

Effect of Methyl Bromide Additions on the Flame Speed of Methane

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The effect of small quantities of methyl bromide, up to 0.5 percent by volume, on the flame speed of methane-air mixtures has been determined. Maximum flame speeds, at given experimental conditions, are reduced proportionately to the amount of methyl bromide added. Flame speeds of rich mixtures are reduced much more than are flame speeds of lean mixtures. Reaction zone thickness of methane-air flames is increased by the addition of methyl bromide and the thickness increases with the amount of methyl bromide.

1. Introduction

Halogenated hydrocarbons have long been used to extinguish fires, and the effect of these combustion inhibitors on various combustion parameters has been the subject of many investigations [1–10].¹ Limits of flammability, quenching distance, and laminar flame speed all have been found to be affected by these inhibitors. Effect of inhibitors on the limit of flammability has been the chief topic of these investigations. The effect on flame speed has been little studied and what work that has been published usually treats of the effects of several inhibitors on a given fuel; description of the effects of other experimental conditions are usually lacking [1,2,9,10]. It was felt that a study of the effect of one inhibitor on flame speed under controlled experimental conditions would be of interest and of value. Methane was chosen as the fuel since we have had considerable experience in the determination of the flame speed of methane-air mixtures. Methyl bromide was chosen as the inhibitor.

2. Apparatus and Procedure

A description of the apparatus and method used to measure flame speeds has been presented earlier [14]. Briefly, the apparatus consists of drying and metering systems for air and fuel, and a nozzle, the exit of which is the burner port. Means are provided to control the temperature of the combustible mixture issuing from the nozzle. Flame speeds are determined by a total-area method, which is based on the measurement of the area of an enlarged photograph of the schlieren image of the flame.

It was decided to prepare mixtures of air and methyl bromide of the desired strength and to meter these mixtures, rather than to set up a third metering system for the small quantities of methyl bromide that would be required. Some error is introduced in the metering of these mixtures, since the sharp-

edged orifice used was calibrated for air. However, since the maximum amount of methyl bromide added was only 0.5 percent by volume of the air, it was considered that the error would be tolerable.

The mixtures of methyl bromide and air were prepared in a 120 gallon (16 ft³) steel tank. The tank was evacuated to a pressure of several microns and the methyl bromide admitted from its container. Rise in pressure was measured on a mercury manometer, read to 0.01 in. Air from a compressor was dried by passing first through a column of activated alumina and then through a cold trap immersed in a slush of dry ice in a mixture of equal parts by weight of chloroform and carbon tetrachloride. Water content of the air is thus kept at 0.03 percent by volume. The dried air was admitted slowly to the tank, and the final pressure, generally 130 psig, was read on a calibrated Bourdon gage to 0.1 psig.

The products of combustion, which contain hydrogen bromide and bromine, were drawn from the enclosure surrounding the burner by a large capacity vacuum pump. Air currents, set up by the pump, so disturbed the flames that the pump was shut off when photographs were taken.

Mixtures of 0.1, 0.2, 0.3, 0.4, and 0.5 percent by volume of methyl bromide in air were prepared. For each mixture, the variation of flame speed with mixture ratio, by weight, of methane to air plus methyl bromide was determined, gas velocity at the exit of the nozzle being constant. The ratio, by weight, of methane to air plus methyl bromide was varied from 0.054 to 0.072, and the gas velocity at the port of the nozzle was varied from 3 to 6 fps. Control of the temperature of the combustible mixture was such that the maximum change in temperature during a single run of about 3 hr duration was 3.7 °F. Actual gas temperatures ranged from about 90 °F in the summer to about 75 °F in the winter. The variation of flame speed with temperature was determined using a mixture ratio of methane to air of 0.060 (the air contained 0.2% methyl bromide), and a gas velocity of 4 fps; the temperature range in this determination was from 70 to 95 °F. Variation of flame speed with temperature was found to be 0.00328 fps per °F, and this value was used to correct

¹ Figures in brackets indicate the literature references at the end of this paper.

all flame speeds to a constant temperature of 75 °F. It is not expected that the rate of change of flame speed with temperature will differ appreciably with the relatively small amounts of methyl bromide added. Some previously unpublished data in our possession shows that the rate of change of flame speed with temperature is unaffected by changes in mixture ratio.

