	26.8	0.247	2.010	.176	1.448
13	3.2	25.6	0.441	1.888	.191	1.178
14	3.8	23.7	0.355	1.631	.167	0.819
15	4.2	25.6	0.561	1.812	.244	.880

[a]Weight (g) from 12 g urea

[b]Moles per two moles (12 g) urea

[c]No melt recovered

Catalyst left in tube at end of experiment: 1.529 g

UNCLASSIFIED

UNCLASSIFIED

TABLE 18

INSOLUBLES RECOVERED FROM MELTS

Reactants	Weight of Catalyst (g)	Runs	Insolubles in melt (g)	Catalyst recovered (g)	Total Insolubles (g)
a	10.2	11[b]	0	15.16	4.96
a	10.2	13[c]	1.39	14.16	5.35
a	6	13[d]	2.84	8.49	5.33
a	6	3[d]	0.45	7.15	1.60
a	3	7[d]	4.33	3.35	4.68
e	6	13[d]	4.06	11.10	9.16
a	10.2	13[f]	3.99	9.53	3.32
a'	10.2	11[b']	0	9.03	-
a'	10.2	13[c']	0.52	10.09	0.41
a'	10.2	13[f']	5.85	6.98	2.63

(i) Houdry Catalyst

[a] 12 g urea, 16 g ammonium nitrate, boiling tube

[b] 4 h at 160°C

[c] 4 h at 170°C

[d] 3.75 h at 180°C

[e] 12 g urea, 16 g ammonium nitrate, beaker

[f] 100 min at 190°C

(ii) Silica Gel

[a'] 12 g urea, 16 g ammonium nitrate, boiling tube

[b'] 4 h at 160°C

[c'] 4 h at 170°C

[f'] 100 min at 190°C

TABLE 19

CONVERSIONS AND YIELDS FOR BATCH RUNS USING HOUDRY CATALYST, AMMONIUM NITRATE AND UREA

	160°C		170°C		180°C		190°C	
Run	Conversion[a]	Yield[b]	Conversion	Yield	Conversion	Yield	Conversion	Yield
	c		d		e		f	
1	(0.832)	(0.203)	(0.83)	(0.174)	(0.857)	(0.673)	-	-
2	.598	.232	.53	.429	.762	.755	0.90	0.60
3	.485	.298	.61	.577	.731	.805	.82	.762
4	.428	.338	.53	.709	.733	.822	.80	.826
5	.394	.414	.52	.768	.707	.849	.80	.830
6	.373	.426	.62	.687	.701	.888	.783	.892
7	.362	.439	.61	.713	.716	.941	.81	.849
8	.362	.445	.56	.723	.715	1.007	.775	.910
9	.356	.460	.52	.734	.709	1.051	.771	.925
10	.348	.517	.53	.731	.706	1.042	.778	.92
11	.353	.526	.47	.760	.703	1.074	.776	.91
12			.56	.782	.691	1.051	.772	.92
13			.49	.791	.678	1.051		

[a](moles of urea consumed)/(moles introduced)

[b]2(moles of guanidine nitrate formed)/(moles of urea consumed)

[c]4 h runs: 2:2:1.7 [d]4 h runs: 2:2:1.7 [e]3.75 h runs: 2:2:1 [f]100 min runs: 2:2:1.7

TABLE 20

CONVERSIONS AND YIELDS FOR BATCH REACTIONS USING AMMONIUM NITRATE, UREA AND SILICA GEL

	160°C		170°C		180°C		180°C		190°C	
Run	Conversion	Yield	Conversion	Yield	Conversion	Yield	Conversion	Yield	Conversion	Yield
	a		b		c		d		e	
1	(0.656)	(0.076)	(0.190)	(0.913)	(0.837)	(0.158)	(0.981)	(0.139)	(0.870)	(0.535)
2	.478	.178	.364	.694	.709	.252	.926	.376	.786	.761
3	.444	.236	.439	.728	.683	.284	.886	.516	.693	1.087
4	.394	.302	.485	.855	.661	.308	.856	.585	.749	.952
5	.367	.346	.494	.844	.649	.328	.831	.623	.718	1.007
6	.336	.398	.520	.757	.643	.330	.891	.576	.750	.967
7	.303	.466	.522	.655	.615	.367	.874	.580	.724	.998
8	.311	.460	.523	.632	.611	.362	.843	.585	.725	1.013
9	.304	.473	.526	.621	.604	.366	.833	.600	.714	1.051
10	.302	.493	.522	.643	.598	.377	.824	.618	.722	1.068
11	.316	.485	.516	.665	.587	.373	.817	.631	.724	1.058
12			.519	.689	.582	.380	.807	.649	.741	1.006
13			.534	.669			.806	.631	.741	.981
14							.803	.621		
15							.797	.626		

[a]4 h runs, 2:2:1.7; [b]4 h runs, 2:2:1.7; [c]3.75 h runs, 2:2:1; [d]3.75 h runs, 2:2:1.7; [e]100 min runs, 2:2:1.7

UNCLASSIFIED

UNCLASSIFIED

TABLE 21

CONVERSIONS AND YIELDS FOR BATCH REACTIONS, USING UREA, AMMONIUM NITRATE, AND VARYING AMOUNTS OF SILICA GEL (190°C 100 min runs)

Run	2:2:0.25		2:2:0.5		2:2:1.7	
	Conversion	Yield	Conversion	Yield	Conversion	Yield
1	0.512	0.380	0.504	0.420	0.870	0.535
2	.451	.475	.467	.462	.786	.761
3	.421	.622	.444	.545	.693	1.087
4	.399	1.312	.422	.592	.749	.952
5	.388	1.226	.420	.557	.718	1.007
6	.378	1.085	.418	.550	.750	.967
7	.373	1.064	.416	.588	.724	.998
8	.368	.971	.413	.588	.725	1.013
9	.367	.963	.411	.597	.714	1.051
10	.367	.969	.409	.609	.722	1.068
11	.368	.883	.410	.610	.724	1.058
12	.369	.879	.406	.619	.741	1.006
13	.373	.829	.405	.627	.741	.981
14	.370	.834	.407	.630		
15	.369	.834	.415	.610		

UNCLASSIFIED

UNCLASSIFIED

TABLE 22

CONVERSIONS AND YIELDS FOR BATCH RUNS, USING COMMERCIAL SILICA GEL

	U 30 Silica Gel; 2:2:1.7 180°C		U 30 Silica Gel; 2:2:1.7 190°C		Intermediate Density Silica Gel; 2:2:1.7 190°C	
Run	Conversion	Yield	Conversion	Yield	Conversion	Yield
1	(0.937)	(0.155)	-	-	-	-
2	.802	.253	.956	.256	.972	.187
3	.700	.313	.907	.368	.915	.330
4	.652	.309	.854	.488	.858	.464
5	.621	.303	.824	.544	.827	.518
6	.604	.302	.778	.592	.770	.600
7	.583	.253	.751	.619	.733	.604
8	.567	.311	.737	.612	.702	.600
9	.557	.309	.722	.624	.676	.594
10	.535	.324	.710	.638	.657	.586
11	.524	.332	.696	.642	.637	.586
12	.518	.331	.688	.630	.607	.588
13			.674	.636	.592	.582
14			.668	.632	.595	.558
15			.659	.640	.580	.550

UNCLASSIFIED

UNCLASSIFIED

TABLE 23

CUMULATIVE WEIGHT LOSSES vs GUANIDINE NITRATE PRODUCED (EFFICIENCIES) AT 170°C

(a) Houdry catalyst

Weight loss (as mole of ammonium carbamate)	Guanidine Nitrate (mole)
0.074	0.015
.126	.060
.196	.116
.246	.180
.300	.235
.351	.253
.423	.306
.482	.351
.532	.394
.580	.431
.633	.484
.686	.542
.731	.587

(b) Silica gel

0.094	0.017
.133	.050
.174	.096
.212	.166
.255	.208
.295	.235
.337	.238
.385	.263
.424	.293
.476	.335
.518	.377
.560	.428
.603	.463

TABLE 24

CUMULATIVE WEIGHT LOSSES vs GUANIDINE NITRATE PRODUCED (EFFICIENCIES) AT 180°C

Weight loss (as mole of ammonium carbamate)	Guanidine Nitrate (mole)
0.087	0.057₇
.151	.115
.215	.176
.286	.238
.347	.300
.424	.373
.501	.471
.567	.576
.629	.671
.690	.736
.751	.830
.800	.871
.847	.927

TABLE 25

BATCH RUNS (100 min at 190°C) WITH AMMONIUM NITRATE, UREA, AND POROUS GLASS

	Porasil		Porous Glass	
Run	Weight loss[a]	Guanidine Nitrate[b]	Weight loss[a]	Guanidine Nitrate[b]
1	4.0	0.22	2.8	0.10
2	2.5	.91	2.0	.10
3	-	-	1.8	.09

[a]Weight (g) from 6 g urea

[b]Moles per 2 moles (6 g) urea

TABLE 26

RELATIVE CONCENTRATIONS OF GUANIDINE NITRATE, AMMONIUM NITRATE, AND UREA

Time (min)	Guanidine Nitrate	Ammonium Nitrate	Urea
0	0	1.50	2.0
10	.24	1.25	1.20
20	.38	1.11	.91
30	.49	1.01	.73
40	.58	.92	.61
50	.64	.86	.53
60	.70	.80	.47$_5$
120	.85	.65	.16
180	.89	.60	.02

