with one work hardening effect, the dynamic bursting pressure with a double work hardening effect, and the rupture disk rating. The dynamic bursting pressure increased with work hardening.

For one work hardening effect the dynamic bursting pressure increased an average of approximately 16%. The dynamic bursting pressure increased an average of approximately 34% when the disk was dynamically work hardened a second time. However, the dynamic bursting pressure after a double work hardening showed an increase of only an average of 8% over the increase caused by a single work hardening effect.

CONCLUSIONS

Rupture disks used in this study exhibited a higher bursting pressure under dynamic loading than under static loading.

The relationship between dynamic bursting pressure and static bursting pressure was linear for all disks tested.

Stainless steel Type 304, nickel, and cold-rolled steel exhibited dynamic work hardening.

Phosphor bronze did not dynamically work harden.

Stainless steel Type 304 will progressively dynamically work harden.

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Knallgas and Knallgas-Steam Mixtures at High Initial Temperature and Pressure

Calculated Detonation Parameters and Adiabatic Constant-Volume Explosion Properties

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Explosive gas mixtures at certain conditions react in a radically different manner from that normally found in gaseous combustion. This reaction is characterized by an extremely high propagation rate of the combustion wave into the unburned gas, equal to several times the speed of sound, and by pressures behind the wave front much higher than those found in constant-volume adiabatic explosions. For this phenomenon, called detonation, many experimental velocity and some pressure and density measurements have been made for various gas mixtures. Since the work of Chapman and Jouguet around 1900, many theoretical calculations of detonation wave properties have been made which show satisfactory agreement with experimental values. Therefore, calculated detonation parameters provide valuable design information for the safe handling of detonable gas mixtures.

The specific mixtures considered here are knallgas ($2H_2$-O_2) and knallgas saturated with steam. The latter mixture is of particular interest in the atomic energy field because one of the characteristics of homogeneous reactors, in which the nuclear fuel is dissolved in an aqueous medium, is that molecular hydrogen and oxygen are produced in approximately stoichiometric proportions by radiation effects. Thus, a potentially explosive or detonatable gas mixture at high pressure and temperature may be formed. Naturally, the reactor components must be designed to withstand the pressures resulting from any explosion or detonation which might occur.

Gas mixtures which could be produced under typical reactor operating conditions were considered. This range of interest covered the region from room temperature and atmospheric pressure to 300° C. and 150 atm. Presented in Table I are the specific initial conditions considered for dry knallgas and saturated knallgas-steam mixtures.

For each initial condition the detonation pressure, temperature, velocity, and the composition of the detonation products at thermodynamic equilibrium were calculated. These same detonation parameters were also calculated for a reflected detonation wave. The reflected pressure, being more than twice as great as the detonation pressure, is of primary importance since equipment damage will most likely occur at points of reflection. These results represent normal and reflected parameters for stable detonations.

During the formation of a detonation in the transition from deflagration to detonation, pressures significantly higher than

Table I. Initial Properties of Mixtures with Composition in Mole % Knallgas

Pressure, Atm.	Temperature, °K.				
	298.16	423	473	523	573
	Composition, Mole %				
1	100	. . .	. . .	. . .	. . .
5	100	5.78	. . .	. . .	. . .
10	100	51.8	. . .	. . .	. . .
16	. . .	. . .	3.70	. . .	. . .
30	100	83.4	46.0	. . .	. . .
43	. . .	. . .	. . .	7.26	. . .
50	100	89.8	66.4	18.3	. . .
70	100	92.5	75.4	38.6	. . .
90	100	94.1	80.4	50.5	4.11
110	100	95.1	83.6	58.3	17.0
130	100	95.7	85.8	63.8	26.5
150	100	96.2	87.5	67.8	33.9

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the normal stable pressures are attained (*7,16–18*). Points of reflection of these unstable pressures could result in extremely high impact pressures. While the unstable detonation region has been analyzed theoretically (*15*), it is not possible to calculate these pressures from existing theory. Detonation pressures in the unstable detonation region are currently being investigated. It is hoped that unstable detonation pressures may be expressed as multiples of the stable detonation pressure in the future [see Adler and Luker (*1*)].

Where detonation limits of the particular mixture of interest have been established, equipment operation outside these limits—i.e., in the explosive composition range—is often feasible. In such cases, calculated constant-volume adiabatic explosion properties provide adequate design criteria.

Recent experimental work on saturated knallgas-steam mixtures (*1,2*) has indicated, subject to several pertinent features of the experimental system, mixture composition ranges in which detonation is not obtained. It is plausible to use constant-volume explosion properties as design criteria for saturated knallgas-steam mixtures in some instances; the constant-volume explosion properties of saturated knallgas-steam mixtures are reported.