3. Results

Combustion of methane with air to which methyl bromide had been added proceeded smoothly. The outer mantle of the flames was colored brown by the formation of free bromine and the odor of bromine was noticeable. At lean conditions, the brown color began close to the base of the flame and extended to the tip. As flames became richer

in fuel, the normal blue-green color of the inner cone appeared and the brown color was seen only near the tip of the outer mantle. As the concentration of methyl bromide was increased, the brown color became more intense, but in rich flames was visible only near the tip of the outer mantle. It is probable that hydrogen bromide is the original product and is converted to bromine by the overall reaction: $4 \text{HBr} + \text{O}_2 \longrightarrow 2 \text{Br}_2 + 2 \text{H}_2\text{O}$. Apparently there is insufficient oxygen in a rich flame for complete conversion of hydrogen bromide.

The variation of flame speed with mixture ratio for a methane-air flame is shown in figure 1. This is taken from our previous work [14] with the values of flame speed corrected to 75 °F. The maximum flame speed is 1.196 fps, at a fuel-air ratio of 0.062. At a fuel-air ratio of 0.054, flame speed is 1.057 fps, and at a fuel-air ratio of 0.072, flame speed is 0.980 fps.

Results of addition of methyl bromide are shown in figures 2 through 6. It should be noticed that gas mixtures described as having the same mixture ratio but with different amounts of methyl bromide added do not have exactly the same ratio of fuel to air. As the amount of additive increases, the amount of air decreases, and the ratio between fuel and air increases; but this increase is only a matter of about a tenth of a percent. However, these facts should be remembered when comparing results. Figure 2

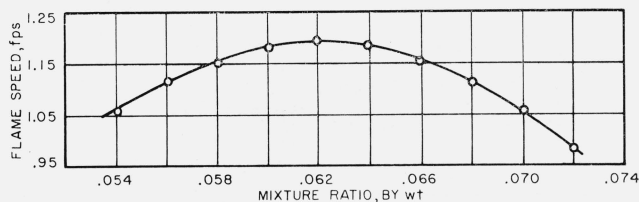


FIGURE 1. Variation of flame speed of methane with mixture ratio.

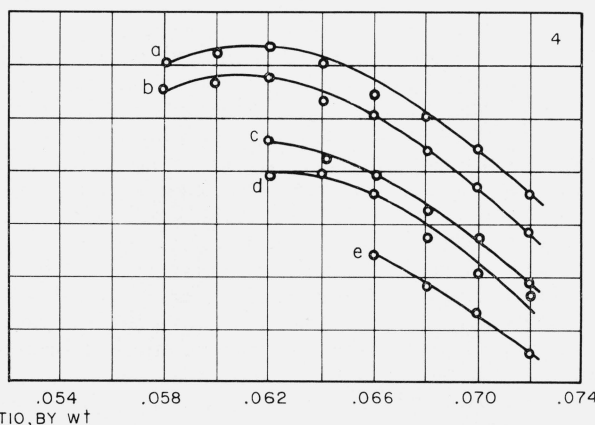
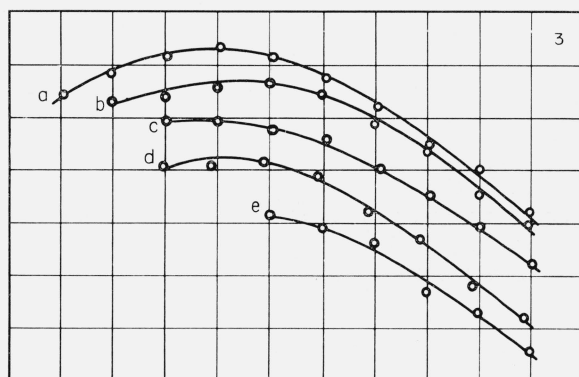
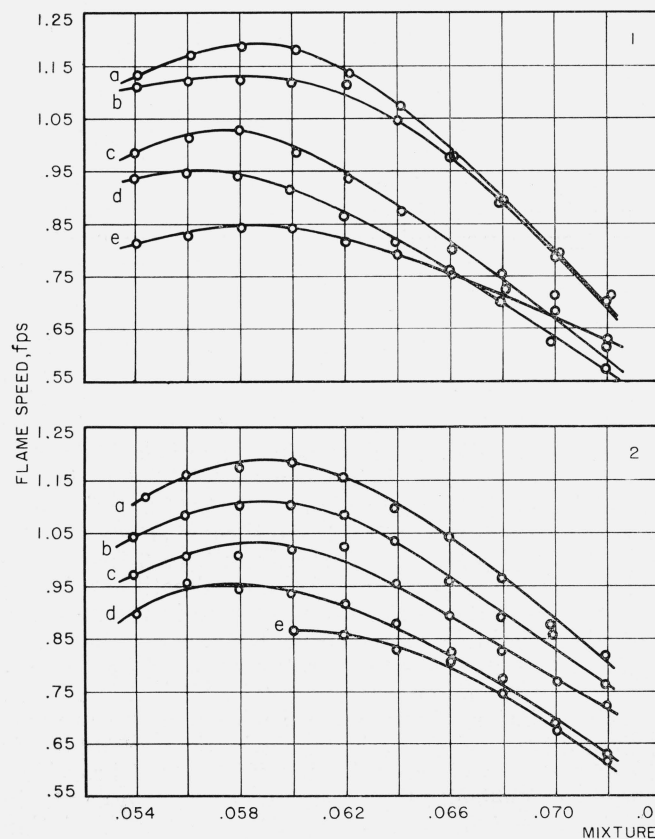