FIGURES 1 - 15

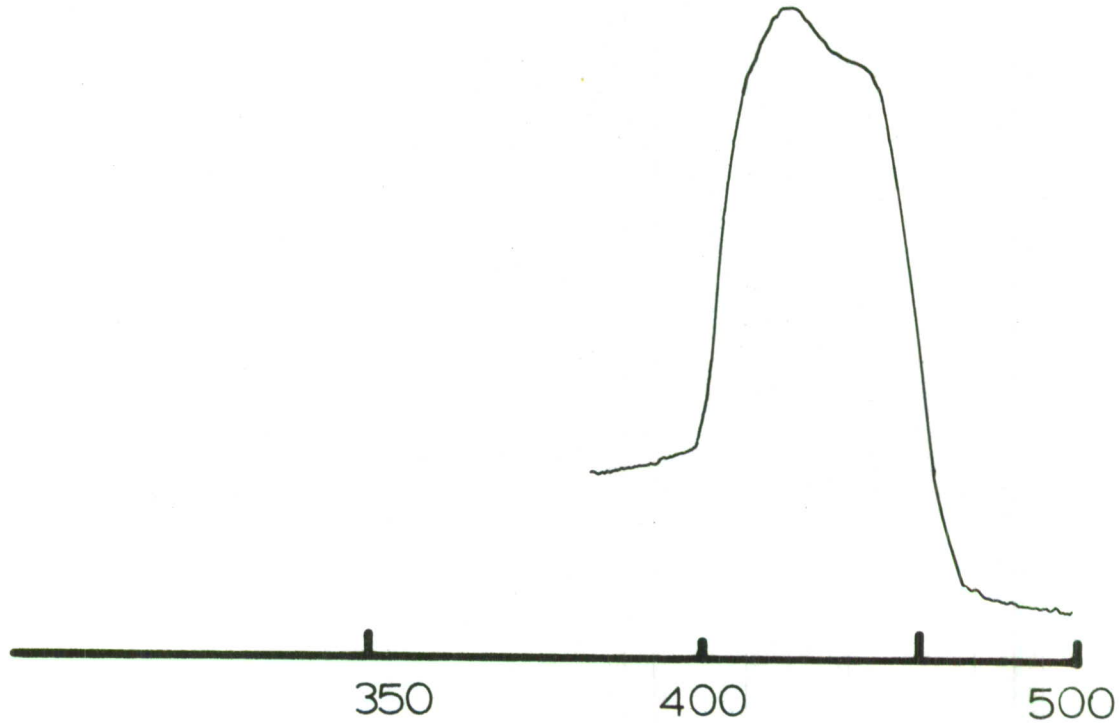
Figure 1. Absorption peaks used for the determination of

(a) urea

(b) total nitrate ion concentrations

(DK2 spectrophotometer, 1 cm silica cells)

ERDE TR 113



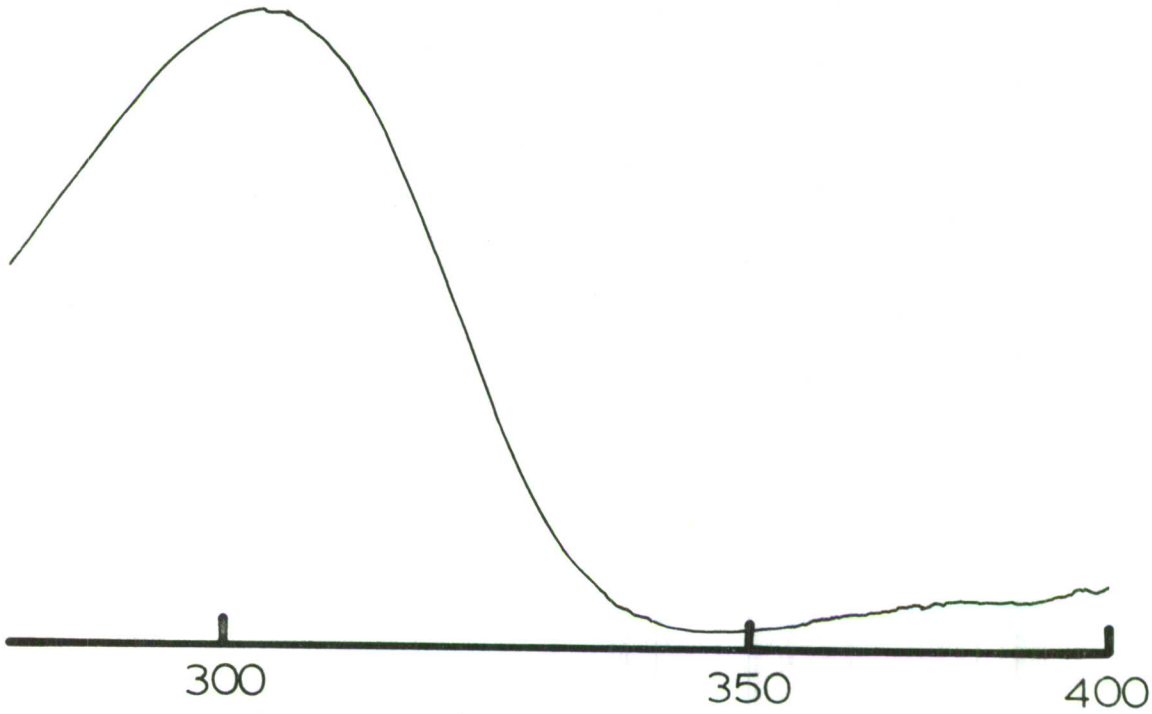


FIG. 1

Figure 2. Apparatus for small scale labelling experiments

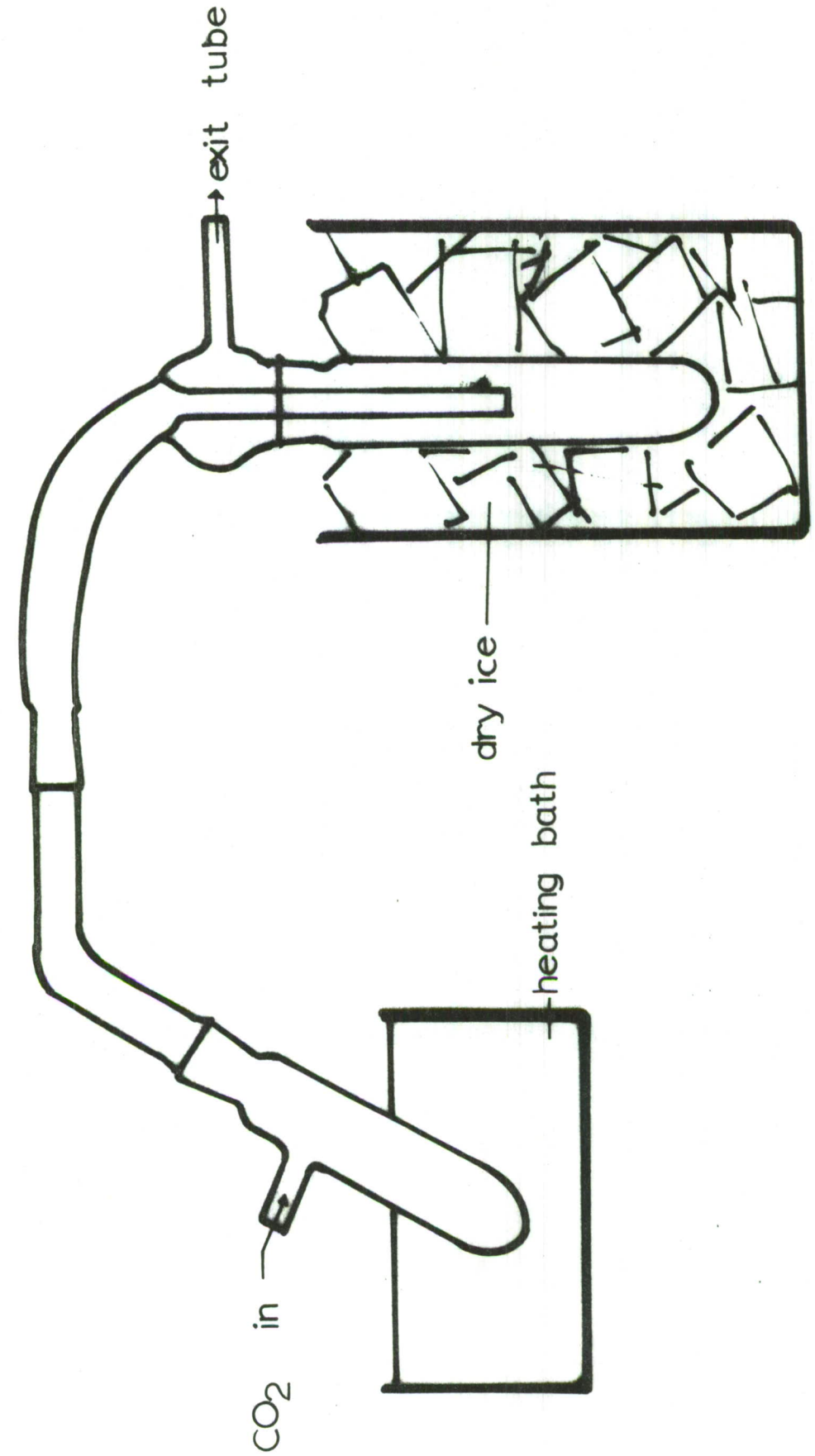


FIG. 2

Figure 3. Time and reactant concentrations (ammonium nitrate:urea:silica gel 2:2:1; 180°C)