GENERAL ANALYSIS

Plane Detonation Waves. The theory of steady state detonation is due primarily to Chapman (*6*), Jouguet (*9*), and Becker (*4*). The governing relationships for plane detonation waves may be developed by considering the physical situation of a shock front moving into stationary unburned gas. As shown in Figure 1, the coordinate system is fixed in the shock front. The following equations may be applied to a unit mass entering a unit area of the shock front with velocity u_1 and leaving with velocity u_2.

$$u_1/V_1 = u_2/V_2 \qquad \text{(conservation of mass)} \qquad (1)$$

$$P_1 + u^2{}_1/V_1 = P_2 + u^2{}_2/V_2 \qquad \text{(conservation of impulse)} \qquad (2)$$

$$E_1 + P_1V_1 + u^2{}_1/2 = E_2 + P_2V_2 + u^2{}_2/2 \qquad \text{(conservation of energy)} \qquad (3)$$

Equations 1, 2, and 3 may be combined to yield the well known Hugoniot relation.

$$E_2 - E_1 = 1/2(P_1 + P_2)(V_1 - V_2) \qquad (4)$$

In Equation 4 the term $E_2 - E_1$ represents the increase in internal energy due to the Hugoniot compression. To apply this equation to a detonation wave, the net energy release due to chemical reaction, ΔE_g, must be added to the compressional change as follows:

$$E_2 - E_1 = 1/2(P_1 + P_2)(V_1 - V_2) + \Delta E_g \qquad (5)$$

If the perfect gas law is applicable to the detonation products, Equation 5 may be further simplified, since the internal energy of a perfect gas is a function of temperature only.

$$\bar{C}_v(T_2 - T_1) - \Delta E_g = 1/2(P_1 + P_2)(V_1 - V_2) \qquad (6)$$

Combination of Equation 6 with the perfect gas law ($PV = nRT$) fails to yield a solution because three unknown quantities exist. The necessary additional relationship was furnished by Chapman (*6*) and Jouguet (*9*), whose hypothesis specifies the exact point on the proper Hugoniot curve which will correspond to physical reality. Essentially the hypothesis assumes that the gas will assume the thermodynamic state of greatest probability consistent with hydrodynamic stability. This hypothesis may be expressed as follows in the form of an equation of stability.

$$\left(\frac{dP_2}{dV_2}\right)_{\text{adiabatic}} = -\gamma_2\frac{P_2}{V_2} = \frac{P_2 - P_1}{V_2 - V_1} \qquad (7)$$

For any specified initial condition, Equations 6 and 7 and the perfect gas law may be solved simultaneously to yield a unique solution for T_2, P_2, and V_2.

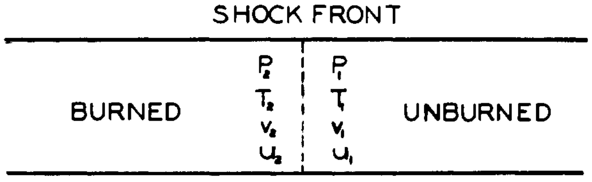

Figure 1. Detonation coordinates

If the coordinate system is transformed to that of a stationary observer, the detonation velocity, D, is equal to u_1. Combination of Equations 1 and 2 relates D to the final conditions.

$$D = u_1 = V_1\left(\frac{P_2 - P_1}{V_1 - V_2}\right)^{1/2} \qquad (8)$$

Experimental and calculated velocities have been shown to agree (*5, 12*) if the chemical reaction in the wave front is assumed to proceed to equilibrium. This assumption was used in calculating all detonation parameters reported.

Reflected Wave. Whenever a detonation wave impinges upon an obstacle in its path a reflected shock wave must be formed to maintain conservation of momentum and energy. Reflection from a rigid surface normal to the incident wave will be considered, because this will yield the maximum attainable reflected pressure. Using the coordinates shown in Figure 1, the following governing equations may be written for a detonation wave traveling with velocity D into a stationary medium.

$$\rho_1(D - u_1) = \rho_2(D - u_2) \qquad \text{(mass balance)} \qquad (9)$$

$$\rho_2(D - u_2)u_2 - \rho_1(D - u_1)u_1 = P_2 - P_1 \qquad \text{(Conservation of momentum)} \qquad (10)$$

Combination of Equations 9 and 10 with boundary condition $u_1 = 0$—i.e., stationary medium—yields

$$P_2 - P_1 = \rho_1 D u_2 \qquad (11)$$

Similar equations may be written for the reflected wave. The properties of the reflected wave will be designated by the subscript 3.

$$\rho_2(D - u_2) = \rho_3(D_3 - u_3) \qquad \text{(mass balance)} \qquad (12)$$

$$P_3 - P_2 = \rho_2(D_3 - u_2)u_2 - \rho_3(D_3 - u_3)u_3 \qquad \text{(Conservation of momentum)} \qquad (13)$$

Combination of Equations 12 and 13 and the boundary condition $u_3 = 0$—i.e., the fluid at the boundary is at rest—yields

$$P_3 - P_2 = \rho_3 D_3 u_2 \qquad (14)$$

Combining Equations 9, 11, 12, and 14, to eliminate velocity terms, and converting densities to specific volumes give the following equation:

$$\frac{P_3 - P_2}{P_2 - P_1} = \frac{V_1 - V_2}{V_2 - V_3} \qquad (15)$$

The reflected wave is a shock wave; thus, the Hugoniot relation will also be applicable.

$$E_3 - E_2 = 1/2(P_2 + P_3)(V_2 - V_3) - \Delta E_{hr} \qquad (16)$$

In writing the Hugoniot relation, Equation 16, it was assumed that in undergoing reflection the equilibrium reaction products in the detonation wave dissociate to a new equilibrium at the temperature T_3 and pressure P_3 in the reflected wave. Thus the ΔE_{hr} term in Equation 16 represents the chemical energy due to dissociation.

