

INFLAMMATION LIMITS AND THEIR PRACTICAL APPLICATION IN HAZARDOUS INDUSTRIAL OPERATIONS¹

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INTRODUCTION

One of the major activities of the United States Bureau of Mines is the promotion of safety in mining and other industries. Investigations are carried out in connection with these activities to determine the explosion hazards of combustible gases, vapors, and solids and to investigate means of controlling and preventing explosions.

The limits of inflammability (explosive limits) of combustibles are not only of theoretical but also of great practical importance, because most industries, at one time or another, must contend with explosive mixtures of combustible gases or vapors in their manufacturing processes. The organic chemical industry has made rapid progress during the last twenty years, and numerous combustible liquids and gases which heretofore were either unknown or were mere laboratory curiosities are now manufactured in large quantities. The manufacture and marketing of these newer chemicals require a knowledge of the explosion hazards involved.

Combustible gases and vapors may be classed as one of the major hazards in present industrial operations, and there is need for a greater appreciation of the hazards involved in handling these gaseous mixtures and a better understanding of means of mitigating and preventing explosions.

LIMITS OF INFLAMMABILITY

Confusion has arisen regarding the meaning of the terms "explosive limits," "inflammation limits," and "limits of inflammability." These different expressions, in the final analysis, mean the same thing. Some authorities regard explosive limits as those limiting mixtures within which flame will propagate through the entire volume of the mixture and develop

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considerable pressure, while inflammation limits or limits of inflammability are regarded as those limiting mixtures within which flame will propagate through the mixture indefinitely, irrespective of whether or not pressure is developed.

It is impossible to distinguish an inflammation from an explosion by the amount of violence produced. Mixtures just within the limits of inflammability, if confined in a long tube and tested by opening one end and igniting at this open end, will propagate flame quietly and slowly through the tube (usually at a uniform speed) and the speed, for a given concentration of combustibles in air, will vary with the direction of flame propagation. This same mixture, if confined in a closed bomb of sufficient size and ignited when the gases are in motion or gentle turbulence, will propagate flame at a speed many times as fast as that in the open tube and develop pressures ranging up to 30 lb. or more per square inch. Thus the violence and pressure developed by an inflammable mixture depend upon the environment and direction of flame propagation; therefore no differentiation should, or can, be made between explosive limits and limits of inflammability.

1. Factors affecting the limits of inflammability

Only a brief discussion of the various factors affecting the limits of inflammability will be given. A more complete discussion is given in published reports (5, 6, 8). The limits are affected by the direction of flame propagation, the design, diameter, and length of the test apparatus, the temperature and pressure of the mixture at the time of ignition, the percentage of water vapor present, and indirectly by the source of ignition.

Wider limits are obtained for upward propagation of flame than for horizontal or downward propagation, therefore the risk of an explosion is greater when the mixtures are ignited from below than when ignited from above.

The limits of inflammability are widened as the diameter of the apparatus is increased, rapidly at first and then more slowly as the diameter approaches 2 in. Apparatus greater than 2 in. in diameter gives limit values very little different from those obtained with 2-in. apparatus.

The apparatus must be long enough to insure continued propagation of flame after the heat imparted to the mixture by the source of ignition has been dissipated. An apparatus 3 ft. or more in length is sufficient.

It has been found that, if the apparatus is closed when the mixtures are ignited and ignition is initiated near the closed end when the gases are in gentle turbulence, the lower limit is reduced slightly (15).

Ordinary variations of laboratory temperatures have no appreciable effect on the limits of inflammability. Elevated temperatures cause widening of the limits.

Normal variations of atmospheric pressure have no appreciable effect on the limits. The effect of high pressures on the limits is neither simple nor uniform, but is specific for each inflammable mixture. As yet, no means has been developed for predicting the effect of high pressures on the limits of inflammability for any given combustible in air. In certain cases both limits are raised, in others the limits are narrowed, and in some both limits are changed as the pressure is increased.

The normal quantity of water vapor present in atmospheres at laboratory temperatures affects the lower limit of inflammability only to a slight extent. The presence of water vapor reduces the upper limit because some of the oxygen in the mixture is displaced by the water vapor, and, since the oxygen concentration is the important factor in an upper-limits mixture, as the oxygen is lowered the amount of combustible that can be burned is decreased, and so the limit is lowered.

2. Limits of inflammability of gases and vapors

Industrial safety requires that only values for the limits of inflammability of gases and vapors in air, which are obtained in apparatus giving the widest limits, be used. Keeping the above fact in mind, tabulations of the limits of inflammability of combustible gases and vapors have been made and are given in tables 1, 2, and 3. Values reported in the literature that were obtained in small apparatus and those in which the direction of flame propagation was other than upward have not been used, except where no other reported values were available. In some cases values reported by several investigators were found to be in good agreement; however, only one reference has been given.

The ratios between the amount of combustible in the limit mixtures and the amount of combustible required for theoretical complete combustion with air and the relationship between the amounts of combustible in the limit mixtures and their net heats of combustion are given.

Burgess and Wheeler (3) first showed that there was a definite relationship between the calorific value of the combustible and its lower limit of inflammability; that is, the calorific values of the pure paraffin hydrocarbons times their lower limits of inflammability were a constant and that a lower-limit mixture of any of the paraffin hydrocarbons with air on combustion liberates the same amount of heat. Most of the "hot wire" combustible-gas indicators operate on this principle.

Some time later Thornton (34) announced that the upper limit bears a direct relation to the amount of oxygen needed for perfect combustion (theoretical complete combustion). He stated that in the case of paraffins the upper limit contained twice as great a volume of gas as the mixture for perfect combustion, acetylene and carbon disulfide three times the volume, hydrogen four times, and carbon monoxide six times the volume.

