DISCUSSION—SECOND SESSION

The CHAIRMAN asked Dr. Rutledge how the fractionation actually took place bearing in mind the rate of decomposition which was stated to depend on the area.

He also asked to what extent the results might have been influenced by the dilution which occurred because of the decomposition products.

The answer about distillation, replied Dr. RUTLEDGE, was that on a large scale it was necessary to keep decomposition to acceptable levels. In the work that he had described, he had not drawn delegates' attention to the fact that decomposition was used to obtain the composition required. Peroxide was allowed to decompose down to a known level. It was then put into the detonation tube and a sample was drawn off at the same time.

Addressing a question to Dr. Rutledge, Dr. NAPIER wondered what the flame that Dr. Rutledge had mentioned at the beginning looked like. He remembered some of the early experiments that Dr. Hart had carried out at A.M.L. around 1950. The flames seemed to be coloured with sodium. Dr. Napier wondered whether there was any more information on species present in the flames or any interesting developments in that general area.

The flame was virtually transparent in colour, said Dr. RUTLEDGE. You could not see anything unless there happened to be sodium there as the flame passed through: but in all these experiments they never saw any reactions. They had not investigated the decomposition species.

Dr. M. A. NETTLETON wondered how Dr. Rutledge discriminated between the effect of packing in increasing turbulence and its effect in producing pressure fronts reflecting back towards the flame. He saw in Fig. 1 of the paper that there was a constriction at the end of the detonation tube which would also reflect pressure waves back towards the flame inducing acceleration of the flame.

Dr. RUTLEDGE said that as to whether detonation was obtained, they used a test to see whether it was reaching probe five or whether it was detonating before it got to the far end and there was not time for it to be reflected back off the end.

The packing was put in at the ignition end of the tube and that effectively reduced the run-up. It was slightly complicated because you had so many variables; one was pressure, one was composition, and one was the tube diameter. If you put a packed section in the tube, you could get detonation at lower pressures and weaker peroxide composition.

Did it, Dr. NETTLETON queried, pass up, reflecting back, and therefore increase the pressure into which the flame had moved.

Dr. RUTLEDGE replied that the packing section was only a little way from the ignition end. He did not think it had time to do any reflecting; it was still accelerating at the point at which it reached the packing.

The packing was situated 30 centimetres from the ignition end and there were 5·2 metres following that so it should have showed the effect of putting the packing in without having a detonation at that point.

A SPEAKER asked Dr. Carver whether any work had been done on saturated hydrocarbon dilution.

Some had been done, replied Dr. CARVER, but not recently. Most of the work they had been doing had been done on unsaturated hydrocarbons. He could not recall any specific work which dealt with the effect of saturated hydrocarbons.

Dr. SMITH said a certain amount of work had been done on this a long time ago and he thought the results were available. There had been no further work except an *ad hoc* investigation into the likelihood of self decomposition in gases produced by the pyrolysis of naptha under Wulff conditions.

Mr. R. B. THOMSON asked Dr. Carver whether he could give further information on the rule of thumb which he had developed.

Answering for Dr. Carver, Dr. SMITH said that, as delegates probably knew, the commercial use of acetylene as a starting point for derivatives only began after the end of the War when the work of Reppe became well known here and in the States. Many of the big chemical companies had been interested in setting up plants.

As Dr. Carver had said, the use of acetylene was controlled by the Home Office and plant designs and processes were a matter for mutual consideration with the firms. In order that the plants might be built at all some basis had to be laid down and that is how " the rules of thumb " arose.

Since it was obviously not possible to make a plant sufficiently strong not to fragment under all conditions that could arise, compromises had to be agreed. The plant could be treated in two parts—the transport pipelines and the vessels.

Long lengths of pipeline with consequent large free volumes were often necessary and if an ignition occurred, progress to detonation could be expected. It was agreed that the design pressure should be 10 to 12 times the working pressure absolute with a minimum safety factor of four and a corrosion allowance. The bursting pressure would thus be some 50 times the working pressure. This figure relates to the fact that at detonation the C.J. pressure developed rises to 20 to 25 times the initial pressure. How to arrest a detonation in the pipe had now to be considered.