FIGURE 2. Effect of addition of methyl bromide on the flame speed of methane.

Percentage methyl bromide added: a=0.1; b=0.2; c=0.3; d=0.4; and e=0.5. Gas velocity=1, 3 fps; 2, 4 fps; 3, 5 fps; and 4, 6 fps.

shows the variation of flame speed with mixture ratio, by weight, of methane to air plus methyl bromide, when 0.1, 0.2, 0.3, 0.4, and 0.5 percent by volume, respectively, of methyl bromide is added to air, and at gas velocities of 3, 4, 5, and 6 fps.

For each addition of methyl bromide and at each gas velocity, there is found one value of mixture ratio at which flame speed is greatest. Maximum flame speed for a methane-air flame occurs at mixture ratio 0.062; addition of methyl bromide causes maximum flame speed to shift to leaner conditions, especially at the lower gas velocities. (Stoichiometric for a methane-air flame is equivalent to a mixture ratio of 0.0583.) Table 1 lists the maximum flame speeds and the experimental conditions at which they were observed.

TABLE 1. *Maximum flame speeds*

Flame speed	Wt CH ₄	Percent CH ₃ Br added to air	Flame speed	Gas velocity
	Wt air+CH ₃ Br		Flame speed CH ₄ -air	
<i>fps</i> 1.196	0.062	0	-----	<i>fps</i> 6
1.186	.058	0.1	0.992	3
1.125	.058	.2	.941	3
1.029	.058	.3	.860	3
0.945	.056	.4	.790	3
.843	.060	.5	.704	3
1.186	.060	.1	.992	4
1.103	.060	.2	.922	4
1.029	.062	.3	.860	4
0.958	.056	.4	.801	4
.864	.060	.5	.722	4
1.185	.060	.1	.991	5
1.117	.062	.2	.934	5
1.047	.058	.3	.875	5
0.967	.062	.4	.806	5
.867	.062	.5	.724	5
1.186	.062	.1	.992	6
1.127	.062	.2	.942	6
1.006	.062	.3	.841	6
0.945	.064	.4	.790	6
.790	.066	.5	.661	6

^a Blow-off occurred at 0.064.

Flash-back which represents the rich limit of operation of the burner was not encountered at any of the experimental conditions used. Blow-off which represents the lean limit of operation was rather frequent especially at gas velocities of 5 and 6 fps. No cases of blow-off were encountered at 3 fps and only one at 4 fps; this occurred at mixture ratio of 0.058 with 0.5 percent CH₃Br added to the air. Table 2 lists the conditions at which the leanest flame could exist before blow-off occurred. It can be noted that as the amount of methyl bromide increases, the lean limit shifts toward fuel-rich conditions, while the flame speed becomes less. Rich flames are thus stabilized when methyl bromide is present.