ERDE TR 113

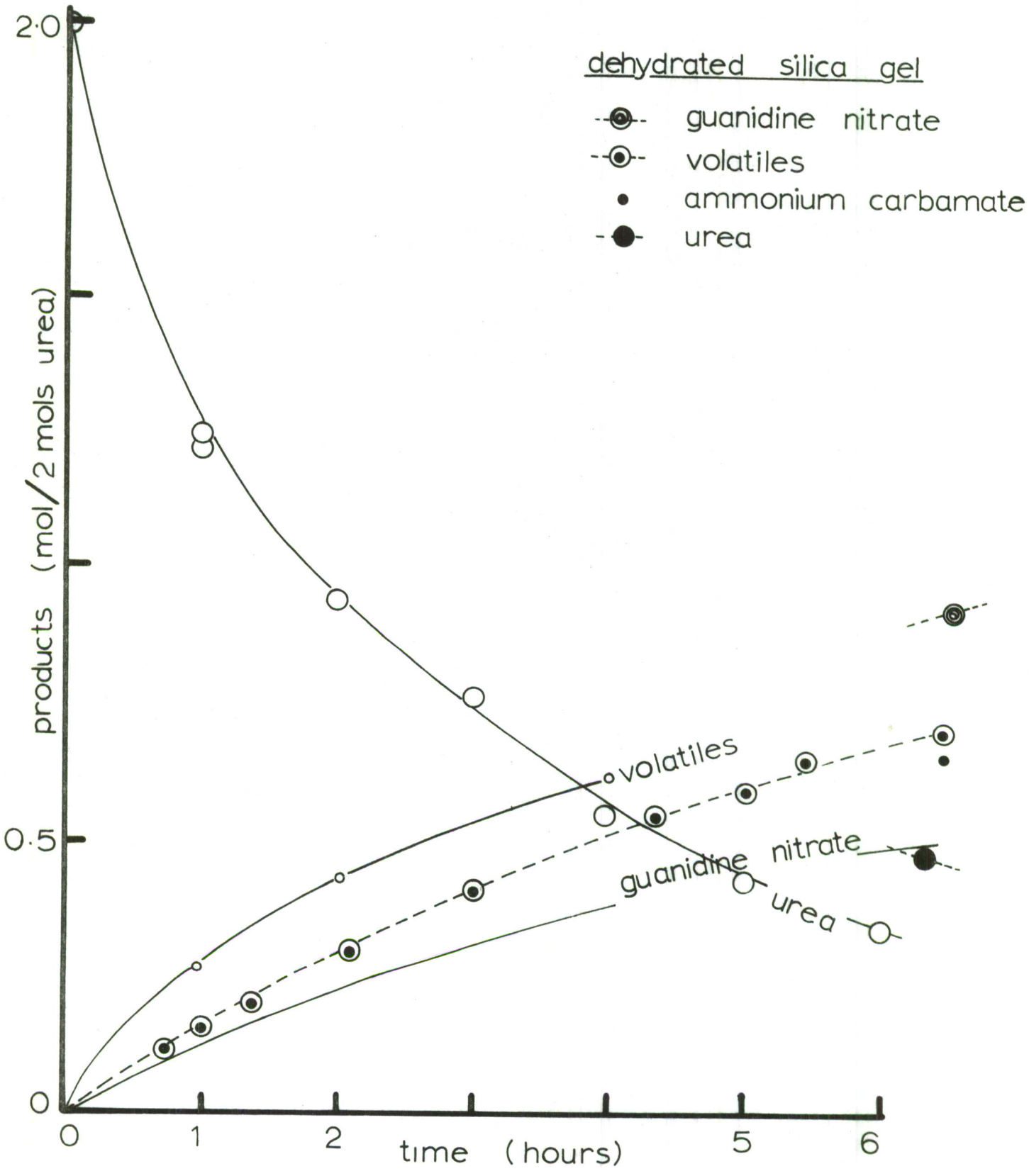


FIG. 3

Figure 4. Batch processes - 180°C; production of guanidine nitrate per run (reaction efficiency)

ERDE TR 113

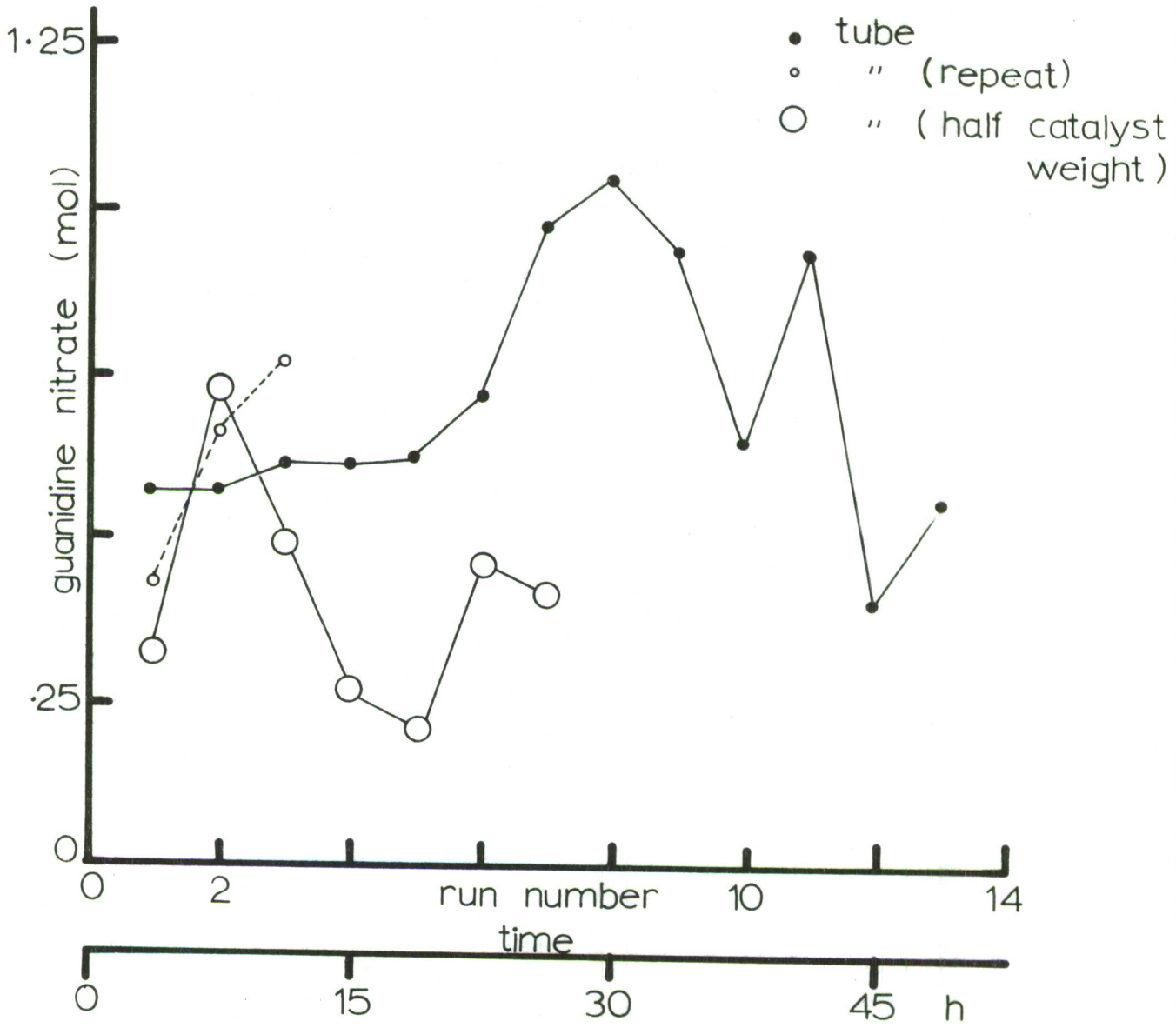


FIG. 4

Figure 5. Comparison of Catalysts: 190°C (reaction efficiency)

