

FLAMMABILITY LIMITS OF HALOGENATED HYDROCARBONS

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SYNOPSIS

Lower flammability limits have been determined by upward propagation for a number of chlorinated and brominated hydrocarbons in two, four, and nine inch diameter vessels open at the lower end. Two effects have been differentiated. With vertical tubes completely open at the lower end, loss of heavier-than-air fuel-air mixture prior to ignition can lead to appreciable errors when limit mixtures are more than about five per cent more dense than air. Loss of material can be eliminated by use of a spring-loaded closure which opens to vent product gases when the pressure rise exceeds about 1 mm Hg. Using this closure the results in two and nine inch diameter vessels show evidence of a diameter dependence of the lower limits for slow-burning fuels, such as methyl and ethyl chlorides and the dichloroethanes, which can lower the lower flammable limit by a factor of 0.9.

It is concluded that the conventional use of an open-ended two inch diameter flame tube gives qualitative indications of lower flammable limits useful in many instances in hazard evaluation, but that the values obtained may be too high.

The following lower limits for upward propagation obtained in the nine inch vessel with a spring-loaded seal are believed to be the most reliable currently available for practical application in unconfined situations:

methyl chloride	8.8
1, 1-dichloroethane	5.3
1, 2-dichloroethane	5.5
ethyl chloride	3.5
<i>n</i> -propyl bromide	4.6

Corrected values for three further materials are:

<i>n</i> -propyl chloride	2.5
<i>n</i> -butyl chloride	1.8
<i>n</i> -butyl bromide	2.5

Ethyl bromide-air mixtures were non-flammable under all our experimental conditions, but in the nine inch vessel a narrow band of concentrations was on the verge of flammability.

Introduction

This work arose from an interest in assessing the explosive hazard rating of halogenated hydrocarbons when handled on an industrial scale. A fundamental requirement for such assessment is a knowledge of the lower flammability limits. These are conventionally determined in the apparatus described by Coward and Jones¹ which consists of a two inch diameter tube some 4 ft 6 in in length. It has been shown that, for conventional hydrocarbon fuels, the lower flammable limits in air are dependent on diameter at diameters less than two inches, but become independent of diameter in larger tubes. There has been no systematic investigation of the effect of diameter on the limits of slow burning fuels though it has been suggested² that a diameter effect might persist to diameters greater than two inches, for example, with halogenated hydrocarbon/air mixtures.

There are a number of indications that this may be so. As the pressure in a fuel/air system is decreased below atmospheric the flammable region eventually contracts and the fuel/air mixture becomes non-flammable when the quenching distance becomes comparable with the dimensions of the enclosure. Quenching diameters of halogenated hydrocarbons, where known, are greater than those for most hydrocarbon fuels; it is likely therefore that wall quenching will be important at higher pressures for slow burning materials such as halogenated hydrocarbons than for faster burning hydrocarbon fuels, and may well be important at or around atmospheric pressure. There is some evidence that limits of some

halogenated hydrocarbons in air are sensitive to vessel diameter and to relatively small fluctuations in pressure and temperature; for example, ethyl bromide is reported to be non-flammable in small, open vessels but flammable in larger diameter vessels with only limited venting;^{3, 4} methyl bromide/air mixtures, while reportedly non-flammable^{1, 2} have been held responsible for large-scale explosions.⁵

It is also plain from published work^{2, 5} that the limits of flammability of halogenated hydrocarbons can be very dependent on the energy of the initiation source. The criterion for the flame propagation limit which has been adopted here is that the limit lies between two fuel concentrations: (a) that at which a flame front once established across the whole diameter of the tube would propagate the whole length of the tube and (b) that at which the front, although propagating over an appreciable distance, failed before reaching the top of the tube. The effective source of ignition has thus been a flame front extending right across the tube and it is thought that the limits obtained are for true flame propagation and are not influenced by the primary initiation. Establishment of a stable flame front has been aided where necessary by injection of small quantities of secondary hydrocarbon fuel around the spark gap prior to passage of the spark.