Simultaneous solution of Equations 15, 16, and an equation of state (perfect gas law) determines the properties of the reflected wave.

DETONATION PARAMETERS

Calculations. The detonation and reflected wave properties were calculated with the aid of an electronic computer. Because initial mixture properties have a significant effect on the detonation parameters, it was felt that the use of the perfect gas law should be avoided in calculating the P-V-T relations of the initial hydrogen-oxygen-steam mixtures. Recently, (*13*) it was found that the saturation composition and the P-V-T data of steam-oxygen mixtures could be predicted to within 1% by use of Dalton's law of additive pressures and the individual constituents' P-V-T data. This method was used with the P-V-T data for steam (*11*) and the P-V-T data for knallgas ($2H_2$-O_2) as estimated by the Beattie equation of state (*3*) to calculate initial gas compositions and the P-V-T data for the initial mixtures.

For ease of calculation the initial gas mixtures were considered to undergo the following changes.

Complete reaction at T_1 to H_2O (gas) with a liberation of energy equal to ΔE_s.

Dissociation at T_1 to the composition which would exist in equilibrium at T_2 and P_2, with an absorption of energy equal to ΔE_h.

The net energy remaining, $\Delta E_g = \Delta E_s - \Delta E_h$, was used to heat the products to T_2.

A unit mass was chosen as the calculation basis, because the number of moles, n, is not constant. The molecular species assumed to be present in the detonation wave were H_2O, H_2, O_2, OH, H, and O, thus, the following four equilibria were considered:

$$2H_2) = 2H_2 + O_2, \qquad K = \frac{(p_{H_2})^2(p_{O_2})}{(p_{H_2O})^2}$$

$$H_2O = 1/2\ H_2 + OH, \qquad K = \frac{(p_{H_2})^{1/2}(p_{OH})}{H_2O\backslash p}$$

$$1/2\ H_2 = H, \qquad K = \frac{(p_H)}{(p_{H_2})^{1/2}}$$

$$H_2O = H_2 + O, \qquad K = \frac{(p_{H_2})(p_O)}{(p_{H_2O}}$$

All thermodynamic data used in the calculations were taken from NACA Report 1037 (*8*). Algebraic equations were derived for the heat capacity and equilibrium constant data which were used. Heats of reaction and dissociation were tabulated at the initial conditions to be considered. The basic steps in solving for the equilibrium composition in the detonation front were as follows:

1. Assume a value of T_2 and P_2.
2. Calculate equilibrium constants.
3. Calculate the moles of each constituent present at equilibrium.

In solving this part of the problem the method of Kandiner and Brinkley (*10*) was used. All stoichiometric and dissocia-

