

Comparison with velocities calculated by the Chapman-Jouguet theory shows agreement only for mixtures with a ratio of hydrogen to oxygen not far from stoichiometric. The deviations from the theory are only partially explainable by losses of energy to the walls of the tube. Evidence is presented to show that the internal

heat capacity of polyatomic gases may not be fully excited and also that the chemical reactions may not reach the state of thermodynamic equilibrium in the Chapman-Jouguet plane of some detonation waves.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

## Gaseous Detonations. II. Initiation by Shock Waves<sup>1</sup>

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Extensive studies of the initiation of gaseous detonation have shown no single sequence of events.<sup>1a</sup> The primary result of a thermal initiation appears always to be a flame, which propagates with subsonic speed. Where conditions are such that the flame causes adiabatic compression of the still unreacted material ahead of it, its velocity speeds up. In some of the observations the speed of the flame seems gradually to rise until it equals that of the detonation wave. Normally a discontinuous change of velocity is observed from the low flame velocity to the high speed of detonation. In still other observations the detonation wave has been observed to originate apparently spontaneously some distance ahead of the flame front. The place of origin has been shown to coincide with the location of a shock wave sent out by the expanding gases of the flame. The observed phenomena are quite complex and exceptions may easily be taken to this synopsis, but we believe that it is as accurate as a brief summary can be.

The theoretical problem of transitions from flames to detonations has not been extensively treated, except by Zeldovich<sup>2</sup> and by Shchelkin<sup>3</sup> who attribute it to turbulence near the front of the flame. Other less quantitative ideas attribute the initiation of detonations to chain carriers,<sup>4</sup> etc. Le Chatelier proposed that adiabatic compression by a shock is the cause of detonations and initiation by shock waves has been a subject of extensive experimental work, Laffitte,<sup>5</sup> Wendlandt,<sup>6</sup> Payman,<sup>7</sup> Dixon,<sup>8</sup> Bone<sup>9</sup> and others having participated in it. The gist of their findings is that det-

onation waves may be started by shock waves, even when these arrive from chemically inert media. Very intense shocks appear to start the detonation instantly and even to overdrive it initially to an excess velocity. Weaker shocks appear to cause ignitions, which eventually change into detonations. Still weaker shocks produce no chemical effects. In view of the usually discontinuous character of detonation initiation by flames and other evidence<sup>10</sup> it may be surmised that shocks are the normal if not the exclusive cause of detonation waves. This mode of initiation has therefore particular interest and yet previous experimental work has been far from exhaustive or even quantitative. The initiation by shocks arriving from inert media should possess, relatively speaking, maximum simplicity because the transfer of the reaction by chain carriers is excluded and the theory of shocks is sufficiently well developed so that initial conditions in the explosive gas mixture may be deduced, except for the uncertainty of incomplete equilibration of the internal degrees of freedom in the molecules.

The present paper describes experiments on the initiation of gaseous detonations by plane shock waves transmitted by inert gases.

### Experimental Details

The same equipment as described in the preceding paper, but with suitable additions, was used. The experiments were carried out in the 10-cm. pipe, which was assembled by bolting together flanged sections 50, 20, 10 and 100 cm. long. The first two sections contained the initiating mixture. Separated from it by a cellophane diaphragm 0.001" thick was a 10-cm. buffer layer of air and beyond the next cellophane diaphragm was the experimental gas mixture. Gases were taken from commercial high-pressure cylinders without further purification. The first piezoelectric gage was located about 5 cm. ahead of the first cellophane diaphragm and was used to trigger the oscilloscope sweep. The next gage was located midway in the buffer section. The experimental section had twelve gages spaced 5 cm. apart, followed by three more at 10-cm. intervals. The same piezoelectric gages and amplifiers were used as described in the first paper, except that the resistances on the diode filters were altered when weaker waves were expected, or the diodes were even omitted altogether to permit the amplification of still weaker signals.

Some of the phenomena observed suggested the possibility that the waves transmitted through the cellophane

(1) The research reported in this document was made possible by funds extended Harvard University under O. N. R. Contract N5ori-76 T. O. XIX NR-053-094.

(1a) For a review see Lewis and v. Elbe, "Combustion, Flames and Explosions of Gases," Cambridge University Press, Cambridge, England, 1938.