Theoretically, the velocity with which combustible gas issues from a burner should have no effect on the flame speed. In practice, some variation of flame speed with gas velocity is noted [14]. In this present work, a small decrease of flame speed with increasing gas velocity, amounting to about 2 percent of the average value over the gas velocity range covered, was found at mixture ratios yielding maximum flame

TABLE 2. *Lean limit of operation of burner*

Percent CH ₃ Br added to air	Wt CH ₄	Gas velocity	Flame speed
	Wt air+CH ₃ Br		
0.1	0.058	<i>fps</i> 6	<i>fps</i> 1.156
.2	.056	5	1.084
.2	.058	6	1.103
.3	.058	5	1.047
.3	.062	6	1.006
.4	.058	5	.958
.4	.062	6	.941
.5	.060	4	.864
.5	.062	5	.867
.5	.066	6	.790

speeds, and at leaner conditions. At rich conditions, flame speed increased with gas velocity, and the variation amounted to as much as 15 percent of the average value. Rich flames, however, are very tall as the flame speed is very low, and tall flames are very susceptible to disturbances. It is possible, therefore, that the increased variation of flame speed with gas velocity may be due to these disturbances.

The addition of methyl bromide to the combustion air reduces the maximum flame speed and the more methyl bromide added, the greater is the reduction in flame speed. Flames burning at mixture ratios greater than that at which maximum flame speed occurred are more affected by methyl bromide than are those burning at leaner conditions. At 0.1 percent methyl bromide addition, for example, and at a gas velocity of 3 fps, the maximum flame speed is 1.186 fps at a mixture ratio of 0.058. At a mixture ratio of 0.072 flame speed is 0.718 fps which is 60.6 percent of the maximum, while at mixture ratio 0.054, flame speed is 1.134 fps which is 95.6 percent of the maximum. The corresponding percentages for the methane-air flame are 82.0 percent at mixture ratio 0.072 and 88.4 percent at mixture ratio 0.054. The addition of 0.1 and 0.2 percent of methyl bromide even increases the flame speed at lean conditions. At a gas velocity of 3 fps, the flame speed at mixture ratio 0.054 is 1.134 fps for a 1 percent addition and 1.120 fps for 0.2 percent addition. For a methane-air flame, flame speed is 1.057 fps at mixture ratio 0.054 and a gas velocity of 6 fps.

In figure 3, flame speed is plotted against the percent of methyl bromide added to the combustion air. Mixture ratio is 0.062 and gas velocity is 5 fps. Flame speed decreases as the percentage of methyl bromide increases, and the data points fall along a straight line. For all experimental conditions of mixture ratio, gas velocity and methyl bromide addition, similar results were found. Hence, it may be deduced that the reduction in flame speed is directly proportional to the amount of methyl bromide, at least in the range of addition used in this work. In figure 4, the maximum flame speed at each addition of methyl bromide, at constant gas velocity, is plotted against the percentage of methyl bromide, and again the data points fall on a straight line, and the slopes of these lines are of similar magnitude.

The reduction in maximum flame speed is directly proportional to the amount of methyl bromide added and amounts to 0.0828 fps for each tenth percent of methyl bromide added.

In the method used for determining flame speeds, photographs of the schlieren and visible images of the flame are taken simultaneously on the same film. The schlieren image which depends on the change in density and thus on the change in temperature marks the position where chemical reactions begin in the flame [15]. The visible image indicates the region in the flame where reactions are completed [16] except for equilibrium changes. Hence, the separation between the schlieren and visible images is a measure of the thickness of the reaction zone. However, since both images in an enlarged photograph are rather diffuse, these measurements cannot be considered exact.

It is found that the thickness of the reaction zone varies with the flame speed; the greater the flame speed, the less is the thickness of the reaction zone. Figure 5 shows the variation of reaction zone thickness with mixture ratio at constant gas velocity; 0.2

percent methyl bromide was added to the air and the gas velocity was 4 fps. Similar curves are obtained for all the other experimental conditions. Figure 6 shows the variation of reaction zone thickness with added methyl bromide at constant mixture ratio and at constant gas velocity. Mixture ratio was 0.070 and gas velocity was 6 fps. Zone thickness increases with the amount of methyl bromide added, and similar results were obtained at all other experimental conditions of mixture ratio and gas velocity. From some previously unreported experiments, it is found that the reaction zone thickness of a methane-air flame at fuel-air ratio of 0.070 and gas velocity of 6 fps was 0.0180 in. Minimum thickness was 0.015 in. and occurred at mixture ratio 0.062.

