Effect of Initial Mixture Density on the Formation of Detonation in Knallgas Saturated with Water Vapor

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IN an earlier article, Adler, Hobaica, and Luker (*1*) discussed the effects of external properties, detonation tube diameter, and mode and strength of ignition on the formation of detonation in knallgas saturated with water vapor. In this article, the effect of initial mixture density on the formation of detonation at constant external conditions is treated.

Experimental studies of this type have been performed by Dixon (*4*), Laffitte (*6*), Laffite and Dumanois (*7*), Egerton and Gates (*5*), Bollinger and Edse (*3*), and Potter and Wayman (*10*). In each study, increasing gas density shortened the distance traveled by the predetonation flame before detonation was established.

Reported herein are the effect of density on the formation of detonation and the detonation limits in a particular experimental system for a saturated knallgas–steam mixture. This mixture is of particular interest in the atomic energy field as it may be encountered in aqueous homogeneous reactors.

In this investigation, the initial mixture density was varied from 0.64 to 62 gram per liter. A marked decrease in the system detonation limit (composition–mole per cent cent of knallgas) was noted as the density was increased.

Since most explosive and detonation limits for gaseous mixtures are reported at or near atmospheric pressure, the present results are of general interest to engineers confronting the problem of safe handling of combustible media at high pressures.

EXPERIMENTAL

Apparatus. A sketch of the apparatus used in the study is presented in Figure 1.

The reaction tube, 0.434-inch-i.d., was of Type 304 stainless steel, seamless tubing. The reactor was 7 feet, 6 inches long. It was heated electrically in four sections wrapped with Nichrome resistance wire. Each of the four sections of Nichrome wire was independently controlled by a Brown Pyr-O-Vane indicating controller. The temperature of each of these four sections was controlled to within ±1° C. of the set point.

Static pressure readings or mixture pressure before and after reaction were measured with one or three Bourdon-type pressures gages. Their precision is as follows: The Heise gage at 100° C., ±0.1 p.s.i.; at 200° C., ±0.5 p.s.i.; U. S. gage at 300° C., ±2 p.s.i.

Both hot wire and spark ignition were used. In both cases, the source of ignition was located 3 inches from the near end of the reactor.

The hot wire ignitor consisted of a short length of 24 gage Nichrome wire wound in a helix. Constant direct current power was supplied by an automobile battery booster which has a maximum output of 10 volts and 6.3 amperes. Time of current application was recorded manually by the use of a timer.

Spark ignition was furnished by discharge of a 0.02-microfarad capacitor charged to a potential of 6000 volts. Switching losses were minimized by the use of a thyratron tube; tungsten rods 0.060 inch in diameter were used as electrodes. A constant spark gap setting of 0.05 inch was employed.

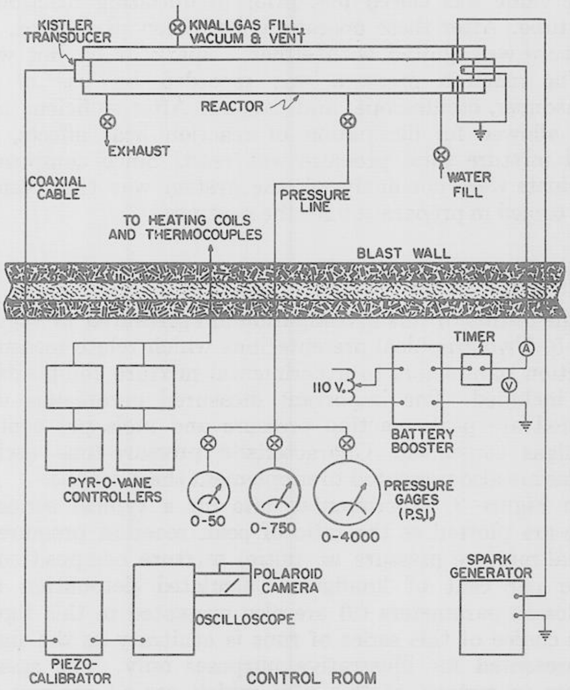

Figure 1. Experimental system

Reaction pressures were measured as reflected pressures with a quartz pressure transducer. (Kistler Instrument Co. SLM PZ-14). The transducer was located at the far end of the tube. The electrical output of the transducer was monitored with a amplifier calibrator (Kistler PC-14H) and the signal was displayed on a cathode ray oscilloscope (DuMont Type 324) as a pressure-time pulse. The pressure-time signal was recorded with a Polaroid land camera (DuMont Type 302). The range of the Kistler transducer was 0 to 3000 p.s.i., but by using a high pressure adaptor the range was extended to 30,000 p.s.i. The pressure pickup was calibrated statically with a dead-weight tester (Crosby Style CD-210). The resultant pressure measurements obtained from this instrument should not be considered quantitatively as such; however, they were reproducible and may be used on a comparative basis.