TABLE I
Limits of inflammability of hydrocarbons in air

(1) TYPE	(2) NAME	(3) FORMULA	(4) LIMITS OF INFLAMMABILITY, PER CENT BY VOLUME		(5) PER CENT COMBUSTIBLE IN AIR, MIX- TURE FOR THEORETICAL COMPLETE COMBUSTION	(7) RATIO OF LOWER LIMIT TO P.C.C.† = COLUMN 4 ÷ COLUMN 6	(8) RATIO OF UPPER LIMIT TO P.C.C. = COLUMN 5 ÷ COLUMN 6	(9) NET HEAT OF COMBUS- TION, IN KG.-CAL. PER MOLE	(10) LOWER LIMIT × H.C.I. = COLUMN 4 × COLUMN 9	(11) UPPER LIMIT × H.C. = COLUMN 5 × COLUMN 9
			Lower	Upper						
Paraffin hydrocar- bons.....	Methane	CH ₄	5.00 ⁽¹⁸⁾ §	15.00 ⁽¹⁸⁾	9.47	0.53	1.58	191.7	958	2876
	Ethane	C ₂ H ₆	3.22 ⁽⁸⁾	12.45 ⁽⁸⁾	5.64	0.57	2.21	336.7	1084	4192
	Propane	C ₃ H ₈	2.37 ⁽⁸⁾	9.50 ⁽⁸⁾	4.02	0.59	2.36	484.1	1147	4599
	Butane	C ₄ H ₁₀	1.86 ⁽⁸⁾	8.41 ⁽⁸⁾	3.12	0.60	2.70	634.4	1180	5335
	Isobutane	C ₄ H ₁₀	1.80 ⁽¹⁷⁾	8.44 ⁽¹⁷⁾	3.12	0.58	2.71	630.6	1135	5322
	Pentane	C ₅ H ₁₂	1.40 ⁽¹⁷⁾	7.80 ⁽¹⁷⁾	2.55	0.55	3.06	774.9	1085	6044
	Isopentane	C ₅ H ₁₂	1.32 ⁽⁸⁾		2.55	0.52		780.1	1030	
	Hexane	C ₆ H ₁₄	1.25 ⁽¹⁷⁾	6.90 ⁽¹⁷⁾	2.16	0.58	3.19	915.9	1145	6320
	Heptane	C ₇ H ₁₆	1.00 ⁽²¹⁾	6.00 ⁽²¹⁾	1.87	0.53	3.21	1064.5	1065	6387
	Octane	C ₈ H ₁₈	0.95 ⁽¹⁷⁾		1.65	0.58		1207.7	1147	
	Nonane	C ₉ H ₂₀	0.83 ⁽²³⁾		1.47	0.56		1353.0*	1123	
	Decane	C ₁₀ H ₂₂	0.67 ⁽²¹⁾		1.33	0.50		1494.0	1001	
	Olefins.....	Ethylene	C ₂ H ₄	2.75 ⁽²⁵⁾	28.60 ⁽²⁵⁾	6.52	0.42	4.39	310.9	855
Propylene		C ₃ H ₆	2.00 ⁽¹⁷⁾	11.10 ⁽¹⁷⁾	4.44	0.45	2.50	460.5	921	5112
Butylene		C ₄ H ₈	1.70 ⁽²⁶⁾	9.00 ⁽²⁶⁾	3.37	0.50	2.67	611.7	1040	5505
Amylene		C ₆ H ₁₀	1.60 ⁽²⁹⁾		2.71	0.59		750.6	1201	
Acetylenes.....	Acetylene	C ₂ H ₂	2.50 ⁽¹⁷⁾	80.00 ⁽²⁶⁾	7.72	0.32	10.36	301.5	754	24120
Aromatics.....	Benzene	C ₆ H ₆	1.41 ⁽¹⁷⁾	6.75 ⁽¹⁷⁾	2.71	0.52	2.49	750.6	1058	5067
	Toluene	C ₇ H ₈	1.27 ⁽¹³⁾	6.75 ⁽²⁷⁾	2.27	0.56	2.97	892.0	1133	6021
	o-Xylene	C ₈ H ₁₀	1.00 ⁽²¹⁾	6.00 ⁽²¹⁾	1.95	0.51	3.08	1038.9	1039	6233

Cyclic hydrocarbons.....	Cyclopropane	C ₃ H ₆	2.40 ⁽¹⁷⁾	10.40 ⁽¹⁷⁾	4.44	0.54	2.34	465.1	1116	4837
	Cyclohexane	C ₆ H ₁₂	1.33 ⁽²⁾	8.35 ⁽²⁾	2.27	0.59	3.68	875.6	1165	7311
	Methylcyclohexane	C ₇ H ₁₄	1.15 ⁽²⁰⁾		1.95	0.59		1017.9	1171	
Terpenes.....	Turpentine	C ₁₀ H ₁₆	0.80 ⁽²¹⁾		1.47	0.55		1385.5	1108	

* Estimated.

† p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

‡ h.c. = net heat of combustion.

§ Superior numbers in parentheses are reference numbers.

TABLE 2
Limits of inflammability of alcohols, aldehydes, ethers, ketones, acids, and esters in air

(1) TYPE	(2) NAME	(3) FORMULA	(4) LIMITS OF INFLAMMABILITY, PER CENT BY VOLUME		(6) PER CENT COMBUSTIBLE MATERIAL TIME FOR THEORETICAL COMPLETE COMBUSTION	(7) RATIO OF LOWER LIMIT TO P.C.C. = COLUMN 4 ÷ COLUMN 6	(8) RATIO OF UPPER LIMIT TO P.C.C. = COLUMN 5 ÷ COLUMN 6	(9) NET HEAT OF COMBUS- TION, IN KG.-CAL. PER MOLE	(10) LOWER LIMIT X H.C.I. = COLUMN 4 X COLUMN 9	(11) UPPER LIMIT X H.C. = COLUMN 5 X COLUMN 9
			Lower	Upper						
Alcohols.....	Methyl alcohol	CH ₄ O	6.72 ⁽²²⁾ §	36.50 ⁽³⁷⁾	12.24	0.55	2.98	149.8	1007	5468
	Ethyl alcohol	C ₂ H ₆ O	3.28 ⁽¹³⁾	18.95 ⁽²⁸⁾	6.52	0.50	2.91	295.9	971	5607
	Propyl alcohol	C ₃ H ₈ O	2.55 ⁽²⁸⁾		4.44	0.57		438.3	1118	
	Isopropyl alcohol	C ₃ H ₈ O	2.65 ⁽²⁸⁾		4.44	0.60		432.6	1146	
	Butyl alcohol	C ₄ H ₁₀ O	1.70 ⁽³¹⁾		3.37	0.50		585.8	996	
	Isobutyl alcohol	C ₄ H ₁₀ O	1.68 ⁽²⁸⁾		3.37	0.50		585.4	983	
	Amyl alcohol	C ₅ H ₁₂ O	1.19 ⁽²⁸⁾		2.71	0.44		730.3	869	
Aldehydes.....	Isoamyl alcohol	C ₅ H ₁₂ O	1.20 ⁽³¹⁾		2.71	0.44		711.6	854	
	Allyl alcohol	C ₃ H ₆ O	2.40 ⁽³¹⁾		4.97	0.48		410.6	985	
	Acetaldehyde	C ₂ H ₄ O	3.97 ⁽³⁷⁾	57.00 ⁽³⁷⁾	7.72	0.51	7.38	257.8	1023	14695
	Crotonaldehyde	C ₄ H ₆ O	2.12 ⁽²²⁾	15.50 ⁽¹⁷⁾	4.02	0.53	3.86	510.4	1082	7911
	Furfural	C ₅ H ₄ O ₂	2.10 ⁽²¹⁾		4.02	0.52		538.4	1131	
	Paraldehyde	C ₆ H ₁₂ O ₃	1.30 ⁽³¹⁾		2.71	0.48		788.1*	1025	
Ethers.....	Methyl ethyl ether	C ₃ H ₈ O	2.00 ⁽³¹⁾	10.10 ⁽³¹⁾	4.44	0.45	2.27	461.1	922	4657
	Diethyl ether	C ₄ H ₁₀ O	1.85 ⁽²⁶⁾	36.50 ⁽²⁶⁾	3.37	0.55	10.83	598.8	1108	21856
	Divinyl ether	C ₄ H ₆ O	1.70 ⁽¹⁵⁾	27.00 ⁽¹⁴⁾	4.02	0.42	6.72	569.1	967	15366
	Acetone	C ₃ H ₆ O	2.55 ⁽¹⁵⁾	12.80 ⁽¹⁶⁾	4.97	0.51	2.58	395.0	1007	5056
Ketones.....	Methyl ethyl ke- tone	C ₄ H ₈ O	1.81 ⁽¹⁷⁾	9.50 ⁽¹⁷⁾	3.67	0.49	2.59	540.1	978	5131
	Methyl propyl ke- tone	C ₅ H ₁₀ O	1.55 ⁽¹⁷⁾	8.15 ⁽¹⁷⁾	2.90	0.53	2.81	682.8	1058	5565
	Methyl butyl ke- tone	C ₆ H ₁₂ O	1.22 ⁽¹⁷⁾	8.00 ⁽¹⁷⁾	2.40	0.51	3.33	831.8	1015	6654