The mechanism of combustion inhibition by halogenated hydrocarbons is not fully understood [5, 9, 11, 12]. Since the combustion of hydrocarbons in air involves the propagation of chain reactions by free radicals, it is plausible to assume that the presence of halogen results in the deactivation of one or more of the chain carrying radicals. Since deactivation would effectively decrease the rate of reaction, the general effect of chemical inhibitors in decreasing flame speeds would be explained. The increased reaction zone thickness which results on the addition of methyl bromide may also be explained by the effective decrease in reaction velocity.

The increase in flame speed noted at lean conditions at additions of 0.1 and 0.2 percent methyl bromide cannot be so explained. Since there is more oxygen in a lean flame, it may be that methyl bromide acts as a fuel rather than an inhibitor at this condition and the reaction mechanism is different. If methyl bromide acts as a fuel, then the mixture ratio should be expressed as $\frac{\text{wt methane} + \text{wt methyl bromide}}{\text{wt air}}$, in which case the

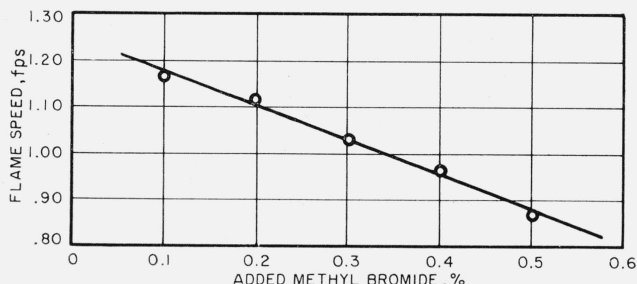


FIGURE 3. Variation of flame speed with added methyl bromide.

Mixture ratio, by weight, = 0.062. Gas velocity = 5 fps.

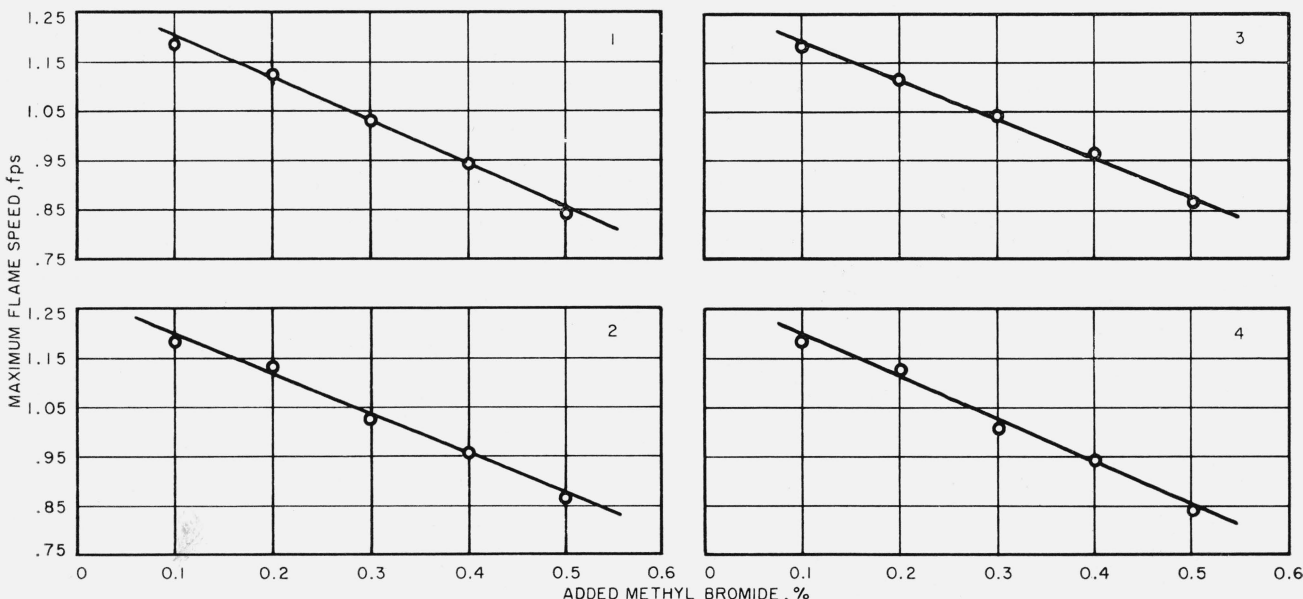


FIGURE 4. Variation of maximum flame speed with added methyl bromide.