Table II. Calculated Detonation Wave Parameters

T_1	p_1	p_2	T_2	D	$n_2 \times 10^2$	$n_a \times 10^2$	$n_b \times 10^2$	$n_c \times 10^2$	$n_d \times 10^2$	$n_e \times 10^2$	$n_f \times 10^2$
298.16	1	18.096	3673.9	2845.0	6.9192	3.6685	1.1556	0.3541	0.8860	0.5671	0.2880
	5	96.690	3997.3	2945.6	6.7523	3.8088	1.0811	0.3129	0.8878	0.4337	0.2281
	10	198.02	4144.3	2981.4	6.6760	3.8812	1.0408	0.2945	0.8782	0.3791	0.2022
	30	617.22	4388.3	3060.6	6.5510	4.0102	0.9669	0.2643	0.8495	0.2979	0.1622
	50	1034.0	4500.6	3080.3	6.4927	4.0753	0.9289	0.2503	0.8300	0.2635	0.1447
	70	1438.5	4572.3	3078.2	6.4559	4.1172	0.9038	0.2415	0.8162	0.2430	0.1343
	90	1830.7	4624.2	3072.3	6.4287	4.1497	0.8847	0.2349	0.8045	0.2283	0.1266
	110	Computer malfunction			. . .	. . .	. . .	. . .	. . .	. . .	. . .
	130	2612.2	4702.7	3100.8	6.3851	4.2027	0.8529	0.2245	0.7838	0.2061	0.1150
	150	2980.6	4731.6	3105.7	6.3696	4.2219	0.8414	0.2208	0.7762	0.1985	0.1109
423	5[a]	15.57	840	1076.1	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	10	107.98	2977.2	2294.2	5.6925	5.2879	0.1957	0.0683	0.1196	0.0145	0.0065
	30	398.38	3950.5	2768.4	6.1855	4.5092	0.6864	0.2013	0.5600	0.1498	0.0787
	50	697.77	4198.8	2881.0	6.2948	4.3485	0.7772	0.2192	0.6636	0.1863	0.1001
	70	974.67	4333.6	2934.9	6.3315	4.2927	0.8073	0.2233	0.7045	0.1969	0.1069
	90	1258.7	4424.2	2969.7	6.3461	4.2685	0.8196	0.2238	0.7253	0.1991	0.1095
	110	1535.7	4490.3	2988.9	6.3507	4.2589	0.8240	0.2230	0.7362	0.1991	0.1095
	130	1800.4	4540.6	2991.9	6.3520	4.2552	0.8256	0.2219	0.7427	0.1977	0.1091
	150	2070.2	4583.4	3017.1	6.3464	4.2606	0.8217	0.2197	0.7434	0.1938	0.1072
473	16	41.3	760.0	990.3	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	30	286.59	2852.7	2214.4	5.6225	5.4130	0.1051	0.0375	0.0607	0.0043	0.0019
	50	559.50	3572.0	2547.9	5.8409	5.0328	0.3617	0.1132	0.2703	0.0418	0.0210
	70	823.34	3874.4	2695.8	5.9754	4.8157	0.4974	0.1480	0.3996	0.0753	0.0393
	90	1079.1	4054.2	2771.8	6.0586	4.6856	0.5759	0.1665	0.4797	0.0987	0.0524
	110	1330.0	4177.0	2821.2	6.1114	4.6042	0.6238	0.1770	0.5312	0.1140	0.0613
	130	1572.5	4267.0	2849.4	6.1467	4.5502	0.6551	0.1834	0.5663	0.1244	0.0673
	150	1809.8	4336.5	2870.3	6.1697	4.5146	0.6753	0.1872	0.5902	0.1310	0.0713
523	43[a]	154.7	1024	1124.4	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	50[a]	285.0	1620	1454.7	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	70	592.42	2602.7	2091.6	5.5771	5.4986	0.0412	0.0154	0.0208	0.0007	0.0003
	90	856.18	3103.0	2311.3	5.6438	5.3732	0.1320	0.0449	0.0848	0.0062	0.0028
	110	1103.1	3402.6	2444.4	5.7142	5.2465	0.2185	0.0705	0.1556	0.0155	0.0076
	130	1345.1	3607.8	2543.3	5.7754	5.1398	0.2889	0.0899	0.2179	0.0258	0.0130
	150	1562.2	3760.7	2584.2	5.8306	5.0460	0.3494	0.1060	0.2738	0.0366	0.0189
573	90[a]	300.0	890	1120.2	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	110[a]	645.5	1596	1594.9	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	130	935.60	2074.7	1840.4	5.5524	. . .	. . .	. . .	. . .	. . .	. . .
	150	1209.8	2447.5	2012.3	5.5629	5.5262	0.0198	0.0076	0.0090	0.0002	0.0001

[a] Hand calculations, dissociation neglected.

Table III. Calculated Reflected Wave Parameters

T_1	p_1	p_3	T_3	$n_3 \times 10^2$	$n_a \times 10^2$	$n_b \times 10^2$	$n_c \times 10^2$	$n_d \times 10^2$	$n_e \times 10^2$	$n_f \times 10^2$
298.16	1	42.837	3964.3	7.1518	3.3996	1.2832	0.3722	1.0453	0.6903	0.3612
	5	231.94	4354.7	6.9692	3.5393	1.2144	0.3316	1.0581	0.5358	0.2900
	10	476.34	4533.7	6.8844	3.6132	1.1757	0.3134	1.0519	0.4715	0.2587
	30	1501.1	4837.3	6.7474	3.7436	1.1047	0.2839	1.0286	0.3760	0.2106
	50	2515.1	4976.2	6.6798	3.8142	1.0654	0.2697	1.0084	0.3336	0.1886
	70	3484.0	5063.2	6.6346	3.8639	1.0375	0.2603	0.9916	0.3069	0.1744
	90	4413.8	5126.0	6.6014	3.9014	1.0162	0.2534	0.9780	0.2880	0.1644
	110	Computer malfunction			. . .	. . .	. . .	. . .	. . .	. . .
	130	6327.6	5224.9	6.5533	3.9568	0.9844	0.2432	0.9574	0.2615	0.1501
	150	7219.3	5260.5	6.5350	3.9785	0.9719	0.2393	0.9487	0.2518	0.1449
423	5[a]	29.775	967.5	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	10	228.70	3246.6	5.7583	5.1733	0.2722	0.0903	0.1844	0.0258	0.0123
	30	942.83	4331.5	6.3377	4.2846	0.8121	0.2247	0.7082	0.1998	0.1085
	50	1631.0	4616.5	6.4572	4.1132	0.9054	0.2406	0.8222	0.2418	0.1340
	70	2313.0	4774.2	6.4962	4.0542	0.9362	0.2437	0.8672	0.2532	0.1417
	90	2989.5	4881.6	6.5103	4.0303	0.9480	0.2436	0.8894	0.2553	0.1438
	110	3644.4	4959.6	6.5134	4.0221	0.9515	0.2423	0.9005	0.2536	0.1435
	130	4254.5	5018.3	6.5124	4.0202	0.9517	0.2407	0.9066	0.2508	0.1424
	150	4921.0	5070.2	6.5071	4.0243	0.9487	0.2386	0.9088	0.2464	0.1403
473	16[a]	74.302	864.8	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	30	666.43	3186.6	5.6743	5.3181	0.1709	0.0573	0.1133	0.0101	0.0048
	50	1316.1	3938.4	5.9460	4.8590	0.4685	0.1381	0.3814	0.0650	0.0342
	70	1947.1	4268.8	6.1002	4.6174	0.6139	0.1720	0.5309	0.1077	0.0583
	90	2548.8	4469.1	6.1921	4.4778	0.6951	0.1892	0.6197	0.1356	0.0745
	110	3138.1	4607.4	6.2493	4.3918	0.7441	0.1988	0.6761	0.1535	0.0851
	130	Computer malfunction			. . .	. . .	. . .	. . .	. . .	. . .
	150	4246.6	4786.6	6.3107	4.2992	0.7955	0.2076	0.7394	0.1722	0.0967
	43[a]	308.1	1181	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	50[a]	623.4	1866	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	70	1364.6	2941.0	5.6038	5.4475	0.0784	0.0275	0.0471	0.0023	0.0010
	90	1989.4	3462.9	5.7003	5.2704	0.2010	0.0641	0.1457	0.0128	0.0063
	110	2574.9	3778.0	5.7901	5.1130	0.3043	0.0921	0.2393	0.0273	0.0141
	130	3157.0	3998.4	5.8648	4.9865	0.3846	0.1124	0.3170	0.0420	0.0222
	150	3635.2	4159.5	5.9266	4.8844	0.4480	0.1278	0.3806	0.0558	0.0299
573	90[a]	586	1027	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	110[a]	1422	1849	5.5506	5.5506	. . .	. . .	. . .	. . .	. . .
	130	2118.0	2384.3	5.5587	5.5347	0.0131	0.0051	0.0057	0.0001	. . .
	150	2766.3	2783.1	5.5778	5.4972	0.0415	0.0150	0.0231	0.0007	0.0003