Acids.....	Acetic acid	$C_2H_4O_2$	4.05 ⁽²⁹⁾	9.47	0.43	2.79	188.3	763
	Hydrocyanic acid	HCN	5.60 ⁽³²⁾	14.34	0.39		154.4	865
Esters.....	Methyl formate	$C_2H_4O_2$	5.05 ⁽²³⁾	9.47	0.53	2.40	212.0	1071
	Ethyl formate	$C_3H_6O_2$	2.75 ⁽²²⁾	5.64	0.49	2.91	359.9	990
	Methyl acetate	$C_3H_6O_2$	3.15 ⁽²²⁾	5.64	0.56	2.77	349.4	1101
	Ethyl acetate	$C_4H_8O_2$	2.18 ⁽¹⁹⁾	4.02	0.54	2.84	494.7	1078
	Propyl acetate	$C_6H_{10}O_2$	2.05 ⁽²⁾	3.12	0.66		633.0*	1298
	Isopropyl acetate	$C_6H_{10}O_2$	2.00 ⁽³²⁾	3.12	0.64		638.0	1276
	Butyl acetate	$C_6H_{12}O_2$	1.70 ⁽²⁾	2.55	0.67		768.4	1306
Amyl acetate	$C_7H_{14}O_2$	1.10 ⁽³¹⁾	2.16	0.51		968.6	1065	

* Estimated.

† p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

‡ h.c. = net heat of combustion.

§ Superior numbers in parentheses are reference numbers.

TABLE 3
Limits of inflammability of miscellaneous combustible gases and vapors in air

(1) TYPE	(2) NAME	(3) FORMULA	(4) LIMITS OF INFLAMMABILITY PER CENT BY VOLUME		(5) PER CENT COMBUSTIBLE IN AIR. MIX- TURE FOR THEORETICAL COMPLETE COMBUSTION	(7) RATIO OF LOWER LIMIT TO P.C.C.† = COLUMN 4 ÷ COLUMN 6	(8) RATIO OF UPPER LIMIT TO P.C.C. = COLUMN 5 ÷ COLUMN 6	(9) NET HEAT OF COMBUS- TION, IN K.G.-CAL. PER MOLE	(10) LOWER LIMIT X H.C.† = COLUMN 4 X COLUMN 9	(11) UPPER LIMIT X H.C. = COLUMN 5 X COLUMN 9
			Lower	Upper						
Hydrogen..... Carbon mon- oxide.....	Hydrogen	H ₂	4.00 ⁽¹⁾ §	74.20 ⁽⁴⁾	29.50	0.14	2.52	57.8	231	4289
	Carbon monoxide	CO	12.50 ⁽⁶⁾	74.20 ⁽⁴⁾	29.50	0.42	2.52	67.6	845	5016
Nitrogen compounds	Ammonia	NH ₃	15.50 ⁽⁹⁾	27.00*	21.82	0.71	1.24	76.2	1181	2057
	Cyanogen	C ₂ N ₂	6.60 ⁽⁴⁾	42.60 ⁽¹⁾	9.47	0.70	4.50	258.3	1705	11004
	Pyridine	C ₅ H ₅ N	1.81 ⁽²⁷⁾	12.40 ⁽²⁷⁾	3.24	0.56	3.83	652.1	1180	8086
	Ethyl nitrate	C ₂ H ₅ NO ₂	3.80 ⁽²³⁾		10.68	0.36		296.0	1125	
	Ethyl nitrite	C ₂ H ₅ NO	3.01 ⁽²⁷⁾		8.51	0.35		306.2	922	15310
Oxides.....	Ethylene oxide	C ₂ H ₄ O	3.00 ⁽¹⁸⁾	80.00 ⁽¹⁹⁾	7.72	0.39	10.36	281.0	843	22480
	Propylene oxide	C ₃ H ₆ O	2.00 ⁽²⁷⁾	22.00 ⁽²⁷⁾	4.97	0.40	4.43			
	Dioxan oxide	C ₄ H ₈ O ₂	1.97 ⁽²⁴⁾	22.25 ⁽²⁴⁾	4.02	0.49	5.53	539.8	1063	12011
	Diethyl peroxide	C ₄ H ₁₀ O ₂	2.34 ⁽²⁸⁾		3.67	0.64				
Sulfides.....	Carbon disulfide	CS ₂	1.25 ⁽¹⁷⁾	50.00 ⁽³⁷⁾	6.52	0.19	7.67	246.6	308	12330
	Hydrogen sulfide	H ₂ S	4.30 ⁽³⁶⁾	45.50 ⁽³⁶⁾	12.24	0.35	3.72	122.5	527	5574
	Carbon oxysulfide	COS	11.90 ⁽¹⁰⁾	28.50 ⁽¹⁰⁾	12.24	0.97	2.33	130.5	1553	3719
Chlorides.....	Methyl chloride	CH ₃ Cl	8.25 ⁽¹²⁾	18.70 ⁽¹²⁾	12.24	0.67	1.53	153.7	1268	2874
	Vinyl chloride	C ₂ H ₃ Cl	4.00 ⁽¹⁷⁾	21.70 ⁽¹⁷⁾	7.72	0.52	2.81	270.9	1084	5879
	Ethyl chloride	C ₂ H ₅ Cl	4.00 ⁽¹²⁾	14.80 ⁽¹²⁾	6.52	0.61	2.27	295.6	1182	4375

Chlorides.....	Amyl chloride	$C_5H_{11}Cl$	1.40 ⁽¹⁷⁾	12.80 ⁽⁷⁾	2.71	0.52	1.35	731.9	1025	2874
	Dichloroethylene	$C_2H_2Cl_2$	9.70 ⁽⁷⁾	15.90 ⁽¹⁹⁾	9.47	1.02	2.06	224.5	2178	3973
	Ethylene dichloride	$C_2H_4Cl_2$	6.20 ⁽¹⁹⁾	14.50 ⁽²⁵⁾	7.72	0.80	2.92	249.9	1549	5743
Bromides.....	Propylene dichloride	$C_3H_6Cl_2$	3.40 ⁽²⁵⁾	14.50 ⁽¹²⁾	4.97	0.68	1.18	396.1	2342	2516
	Methyl bromide	CH_3Br	13.50 ⁽¹²⁾	11.25 ⁽¹²⁾	12.24	1.10	1.73	173.5	2156	3593
	Ethyl bromide	C_2H_5Br	6.75 ⁽¹²⁾		6.52	1.04		319.4		

* Average of several reported values.