Experimental Method

Lower flammable limits were determined by upward propagation in nominally two, four and nine inch diameter flame tubes. The internal diameters were 2.1, 3.7, and 8.4 inches respectively. All the tubes were approximately 4 ft 6 in long. Each of the two and four inch vessels was

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pivoted about its centre of gravity and mixing was achieved by a free vane which fell through the gas mixture when the tube was inverted. The bottom ends of these tubes were closed by lightly greased ground glass covers, which were removed by hand before ignition. The nine inch diameter vessel was remotely operated, and mixing was achieved by a fan mounted at the top driven through a high vacuum seal by an electric motor. The lower end was closed by a pneumatically controlled aluminium plate seating on an "O" ring. The lower end was opened before ignition by dropping the plate and swinging it away from the mouth of the tube.

Mixtures were made up by admitting a pressure of fuel vapour, measured on a mercury manometer, to the previously evacuated vessel, followed by air to ambient pressure. In the smaller vessels, mixing for 10 minutes was adequate; up to 30 minutes' stirring was necessary in the larger vessel. Spark ignition was used in all cases; an oscillatory spark (peak voltage 14 kV, frequency 10 kHz, duration 150 ms, energy of each spark *ca* 0.3 mJ) was found to give more reproducible results than condenser or ignition coil discharges. Just before ignition, the bottom plate was removed from the vessel and if necessary several millilitres of a secondary fuel vapour (methane or ethane) could be injected around the spark gap. Secondary fuel was used when it was not otherwise possible to establish a flame front which died before propagation was complete, that is, when the leanest flame which could be established propagated the whole length of the tube and no flame propagation at all could be observed in weaker mixtures. In the two and four inch vessels, 2 or 5 ml of secondary fuel were used, while in the nine inch vessel up to 15 ml of secondary fuel were injected. The bottom plate and secondary fuel injection systems are shown schematically in Fig. 1.

Errors in making up mixtures were checked in the nine inch vessel as follows. Mixtures of carbon dioxide (about five per cent by volume) in nitrogen were made up and mixing started. In each run, five samples were removed at intervals through a probe and the carbon dioxide absorbed in 0.02 M strontium hydroxide and determined conductimetrically.⁶ In each of five runs the mean estimated concentrations were within 0.02% v/v of the expected values, while the scatter within each run was about 0.04% v/v. It is concluded that the making-up error was of the magnitude expected from the errors in reading mercury manometers; also that the absolute errors and inhomogeneities within a given mixture were each comparable in magnitude with the spread due to bracketing. This is consistent with the degree of reproducibility experienced

while carrying out the bracketing. In addition, three independent determinations of the limit for methyl chloride in the nine inch diameter vessel were found to agree within $\pm 0.1\%$.

Difficulties were met while determining the lower limits of *n*-propyl and ethyl bromides in the nine inch diameter vessel. With *n*-propyl bromide the limit in the nine inch vessel was found to be 5.1% which is higher than the values in the smaller vessels. This anomalous result was accompanied by the observation of persistent burning at the mouth of the tube. With ethyl bromide, also, flame would propagate less than three-quarters of the way up the tube before dying and again a ball of flame burnt for considerable periods at the exit of the tube. It was thought that these difficulties might be due to a tendency for the heavy fuel/air mixture to pour from the tube as soon as the end plate was removed.

Attempts were made to limit the escape of vapour by restricting the tube exit but although a slight reduction in the amount of burning at the mouth of the tube was achieved, there was no detectable effect on the lower limit of *n*-propyl bromide.

The mouth of the tube was then completely closed by a light plate a quarter of whose area was spring loaded⁷ to allow venting of hot product gases. The plate prevented loss of fuel/air mixture before ignition but opened at a pressure differential of less than one mm Hg. A water manometer fitted to a side arm above the spring-loaded plate confirmed that the pressure rise during the passage of flames never exceeded 1.5 cm water. Using the plate, a lower limit of 4.64% was obtained for *n*-propyl bromide in air. The same device was used with ethyl bromide; although loss of mixture was greatly reduced so that there was little burning outside the tube, no mixture of ethyl bromide in air would allow a flame to propagate the full length of the tube. Propagation over three-quarters of the length of the tube could be observed with mixtures containing between 9.6 and 11.0% ethyl bromide in air, but the flame front always broke up before travelling the whole length of the tube.

Similar effects were noticed with ethyl bromide in the two and four inch diameter vessels but in these smaller vessels the tendency to propagate flame was very much less marked. Figure 2 shows the spring-loaded plate.