[a] Hand calculations, dissociation neglected.

tion relationships were expressed in the form they suggested. An iteration on n_2 (total moles at equilibrium) was performed until successive values of n_2 did not differ in the fourth significant figure.

After the equilibrium compositions were calculated the validity of Equations 6 and 7 was tested for the assumed values of P_2, T_2. At this point a modified Newton-Raphson method [Luker and McGill (*14*)] was applied to obtain a new assumption for T_2 and P_2. The entire calculation was then repeated until successive values of T_2 and P_2 did not change in the third significant place. After T_2 and P_2 were established, the detonation velocity was calculated from Equation 8.

The calculations for the reflected wave were made in a similar manner using Equations 15 and 16 and associated stoichiometric and energy relationships. It was assumed that chemical equilibrium was attained in the reflected shock front and that the perfect gas law was applicable at the terminal conditions. For details concerning these calculations the reader is referred to a final report (*14*).

Results. The calculated results are tabulated in Tables II and III, and are presented graphically in Figures 2 to 4.

These calculated parameters may be of value to the design engineer until more data are available on detonation limits of gaseous mixtures at elevated conditions. The detonation limits for these mixtures are currently being investigated at this laboratory.

Comparison of these calculated parameters with experimentally measured properties will be of interest to ascertain whether steam acts as a diluent or as a reaction inhibitor.

CONSTANT-VOLUME EXPLOSIONS

Dry Knallgas at 298.16° K. (25° C.) is presented for comparison. The initial conditions for saturated mixtures were 1 to 150 atm. and 373.16°, 473.16°, and 573.16° K. (100°, 200°, and 300° C.) All calculated results are presented in Table IV; constant-volume explosion pressures are plotted as the ratio of explosion pressure to initial pressure *vs.* initial pressure in Figure 5.

The explosion calculations were performed with an IBM 650 digital computer. Initial mixture *P-V-T* data and initial mixture compositions were calculated using Dalton's law of additive pressures with *P-V-T* data for the pure mixture constituents; Dalton's law has been shown to be applicable for this type of mixture by Luker, Gniewek, and Johnson (*13*). The *P-V-T* data for steam were taken from Keenan and Keyes (*11*), while the *P-V-T* data for knallgas ($2H_2 + O_2$) were estimated from the Beattie equation of state (*3*).

The three basic equations used in performing the calculations were:

Heat Balance

$$\Delta E_s = \Delta E_h + \sum_{j=1}^{6} n_j (\overline{C_v})_j (T_4 - T_1) \qquad (1)$$