† p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

‡ h.c. = net heat of combustion.

§ Superior numbers in parentheses are reference numbers.

Lower-limit mixtures which just failed to propagate flame contained twice the volume of oxygen needed for perfect combustion in the case of the paraffins, and thrice the volume in the case of the other gases. The values given in tables 1, 2, and 3 show that some of the predictions given by Thornton are approximately correct, while in other cases there are extremely wide variations, and that the classification is not nearly so simple as Thornton predicted.

The relationship between the calorific value of the combustibles, the oxygen required for perfect combustion, and the limits of inflammability

TABLE 4

Limits of inflammability of selected gases and vapors in air showing variation of ratios between the percentage of combustibles in the limit mixtures and that required for theoretical complete combustion and the relationship between the limits and net heats of combustion

(1) COMBUSTIBLE	(2) FORMULA	(3) (4) LIMITS OF INFLAMMABILITY, PERCENT BY VOLUME		(5) PER CENT COMBUSTIBLE IN AIR. MIXTURE FOR THEORETICAL COMPLETE COMBUSTION	(6) RATIO OF LOWER LIMIT TO P.C.C.* = COL-UMN 3 ÷ COL-UMN 5	(7) RATIO OF UPPER LIMIT TO P.C.C. = COL-UMN 4 ÷ COL-UMN 5	(8) NET HEAT OF COMBUSTION, IN KG.-CAL. PER MOLE	(9) LOWER LIMIT × H.C. † = COL-UMN 3 × COL-UMN 8	(10) UPPER LIMIT × H.C. = COL-UMN 4 × COL-UMN 8
		Lower	Upper						
Hydrogen.....	H ₂	4.00	74.20	29.50	0.14	2.52	57.8	231	4289
Carbon disulfide....	CS ₂	1.25	50.00	6.52	0.19	7.67	246.6	308	12330
Acetylene.....	C ₂ H ₂	2.50	80.00	7.72	0.32	10.36	301.5	754	24120
Hydrogen sulfide...	H ₂ S	4.30	45.50	12.24	0.35	3.72	122.5	527	5574
Ethylene oxide.....	C ₂ H ₄ O	3.00	80.00	7.72	0.39	10.36	281.0	843	22480
Ethylene.....	C ₂ H ₄	2.75	28.60	6.52	0.42	4.39	310.9	855	8892
Methane.....	CH ₄	5.00	15.00	9.47	0.53	1.58	191.7	958	2876
Methyl alcohol.....	CH ₄ O	6.72	36.50	12.24	0.55	2.98	149.8	1007	5468
Methyl acetate.....	C ₃ H ₆ O ₂	3.15	15.60	5.64	0.56	2.77	349.4	1101	5451
Methyl chloride....	CH ₃ Cl	8.25	18.70	12.24	0.67	1.53	153.7	1268	2874
Methyl bromide....	CH ₃ Br	13.50	14.50	12.24	1.10	1.18	173.5	2342	2516

* p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

† h.c. = net heat of combustion.

was investigated and extended by White (37) to cover a number of solvent vapors. He found that for all solvents examined, except one, the lower limit for downward propagation of flame was approximately inversely proportional to the net calorific value of the vapor used. The corresponding upper limit roughly followed a similar rule, it being about 3.5 times the lower limit. He also found that the amount of oxygen available for the combustion of a vapor in its limit mixture bore a fairly constant ratio to the amount required for the perfect combustion of 1 mole of the vapor. Thus the amount of solvent in a lower-limit mixture for downward propagation of flame was 0.57 of that present in the mixture for per-

fect combustion, while the ratio for the upper-limit mixture was just under 2.

The results given in table 4 show that no general relationship of the limits of combustible gases and vapors either to the amount of oxygen required for theoretical complete combustion or to the calorific value of the gases or vapors exists, nor do they give even approximately correct results if used indiscriminately.

On the other hand, if the combustibles are classified according to types of compounds the relationship between the limits and the oxygen required for theoretical complete combustion is of value in predicting the limits of inflammability of new compounds, the limits of which have not already been determined, as will be shown later.

3. Calculation of limits of inflammability of mixtures of combustibles

The calculation of the limits of inflammability of combustible mixtures from a knowledge of the limits of each combustible in air and the percentages of each combustible present in the mixture can be done quite accurately for a great number of mixtures by the application of the so-called "mixture law."

Le Chatelier (28) first applied the law to the limits of inflammability of gases. The law states that if we have, say, separate limit combustible-air mixtures and mix them, then this mixture will also be a limit mixture. The equation for expressing this law in its simplest form is written as follows:

$$L = \frac{100}{\frac{P_1}{N_1} + \frac{P_2}{N_2} + \frac{P_3}{N_3} + \frac{P_4}{N_4}}$$

where P_1 , P_2 , P_3 , and P_4 are the proportions of each combustible gas present in the original mixture, free from air and inerts, so that $P_1 + P_2 + P_3 + P_4 = 100$, and N_1 , N_2 , N_3 , and N_4 are the lower limits of inflammability of each combustible in air.

As an example of the application of this law we may take a natural gas of the following composition:

HYDROCARBON PRESENT	PER CENT BY VOLUME	LOWER LIMIT
Methane.....	80.0	5.00
Ethane.....	15.0	3.22
Propane.....	4.0	2.37
Butane.....	1.0	1.86

$$\text{Lower limit} = \frac{100}{\frac{80.0}{5.00} + \frac{15.0}{3.22} + \frac{4.0}{2.37} + \frac{1.0}{1.86}} = 4.37$$

This law has been tested by Coward, Carpenter, and Payman (5) and proved to hold for hydrogen, carbon monoxide, and methane containing no inert gases in normal air. Subsequent tests made with paraffin hydrocarbons in air (8) showed that the law could also be applied to these mixtures. Exceptions have been found in tests made with some inflammable gases. White (37) found that the law does not hold strictly for hydrogen-ethylene-air mixtures, acetylene-hydrogen-air mixtures, hydrogen sulfide-methane-air mixtures, and mixtures containing carbon disulfide. Also, in tests on some chlorinated hydrocarbons, Coward and Jones (7) found that the law did not hold for methane-dichloroethylene-air mixtures, and more recently it was found (12) that the law was only approximately correct for mixtures of methyl and ethyl chlorides. It is therefore apparent that the mixture law, useful when its application has been proved, cannot be applied indiscriminately, but must first be proved to hold for the gases being investigated.