—○— silica gel

—●— Houdry catalyst

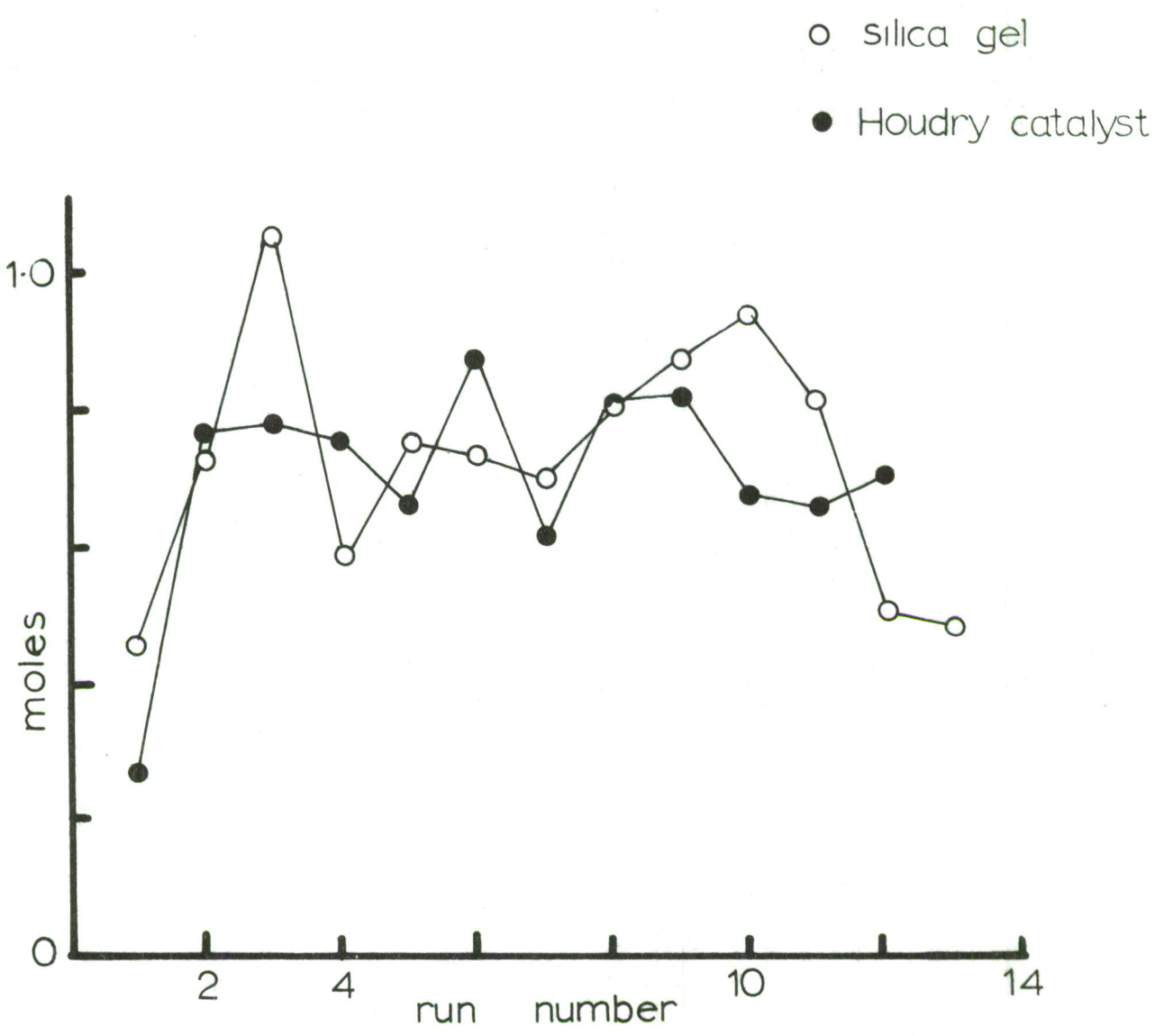


FIG. 5

Figure 6. Batch processes. Insolubles in melt, per run

—●— Houdry catalyst

—○— silica gel

(2:2:1.7 190°C 100 min runs)

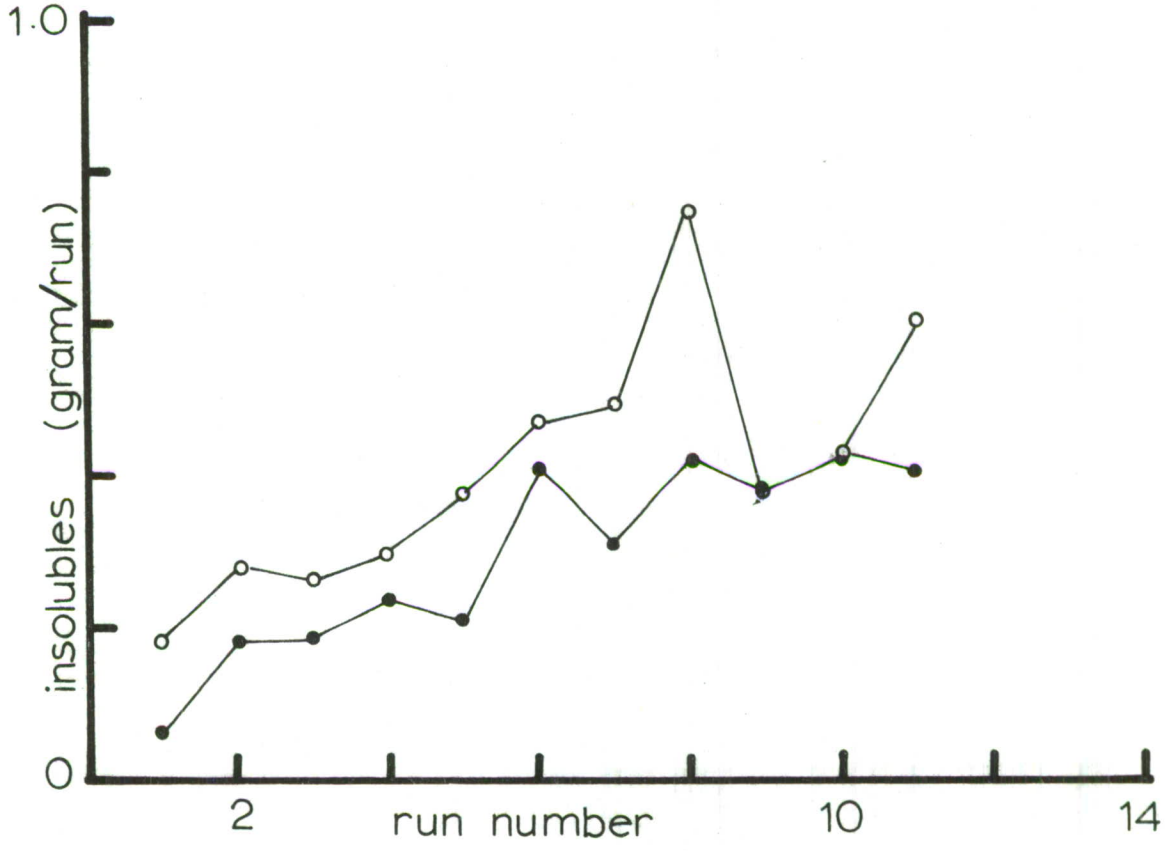


FIG. 6

Figure 7. Biuret formation in the early stages of the reaction.[10]