During the symposium at which this paper was first presented (Fourth Symposium on Chemical Process Hazards with Special Reference to Plant Design, Institution of Chemical Engineers, UMIST, 6-7 April, 1971), discussions

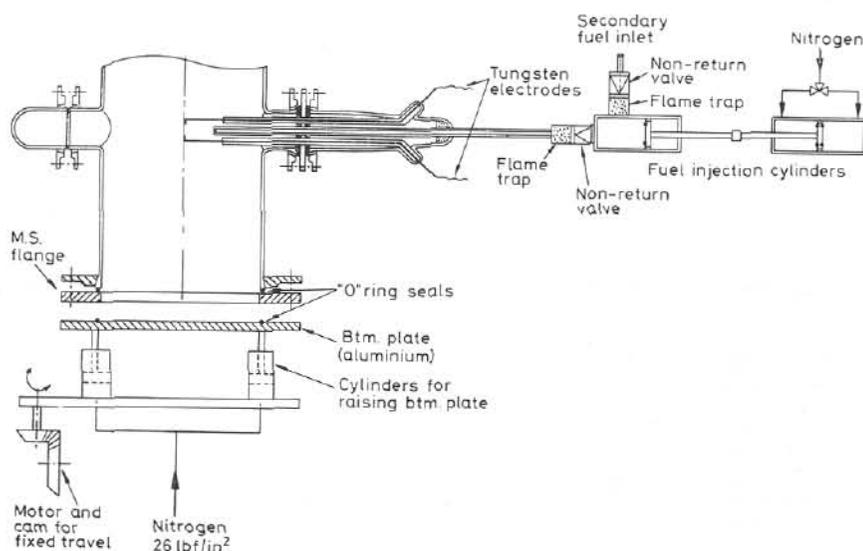


Fig. 1.—Bottom plate and secondary fuel injection systems

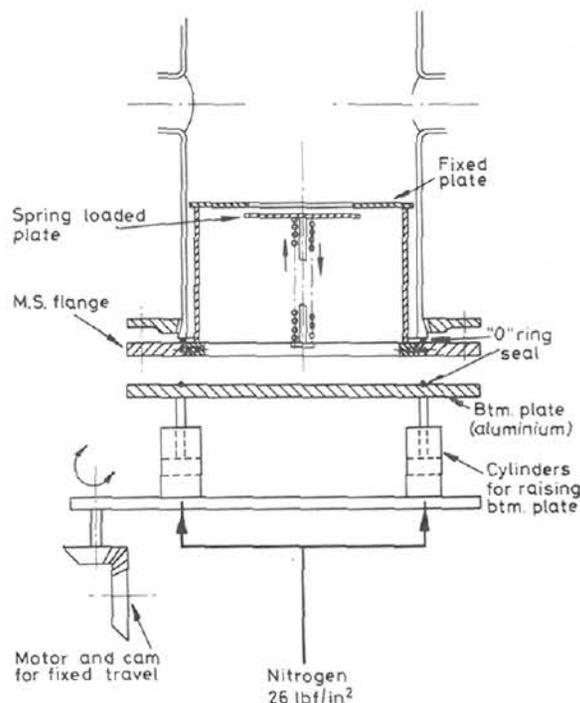


Fig. 2.—Spring-loaded plate

with Dr. D. Lewis and Dr. G. Artingstall emphasised that loss of material from the open end of the flame tube before and during flame propagation might seriously affect the determination of lower flammable limits for all those materials whose limit mixtures are appreciably more dense than air. Further work was therefore carried out using a spring-loaded closure in both two and nine inch flame tubes on five halogenated hydrocarbons and on ethane, to separate and determine the effects of mixture density and of flame tube diameter. The materials were selected because of their direct practical interest and to cover a reasonably wide range of limit mixture density.