Many industrial processes require the use of mixtures of various solvents in their processes, and although the limits of inflammability of the various individual constituents in the mixture may be known, it is not at all certain what the inflammability limits will be for the various mixtures. Investigations of the lower limits of inflammability of solvent mixtures have shown that where the ratios of the lower limits of the individual constituents to the amount of oxygen required for theoretical perfect combustion are about the same, the limits of mixtures of the constituents may be determined accurately by calculation. For example, the limits of mixtures of ethyl alcohol, benzene, furfural, and acetone in which the ratios range from 0.50 to 0.53 (tables 1, 2, and 3) may be calculated, and mixtures of ethyl acetate, ethyl alcohol, and toluene, whose ratios vary from 0.50 to 0.56, have been found also to give calculated results agreeing closely with experimental results (13).

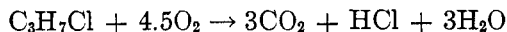
At the present time, the accuracy of the above prediction has been proved only for a limited number of mixtures; however, as information on the subject is accumulated, the classification of compounds according to the ratios should be of great value in predicting and calculating the limits of inflammability of mixtures of combustible gases and vapors.

As an example to show the application of this method for predicting the limits of inflammability of combustibles whose limits have not been determined, propyl chloride may be used. The ratio of the lower limit of certain gases to that for theoretical complete combustion is as follows:

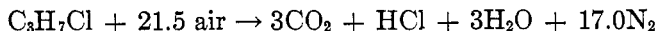
methane.....	0.52	methyl chloride.....	0.67
ethane.....	0.57	ethyl chloride.....	0.61
propane.....	0.59	propyl chloride.....	not known

The addition of one chlorine atom to methane has raised the ratio 0.15, while the addition of one chlorine atom to ethane has raised the ratio only 0.04. One chlorine atom added to propane should raise the ratio even less, say 0.02, thus giving a ratio of 0.61 for propyl chloride.

When propyl chloride is burned with the theoretical amount of oxygen to give complete combustion, the following reaction takes place:



or with air



The percentage of propyl chloride in a mixture with air to give theoretical complete combustion = $\frac{1 \times 100}{22.5} = 4.44$ per cent. Using the ratio 0.61 for propyl chloride given above, the predicted lower limit of inflammability = $4.44 \times 0.61 = 2.71$ per cent.

4. *Limits of inflammability of complex mixtures*

It is possible to calculate closely the limits of inflammability not only of certain mixtures of combustible gases and vapors in air but also of mixtures containing varying amounts of inert gases. The limits of inflammability of natural, manufactured, producer, blast furnace, automobile, and sewage gases may be calculated from a knowledge of the composition of constituents composing the gases and their limits of inflammability. The actual procedure is rather long and complicated, so only a reference to this method will be given in this report (6, 11, 20, 40).

PRACTICAL MEANS OF ELIMINATING OR MINIMIZING EXPLOSIONS IN INDUSTRIAL OPERATIONS

1. *Control of the oxygen content of the atmosphere*

The fact that all combustible gases, vapors, mists, and pulverized solids will not burn or explode when the oxygen content is reduced below certain definite values, varying with the combustible materials under consideration, gives the safety engineer a means of definitely controlling and eliminating explosions.

The oxygen present in an explosive mixture may be reduced by direct absorption by means of special reagents, by dilution with inert gases such as nitrogen or carbon dioxide, or by combinations of these inert gases as represented by flue gas or exhaust gas from an internal-combustion engine. Flue gases made by burning fuel gas or fuel oil with the proper proportions of air and automobile exhaust gas both have a low oxygen content and are ideally suited for reducing the oxygen content of atmospheres. Carbon

dioxide compressed in cylinders, carbon tetrachloride, and dichlorodifluoromethane have been used also for this purpose.

The critical oxygen values below which flames will not propagate or explosions take place when the reduction of the oxygen content of the atmosphere is brought about by the addition of nitrogen and carbon dioxide for several hydrocarbons are shown graphically in figure 1. The critical oxygen value for any given combustible varies with the concentration of the combustible present; however, the values given in figure 1 are minimum ones and cover all concentrations of the combustible that might be present. The relationship between concentration of combustible and the critical oxygen requirements to prevent explosions is shown to better advantage in figure 2. This graph shows the explosive areas of all possible mixtures of pentane, air, and added nitrogen or carbon dioxide. The straight line *AD* represents the composition of mixtures of pentane and pure air containing up to 15 per cent pentane. The limits as shown on this line are seen to be 1.4 per cent for the lower and 7.8 per cent for the upper limit. All mixtures between these limits are explosive. As nitrogen or carbon dioxide is added the oxygen concentration is lowered and, as shown, the limits are narrowed. Finally when the oxygen content is reduced to 11.7 per cent all mixtures of pentane, air, and added nitrogen become non-explosive. The mixture which will propagate flame with a minimum concentration of oxygen contains 2.10 per cent of pentane. If the atmosphere contains 5.00 per cent of pentane the graph shows that the oxygen concentration needs to be reduced to only 15.6 per cent. Although this mixture having 5.00 per cent of pentane will not explode when the oxygen content is below 15.6 per cent, the graph shows that if air is added to the mixture it becomes explosive, since addition of air shifts the composition of the mixture along the line to the left and towards the *A*-axis, so that the composition passes through a range of mixtures which are explosive.

The usual problem in dealing with pentane-air mixtures is to control the atmosphere so that the composition at all times is outside the explosive area bounded by *BCE* (when added nitrogen is used as the diluent). A graph of this type enables one to determine at a glance the explosive hazards involved. If an analysis is made of an atmosphere and it is found to contain, say, 12 per cent oxygen and 8.40 per cent pentane, this mixture, as indicated by the point *J* on the graph, shows at once that the mixture cannot explode until air is added; however, if the equipment is to be taken out of service and it is desired to do so without possibility of explosions, the atmosphere must be altered so as to pass around the explosive area. It becomes necessary to alter the composition of the atmosphere until it falls into the area to the left of the line *AEF*, and in no case should it

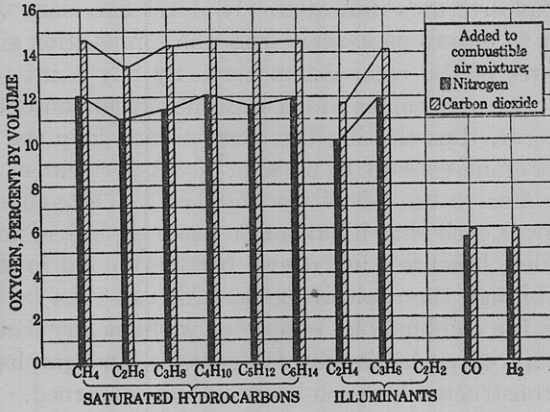


FIG. 1. Per cent oxygen by volume in gas mixtures below which explosions are prevented at ordinary temperatures and pressures.