The knallgas ($2H_2 + O_2$) was prepared by premixing electrolytic hydrogen, purity better than 99.9 mole %, and oxygen of 99.6 U.S.P. grade mole % purity. Sufficient mixing time was allowed so that the composition of knallgas never deviated more than 0.5 mole % from stoichiometric.

More details concerning the apparatus and calibration of components are given by (*2*).

Procedure. The same procedure was used for each run. The reactor was evacuated and a sufficient quantity of distilled water was added to form a saturated mixture at the temperature studied. Sufficient knallgas was then introduced into the reactor to yield the desired composition. The tube was heated to the selected temperature (100°, 200°, or 300° C.) and was maintained at the control temperature for 3 hours.

Prior to initiation of the actual detonation experimen-

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tation, an equilibrium-composition study was conducted. Analysis of gas samples periodically withdrawn from the reactor showed that composition in the reactor approached saturation composition and remained constant after a 2-hour heating period. Thus, the 3-hour equilibration period was selected to be certain saturated conditions were established.

The total mixture pressure was recorded and the reactor gage value was closed just prior to initiating reaction in the tube. After these operations had been performed, the mixture was ignited with either a spark or by hot wire.

The reaction pressure was recorded by use of the transducer, oscilloscope, and camera. After sufficient time was allowed for dissipation of reaction heat effects, the final mixture total pressure was read. Since combustion products were not analyzed, the system was then vented and cooled in preparation for the next run.

RESULTS AND DISCUSSION

The results of this investigation are presented in Figures 2 to 5. Two graphical presentations which relate measured reaction parameters to experimental mixture compositions are included. The important measured parameters considered are peak reaction pressure and mole per cent of knallgas consumed. Characteristic pressure-time oscillograms are also presented to supplement these graphs.

In Figure 2, experimental data for a typical series of runs are plotted as the ratio of peak reaction pressure to initial mixture pressure *vs.* initial mixture composition in mole per cent of knallgas. Calculated detonation and explosion parameters (*9*) are also presented in this figure. The choice of this series of runs is arbitrary as the figure is presented for illustrative purposes only. The specific points or regions of this plot which are of interest are the no reaction limit, the predetonation zone, the induction composition, and the overpressure region.

The no reaction limit designates the initial mixture composition in mole per cent of knallgas below which no detectable reaction occurred when a source of ignition was applied. The predetonation zone is defined as the initial mixture composition range from the no reaction limit to the intersection of the calculated stable detonation curve with the experimental curve. This point of intersection or the leanest initial mixture composition which will result in an experimental reflected detonation pressure equal to the calculated reflected stable pressure is termed the induction composition. Mixtures richer than the induction composition exhibit overpressure associated with unstable detonation (*2*).