Results

The results obtained in the original work using completely open tubes are listed in Table IA, together with the spread due to bracketing. Results subsequently obtained in spring-loaded two and nine inch diameter vessels are compared in

TABLE I.—Lower Flammable Limits in two, four, and nine inch Diameter Tubes

Fuel	A In open tubes (% v/v)			B Spring-closed tube (% v/v)		C Density of limit mixtures (air = 100)
	two inch diameter	four inch diameter	nine inch diameter	two inch diameter	nine inch diameter	
ethane	3.10 ± 0.05	—	2.98 ± 0.02	2.96 ± 0.02	2.88 ± 0.03	100.1
methyl chloride	9.80 ± 0.04	9.69 ± 0.09	9.47 ± 0.05	9.51 ± 0.03	8.80 ± 0.04	108
1, 1-dichloroethane	6.09 ± 0.04	6.09 ± 0.04	5.99 ± 0.02	5.84 ± 0.02	5.30 ± 0.03	115
1, 2-dichloroethane	5.85 ± 0.07	5.87 ± 0.07	5.50 ± 0.03	5.66 ± 0.04	5.50 ± 0.03	114
ethyl chloride	3.84 ± 0.04	3.78 ± 0.03	3.65 ± 0.03	3.75 ± 0.07	3.50 ± 0.05	105
<i>n</i> -propyl chloride	3.00 ± 0.07	3.00 ± 0.04	2.69 ± 0.09	—	—	105
<i>n</i> -butyl chloride	1.93 ± 0.02	1.91 ± 0.06	1.90 ± 0.01	—	—	104
ethyl bromide	—	non-flammable	—	non-flammable	—	—
<i>n</i> -propyl bromide	5.00 ± 0.02	4.87 ± 0.03	5.1	4.66 ± 0.04	4.64 ± 0.04	116
<i>n</i> -butyl bromide	3.08 ± 0.05	3.04 ± 0.04	2.78 ± 0.04	—	—	111

Table IB; Table IC lists the densities of lower limit mixtures relative to air.

Adiabatic limit flame temperatures for the chlorinated hydrocarbons have been computed by Dr. R. F. Simmons at UMIST. The calculated values are listed in Table II.

TABLE II.—Calculated Adiabatic Limit Flame Temperatures

Fuel	Lower flammable limit (% v/v)	Adiabatic limit flame temperature (K)
methyl chloride	8.80	1820
1, 1-dichloroethane	5.30	1790
1, 2-dichloroethane	5.50	1830
ethyl chloride	3.50	1520
<i>n</i> -propyl chloride	~2.55*	~1640*
<i>n</i> -butyl chloride	~1.8*	~1600*
ethyl bromide	—	(2206)**
<i>n</i> -propyl bromide	4.64	2306
<i>n</i> -butyl bromide	2.5*	2000*
methane	5.23	1530
ethane	2.90	1500
<i>n</i> -propane	2.20	1580
<i>n</i> -hexane	1.2	1680
<i>n</i> -heptane	1.1	1640
<i>n</i> -octane	0.95	1680
<i>n</i> -decane	0.75	1620

For the halogenated materials the limit values are from the present work in the nine inch diameter vessel with spring-loaded plate, and the flame temperatures were calculated by Dr. R. F. Simmons. Data for the hydrocarbons are from References 2 and 11.

* Estimated values

** For stoichiometric mixture

Discussion

Comparison with other work

There are wide discrepancies in the experimental values reported for the lower flammable limits of halogenated hydrocarbon/air mixtures but these could be due to the wide variety of vessels and experimental conditions which have been used. The principal collections of flammability data are References 1, 2, and 8 and Table III compares the values from these sources.

The present work in open two inch tubes is in reasonable agreement with literature values of lower flammable limits which were determined in conventional two inch diameter vessels under comparable conditions. This is the case for 1, 2-dichloroethane,¹ ethyl chloride^{1, 2} and *n*-butyl chloride.² Such agreement is rather surprising in view of the effect of loss of material on lower limit determinations which has now

TABLE III.—Comparison of Lower Flammable Limit Values

Fuel	Coward and Jones ¹ (% v/v)	Zabetakis ² (% v/v)	Nabert and Schön ⁸ (% v/v)	Present work open two inch tube (% v/v)
methyl chloride	10.75	7.0*	7.10	9.80
1, 1-dichloroethane	—	—	5.6	6.09
1, 2-dichloroethane	6.2	—	6.2	5.85
ethyl chloride	3.85	3.8	3.6	3.84
<i>n</i> -propyl chloride	2.6‡	2.4*	2.60	3.00
<i>n</i> -butyl chloride	4.1**	1.80	1.80	1.93
ethyl bromide	non-flammable	—	6.70	—
<i>n</i> -propyl bromide	non-flammable	—	non-flammable	5.00
<i>n</i> -butyl bromide	5.2**	2.50†	4.00	3.08