In Germany in 1954 a self decomposition occurred in an acetylene pipeline leading to the almost complete destruction of the purification plant gasometer and acetylene pipe network. The accident lead to an investigation into methods of slowing down or quenching a decomposition. It was found that the most effective means was to use a tower filled with Raschig rings (a heat sink) preferably irrigated and designed to reduce the flow velocity in conjunction with an automatically operated quick shut-off valve. The tower diameter should be not less than 0·55 metres, the ring diameter not greater than

0·035 metres and the depth of ring bed not less than 4·0 metres. The flow velocity should be in the region of six to seven metres per second. The inlet and outlet to the tower should be " 'round the corner " so that an advancing detonation wave could not strike the tower frontally and be released through a bursting disc, (failure of which should be used to operate an isolation valve).

The towers could be one to two metres in diameter. The design pressure is calculated on the same basis as for pipelines, *i.e.*, a bursting pressure of some 50 times the working pressure absolute.

Vessels designed on a similar basis are inviting but are economically not a proposition. Since it was found that the length to diameter ratios of free spaces in vessels could be kept low ($L/D \not> 4$), the basis was related to the adiabatic decomposition pressure, *viz.*, 10 to 12 times the working pressure absolute. It was agreed that the design pressure should be 5 to 6 times the working pressure absolute with a minimum safety factor of four and corrosion allowance, giving a bursting pressure of about 25 times.

The plant design and location should avoid as far as humanly possible potential sources of ignition within and without the system. Instrumentation should be fitted to warn automatically of the possibility of a runaway condition arising in regard to pressure or temperature and arranged in part to shut down the plant automatically.

A SPEAKER asked Dr. Rutledge and Dr. Carver the same question. Both systems they described were, he said, one-dimensional, and he wanted to know whether there was any available information on the situation which could arise in the event of a tanker being involved in a collision causing a spillage in free space. Could one expect a problem from detonation or would one expect an ordinary deflagration under those circumstances?

In reply, Dr. RUTLEDGE said that a vapour detonation hazard could not arise from a road tanker accident If the peroxide concentration was high, fire was a hazard, but not the vapour detonation hazard they had been studying

You must have temperatures over 100 to 150°C in order to get the vapour pressure necessary to support detonation. Since peroxide is, and must be carried at ambient temperatures, the question just did not arise.

Dr. CARVER thought that in the case of acetylene such a situation was unlikely to arise because of the legislation controlling its transportation. However, if there was by chance a major spillage, he thought that there was a danger of detonation if the right sort of acetylene-air mixture was obtained. As far as he was aware, no one had tried to reproduce such a condition.

A SPEAKER asked whether it would be illegal to transport acetylene in that way.

Dr. CARVER replied that it was not legal to transport it except within clyinders. To condense or solidify it was against the law.

A SPEAKER commented that one could transport carbide which would presumably give the same sort of hazard.

Dr. CARVER said that that would be true up to a point but one had still to generate the acetylene and one had to get plenty of moisture to decompose it. He thought that under normal spillage of carbide the process would be quite slow.

Mr. G. H. IRELAND said that he was interested in the question about the unreliability of impact testing. He was wondering whether they could be given any further information about it. He had a drop hammer built precisely the same as his colleagues had done in Basle, Switzerland and everything was diagrammatically the same but he could not produce the same results with the same equipment.

His experience was apparently similar to that which many other people had had, replied Mr. CLANCEY. It was a well established feature of impact testing.

A few years ago national laboratories in seven different countries had carried out trials on samples of thirty-two compounds from the same sources. Whilst they tended on the whole to put the compounds into the same order of sensitivities there were occasional anomalies and the absolute values were sometimes different.

This was understandable in the case of liquids. It was known from Bowden's work that small bubbles played a marked part in sensitising liquids so that very small differences in techniques or apparatus which might affect the inclusion of bubbles, deliberately or accidentally, could influence the results strongly.