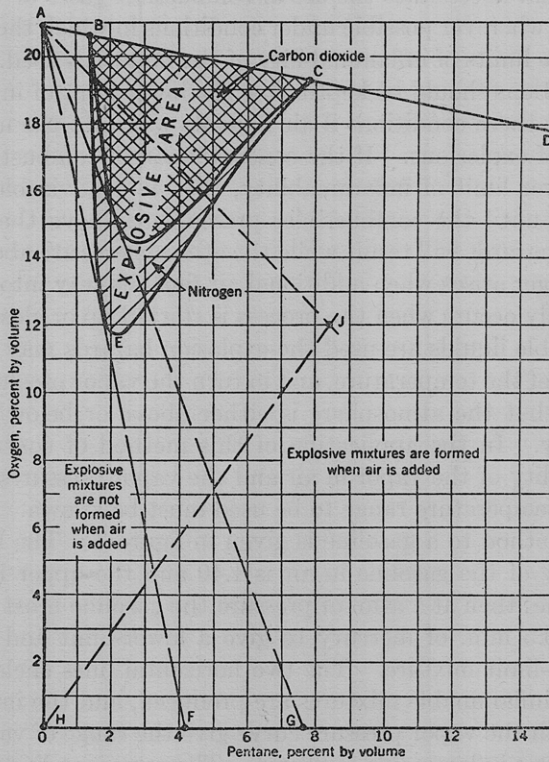


FIG. 2. Explosibility of mixtures of pentane, air, added nitrogen, and carbon dioxide

fall into the explosive area indicated. It is not necessary to reduce the oxygen content to zero to pass safely from the composition given by point *J* to atmospheres of the composition given by any point to the left of the line *AEF*. Nitrogen can be added until the oxygen content is reduced to below 4.6 per cent, thus shifting the composition along the line *JH* and reducing the pentane content to a value of 3.3 per cent or less, until it passes into the area to the left of the line *AEF*. The composition of the atmosphere now is such that it cannot be made explosive, no matter how much air is added, because a line drawn from any point in this area to *A* will not pass through the explosive area. Air can then be added to the equipment and the combustibles swept out without any danger of explosions. The graph given holds only for pentane, and graphs of a similar type must be constructed for each hydrocarbon concerned.

2. Carrying out operations so that the percentages of combustibles present are outside the limits of inflammability

Processes that necessitate the use of combustible gases or vapors should be carried out wherever possible under conditions in which the atmospheres are outside the limits of inflammability of the materials used. If possible, the concentrations should be kept below the lower limit of inflammability, because under these conditions if air finds its way into the mixture, there is no danger of explosions. If the concentration of combustibles must be above the lower limit of inflammability, then it is advisable to raise the concentration until the combustibles present are above the upper limit. No explosion hazards will result while the atmospheres are above the upper limit; the danger arises when additional air finds its way into the mixture, and this usually occurs when the process is started up or closed down.

If combustible liquids are used the explosion hazards may be controlled by regulation of the temperature, and in turn the vapor pressures should be so regulated that the atmosphere is either above or below the limits of inflammability. In the application of this method of control the limits of inflammability of the vapor in air and the vapor pressures of the material over the temperature range to be used must be known. The application of this method to a gasoline is given in figure 3. The lower limit of inflammability of the gasoline in air is 1.40 and the upper limit 6.90 per cent by volume; then at 1 atm. of pressure the gasoline must have a vapor pressure of 10.5 mm. of mercury to give a lower-limit and 52.5 mm. to give an upper-limit mixture. The two horizontal lines enclose the limits within which inflammable mixtures are produced, and the intersections of these lines with the vapor pressure curve give the range of vapor pressures that can produce inflammable mixtures. The corresponding temperatures in this particular case are 4°F. and 77°F. The graph shows that this

gasoline should be used at temperatures either below 4°F. or above 77°F., if the process is to be carried out under conditions where explosive mixtures will not be present.

If combustible liquids or mixtures of which the vapor pressures are not known are used in a process, the temperature range over which explosive mixtures may be present may be easily determined by means of the simple apparatus shown in figure 4. Explosion tube D is 2.5 cm. (1 in.) in diameter and 20 cm. (8 in.) long. E indicates the electrodes across which sparks generated from a transformer M and induction coil N are passed when a test of the explosibility of the atmosphere in tube D is desired. H and H' are mercury seals through which contact is made between the electrodes and the induction coil N. The explosion tube D is immersed in a liquid

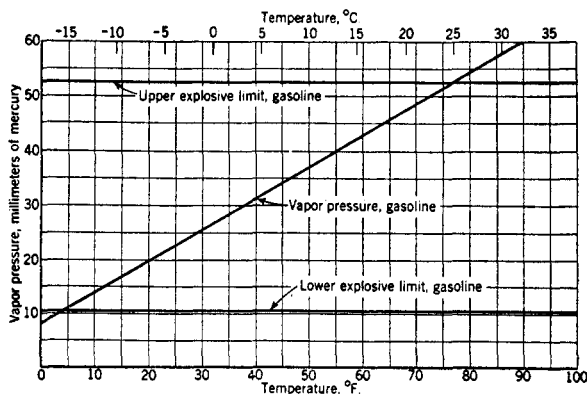


FIG. 3. Relationship between limits of inflammability and vapor pressure of a combustible liquid

bath, C, kept at uniform temperature by stirrer L, and heated to the desired temperature by burner O. K is a thermometer for recording the temperature of the bath.

To determine the temperature range over which a combustible liquid gives explosive mixtures, the combustible liquid is poured into D until the level is about 2 cm. (0.8 in.) below the electrodes, and a cork R, having an opening as shown, is placed in the top of explosion tube D. Air is turned on and adjusted to give at the start three bubbles per second, as indicated by bubbler A. The air is then passed through tower B containing a drying agent, and thence through the glass coil G in the bath to bring the air to the temperature of the bath before it enters the combustible liquid F in explosion tube D. Air is passed through the liquid at the rate given for 5 minutes at a given temperature, and a test for explosibility is made by removing cork R and causing sparks to pass at the elec-

trodes (E). If the combustible liquid gives an explosive mixture with air at the temperature tested, flame will pass up the tube and out the top. Tests are continued by the method of trial and error until a minimum temperature is obtained at which flame carries from the electrodes upward through the tube. The temperature is then kept constant and the rate of air flow changed until a rate is found which gives the lowest temperature that causes inflammation of the mixture in the tube. The temperature of the bath is then raised and the temperature at the upper-limit mixtures is ascertained in a similar manner.