(2) Zeldovich, *J. Exp. Theor. Phys. U. S. S. R.*, **10**, 542 (1940); *J. Tech. Phys., U. S. S. R.*, **17**, 3 (1947).

(3) Shchelkin, *Compt. rend. acad. sci. U. R. S. S.*, **23**, 636 (1939); **47**, 482 (1945).

(4) Lewis, *This Journal*, **52**, 3120 (1930).

(5) P. Laffitte, *Compt. rend.*, **177**, 178 (1923).

(6) W. Wendlandt, *Z. physik. Chem.*, **116**, 227 (1925).

(7) Payman, *Proc. Roy. Soc. (London)*, **A120**, 90 (1928).

(8) Lean and Dixon, *Manch. Lit. Phil. Soc.*, **5**, 16 (1891).

(9) Bone, *et al.*, *Phil. Trans. Roy. Soc. London*, **A235**, 29 (1936).

(10) Kistiakowsky, Third Symposium on Combustion, Flame and Explosion Phenomena, Madison, Wisconsin, 1948.

initiated at a point rather than uniformly throughout the cross section of the pipe. This required a study of the planarity of the waves, for which purpose a gage was mounted at the end of a 0.5-inch pipe, threaded on the outside. This pipe passed through a threaded hole in the center of the plate closing the end of the 10-cm. tube, so that by turning the 0.5-inch pipe the gage could be moved back and forth along the axis of the large tube. In another set-up two piezoelectric gages were mounted in the end-plate, one on the axis of the tube, the other near its periphery.

The pressure in the experimental compartment was kept near 760 mm. in all runs, the gases being at room temperature, averaging 24°. The pressure in the buffer section normally was the same. However, in some runs a variation in the strength of the initiating wave was caused by changing the pressure of the initiator compartment, rather than its composition. This was possible since the cellophane diaphragms withstood pressure differences of about 200 mm. and the technique provided a very convenient method for obtaining reproducible and controlled changes in the initiator strength. The initiating mixture was acetylene and oxygen in all experiments, because with this mixture we were able to establish detonations within the sufficiently short distance of a few centimeters from the initiating spark.

### Results and Interpretation

The experiments presented below provide information on the course of events when shock waves of controlled intensity enter variously composed mixtures of acetylene and oxygen, hydrogen and oxygen, methane and oxygen, and benzene and oxygen. Some experiments on the variation of the duration of the shock were also tried.

To interpret the meaning of the signals from gages next to the cellophane diaphragms, it was necessary to determine the delays caused by the diaphragms in the transmission of the waves. Using a detonating acetylene-oxygen mixture in the entire pipe and assuming constant velocity for it, the delays caused by the diaphragm were found to be 3.0 and 3.2 microseconds, or an average of 3.1, which value was used in all calculations. It may be noted that Campbell, Littler and Whitworth<sup>11</sup> found delays of 45 and 33 microseconds, respectively, in rupturing 0.0028- and 0.0022-inch copper diaphragms. Allowing for the ratio of masses of their and our diaphragms, the observed delays appear to be in satisfactory agreement.

The planarity of the waves was repeatedly investigated. The first experiments were made with the gages set directly into the end-plate and gave simultaneous signals to within the accuracy of these measurements which was not better than 0.3 microsecond because of complicated records caused by signals from the reflected wave. More extensive measurements were undertaken with the gage mounted on the end of the movable pipe. The planarity of a shock wave sent into air from a detonating 16.7% acetylene-oxygen mixture after passing through the buffer and two diaphragms was obtained as follows. The signals from a series of wall gages gave the velocity of the shock wave. From the time difference between the pips from a wall gage and the central gage the