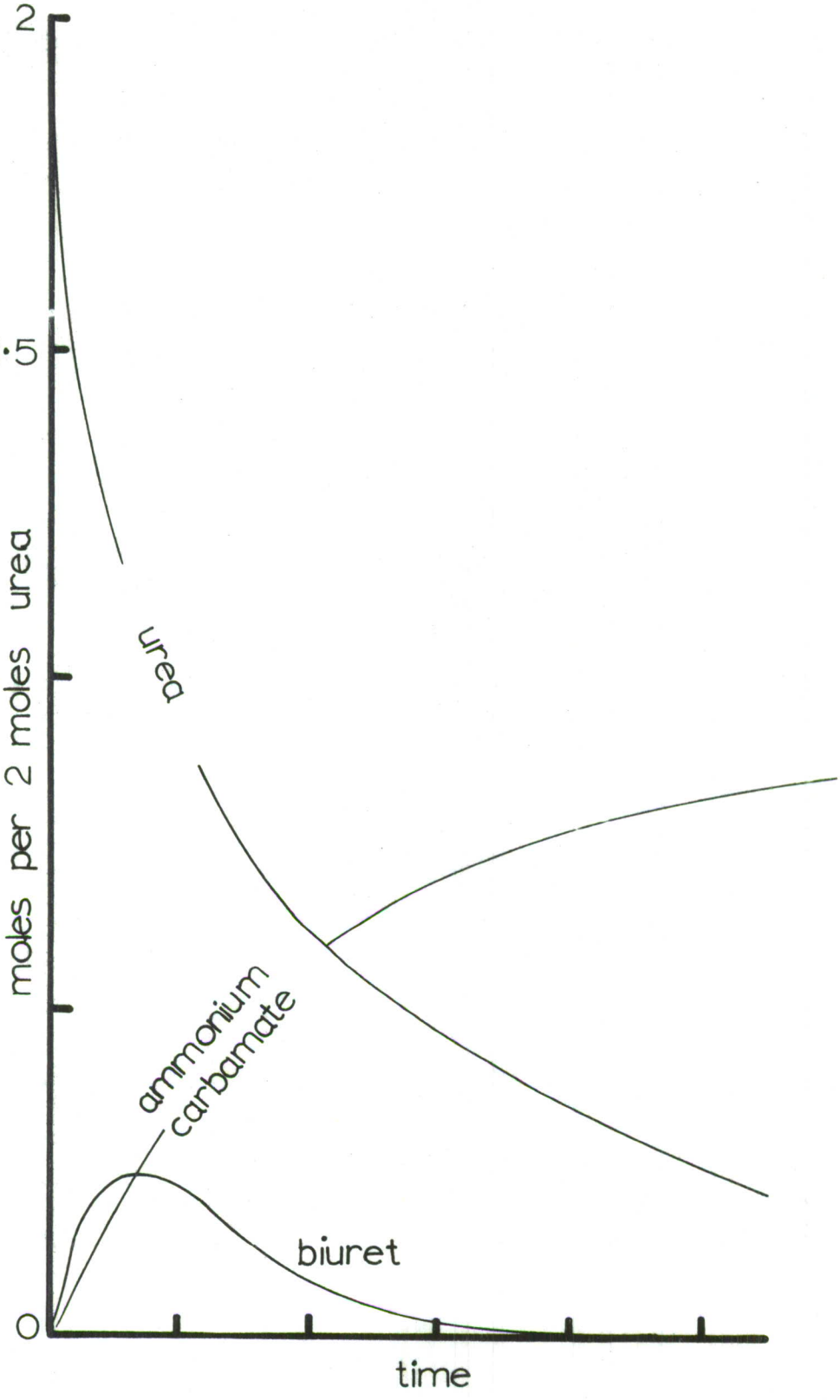

2
1·5
0
moles per 2 moles urea
urea
ammonium carbamate
biuret
time

FIG.7

Figure 8. Relation between volatiles lost (expressed as ammonium carbamate) and the amount of guanidine nitrate formed (180°C; total time of experiment 42h)

ERDE TR 113

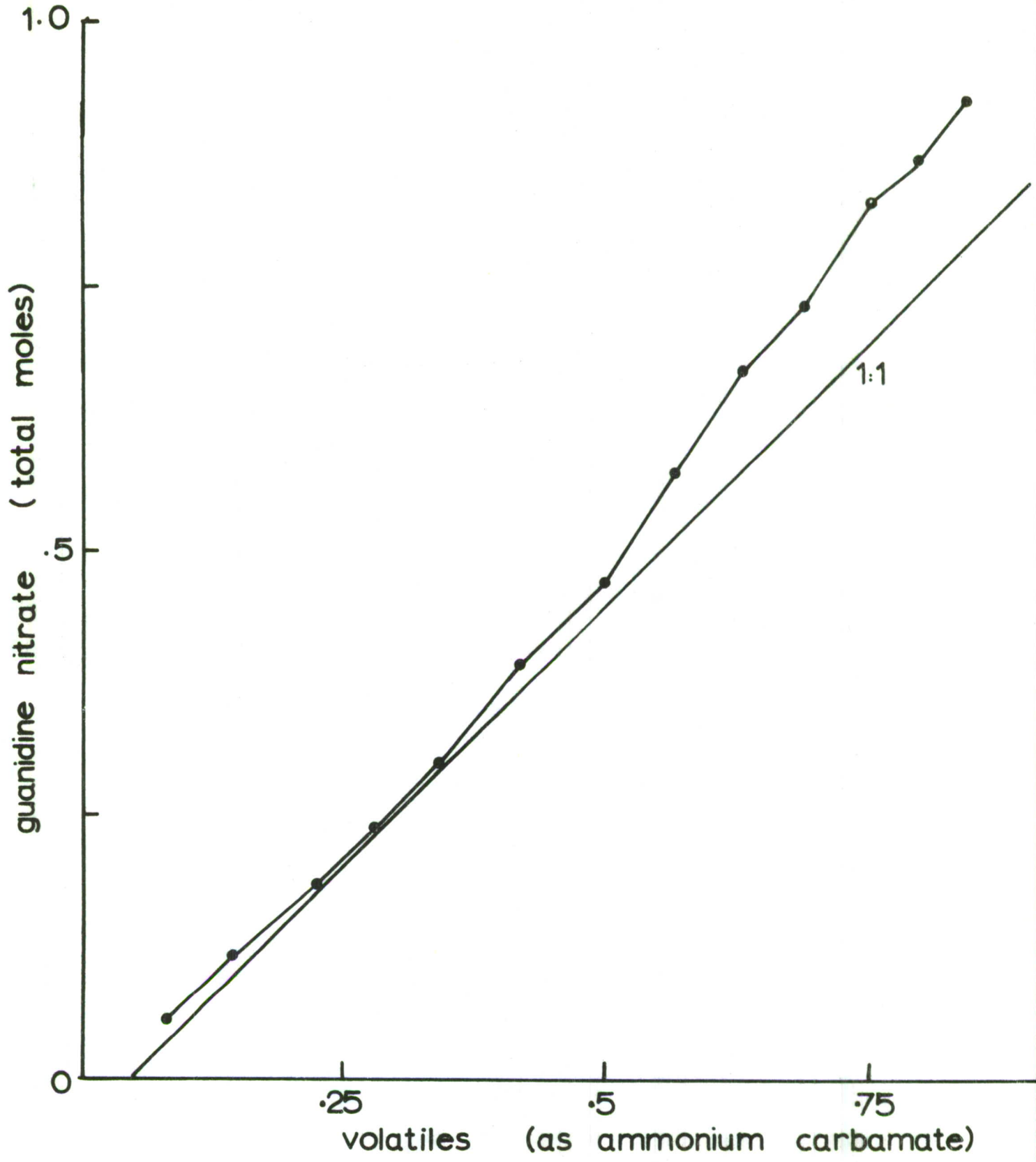


FIG. 8

Figure 9. Insolubles recovered from melts

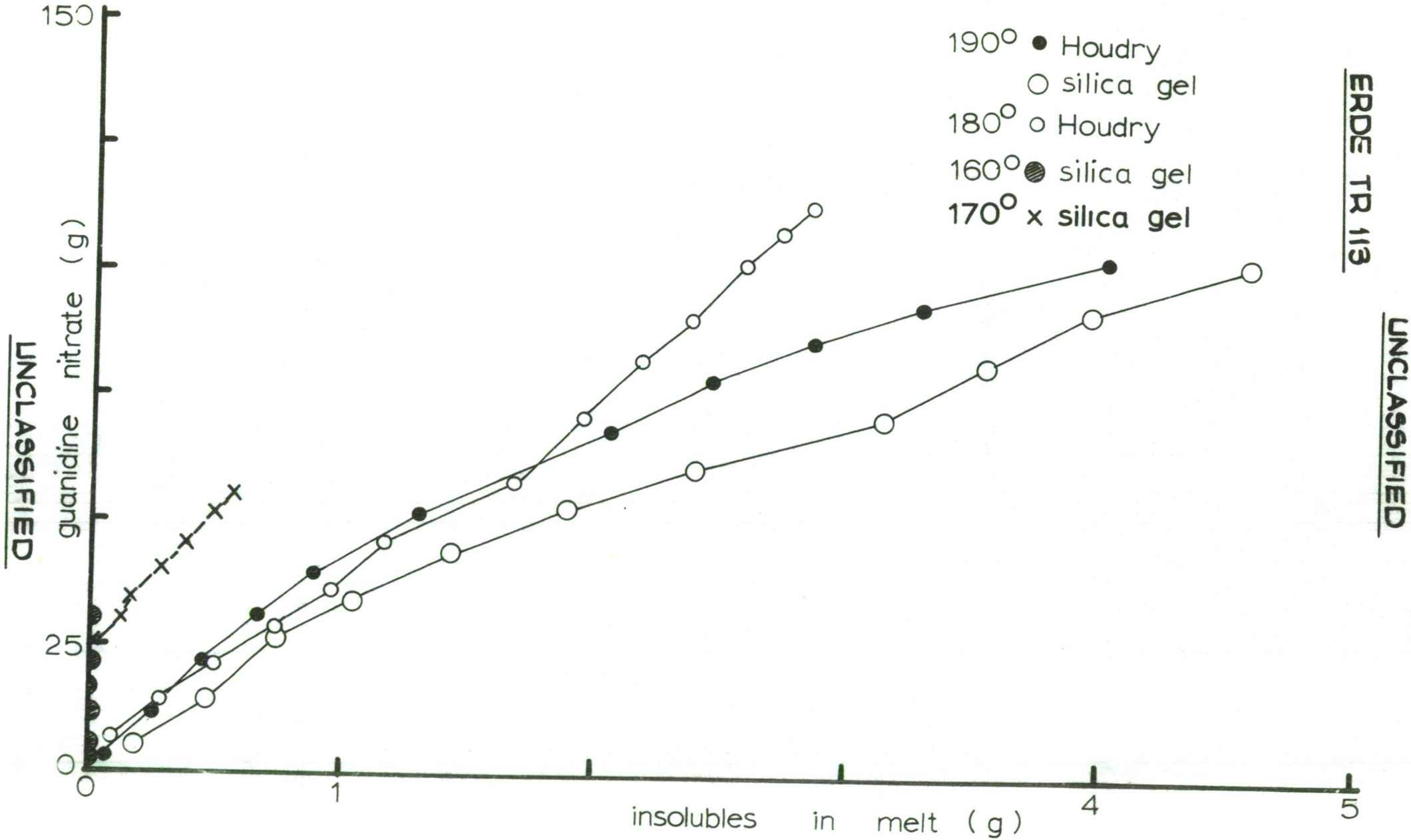

150
25
0
0
1
4
5
guanidine nitrate (g)
insolubles in melt (g)
190° ● Houdry
○ silica gel
180° ○ Houdry
160° ◍ silica gel
170° x silica gel
UNCLASSIFIED
ERDE TR 113
UNCLASSIFIED