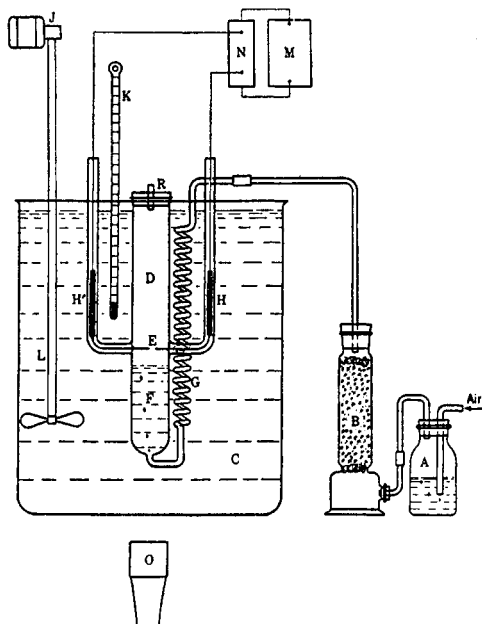


FIG. 4. Apparatus for determining the explosive range of high-boiling hydrocarbons

The limits of inflammability of combustible liquids may be determined rather closely in the apparatus described, provided the vapor pressures of the liquids tested are accurately known. To obtain the limits, the vapor pressure of the liquid at the temperature at which flame is propagated is divided by the barometric pressure at the time of the experiment and multiplied by 100. Tests made both in the apparatus described and in large-scale apparatus have shown approximate agreement.

3. The use of less inflammable combustibles

Wherever possible, solvents or other materials with the least inflammable characteristics should be used. Those materials should be chosen which

have, at the temperatures used, vapor pressures that give atmospheres that are not explosive. When this cannot be done the use of chlorinated hydrocarbons should be considered. Table 5 shows how a combustible gas which has one or more hydrogen atoms replaced by chlorine gives resulting materials with reduced explosive characteristics.

Methane becomes highly explosive when mixed with the proper proportions of air. While methyl chloride does not produce as violent explosions as methane-air mixtures, nevertheless explosions of this substance in air may do considerable damage. Methylene chloride is entirely safe when mixed with air at ordinary temperatures and pressures; however, when mixed with pure oxygen in the right proportions, it becomes highly explosive. Chloroform has no explosive properties. Carbon tetrachloride is entirely non-explosive with air in any proportions, and is used to good advantage in the preparation of non-combustible and non-explosive safety

TABLE 5

Effect of substitution of chlorine atoms for hydrogen upon the explosibility of methane

SUBSTANCE	FORMULA	EXPLOSIBILITY	LIMITS OF INFLAMMABILITY, PER CENT BY VOLUME	
			Lower	Upper
Methane	CH ₄	Highly explosive with air	5.00	15.00
Methyl chloride.....	CH ₃ Cl	Moderately explosive with air	8.20	18.70
Methylene chloride..	CH ₂ Cl ₂	Not explosive with air	No explosive limits	
Chloroform.....	CHCl ₃	Not explosive with air	No explosive limits	

cleaning compounds when added in the proper proportions to combustible liquids such as naphtha and petroleum distillates.

4. *Elimination of ignition sources*

Combustible gases and vapors, mixed with air or pure oxygen in the proportions to give explosive mixtures, may be safely used provided all sources of ignition are eliminated. Before a mixture can be made to explode, a portion of it must be heated to its ignition temperature. The ignition temperature may be defined as that temperature at which rapid combustion becomes independent of external supplies of heat.

It is not the purpose of this report to discuss ignition temperatures other than to state briefly that values reported in the literature are variable, can be used only in a relative sense, and may be even misleading unless complete details of the procedure by which the results were obtained are given. The results obtained depend upon and are affected by a number of variables, the most important of which are the percentage of combustible

in the mixture, the oxygen concentration, the "lag" or time required at a given temperature to cause ignition, the size, composition, and dimensions of the equipment in which the tests are made, the pressure at which the mixture is confined at the time of ignition, and the presence of catalysts and impurities in the mixtures.

The safety engineer is primarily interested in the sources of ignition that may cause explosions. These sources may be represented by the classification given below:

Ignition sources . . .	Flames	{	Open lights
			Matches and cigarette lighters
			Fires in boilers; water heaters
Sparks	{	Burning material; incinerators	
		Static electricity	
		Electrical shorts	
Heated materials	{	Lightning	
		Sparks from tools	
		Glowing metals, cinders, and filaments	
		{	Electric lights

Most of the sources of ignition given above can be taken care of by establishing proper safety regulations and installing flame-proof electrical equipment; others by designing the plants so that boilers, water heaters, and other equipment where there are open flames and incandescent materials are installed in other buildings at a safe distance from the place where the hazardous processes are carried out.

Static electricity has caused many serious fires and explosions and is one of the most serious ignition hazards to control. There are few operations in which it may not be present, and it is more serious in dry atmospheres when the relative humidity is below 60 per cent. Static is generated by friction, that is, by slipping belts, pulleys, and revolving machinery and by the passage of solids, liquids, or gases at high velocity through small openings.

Static electricity may be eliminated by grounding all machinery, pipes, and other equipment where charges may accumulate. To accomplish this, permanent metallic conductors should be connected to the pipes of the water system. In the case of moving equipment, metallic collectors or "combs" should contact the moving parts and so ground the charges that may collect on the equipment.

5. Segregation of hazardous operations

Operations which through necessity rather than choice require the use of inflammable gases or vapors should be segregated from other operations.

This requires the installation of hazardous processes in buildings at a safe distance from others and, if heavy combustible vapors are used, the elevation should be below that of other buildings so that in case of a fire or explosion the liquids and vapor that may be released will not flow toward other adjacent buildings. A hill or artificial earth barrier should be constructed where the operations are exceedingly dangerous.

6. The provision of adequate ventilation

The necessity for adequate ventilation in buildings cannot be too strongly emphasized where inflammable gases and vapors are handled and used. This includes not only the buildings in which the vapors are used but also all conduits, trenches, and tunnels where lines for conveying inflammable gases and vapors, and pipe lines for conveying inflammable liquids, are installed. Such lines should be carried in the open air above ground from one building to another, and in buildings they should be suspended above the floor level where they can be inspected readily for leaks.

Buildings should be made of light material which will offer not too great a resistance to pressure if an explosion occurs. The top should be provided with open ventilators, and windows should be installed in sashes of the tilting type which open when pressure is exerted from the inside.

It is impossible to have too much ventilation around hazardous operations. Where possible the operations should be carried out entirely in the open air, with no buildings whatever except those to house recording and other delicate instruments.

7. Construction of smooth fireproof floors

Smooth, fireproof floors resistant to the penetration of liquid combustibles should be used in buildings where hazardous operations are carried out. The floors should be laid directly on an earth foundation with no unventilated spaces underneath. They should be cleaned and scoured periodically. Many disastrous fires have been due to oils, greases, and hydrocarbon deposits being allowed to accumulate on the floors. Although such deposits are normally safe from explosion hazards, they may become exceedingly hazardous if a small fire or explosion develops in the plant, since because of the resulting high temperature the deposits vaporize and burn and are very difficult to extinguish when once set on fire.

8. Release diaphragm

Adequate light-weight release diaphragms should be provided on all equipment in which explosive mixtures may be present. The ideal release diaphragm is that having zero mass and an infinite area. This cannot be realized in practice; however, the construction and size of release openings

should approach the above ideal as closely as possible, yet be of sufficient strength to sustain the operating pressure within the equipment without danger of rupture or leakage except in the case of an explosion within the equipment.