position of the latter was then calculated to be 0.69 cm. behind the wall gage. This calculation assumed perfect planarity of the wave over the entire cross section of the pipe. The actual distance of the front of the central gage was 0.58 cm. behind the middle and 0.74 cm. behind the leading edge of the wall gage, showing that the wave was plane over its 5-cm. radius to within 0.1 cm. Three runs were made with detonating 25% acetylene-oxygen mixtures filling the entire pipe. The maximum observed deviation from planarity was 0.2 cm. The investigation of the planarity of incipient detonation waves starting in the experimental compartment some distance behind the diaphragm presented considerable difficulties because of uncertainties in the place of initiation and the identification of pips on the complex records. However, three sets of reliable data were obtained with a 85.7% hydrogen-oxygen mixture initiated by a 50% acetylene-oxygen mixture at a pressure of 775 mm., the center gage being 65 cm. behind the cellophane diaphragm and about 4 cm. behind the plane in which the detonation started. These runs showed a wave plane to within 0.2 cm. In view of these results we feel confident that in all experiments the observed waves were very nearly planar and that initiation of detonation occurred not at a point but uniformly over the entire cross section of the pipe.

The presentation of the main body of the results creates an awkward problem because they are unsuited to tabular form and graphs of a hundred runs would tax the leniency of the readers and the Editor of this Journal. In the following figures we show, therefore, only a few characteristic runs explaining the main features of various observations. Details will be found elsewhere.<sup>12</sup> The figures are plots of velocities against distance of travel in the buffer and experimental sections. The points represent observed velocities, whose values were obtained on dividing the distance between adjacent gages by the time difference of their signals. The points are located in the graph half-way between the gages. The straight lines joining them are not intended to have physical meaning. Small fluctuations in velocity are due to experimental errors, but several of the runs suggest that real oscillations of velocities persisted in the pipe for considerable distances. The discontinuous nature of our observations does not permit a distinction between a rapid smooth change in velocity and a truly discontinuous one.

The first line in Fig. 1 shows the decaying velocity of a shock wave transmitted into the experimental section filled with air. A wholly analogous result is obtained when the section contains an explosive mixture and the initiating shock is sufficiently weak, as is shown by line no. 2. The mapping of the region of decaying mechanical shock waves in explosive mixtures, as a function of the strength of the initiating wave and the

(11) Campbell, Littler and Whitworth, *Proc. Roy. Soc. (London)*, **A137**, 380 (1932).

(12) E. F. Greene, Ph.D. Thesis, Harvard University, 1949.

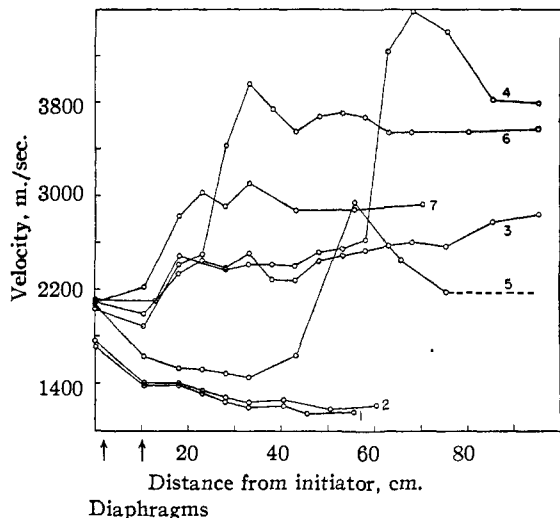


Fig. 1.—Wave velocity vs. distance from initiating section for various gas mixtures and initiating shock intensities.

composition of the reactive mixture, was not very detailed. It is possible, however, to draw a definite conclusion that explosive mixtures nearer the limits of detonable compositions will transmit much stronger mechanical shocks without evidence of self-acceleration. This was investigated with acetylene-oxygen and hydrogen-oxygen mixtures but probably applies to others as well.

The third line in the figure shows the results obtained when more intense initiation is used on hydrogen-oxygen mixtures. The shock wave shows steady acceleration instead of decay, although its velocity remains far below that of stationary detonation over the entire distance investigated.<sup>13</sup> This type of result was obtained *only* with experimental mixtures containing large concentrations of hydrogen. With methane only one composition was studied, containing 33.3% methane, and it did not show such behavior.