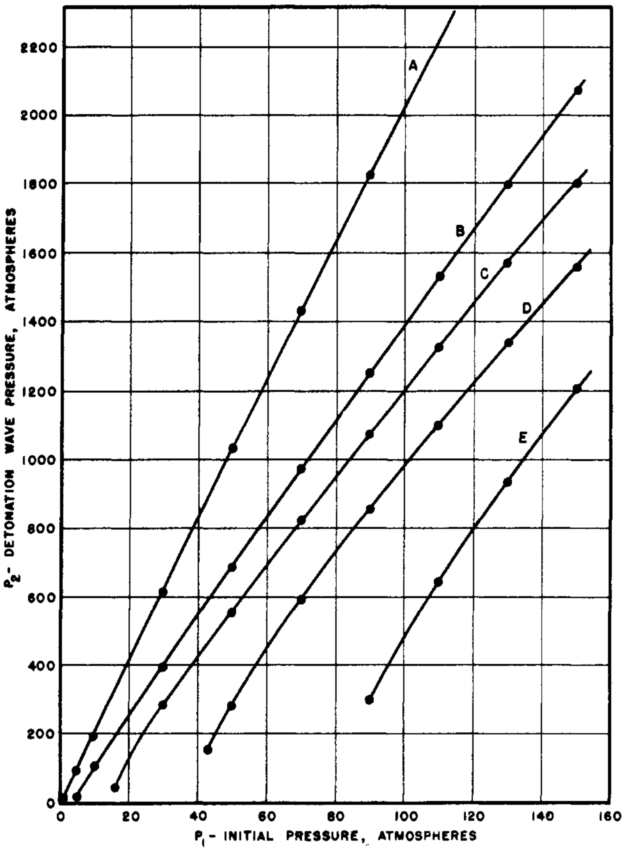

Figure 2. Calculated detonation wave pressures for dry knallgas and knallgas–steam mixtures

	Initial Temperature, °K.	Condition
A	298	Dry
B	423	Saturated
C	473	Saturated
D	523	Saturated
E	573	Saturated

Perfect Gas Law

$$P_4v_4 = \sum_{j=1}^{6} n_jRT_4 \qquad (2)$$

Volume Balance

$$v_1 = v_4 \qquad (3)$$

All thermodynamic data employed were taken from NACA Report 1037 (*8*). Molecular species assumed to be present at the explosion equilibrium were H_2O, H_2, O_2, OH, H, and O; stoichiometric and dissociation relationships were formulated as suggested by Kandiner and Brinkley (*10*). A 1-gram basis of calculation was used.

In solving Equations 1, 2, and 3 for a given set of initial conditions, T_4 and P_4 were assumed; an iteration on n_4 (total moles at equilibrium) was then performed until successive values of n_4 did not differ in the fourth significant figure. Next, a modified Newton-Raphson method [Luker and McGill (*14*)] was applied to Equations 1, 2, and 3 and a corrected assumption of T_4 and P_4 obtained. The entire calculation was then repeated until convergence of T_4 and P_4 to the fourth significant figure was obtained.

NOMENCLATURE

$\overline{C}_v$ = average specific heat at constant volume between T_1 and final temperature
D = detonation velocity, meters/second
E = internal energy
ΔE_g = net energy release from chemical reaction and dissociation
ΔE_h = energy absorbed in dissociation

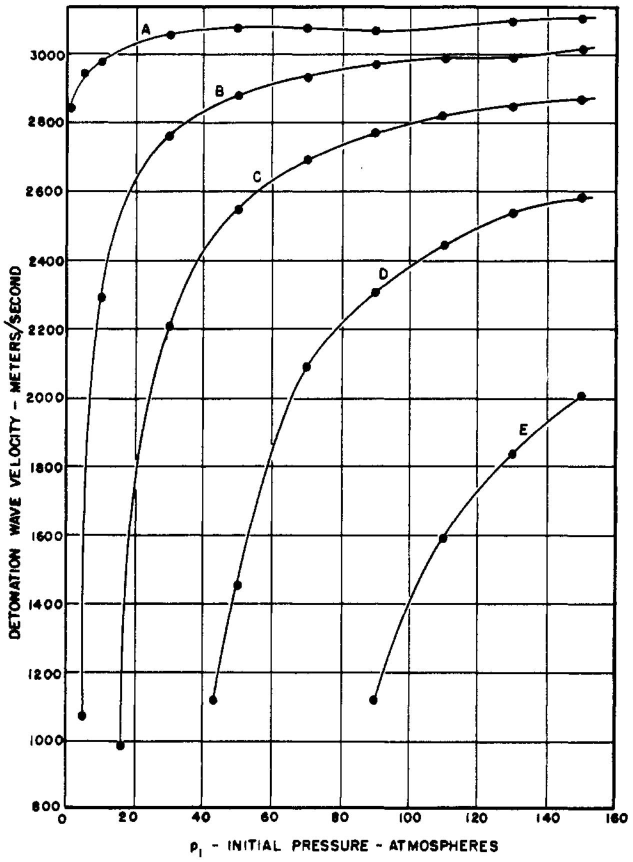

Figure 3. Calculated detonation wave velocities for dry knallgas and knallgas–steam mixtures

(See legend, Figure 2.)