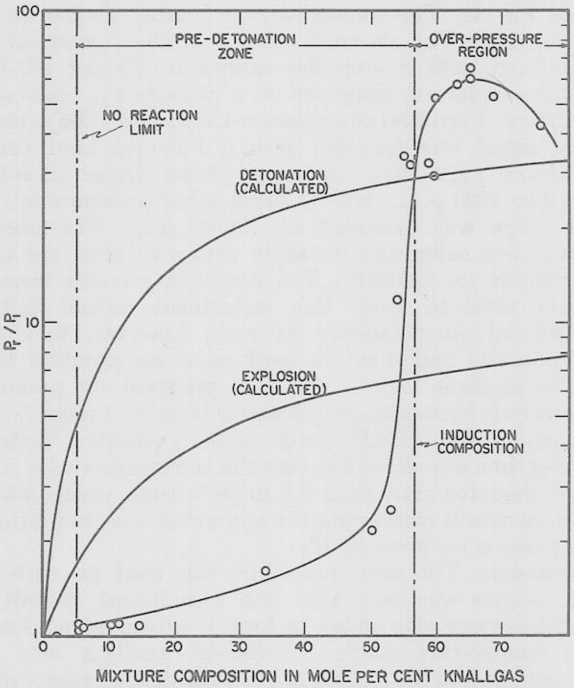
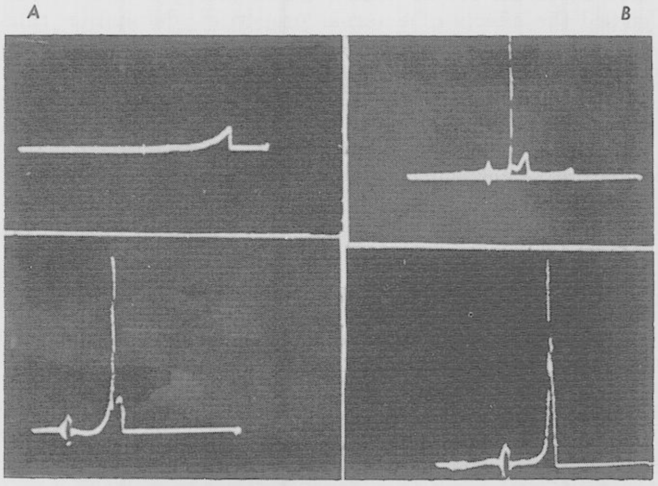


Figure 2. Ratio of peak reaction pressure to initial mixture pressure *vs.* composition of knallgas with water vapor at 100° C.

Spark ignition. Energy level, 360 mj.

In Figure 3, four typical reaction pressure *vs.* time oscillograms are presented. The oscillogram shown in Figure 3*A*, is characteristic of the relatively weak combustion waves generated in the initial composition range of 6 to 50 mole % of knallgas (predetonation region). In this region the measured reaction pressures were significantly lower than the calculated constant volume explosion pressures. The mole per cent of knallgas reacted or consumed in this region was approximately 25%.



Vertical axis, pressure. Horizontal axis, time.

	A	*B*	*C*	*D*
Initial composition, mole, %	34.3	55.2	63.5	66.0
Peak reaction pressure, p.s.i.a.	39.3	1100.0	2320.0	2823.0
Knallgas reacted, %	25.0	86.0	81.0	80.0
P_r/P_I	1.75	33.5	57.9	65.5
Sweep speed, mseconds per cm.	2.5	1.0	0.5	0.5

Figure 3. Pressure *vs.* time records of typical reactions of knallgas

As the induction composition or system detonation limit was approached, oscillograms such as shown in Figure 3*B*, were obtained. The figure shows compressional shocks preceding the detonation front in a manner consistent with the generally accepted picture of the development of detonation. In addition, a sharp rise in reaction pressure and in the mole per cent of knallgas reacted occurred as the induction composition was approached. All of the afore mentioned evidence indicates that the mechanism of reaction is changing from deflagration to a shock-propagated mechanism at or near the induction composition.

In Figure 3*C*, the leading shock waves are beginning to coalesce to form an unstable detonation wave. The entire region of compositions above the induction composition shown in Figure 2 is the overpressure region corresponding to unstable detonation. Figure 3*D*, shows a typical oscillogram in the overpressure region where the detonation front and leading shocks have coalesced to form an unstable detonation wave. If the initial compositions had been further enriched above 76 mole % of knallgas, stable detonations would undoubtedly have resulted.

The method of analysis as cited above was subsequently applied to show the effect of initial density on the formation of detonation. All data presented herein concerning detonation limits or induction compositions are characteristic only for the particular experimental system used. The effect of external factors on such properties may be ascertained by referring to the earlier article by Adler, Hobaica, and Luker (*1*).

In investigating the effect of initial mixture density on the formation of detonation, the initial density of the mixture was varied by controlling the initial mixture composition (mole per cent of knallgas) at temperatures of 100°, 200°, and 300° C. Initial mixture density ranges investigated were as follows:

100° C.	0.64 to 1.8 grams/per liter
200° C.	8.5 to 16 grams/per liter
300° C.	46 to 62 grams/per liter

Investigation of the effect of initial mixture density was conducted with hot wire ignition. While spark ignition functioned exceedingly well in these saturated mixtures at 100° C., the spark ignitor exhibited very erratic behavior and failed to fire in many instances at 200° and 300° C. After several months of operation, use of spark ignition in the investigation of the density parameter was abandoned in favor of hot wire ignition.