Line no. 4 illustrates the behavior of experimental mixtures after a still stronger initiation. One notes the self-acceleration of the shock wave over some 50-cm. distance, followed by a rapid or sudden development of the detonation wave. The initial velocity of the latter is far greater than the steady value ultimately reached.<sup>14</sup> The acceleration in the predetonation period is particularly pronounced with mixtures rich in hydrogen, and does not appear to be essential to the initiation of the detonation wave, as is shown by line no. 5 in which the shock velocity continued to decrease until the onset of detonation. In still other experiments, particularly with other combustibles than hydrogen, the shock propagated at constant

(13) The rapid rise in velocity after leaving the last cellophane diaphragm is a normal acceleration of a shock wave due to the lower density of the experimental mixture compared with the air filling the buffer section.

(14) Cf. Bone, Fraser and Wheeler, *Phil. Trans. Roy. Soc. London*, **A235**, 29 (1936), for similar finding.

velocity, within the accuracy of our measurements, before detonating. The longest distance of travel through the experimental section before the change-over into detonation occurred, was about 50 cm. If it did not occur within this distance, records typified by line no. 3 resulted.

There does not appear to be a definite shock velocity for a given experimental mixture at which transition into detonation takes place. Instead these velocities depend on the initiating shock wave and extend over a moderate range. In fact, the shock velocities which may be obtained on gradual acceleration after weaker initiation (as in line no. 3) are occasionally higher than those at which detonation occurs after stronger initiation. This is noteworthy because temperature and pressure of a shock wave are definite functions of its velocity.

The overshoot of the steady detonation velocity upon initiation was consistently observed and amounted in some experiments to over 30% excess velocity. Because of the discontinuous nature of our readings the extent of overshoot could not be accurately measured. It may be surmised that the instantaneous velocities rose to even higher values than the 5 cm. averages here reported.

With increasing strength of initiation the distance traveled by the shock wave before conversion into detonation decreased, as shown by line no. 6. This was accompanied by a consistent decrease in the magnitude of the overshoot. Such behavior was observed with acetylene, methane and hydrogen as combustibles in the experimental section.

The strongest initiation resulted in immediate formation of the detonation wave, as shown by line no. 7. The overshoot was small, but the detonation velocity showed oscillations which, while not very large compared to experimental errors, are nonetheless probably real.

The described details of the initiation process appeared to be entirely reproducible, provided the compositions and total pressures in the three sections were carefully controlled. The control was essential because the range of initiator strength over which the entire pattern was observed is rather small. Thus using a 85.7% hydrogen-14.3% oxygen mixture at 760 mm. pressure in the experimental section and a 50% acetylene-50% oxygen mixture in the initiator section, the pattern could be reproduced by increasing the pressure of the initiator from 760 to 852 mm. This corresponds to an increase in the pressure of the buffer shock wave by about 12%.

The changes of velocities along the experimental section, shown in Fig. 1, are characteristic of experimental mixtures whose composition is well within the accepted range of detonable mixtures. No difficulties arise here in determining whether and when the gases underwent detonation. A different situation is encountered when a strong ini-

tiator is used on compositions which are near the detonability limits. In fact, our experiments under these conditions show no evidence of sharp detonation limits. According to Laffitte<sup>15</sup> this limit for hydrogen-oxygen mixtures is at 14.9% hydrogen. The following Fig. 2 shows data obtained with mixtures of low hydrogen content, but using a strong initiating mixture, 50% acetylene-oxygen. The first line, for comparison, shows the propagation of a shock wave induced by a weaker initiator, in a 14.3% hydrogen mixture. The following lines nos. 3 to 6 inclusive show propagation of waves induced by strong initiators in mixtures of decreasing hydrogen content. Line no. 2 shows a shock wave in air produced by the same initiator. It is evident from these data that nearly self-supporting shock waves are propagated in the 14.2% hydrogen mixture the length of the experimental section. Their velocity is higher than the stationary value deducible from the data of the first paper of this series. Even in still leaner mixtures, which are considered to be well outside the detonation limits, the waves propagate with high velocities, but show increasing signs of decay. The change in shock behavior from that in normally detonating mixtures to that in pure air appears to be a gradual one and the detonation limit is not sharply defined.