* calculated

‡ closed bomb

** downward propagation

† at 100°C

been demonstrated. This loss is shown not only by the use of the spring-loaded plate (see below) but by a dependence of the limit on the time allowed between opening of the lower end of the tube and ignition in both two and nine inch vessels. The standard delay in these vessels was two seconds. For example, with methyl chloride in the two inch tube a limit of 9.8% was obtained using a delay of two seconds; increasing the delay to five seconds raised the limit of 10.9% in agreement with Coward's and Jones' value.¹

Coward and Jones¹ report a higher value for *n*-butyl chloride in a two inch tube but this was determined by downward propagation. A much lower figure of 2.5% quoted for *n*-butyl bromide by Zabetakis² was determined at 100°C.

Other reports in the literature are based on work in narrow tubes which yield much higher results than those from the present work. *N*-propyl bromide has been said to be non-flammable¹ on the basis of work in a 0.6 inch diameter vessel. The high value quoted by Coward and Jones¹ for *n*-butyl bromide (5.2%) arose from downward propagation work in a 1.5 cm diameter tube.

Of the values lower than the present ones, Nabert's and Schön's⁸ value for ethyl chloride probably derives from Deiss,⁹ who used a partially closed pipette. Zabetakis's² figures for methyl chloride and *n*-propyl chloride are listed as calculated values, but no details of the method of calculation are given. They are consistent with assuming that the heat of combustion per unit volume at the limit for these materials is the same as that for conventional hydrocarbons, that is, 11.5 to 12 kcal/mol combustible mixture.

Effect of loss of material from open tube

It is clear from the experimental results listed in Table I that two factors are affecting the values of lower flammable limits for the fuels tested. Comparison of the results in the two inch diameter flame tubes with and without the spring-loaded plate shows that with fuels such as ethane and ethyl chloride whose lower limit mixtures are similar in density to air, use of the spring-loaded plate has only a small effect on the lower flammable limit. As the density of lower flammable limit mixture increases, so the percentage change in lower flammable limit on use of a spring-loaded plate increases. These observations, together with the effect of time between opening the tube and ignition, strongly suggest that heavier-than-air limit mixtures tend to be lost from the open end of the tube. Dimensional analysis shows¹⁰ that the flow of heavy gas from

a tube should follow an expression of the type:

$$Q \propto \left(g \frac{\Delta\rho}{\rho_2} D^5 \right)^{\frac{1}{2}} \quad \dots \quad (1)$$

where:

Q = rate of influx of light gas

g = gravitational constant

D = vessel diameter

$$\Delta\rho/\rho_2 = \frac{\rho_2 - \rho_{\text{air}}}{\rho_2}$$

ρ_2 = density of heavy gas

If one assumes that the buoyancy-driven flow from a vertical pipe is governed by an expression of this form, that the time between tube opening and ignition is constant, and that there is complete mixing of the inflowing air with the remaining fuel-air mixture then:

$$\Delta L/L \propto (\Delta\rho/\rho)^{\frac{1}{2}} \quad \dots \quad (2)$$

where $\Delta L/L$ is the relative change in the lower limit on changing from an open tube to one from which no material is lost.

Figure 3 shows plots of equation (2) for the two and nine inch tubes. These show that the differences between the limits in the open and spring-closed tubes are consistent with loss of material by buoyancy-driven flow from the open tubes. (The point for 1, 2-dichloroethane in the nine inch vessel is anomalous and is not shown in Fig. 3).

N-butyl chloride, *n*-propyl chloride and *n*-butyl bromide have not been examined using the spring-loaded closure. However, the observed dependence of $\Delta L/L$ on relative density difference allows estimates to be made of the true limits from the experimental results in open tubes. For *n*-propyl and *n*-butyl chloride the estimated nine inch limits are each about a factor 0.95 lower than the values in the open tubes, that is, 2.55 and 1.8% respectively. The limit mixture for *n*-butyl bromide is more dense and a lower limit of ca 2.5% might be expected in a nine inch tube fitted with a spring-loaded plate.