FIG. 9

Figure 10. Variations observed in some peak heights in the mass spectrum of the reaction mixture (quadrupole spectrometer, 120°C)

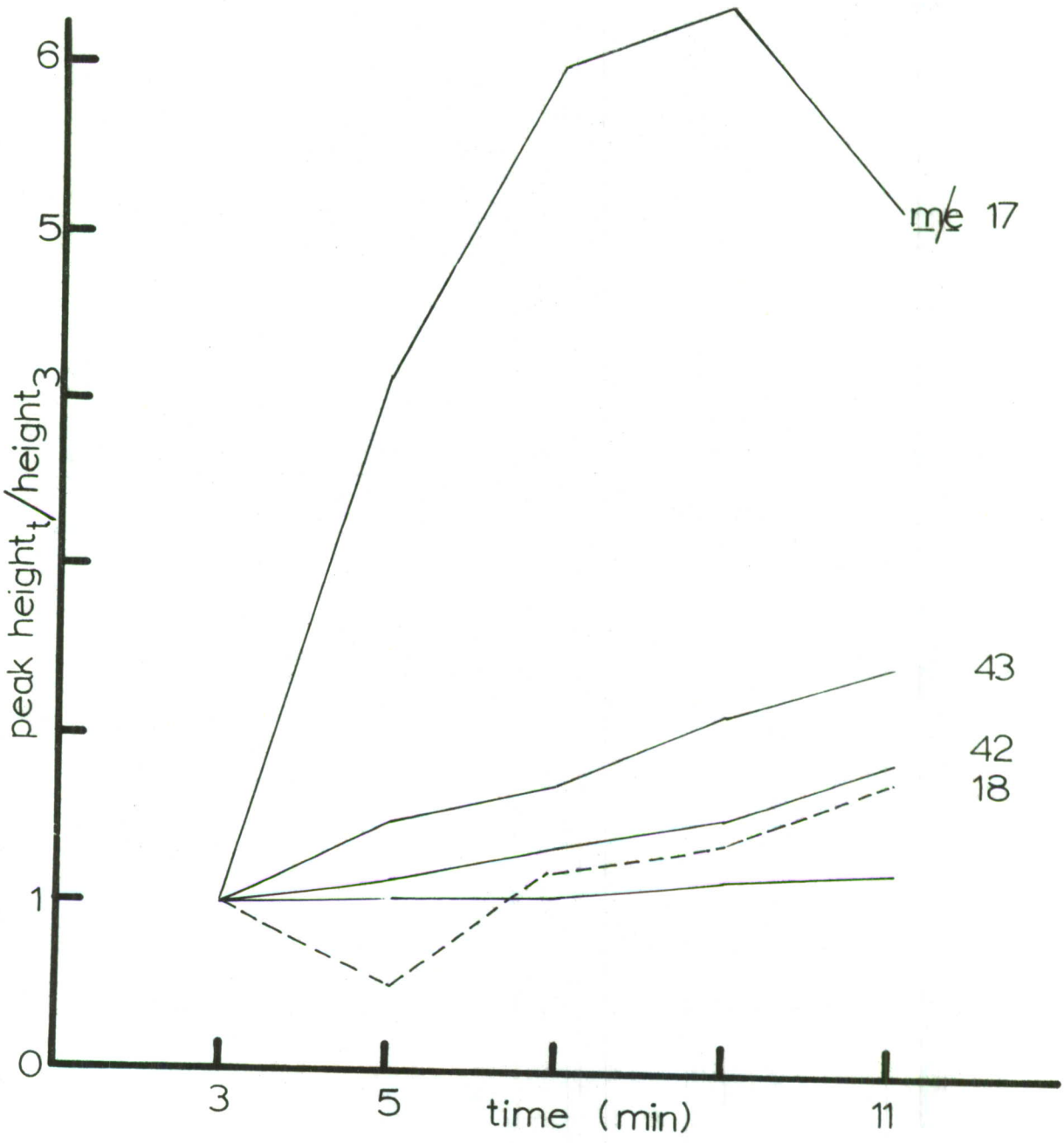


FIG. 10

Figure 11. Mass spectra of the reaction mixture (ammonium nitrate, urea, silica gel) at 120 and 180°C (quadrupole spectrometer)