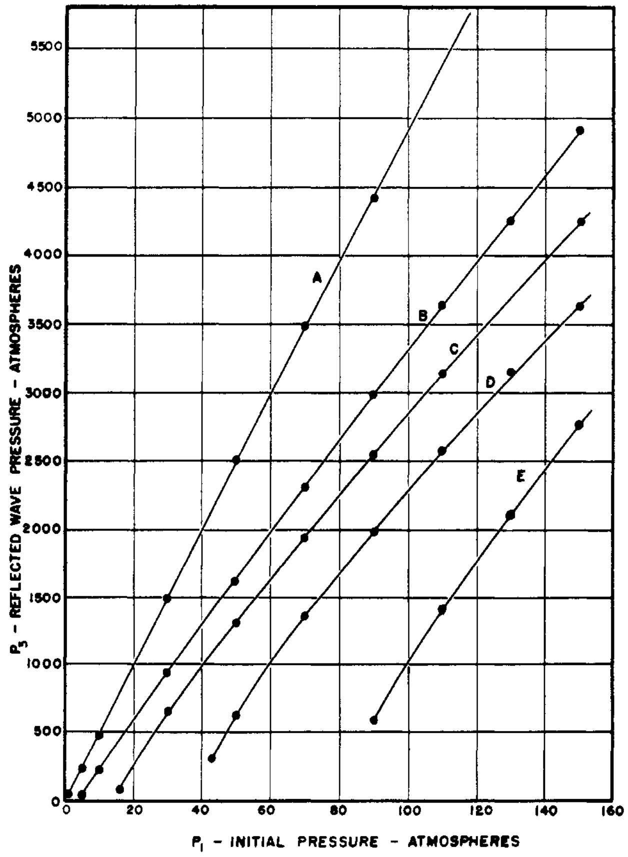

Figure 4. Calculated reflected wave pressures for dry knallgas and knallgas–steam mixtures

(See legend, Figure 2.)

Table IV. Theoretical Properties of Constant-Volume Explosion in Knallgas-Steam Mixtures

P_1, Atm.	y_k	T_4, °K.	P_4, Atm.	P_4/P_1	y_a	y_b	y_c	y_d	y_e	y_f
				T_1 = 298.16° K. (Dry)						
1	1.0000	3512	9.662	9.662	0.5527	0.1613	0.0511	0.1188	0.0775	0.0386
5	1.0000	3801	50.81	10.16	0.5868	0.1539	0.0461	0.1214	0.0605	0.0313
10	1.0000	3932	103.4	10.34	0.6038	0.1496	0.0439	0.1213	0.0535	0.0279
30	1.0000	4143	313.6	10.45	0.6334	0.1413	0.0401	0.1193	0.0429	0.0230
50	1.0000	4241	518.1	10.36	0.6480	0.1370	0.0383	0.1176	0.0385	0.0206
70	1.0000	4304	714.5	10.21	0.6577	0.1339	0.0376	0.1162	0.0357	0.0193
90	1.0000	4350	902.0	10.02	0.6649	0.1317	0.0363	0.1151	0.0337	0.0183
110	1.0000	4385	1080	9.818	0.6706	0.1298	0.0357	0.1141	0.0322	0.0176
130	1.0000	4414	1249	9.608	0.6752	0.1283	0.0351	0.1133	0.0311	0.0170
150	1.0000	4438	1409	9.393	0.6791	0.1270	0.0347	0.1126	0.0301	0.0165
				T_1 = 373.16° K. (Saturated)						
1.2	0.1645	1296	3.991	3.326	1.0000	0	0	0	0	0
1.5	0.3298	2062	7.463	4.975	0.9929	0.0040	0.0017	0.0013	0.0001	0
2	0.4959	2654	12.22	6.110	0.9387	0.0306	0.0114	0.0160	0.0023	0.0010
3	0.6628	3092	20.68	6.893	0.8379	0.0727	0.0249	0.0467	0.0122	0.0056
4	0.7465	3293	28.97	7.243	0.7800	0.0941	0.0310	0.0649	0.0202	0.0098
5	0.7968	3418	37.29	7.458	0.7449	0.1063	0.0342	0.0762	0.0258	0.0126
10	0.8977	3711	79.20	7.920	0.6790	0.1276	0.0389	0.0987	0.0370	0.0188
30	0.9651	4038	247.6	8.253	0.6515	0.1359	0.0392	0.1126	0.0397	0.0211
50	0.9786	4162	412.5	8.250	0.6545	0.1350	0.0382	0.1144	0.0377	0.0202
70	0.9844	4238	571.8	8.169	0.6592	0.1335	0.0374	0.1146	0.0360	0.0193
90	0.9876	4291	725.0	8.056	0.6637	0.1321	0.0367	0.1144	0.0345	0.0186
110	0.9896	4332	871.8	7.925	0.6677	0.1308	0.0362	0.1140	0.0333	0.0180
130	0.9910	4365	1012	7.785	0.6712	0.1297	0.0357	0.1136	0.0323	0.0175
150	0.9920	4392	1147	7.647	0.6742	0.1286	0.0353	0.1132	0.0314	0.0173
				T_1 = 473.16° K. (Saturated)						
16	0.03702	699.0	25.67	1.604	1.0000	0	0	0	0	0
18	0.1351	1218	48.15	2.675	1.0000	0	0	0	0	0
21	0.2492	1765	77.23	3.678	0.9994	0.0004	0.0002	0	0	0
25	0.3609	2269	112.1	4.484	0.9927	0.0040	0.0016	0.0016	0.0001	0
30	0.4603	2673	151.6	5.053	0.9722	0.0143	0.0053	0.0075	0.0005	0.0002
50	0.6644	3367	292.2	5.844	0.8806	0.0545	0.0177	0.0385	0.0058	0.0029
70	0.7539	3649	424.2	6.060	0.8276	0.0754	0.0233	0.0575	0.0108	0.0054
90	0.8041	3813	551.6	6.129	0.7971	0.0867	0.0261	0.0687	0.0141	0.0073
110	0.8362	3924	674.5	6.132	0.7778	0.0937	0.0276	0.0760	0.0163	0.0086
130	0.8585	4006	793.2	6.102	0.7650	0.0982	0.0286	0.0810	0.0178	0.0094
150	0.8749	4069	907.5	6.050	0.7559	0.1013	0.0292	0.0846	0.0189	0.0101
				T_1 = 573.16° K. (Saturated)						
90	0.04120	809.7	175.5	1.950	1.0000	0	0	0	0	0
110	0.1700	1458	349.2	3.175	1.0000	0.	0	0	0	0
130	0.2651	1905	497.9	3.830	0.9992	0.0004	0.0002	0.0002	0	0
150	0.3385	2239	633.4	4.223	0.9964	0.0020	0.0008	0.0008	0	0