The main, although not altogether novel, conclusion which can be drawn from the experiments here discussed, is that plane shock waves without any evidence of turbulence or special wall effects produce detonations, either "instantly" or after some distance of travel through a reactive mixture. It may be thought that such initiation is due to extremely high temperatures, and therefore exceptionally fast reaction rates, produced by the shocks. This, however, is not the case, if one trusts calculations of initiating shock temperatures from their velocities under the assumption of no chemical reaction in the shock wave and uses therefore the heat capacities of the initially present gases. On this basis we find, for instance, that a shock with a peak temperature of 657°K. decays in a 85.7% hydrogen + 14.3% oxygen mixture. A shock of 867°K. temperature shows acceleration in the same mixture and when its temperature is still below 1114°K., transition into detonation takes place. Finally, an air shock at an undetermined but not much higher temperature causes what appears to be an instantaneous detonation in the same mixture. Literature data on the ordinary ignition temperatures of hydrogen-oxygen mixtures are somewhat conflicting, which is not surprising in view of the complex kinetics, but 800–900°K. appears to be the range for the gases at atmospheric pressure. Although this figure should be reduced somewhat because of the higher pressures in the shock waves, it is evident nonetheless that initiation by shocks occurs when their temperatures exceed the ignition temperature by, at most,

(15) Laffitte, *cf.* "International Critical Tables."

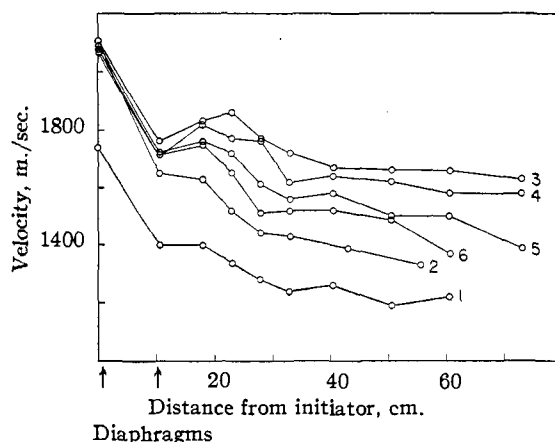


Fig. 2.—Wave velocity vs. distance from initiating section in lean hydrogen-oxygen mixtures: Line 1, weak shock wave in a 14.3% hydrogen–85.7% oxygen mixture; Line 2, stronger shock in air; Lines 3 to 6, stronger waves in hydrogen-oxygen mixtures containing, respectively, 14.2, 13.8, 10.0, 7.7% hydrogen.

a few hundred degrees. A similar result is obtained for acetylene-oxygen mixtures, for which the literature indicates an ignition range from 673 to 713°K. We have been able to obtain detonations from shocks whose temperatures, in the instant before transition, were as low as 756°K. These are temperatures far below those at which other initiating agencies (*e. g.*, electric sparks, glowing wires) produce nothing but flames. The difference between these initiating agencies and shocks is, therefore, not that the latter are able to induce qualitatively different, or at least much faster, chemical reactions. It is that after initiation by other agencies the propagation of the flame is governed by the slow diffusion of chain carriers, or heat conduction, etc. A plane shock, on the other hand, continuously starts the same flame reactions by adiabatic compression as it travels through fresh layers of explosive gases.<sup>16</sup> This concept implies that from the kinetic point of view there is no difference between a flame and the chemical reactions in a detonation wave and indeed there is not. The treatment of detonation waves by v. Neumann<sup>17</sup> shows that to an observer moving with the matter in the detonation wave, the movement of the wave front is subsonic as long as he is in the region between the front and the Chapman-Jouguet plane, that is in the reaction zone. An ordinary flame propagating in a closed tube sends forward a subsonic compressional wave. But so long as one is dealing with what is commonly called a flame, this compressional wave is too weak to cause self-ignition of the gases and the flame depends on diffusion of chain carriers, etc., for its propagation. Eventually, however, this advancing compression

(16) This is not true of a rapidly expanding spherical shock wave, as may be caused by a spark, because of a rapid decrease in intensity.

(17) *Cf.* Courant and Friedrichs, "Supersonic Flow and Shock Waves," Interscience Publishers, Inc., New York, N. Y., 1948.

forms a shock and, when that is strong enough, causes detonation. The flame in a detonation wave also sends forward a continuous compressional wave which keeps the detonation front from decaying. In this it does not differ from other flames. The difference is that the detonation front causes chemical reaction by adiabatic compression and thus automatically maintains the flame burning immediately behind itself. A further but not an essential difference is that this flame burns in highly compressed and preheated gases and burns therefore with extreme rapidity. Now, when a mechanical shock, after entering an explosive gas mixture, is able to produce such a flame burning behind itself, it has initiated detonation. Thus the treatment of the immediate initiation of detonation waves by shocks does not present serious difficulties.