ERDE TR 113

120° ▯ ▮ 180°

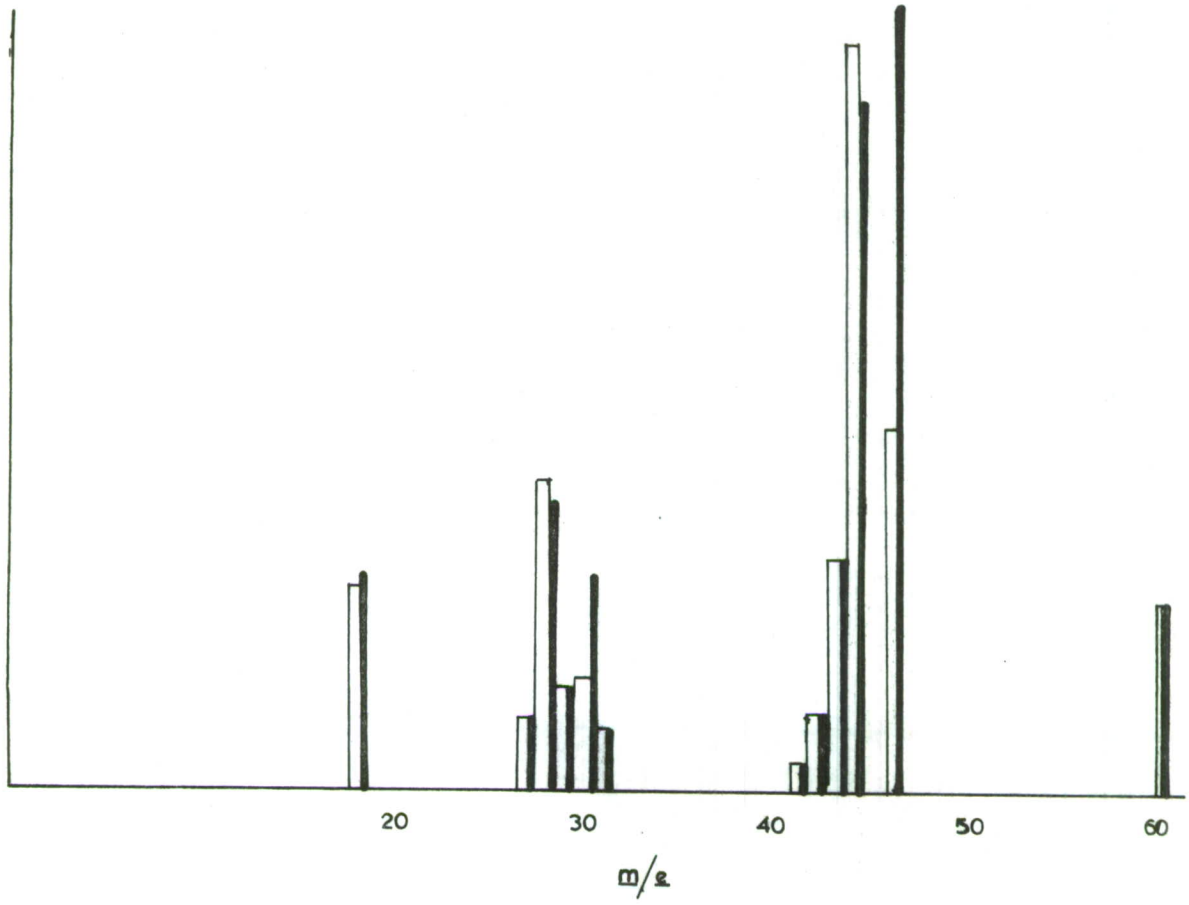


FIG. 11

Figure 12. High resolution spectrum of ammonium carbamate

ERDE TR 113

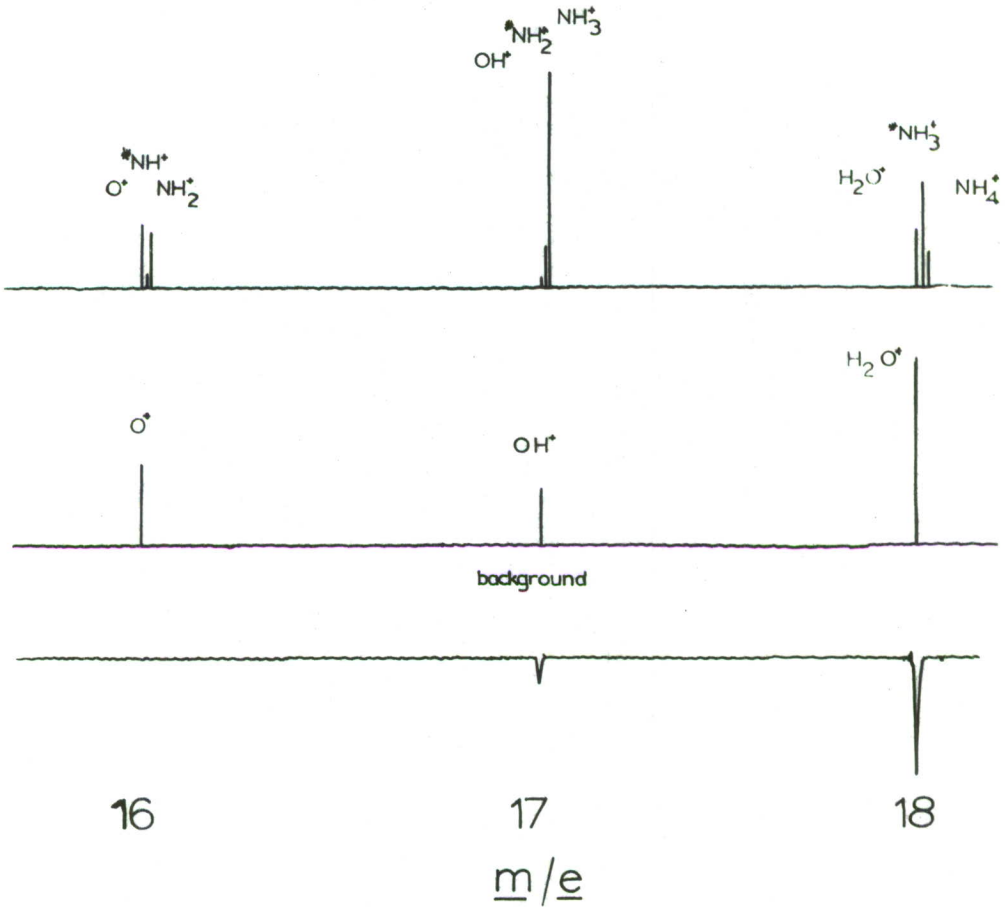


FIG. 12

Figure 13. Low resolution spectrum of guanidine nitrate:

(a) from labelling experiment

(b) unlabelled guanidine nitrate

(c) background

ERDE TR 113

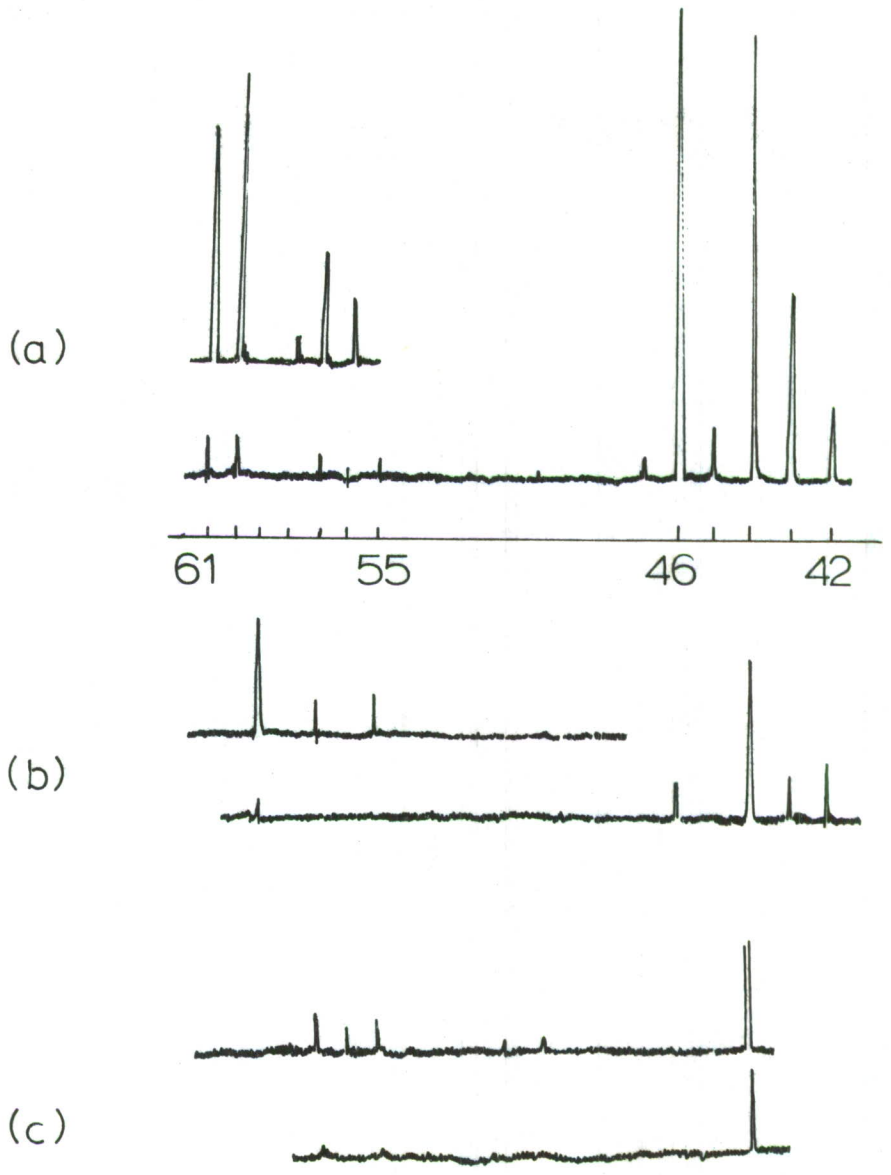


FIG. 13

Figure 14. Residence time distribution for a 2:2:1.7 system; 180°C for $3\frac{3}{4}$ hours:

(a) assuming complete transfer of melt

(b) experimental results for silica gel from tetraethyl silicate

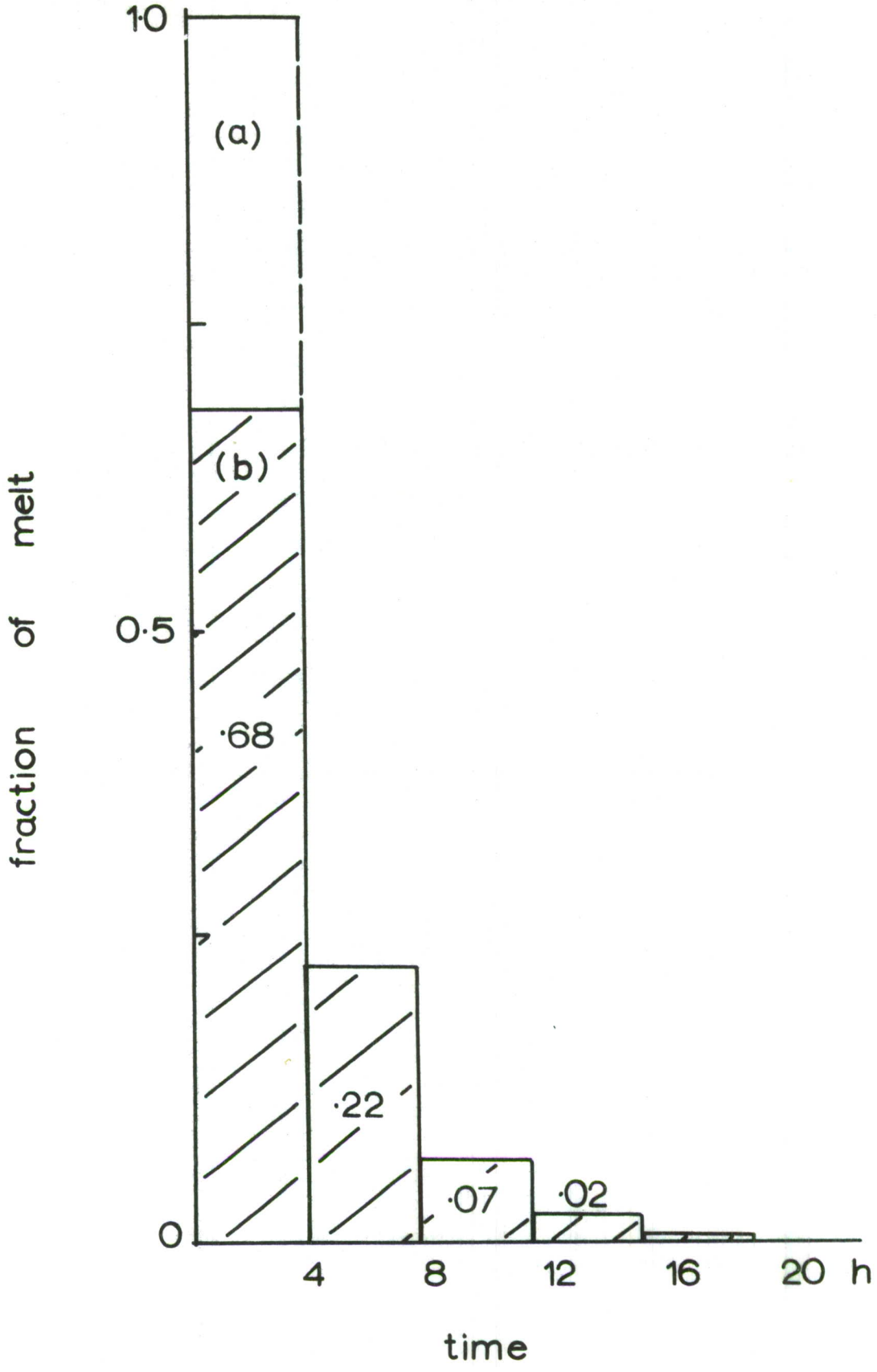


FIG. 14

Figure 15. Calculated and experimental values for guanidine nitrate

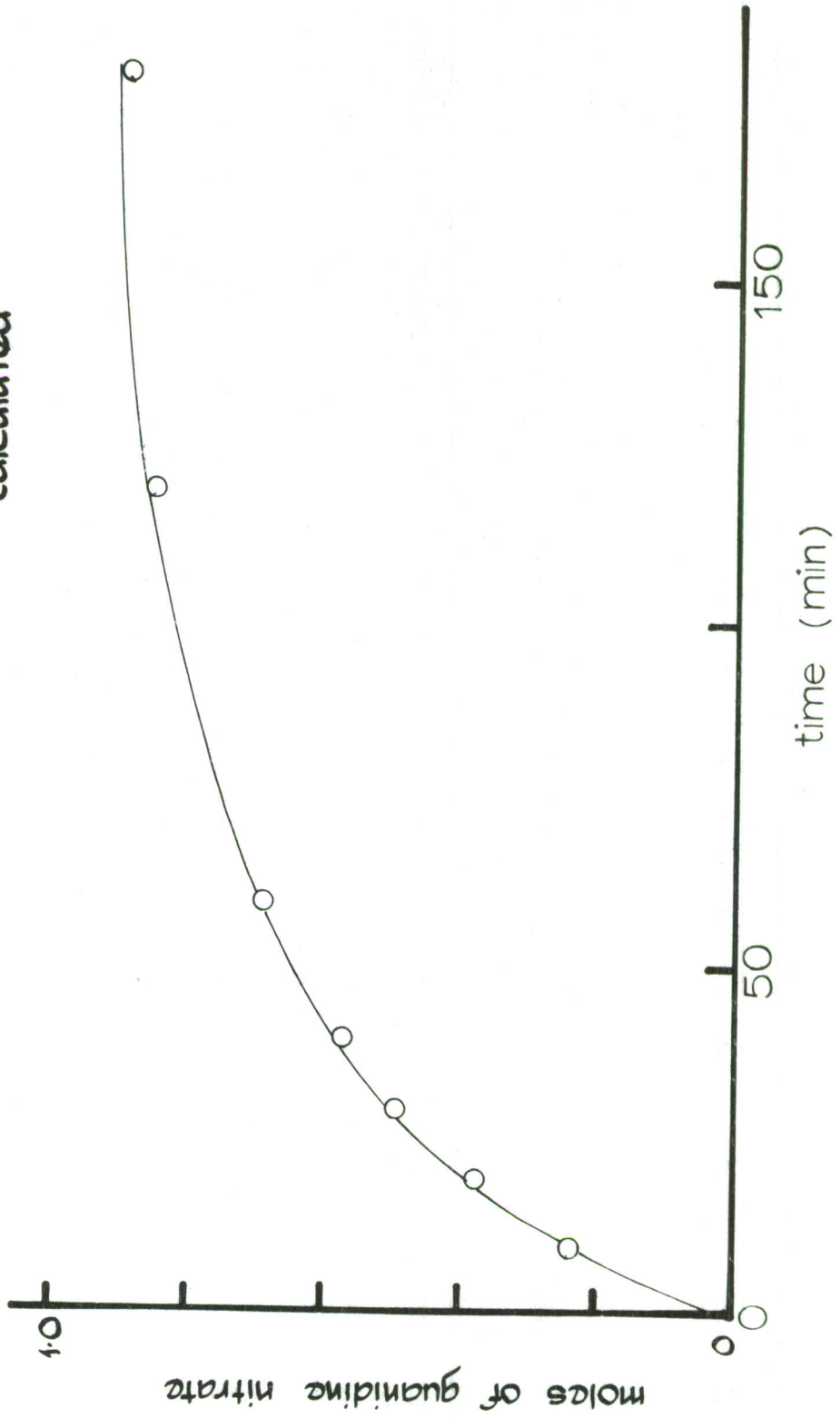

o experimental
— calculated
moles of guanidine nitrate
1·0
0
0
50
150
time (min)

FIG. 15

UNCLASSIFIED

Technical Report No 113
Explosives Research and Development Establishment
THE SILICA GEL PROCESS: SMALL SCALE STUDIES. PART 1: COMPARISON OF CATALYSTS AND LABELLING EXPERIMENTS
Armstrong F A, Fraser R T M
August 1972
48 pp, 26 tabs, 15 figs

Small scale experiments using silica gel, ammonium nitrate and urea show that formation of guanidine nitrate becomes erratic if insolubles build up on the catalyst surface. The rate of production of insolubles increases rapidly with temperature, so that a trade-off between low conversions at lower temperatures and insoluble formation at higher temperatures is possible. The yield/temperature relationship is a property of the silica gel used. Yields of guanidine nitrate can be higher than predicted, possibly because by-product water is removed in the form of ammonium silicates rather than ammonium carbamate. Experiments with ^{15}N and ^{18}O suggest that guanidine nitrate does not result from the direct combination

UNCLASSIFIED /over

UNCLASSIFIED

Technical Report No 113
Explosives Research and Development Establishment
THE SILICA GEL PROCESS: SMALL SCALE STUDIES. PART 1: COMPARISON OF CATALYSTS AND LABELLING EXPERIMENTS
Armstrong F A, Fraser R T M
August 1972
48 pp, 26 tabs, 15 figs

Small scale experiments using silica gel, ammonium nitrate and urea show that formation of guanidine nitrate becomes erratic if insolubles build up on the catalyst surface. The rate of production of insolubles increases rapidly with temperature, so that a trade-off between low conversions at lower temperatures and insoluble formation at higher temperatures is possible. The yield/temperature relationship is a property of the silica gel used. Yields of guanidine nitrate can be higher than predicted, possibly because by-product water is removed in the form of ammonium silicates rather than ammonium carbamate. Experiments with ^{15}N and ^{18}O suggest that guanidine nitrate does not result from the direct combination

UNCLASSIFIED /over

UNCLASSIFIED

Technical Report No 113
Explosives Research and Development Establishment
THE SILICA GEL PROCESS: SMALL SCALE STUDIES. PART 1: COMPARISON OF CATALYSTS AND LABELLING EXPERIMENTS
Armstrong F A, Fraser R T M
August 1972
48 pp, 26 tabs, 15 figs

Small scale experiments using silica gel, ammonium nitrate and urea show that formation of guanidine nitrate becomes erratic if insolubles build up on the catalyst surface. The rate of production of insolubles increases rapidly with temperature, so that a trade-off between low conversions at lower temperatures and insoluble formation at higher temperatures is possible. The yield/temperature relationship is a property of the silica gel used. Yields of guanidine nitrate can be higher than predicted, possibly because by-product water is removed in the form of ammonium silicates rather than ammonium carbamate. Experiments with ^{15}N and ^{18}O suggest that guanidine nitrate does not result from the direct combination

UNCLASSIFIED /over

UNCLASSIFIED

Technical Report No 113
Explosives Research and Development Establishment
THE SILICA GEL PROCESS: SMALL SCALE STUDIES. PART 1: COMPARISON OF CATALYSTS AND LABELLING EXPERIMENTS
Armstrong F A, Fraser R T M
August 1972
48 pp, 26 tabs, 15 figs

Small scale experiments using silica gel, ammonium nitrate and urea show that formation of guanidine nitrate becomes erratic if insolubles build up on the catalyst surface. The rate of production of insolubles increases rapidly with temperature, so that a trade-off between low conversions at lower temperatures and insoluble formation at higher temperatures is possible. The yield/temperature relationship is a property of the silica gel used. Yields of guanidine nitrate can be higher than predicted, possibly because by-product water is removed in the form of ammonium silicates rather than ammonium carbamate. Experiments with ^{15}N and ^{18}O suggest that guanidine nitrate does not result from the direct combination

UNCLASSIFIED /over

[dstl]

Information Centre
Knowledge Services
[dstl] Porton Down
Salisbury
Wilts
SP4 0JQ
22060-6218
Tel: 01980 613753
Fax: 01980 613970

Defense Technical Information Center (DTIC)
8725 John J. Kingman Road, Suit 0944
Fort Belvoir, VA 22060-6218
U.S.A.

AD#: AD908525

Date of Search: 8 December 2008

Record Summary: AVIA 37/1344
Title: Silica gel: small scale studies; Pt 1
Availability Open Document, Open Description, Normal Closure before FOI Act: 30 years
Former reference (Department) ERDE 113/TR/72
Held by The National Archives, Kew

This document is now available at the National Archives, Kew, Surrey, United Kingdom.

DTIC has checked the National Archives Catalogue website (http://www.nationalarchives.gov.uk) and found the document is available and releasable to the public.

Access to UK public records is governed by statute, namely the Public Records Act, 1958, and the Public Records Act, 1967.
The document has been released under the 30 year rule.
(The vast majority of records selected for permanent preservation are made available to the public when they are 30 years old. This is commonly referred to as the 30 year rule and was established by the Public Records Act of 1967).

This document may be treated as UNLIMITED.