To protect properly a given installation containing explosive mixtures, the following factors must be known or determined experimentally. (1) The type and concentration of explosive mixtures that may be present in the equipment. (2) The maximum pressure the equipment will safely stand. (3) The area of release openings necessary to keep the pressures below the safe maximum pressure. (4) The type of diaphragm material that will rupture at the desired pressures. (5) The location of the release diaphragms so that there will be no unprotected dead ends. Space does

TABLE 6

Pressures developed by explosive mixtures of acetone-air with varying sizes of release openings, in pounds per square inch above atmospheric pressure in 8-liter bomb

ACETONE, PER CENT BY VOLUME	ROUND HOLE, DIAMETER OF OPENING							SQUARE HOLE, WIDTH	
	Closed	0.25 in.	0.50 in.	1.00 in.	2.00 in.	3.00 in.	4.00 in.	1.5 in.	2.5 in.
3.00	36	17.0	7.0	2.0	0.5	0.5	0.5	0.5	0.5
4.00	61	40.0	20.0	7.0	2.5	0.5	0.5	2.5	0.5
5.00	74	65.0	45.0	12.0	4.0	1.5	0.5	5.0	1.5
5.50	78		49.0	14.0	4.5	2.0	0.5	6.0	2.0
Ratio = $\frac{\text{volume in cu. ft.}}{\text{area opening in sq. in}}$	Infinite	5.79	1.446	0.362	0.0905	0.0402	0.0226	0.126	0.0454
Area of opening in sq. in. per cu. ft.....	0.00	0.17	0.69	2.77	11.05	24.90	44.30	7.9	22.0

not permit a complete discussion of these factors, so only one example will be given to show how the proper diaphragm releases may be determined.

The pressures developed when mixtures of acetone and air of varying concentration are ignited in the bomb provided with different release openings are given in table 6. The results show that the maximum pressure developed in the bomb occurs when the concentration of acetone equals about 5.5 per cent by volume. Using the values giving the maximum pressure development for the various-size release openings tested, the curve shown in figure 5 is obtained. This gives the pressure developed when the area of release openings is varied from zero opening to 45 sq. in. per cubic foot of space in the equipment. Assume that the equipment should not be subjected to a pressure greater than 10 lb. per square inch, then

the area of release openings should be approximately 5 sq. in. per cubic foot of space.

The next important factor is the determination of the proper size, material, and thickness of the diaphragm material which will provide release of the gases from the equipment at a pressure of 10 lb. or less. In general, lead, tin, aluminum, or copper foil have been found to be most suitable for release material at low pressures.

One example will be shown of tests made on aluminum foil of 0.001 in. thickness in an 8-liter bomb when acetone-air mixtures were used for tests. The rupturing pressures for openings of different sizes and concen-

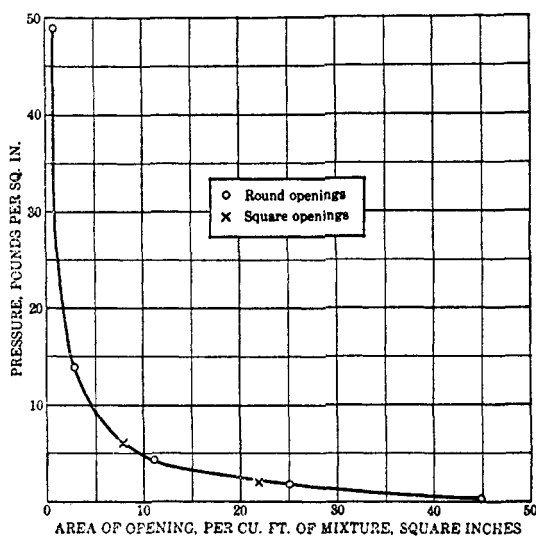


FIG. 5. Curve of relation of pressures produced to area of opening, 5.50 per cent acetone-air mixtures. 8.05-liter bomb.

tration of acetone in air are given in figure 6. The rupturing pressure increases as the area of the opening is reduced. In this example, where the pressure must not exceed 10 lb., the curves show that the diaphragms must be at least 3 in. in diameter if this aluminum foil is used, and the number of release openings should be such as to give 5 sq. in. of diaphragm opening per cubic foot of space in the equipment.

The pressure required to rupture a given diaphragm material is directly proportional to the ratio of the perimeter to the area. This relation can be expressed by the equation

$$P = K \frac{S}{A}$$

in which P is the pressure required in pounds per square inch to rupture the diaphragm, A the area in square inches, S the perimeter in inches, and K a constant characteristic of the particular diaphragm material being used.

In practice, K is determined for any given diaphragm material by making tests of the material in an opening of any given size and determining the pressure developed when the diaphragm is ruptured. The determined value of K can then be used to calculate the rupturing pressure for openings of any size.

In addition to the above requirements demanded of release diaphragms to maintain the maximum developed pressure below a given safe pressure, the location and distribution of the release diaphragms are very important. Experiments made in round ducts 12 in. in diameter and 15 ft. in length with acetone and air mixtures showed that release diaphragms should be

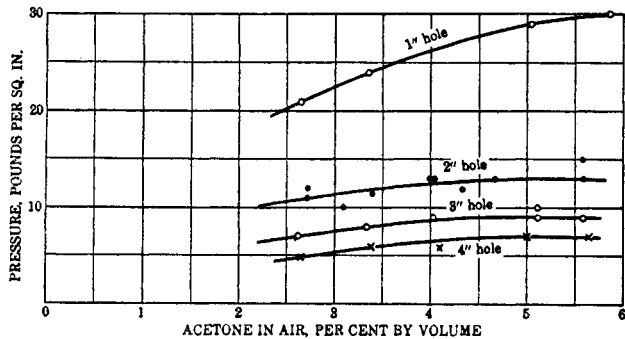


Fig. 6. Tests of aluminum diaphragms, 0.001 in. thick

distributed so that they were not more than 10 ft. apart, and that every dead end and sharp bend needed a diaphragm release to prevent the building up of pressure at these points.

9. *Recorders for determining the concentration of combustibles in hazardous atmospheres*

Combustible gas indicators or recorders should be installed in all equipment where hazardous concentrations of combustibles may be present, and sampling locations should be chosen so that samples may be taken from different locations. Equipment has been developed whereby samples may be taken periodically from twenty or more locations and recorded on one instrument.

It is not the purpose of this report to discuss the merits of indicators and recorders. There are recorders now marketed which operate on the thermal conductivity principle, others on the change in volume resulting

from the burning of the combustibles in the sample, while others depend upon the increase of resistance of a glowing filament when operating in an atmosphere containing combustibles; the greater the amount of combustibles present the greater the temperature of the wire and therefore the greater the resistance.

The performance and success of any of these devices can be determined only by actual installation in a representative plant and calibration of the device by chemical analysis against the particular combustibles used in the process.

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