Effect of tube diameter

The results listed in Table IB show that when the loss of heavier-than-air limit mixtures has been eliminated by use of the spring-loaded closure, there is evidence for a diameter dependence of the lower flammable limit for a number of fuels. With a conventional hydrocarbon fuel, ethane, the

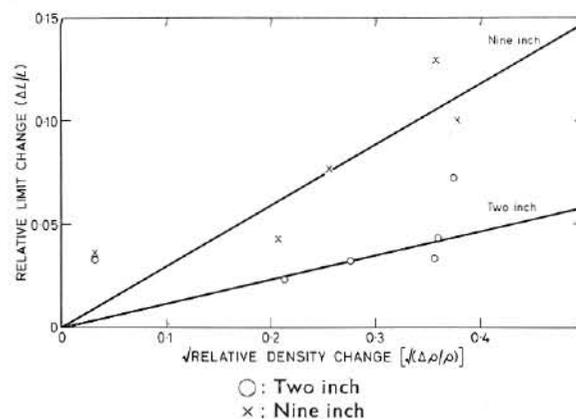


Fig. 3.—Effect of limit mixture density on L.E.L.

difference between the limits in the two tubes is little more than the experimental error. With the other fuels, with the unexpected exception of *n*-propyl bromide, increasing the vessel diameter from two to nine inches lowers the lower limits appreciably, by factors of up to 0.9. There appears to be no good correlation of the magnitude of the observed dependence with other flammable characteristics, although qualitatively it appears that the dependence is most marked with the slowest burning fuels.

Looking at the adiabatic limit flame temperatures of the chlorinated hydrocarbons listed in Table II, it is seen that these fall into two groups. Those for ethyl chloride, *n*-propyl chloride and *n*-butyl chloride form a group whose flame temperatures are only a little higher than those for the corresponding hydrocarbons.¹¹ Those for methyl chloride, 1, 1- and 1, 2-dichloroethane, materials with a higher chlorine: combustible ratio, form a group with substantially higher limit flame temperatures. Addition of halogen to flames inhibits high temperature combustion and so lowers burning velocities, while having little effect on adiabatic flame temperatures.^{12, 13} The increase in limit flame temperature according to the proportion of halogen is therefore required to overcome the reduced reaction rate and so maintain the minimum burning velocity required for flame propagation.

From the evidence presented, it cannot be said that if the vessel diameter were increased beyond nine inches, some lower limits would not drop still further. There may however be a factor which will set a limit to this tendency for the limits to decrease. It is observed that propagation is easier in an upward than in a downward direction, the explanation being that upward propagation is assisted by the buoyancy of the hot products. It has been shown that this buoyancy itself sets a limit on the minimum speed at which a flame can travel up a tube and hence on the lower limit fuel concentration; furthermore this limiting speed actually increases as vessel diameter increases.¹⁴ It may be expected, therefore, that, starting with small tubes in which wall quenching is a major factor, the limit will be observed to drop as the tube diameter increases, but that beyond a certain diameter the limit will rise again when buoyancy becomes the limiting factor. Hence it is reasonable to expect that limit values close to those given here will in fact be applicable to much larger vessels.

Conclusion

For many practical purposes it is not necessary to know lower limit values with great accuracy; a common rule is that certain work can be carried out at concentrations of less than one quarter the lower limit. For this type of application, in view of the discussion above, the conventional use of an open two inch tube will give an adequate indication of lower limits. Where finer control of conditions is required, however,

the two inch flame tube used with unrestricted venting may not give satisfactory limit values. With fuels whose limit mixtures are appreciably more dense than air, loss of material between venting the tube and ignition can have an appreciable effect. (These effects might well be experienced in determining upper limits of even conventional hydrocarbon fuels containing more than three or four carbon atoms.) A spring-loaded plate or similar device which will prevent loss of material without causing an appreciable pressure rise during flame propagation, can minimise the errors due to loss of material. Further, where fuels are relatively slow-burning there is a strong possibility of the lower limits being lower in vessels of diameter greater than two inches.

Acknowledgments

The authors wish to thank Dr. J. H. Burgoyne for many helpful discussions and Dr. R. F. Simmons, UMIST, for computing limit-flame temperatures. Mr. P. S. Gibson assisted in the experimental work.

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The manuscript of this paper was received on 26 January, 1971.