With solids it was more difficult to find an explanation. It was likely that the differences observed between the results with one apparatus, such as that made by Julius Peters and another and that used by the Home Office at Woolwich, were associated with the mechanics of the systems. Initiation depended not only on the energy (weight times height of fall) but also on the time factor. For this reason velocity at impact and the elastic behaviour of all the components were significant.

Differences were found between results when two laboratories were using identical apparatus as mentioned by Mr. Ireland. This was very difficult to understand and so far no satisfactory explanation had been found.

Dr. D. H. NAPIER, addressing a question to Mr. Clancey, said that during the introduction of his most interesting paper Mr. Clancey had dropped a remark that some work was going on which would allow forecasting of larger-scale hazards from the tests. It sounded very interesting and he asked whether they could hear a little of the approach to that.

Mr. CLANCEY exclaimed that if he had said that, he must have dropped not only a remark but also a " clanger ". What he had intended to imply was that work was going on in various laboratories directed towards an understanding of the behaviour of substances in large quantities—energy transfer in large masses, propagation from an origin, the self-confinement effect of a supernatant mass and so on. Hitherto there had been no real knowledge of scaling effects. Judgement of the significance of small-scale tests had been based upon analogy and experience of the safety or otherwise of explosives. As the present work went on it was to be hoped that we would begin to understand the large-scale processes better. An example of the sort of work which was being done was the recent large scale studies by the U.S. Bureau of Mines on initiation of ammonium nitrate/fuel oil.

Dr. J. H. BURGOYNE said that he was worried about Mr. Ireland's point. He wondered whether it would be helpful if the two different laboratories compared one or two standard materials to see if they were working to the same scale.

Mr. CLANCEY thought it would be helpful. Until these problems were resolved the proper procedure would seem to be for each laboratory to keep a stock of a few standard

reference substances. These would be used to " calibrate." the test each time a new substance was being tested. This was done in some laboratories. Tests were carried out alternately on the standard substance and the new substance.

That this was desirable was proved by experience. Tests at different times on a standard substance using the same apparatus in the same laboratory had been found to give different results. The reason for these temporal changes was not clear. They had been observed even when great care had been taken to maintain constant conditions of particle size, moisture content, and temperature.

Mr. R. SIDLOW wondered whether Mr. Clancey would like to make reference to the determination of suitable drying temperatures and the interpretation of the results.

Mr. CLANCEY approached the question by asking himself in what state it was most likely to be dangerous. The drying of hazardous substances raised two questions: the stability of the substance at elevated temperatures and its sensitivity when wet and dry. Generally, substances were less sensitive when wetted with solvent or water than when dry, but this was not universal since there may be reaction with the solvent. In addition to thermal instability many substances become more sensitive at elevated temperatures. It was necessary therefore to carry out explosibility and sensitivity tests at elevated temperatures. In practice one tended to consider what would be most likely yo give rise to a dangerous condition and to carry out a limited number of tests rather than embark upon an exhaustive programme covering the whole range of conditions.

Dr. BURGOYNE was wondering about some sort of hot plate testing.

Mr. CLANCEY said that this was frequently used in one of two forms when the problem was one simply of thermal stability. One method was to place the sample in a tube and raise the temperature at a specified rate of 5° or 10°C per minute and observe the temperature at which the substance flashed off. The other was to drop the sample on to a pre-heated plate and by a series of tests determine the temperature at which it flashed off within a second. Alternatives were to carry out DTA studies or to determine the temperature at which an exothermic reaction occurred under adiabatic conditions. The common practice was then to avoid heating the substance when drying to a temperature within 20 degC of the decomposition temperature—but care is needed to avoid hot spots in ovens, *etc*.

The CHAIRMAN commented that they had heard about experimental work carried out with very extreme initiation mechanisms. Mr. Clancey had said that it was necessary to use judgement. The most difficult thing to decide was the level of initiation to be assumed. Would the author comment?