The results which illustrate the effect of initial density on the formation of detonation are presented in Figures 4 and 5. For reasons of clarity, smoothed curves are presented in these figures. Representative scatter of the experimental data is indicated by the illustrative curve of Figure 2.

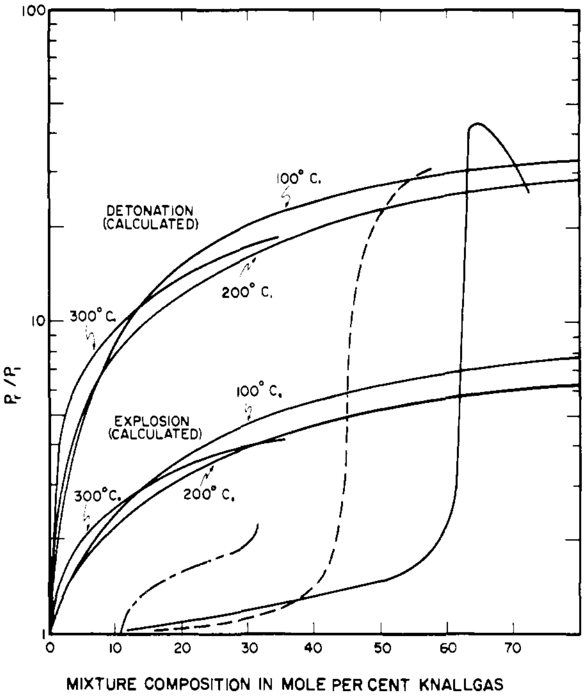


Figure 4. Effect of density on ratio of peak reaction pressure to initial mixture pressure vs. initial mixture composition (hot wire ignition)

—— 100° C. ---- 200° C. – · – 300° C.

Examination of Figure 4 shows that induction composition decreases markedly as initial mixture density is increased. The induction compositions were 62, 44, and less than 36 mole % of knallgas at 100°, 200°, and 300° C. or initial mixture densities of 1.22, 13, and 63 (at 36%) grams per liter, respectively.

In Figure 5, the per cent of knallgas reacted as computed from final pressure and temperature measurements is shown as a function of initial mixture concentration in mole per cent of knallgas at 100°, 200°, and 300° C. Abrupt rises occurred in this figure for each respective temperature in the vicinity of the induction composition.

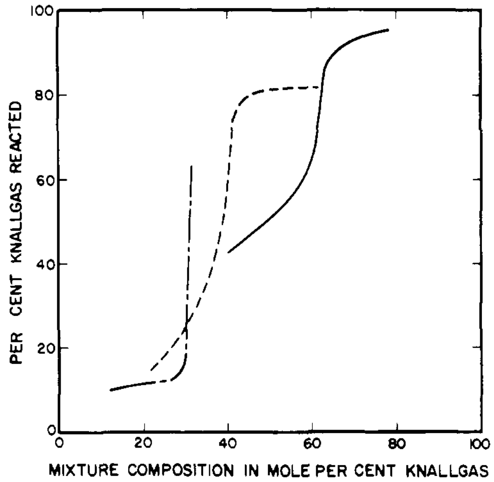


Figure 5. Effect of density on per cent knallgas reacted vs. initial mixture composition

—— 100° C. --- 200° C. –·– 300° C.

Oscillograms characteristic of the predetonation period as illustrated in Figure 3*a*, were obtained at all three temperature levels. At 100° and 200° C., oscillograms characteristic of the transition which occurs at the induction composition (Figure 3*B*, and in the overpressure region (Figure 3*C* and *D*) were obtained.

To compare the moles of knallgas, and consequently the heat of combustion per unit volume, available at the respective temperatures, Figure 6 was prepared. In Figure 6, the partial molal density of knallgas (gram-moles/per liter of mixture) is expressed as a function of mixture composition at 100°, 200°, and 300° C. This figure shows that the partial molal density of knallgas which is proportional to the potential heat release per unit volume increases markedly with temperature. Considering a 40% knallgas composition as an illustration, the moles of knallgas per unit volume of mixture are 0.02, 0.3, and 1.7 gram-moles/per liter at 100°, 200°, and 300° C. respectively.