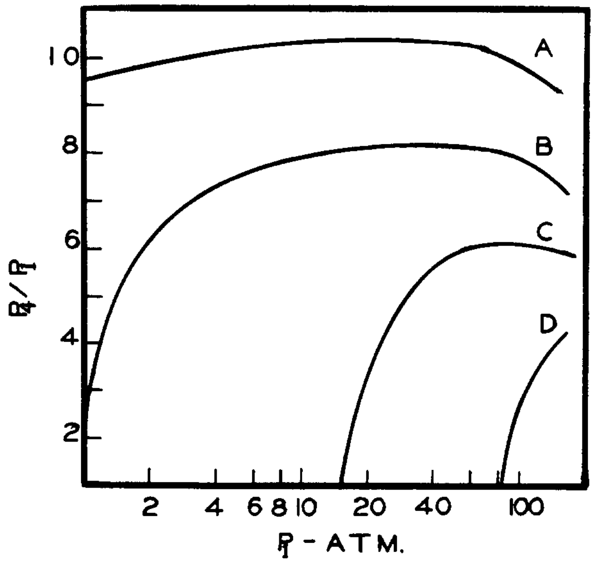

Figure 5. Calculated ratios of explosion pressure to initial pressure for dry knallgas and saturated knallgas-steam mixtures

	Initial Temp., °K.	Gas Condition
A	298.16	Dry
B	373.16	Saturated
C	473.16	Saturated
D	573.16	Saturated

ΔE_s = total energy available for complete reaction (no dissociation)
K = equilibrium constant
n = number of moles per gram
p = absolute pressure, atmospheres
T = absolute temperature, °K.
u = particle velocity, meters/second
v = specific volume, liters/gram
y = mole fraction
γ = ratio of specific heat at constant pressure to specific heat at constant volume
ρ = density, grams/liter

Subscripts

1 refers to unburned gas
2 refers to incident detonation wave
3 refers to reflected detonation wave
4 refers to final explosion condition
a refers to H_2O
b refers to H_2
c refers to O_2
d refers to OH
e refers to H
f refers to O
j refers to jth component
k refers to knallgas
r refers to reflected wave

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Vapor-Liquid Equilibria at Atmospheric and Subatmospheric Pressures for System *n*-Hexane–Methylcyclopentane

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Vapor-liquid equilibrium data at pressures of 760, 600, 400, and 200 mm. of mercury were determined for the system *n*-hexane and methylcyclopentane. This particular binary system was investigated because of the different types of hydrocarbon compounds involved, *n*-hexane being a straight-chain saturated paraffin and methylcyclopentane being a saturated cycloparaffin, and the narrow range of boiling temperatures.

The experimental results show that this binary system behaves ideally in the liquid. The experimental results obtained at a pressure of 760 mm. of mercury are compared with the data obtained by Myers (*4*). The agreement between the two sets of experimental data is reasonably good.

Expressions were developed which would be useful to those who wish to use this binary system to calibrate distillation columns.

PURITY OF COMPOUNDS

The methylcyclopentane and *n*-hexane used in the experimental work were pure grade materials obtained from the Phillips Petroleum Co. and had a minimum purity of 99 mole %. These materials were used without further purification. Table I reports the physical constants for these chemicals and for comparison, similar data on the pure compounds.

EXPERIMENTAL METHOD

The vapor-liquid equilibrium data were determined in a Braun still designed by Hipkin and Myers (*3*). The operating procedure used was essentially the same as used by these authors and has been described by Wagner and Weber (*6*) and Nielsen and Weber (*5*).

The composition of the various mixtures was determined by measuring their refractive indices at 25° C. An Abbé refractometer was used, and the possible error in the readings was ±0.0001. For the system *n*-hexane (η = 1.3723) and methyl-

Table I. Properties of Pure Compounds

	Experimental	Literature
Methylcyclopentane		
Density, 25° C., grams/ml.	0.7443	0.74394 (*1*)
Refractive index, 25° C.	1.4070	1.40700 (*1*)
Vapor pressure, mm. Hg.		
760	71.72° C	71.81° C (*1*)
600	64.32	64.33 (*1*)
400	52.29	52.32 (*1*)
200	39.92	33.96 (*1*)
n-Hexane		
Density, 25° C., grams/ml.	0.6542	0.65481 (*1*)
Refractive index, 25° C.	1.3723	1.37226 (*1*)
Vapor pressure, mm. Hg.		
760	68.77° C	68.74° C (*1*)
600	61.40	61.40 (*1*)
400	49.67	49.63 (*1*)
200	31.68	31.61 (*1*)

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