Mr. CLANCEY said that he did not think that the question could be answered in a vacuum. It was necessary to consider what would be the result of an error of judgement. Would the result be something like the Texas City disaster when two ship loads of ammonium nitrate detonated, killed 600 people and caused 300 million dollars worth of damage? If it could be, the criteria to be applied would be very different from those applicable to a package weighing 10 pounds in a railway carriage.

If the result was going to be disastrous, one had to assume that during the course of its life the material could be subjected to impacts and the like very much greater than those normally used in small-scale testing—for example, in the crashing of

road vehicles. Therefore one had to be very severe. If the result was likely to be a minor one, it was rational to be less stringent. In the case of small packages the packing material might provide a significant degree of protection.

When ammonium nitrate is detonated in the Ballistic Mortar it gives an energy about three-quarters of that of TNT. Thus a large consignment could do a tremendous amount of damage, as it did at Texas City.

In the pure state it was not easy to cause it to detonate and experience has shown that the pure material did not detonate under the conditions met with during handling and transport. Therefore although it has a great potential it was not realised in practice under ordinary conditions and it may be judged to be safe.

When it was mixed with a small amount of organic matter (as it was in the Texas City material) it was initiated much more easily. Such material would have to be judged as being unsafe in a ship—but possibly safe in small quantities, or in special packages or when it was not liable to be exposed to an intense fire.

When considering the transport by ship of pure ammonium nitrate it is necessary to take into account any possibility of it becoming sensitised by contamination—for example by leaking fuel oil or, if in bulk, by residues of previous bulk cargoes, such as sulphur. If that could occur it may be necessary to lay down stowage conditions to avoid the risk.

However there was a limit to the factors to be taken into account. It would be unrealistic to postulate the concurrence of a number of independent unlikely events. The probability would become too small and it would be quite irrational to legislate for it.

Each case had to be judged separately on its merits by relying very heavily on previous experience with other materials which give similar results in the several tests. It was for that reason that one could not lay down a set of numerical criteria to be universally applied.

As far as acetylene was concerned, said Dr. CARVER, one had to consider the consequences if oxygen got into the system, a situation that frequently arises when oxy-acetylene cutting equipment is being used. Oxy-acetylene mixtures have a minimum energy of ignition of 20 microjoules, and when ignited decomposition passes into detonation in a very short distance. The maximum rate of propagation is 3000 metres per second. The danger subsequently is that this detonation can induce a propagating detonation in acetylene further down the line. Therefore it is justified to consider the decomposition of acetylene as a function of pressure using, as the source of ignition, the detonation wave produced in oxy-acetylene mixtures. High explosive initiation of acetylene was used to complete the overall picture. It gave an indication of the effect of increasing the incident shock wave velocity from 3000 metres per second to 6000 metres per second on the lower pressure limit for propagation decomposition in acetylene.

It is necessary to be careful how one interprets results of this sort, and how one uses them in relation to other systems. It is not always the case that the higher the energy of initiation, the lower the limit is for decomposition. He was at the time carrying out some work for industry on the effects of diluents on the lower decomposition limits of a substituted acetylene. A quick assessment of the effects was required. Bearing in mind the results obtained with pure acetylene, his initial consideration was to use the shock wave produced from a detonator to study this effect, as he thought that this would give him the limiting condition. If the material did not decompose under such a stimulus, it was unlikely to decompose under any other. How wrong he was. In the two-litre bomb used for the study, the percentage diluent required to prevent decomposition was much less with detonator ignition than

with ignition from a platinum wire exploded by a discharge of 0·5 joules through it. The mechanisms of ignition were different. With low energy ignition, at an initial pressure of 500–600 kN/m² (abs.), the mixture appeared to burn slowly at first. The burning rate accelerated over a period of two to five seconds and finally part of the mixture exploded violently. In all probability, the acceleration of the burning rate was the result of pressure piling in the vessel. From the records obtained, the pressure in the bomb immediately prior to the explosion was in the region of 5 MN/m² (abs.) It is not known whether there was a transition to detonation in the final stages of the decomposition. With detonative ignition, the mixtures decomposed very rapidly or not at all.