The interpretation of the phenomena involved in accelerating shocks preceding delayed detonation initiation is, on the other hand, rather uncertain. We have some experimental evidence that by speeding chemical reactions but changing little the hydrodynamic properties of the explosive gas mixture it is possible to reproduce the pattern of phenomena shown in Fig. 1, while using an initiating shock wave of unchanged strength. In these experiments initiation was by a 25% acetylene-75% oxygen mixture at 760 mm. and the experimental section was filled with a 14.3% hydrogen-85.7% oxygen mixture. This resulted in a record of the type illustrated by line no. 2 of Fig. 1. Upon addition of 1.5% acetylene to this mixture, a record of the type of line no. 5 was obtained, and 3.3% acetylene caused immediate detonation.

There seems to be no doubt that in the self-accelerating shock waves chemical reaction is proceeding. The front of a mechanical shock wave is associated with the highest temperature and hence it is possible that the chemical reaction develops to full velocity immediately behind the shock front. On the other hand, reactions like the combustion of hydrogen, because of their branching chain<sup>18</sup> mechanism are known to have induction periods. It is therefore possible that the reaction, *i. e.*, the "flame front," develops only some distance behind the shock front. Either mechanism could cause hydrodynamic reinforcement of the shock wave, although the second explains in a much more ready fashion the sudden transitions into detonation waves and is therefore more plausible. The first may be interpreted as an extreme case of a reaction extending back through the Chapman-Jouguet plane, a subject which was discussed in the preceding paper. The reinforcement in this case is a continuous one, of the same nature as the support of a detonation wave by the chemical reactions. If a separate flame front exists, it may form its own shock wave which must eventually overtake the original one and then start the

full detonation. We have at present no experimental evidence to distinguish between these possibilities and will reserve their detailed discussion until such evidence has been obtained by modified experiments now planned.

It remains to comment on the excess velocities observed after delayed initiation of detonation waves. The clue is the observation of so-called retonation waves<sup>19</sup> which were recorded on our gages also for a distance of five or ten cm. backward from the place of initiation. By the conservation laws, the momentum of the forward moving detonation wave must equal the momentum of the retonation wave moving backward from the place of initiation. Added to these is the momentum of the initiating shock wave. Therefore, in reference to a stationary frame, the just formed detonation wave must move with superdetonation velocity, the retonation wave with a subdetonation velocity. Basically not very different from this interpretation is the thought that the superdetonation velocities are due to the overdrive by the high mass velocity of matter in the initiating shock waves. Indeed our calculations show that the mass velocity in the shock wave just prior to initiation are the same as those in the detonation waves moving with the excess velocities. These calculations must be taken cautiously, however, because they apply to the front of the shock wave but to the Chapman-Jouguet plane of the detonation wave.

The rapid decay of the detonation waves to their normal velocities is due to the rapidly rising rate of energy dissipation with velocity. While at the velocities of the initiating shocks this dissipation is just conveniently observable with our experimental arrangement, at the 5,000-4,000 m./sec. velocities of the newly born detonation waves, the energy of the initiating shock is all gone after a short distance of travel. Our observations with discrete gages are not well suited for a detailed exploration of these rapidly changing velocities and it must be reserved for another occasion.

### Summary

Impact of plane shock waves on detonable gas mixtures causes the following pattern of phenomena with increasing strength of shocks: the weakest shocks are transmitted by such mixtures with slow decay, indistinguishable from decay in non-reactive gases; shocks whose peak temperature exceeds the ignition temperature of the gas mixture are propagated with a slowly rising velocity and when the initial shocks are more intense, this phase is followed by the development of a full detonation wave. Such delayed detonation waves are propagated initially with very high velocities which rapidly decay to the stationary values. The strongest shocks produce immediate detonation.

(18) Cf. Semenov, "Chain Reactions and Chemical Kinetics," Oxford University Press, 1935.