In an earlier article (*1*) it was shown that in a 0.434-inch

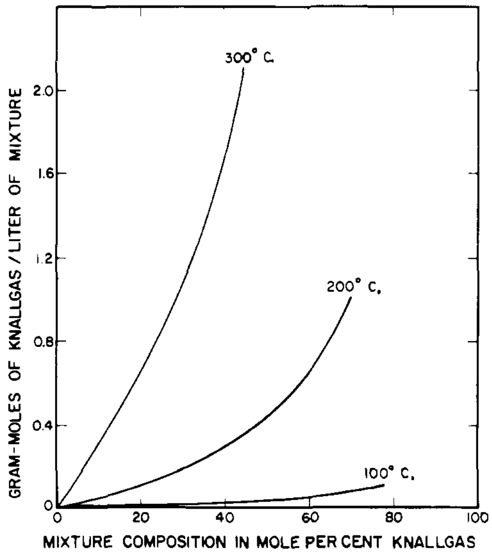


Figure 6. Partial molal density of Knallgas in mixtures saturated with water vapor vs. mixture composition at 100°, 200°, and 300° C.

i.d. reactor such as was used in this study, the high surface to volume ratio of the reactor provides a very effective heat sink. Such a heat sink causes high abstraction of energy due to heat losses, and thus significantly affects the predetonation period. It is conceivable that such action would tend to magnify the effect of density on the formation of detonation and that the effect of density might be less significant in an experimental system where wall effects are minimized.

CONCLUSIONS

The experimental system and procedure used in this investigation provided an excellent simple method for determining the effect of internal properties on the formation of detonation in gaseous mixtures.

Increasing the initial mixture density significantly affected the formation of detonation in mixtures of knallgas saturated with water vapor. The induction composition or system detonation limit decreased markedly with increasing initial mixture density. It is plausible that the effect of density on the formation of detonation as reported was magnified, because of the high surface to volume ratio of the experimental reactor.

The results presented herein are characteristic of only the specific experimental system utilized. It may, however, be generalized that mixture density is an important parameter which must be considered in establishing detonation limits for gaseous mixtures. Neglecting the effect of density on such limits or on the formation process could result in serious errors of estimate, and such procedures should be regarded as an unsafe practice in the handling of combustible gases at elevated pressures.

NOMENCLATURE

P_r = peak reaction pressure, atmospheres
P_1 = initial pressure, atmospheres

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Detonation Properties of Heavy Knallgas, 2 $D_2 + O_2$

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A DETONATION study of heavy knallgas ($2D_2 + O_2$) is warranted from two basic engineering aspects: to provide valuable base data for equipment detonation design, and to determine whether such data can be adequately predicted via Chapman-Jouguet detonation theory (*7, 18*). In particular, measured and predicted detonation properties of heavy knallgas may differ significantly. Although detonation velocities in knallgas ($2H_2 + O_2$) agree well with theory (*3, 11, 12, 24, 27*), the slower reaction kinetics exhibited by deuterium-oxygen mixtures (*4, 8, 16*) suggest increased wave-front energy loss to the detonation tube. Resulting effects on the detonation velocity of heavy knallgas may thus be marked. Deviations may be more prominent, however, if consideration is also given to the detonation pressure. Agreement of theoretical and experimental velocities in itself is not evidence of strict adherence to "ideal" detonation criteria. Rather, detonation velocities may exhibit good agreement with calculated values without denoting exact or near-exact fulfillment of theoretical detonation conditions (*3, 11*). Such may not be true for the detonation pressure. This study thus considers both the stable detonation velocity and reflected, or "impact," detonation pressure in testing the experimental and theoretical detonation agreement of heavy knallgas. Conditions covered are 1 to 15 atm. initial pressure at 25° C. Since adequate comparison is necessary to the analysis, corresponding properties of knallgas have also been determined.

APPARATUS AND PROCEDURE

A schematic of the detonation laboratory is shown in Figure 1. Control valves, gas lines, and placement of the component experimental equipment is indicated.

The detonation tube, 18 feet long, was constructed of round, straight, 1.00-inch i.d. seamless 304 steel tubing.

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