In general, he thought that it was very useful to know the effects of a whole range of levels of initiation energy on such systems. This at least gives one the chance to assess the hazard in relation to a particular practical operation.

Mr. D. G. WILDE mentioned the intensities of radiation quoted in the first column of Table IV on page 60.

It was stated that in the cases of three of the five foams examined there had been flame, or combustion, when the radiation intensities were 8·4 kW/m². Since there was no mention of the use of a pilot flame, it was assumed that the ignitions were caused by the stated level of radiation alone. Mr. Wilde thought that Dr. Napier would agree that a radiation intensity of 8·4 kW/m² was a low value in terms of igniting materials. For example, one could withstand this level of intensity on the skin for several seconds before feeling any pain; wood did not ignite spontaneously until the applied intensity of radiation reached about 29 kW/m².

In experiments at the Safety in Mines Research Establishment it had been found that a common form of polyurethane foam did not ignite spontaneously when it was subjected to a radiation intensity of 40 kW/m² provided that vapour from the foam streamed away from the solid without coming into contact with the source of radiated heat.

He wondered if Dr. Napier would like to comment on the intensities of radiation quoted in Table IV of his paper.

Dr. NAPIER's first comment was that if he had to comment on methods of testing he would draw attention to the fact that the results obtained were influenced considerably by the apparatus used; no one test could be adjudged as giving the complete assessment of the behaviour of the material under all conditions. Thus in the present work the control of the ingress of " ignition air " had some influence on the values of temperature recorded. He suggested that in the standard test referred to in the paper, the temperatures recorded were much higher because to obtain a mixture rich enough for ignition, the rate of production of volatile matter must be sufficiently high to offset the considerable dilution caused by the air stream.

Mr. BOULT added that the values of radiation intensity given were somewhat low; he assured Mr. Wilde that the levels used did cause pain of the hand. He mentioned three further points:

(i) There was no forced ventilation.

(ii) The radiation emanated from a hole in the wall of a furnace.

(iii) Some of the volatiles emitted were inducted into the furnace space.

Mr. M. KNEALE thought that it was interesting to compare the figures for radiation intensity with those given in the paper from Mr. Craven in Session III and he wondered whether Dr. Napier or Mr. Craven would care to comment on measuring radiation of possible ignition sources in the plant area.

Mr. CRAVEN could only reiterate the values in his own paper which was to be presented on the next day. He would not normally consider 6·3 kW/m² (i.e., 0·63 W/cm²) to be dangerous with most materials used on chemical plant.

Dr. NAPIER said that the results reported were those of conditioned spontaneous ignition. They were not speaking of spontaneous ignition in the normal sense of the term.

A SPEAKER pointed out that the history of the foams had not been mentioned. Was that, he asked, because everything was standardised and it was of no importance to the work in question. He was interested to know to what extent information about the previous history of the samples was made available to Dr. Napier and his colleagues, what age they were, and whether he thought it was a matter of significance at all.

Within their limited experience, Dr. NAPIER said that the only difference they had found with ageing over periods of up to two years, was in the composition of the material produced during thermal degradation. Halogenated compounds were trapped in the foam and some of them were lost from the outside but retained in the centre. Referring to the thermal performance of the material, he said that it had not changed appreciably although no special precautions had been taken in storage.

Mr. GAMADIA added that they had found slight migration to the surface taking place during ageing.

Mr. R. B. THOMPSON referred to the fact that they had been talking about one extreme. It appeared that it was purely heat they were concerned with. Had they done anything with extreme cold?

" No ", said Dr. NAPIER.

Mr. COX asked whether Dr. Napier could comment on the difference he had found between the oil-soaked polyurethane and oil-soaked asbestos in Table V.

Dr. NAPIER said that they were concerned with quite different physical arrangements in the two cases.

In the case of oil-soaked asbestos lagging, the oil is spread over an extensive surface and there is relatively free access for replenishment of the oxygen supply to the oil film. On the other hand in the case of the polyurethane foam the cellular structure restricts the access of oxygen to the oil. It is therefore more difficult to replenish the oxygen and the amount of reaction is minimised.