(19) E. g., Bone, Fraser and Wheeler, *Phil. Trans. Roy. Soc. London*, **A235**, 29 (1936).

These observations are discussed and interpreted with the aid of the Chapman-Jouguet-

Neumann treatment of detonation waves.

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## The Heat Capacities and Dielectric Constants of Some Alkyl Halides in the Solid State<sup>1</sup>

BY LAWRENCE M. KUSHNER, ROBERT W. CROWE AND CHARLES P. SMYTH

For a number of years it has been recognized that certain molecules or polyatomic ionic groups in crystalline solids may rotate in the lattice below the freezing point. Two of the more important tools used in the investigation of this phenomenon have been measurements of dielectric constant and heat capacity. Since, in many cases, the effects studied are non-equilibrium in nature and therefore not very reproducible, it seemed advantageous to measure both of these properties simultaneously.

In this investigation, *t*-butyl chloride, *t*-butyl bromide, *i*-propyl bromide and *n*-amyl bromide were studied. The dielectric behavior of these compounds has been previously investigated. The molecules differ in shape, and therefore the ease of rotation in the solid state also varies considerably from compound to compound. The chief objects of the investigation were to correlate the thermal properties of these compounds with their dielectric behavior, and to determine the energy quantities involved in their transition from one phase to another.

### Apparatus and Method of Measurement

The apparatus used for both heat capacity and dielectric constant measurements consisted of a combined heat conduction calorimeter and dielectric cell, constructed in such a way that the two quantities could be determined simultaneously. The principle of the measurement of heat capacity with such a calorimeter<sup>1a</sup> is the comparison of the time required to heat a known weight of sample through a definite temperature interval with that required, under identical conditions, to heat a known weight of a standard compound through that interval. The time required to heat the empty calorimeter through the same temperature interval must also be determined. Knowing these data, it is possible to calculate the average molar heat capacity  $C_{px}$  of the unknown substance in the temperature interval by means of the equation

$$C_{px} = \frac{W_s M_x C_{ps}}{M_s W_x} \cdot \frac{t_x - t_0}{t_s - t_0} \quad (1)$$

In this equation,  $W$ ,  $M$  and  $t$  are weight of sample in grams, molecular weight and time interval in

seconds, respectively. The subscripts  $e$ ,  $s$  and  $x$  refer to empty, standard substance and substance to be measured, respectively.

The calorimetric assembly was enclosed in a double wall glass jacket A (Fig. 1). It consisted of a calorimeter can C, a heating mantle B and a bakelite rod D. The mantle and enclosed calorimeter can were suspended on this rod which was supported by means of a bushing and pin Q. The copper heating mantle was in two parts threaded at point E, so that it could be easily opened in order to fill the enclosed can without disturbing the thermocouple wires. A removable

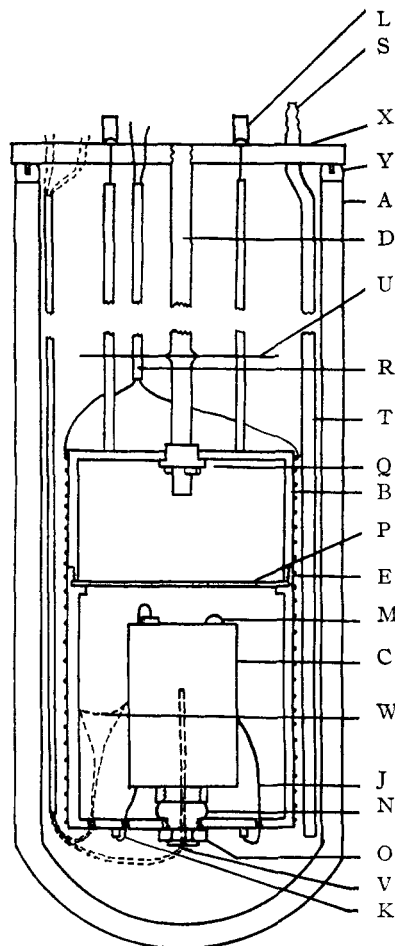


Fig. 1.—Calorimetric assembly.

(1) This research was carried out with the support of the Office of Naval Research.

(1a) Ziegler and Messer, THIS JOURNAL, 63, 2694 (1941).