Gas velocity—1, 3 fps; 2, 4 fps; 3, 5 fps; and 4, 6 fps.

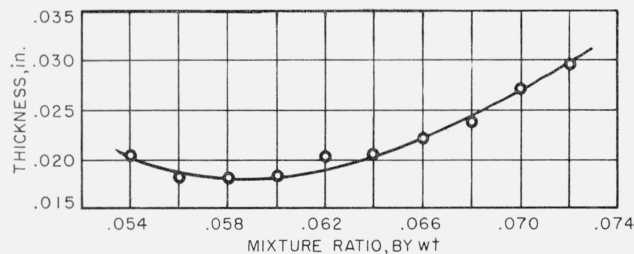


FIGURE 5. Variation of reaction zone thickness with mixture ratio.

0.2 percent methyl bromide added. Gas velocity=4 fps.

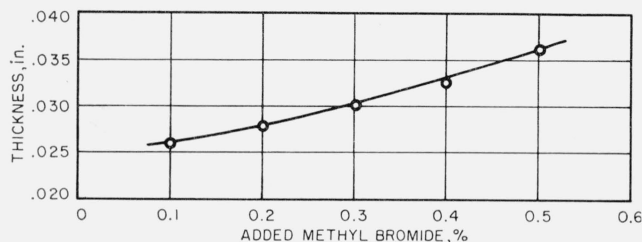


FIGURE 6. Variation of reaction zone thickness with added methyl bromide.

Mixture ratio 0.070. Gas velocity=6 fps.

value is 0.057 instead of 0.054, and 0.059 instead of 0.056 for the addition of 0.1 percent methyl bromide. Then if we superpose the curve for flame speed versus mixture ratio at 0.1 percent methyl bromide addition, using the new values of mixture ratio, on the curve for methane-air, the two curves agree for values of mixture ratio less than that at which maximum flame speed occurred.

4. Experimental Observations

Table 3 presents in detail observations on the effect of some variables on the flame speed and reaction zone thickness.

TABLE 3. Effect of some variables on flame speed

A. 0.1% CH ₃ Br added to air				
Wt CH ₄	Reaction zone thickness	Gas temperature	Flame speed	Flame speed corrected to 75° F
Wt air+CH ₃ Br				
1. Gas velocity=3 fps				
0.05407	0.0155	91.3	1.187	1.134
0.05608	0.0146	91.4	1.224	1.170
0.05807	0.0168	90.0	1.234	1.186
0.06013	0.0165	90.6	1.236	1.185
0.06216	0.0168	90.9	1.190	1.138
0.06410	0.0190	91.2	1.127	1.074
0.06610	0.0200	91.3	1.032	0.979
0.06800	0.0223	91.4	0.944	0.891
0.07013	0.0257	91.4	0.834	0.780
0.07214	0.0305	91.3	0.771	0.718

TABLE 3. Effect of some variables on flame speed—Continued

Wt CH ₄	Reaction zone thickness	Gas temperature	Flame speed	Flame speed corrected to 75° F
Wt air+CH ₃ Br				
2. Gas velocity=4 fps				
0.05436	0.0192	89.6	1.168	1.120
0.05592	0.0172	87.8	1.203	1.167
0.05794	0.0179	88.3	1.217	1.174
0.05992	0.0202	88.9	1.232	1.186
0.06189	0.0191	89.2	1.203	1.156
0.06387	0.0195	89.6	1.143	1.094
0.06594	0.0219	89.6	1.090	1.042
0.06794	0.0235	89.3	1.014	0.967
0.06989	0.0272	89.3	0.923	0.876
0.07196	0.0295	89.3	0.866	0.818
3. Gas velocity=5 fps				
0.05409	0.0198	86.6	1.133	1.094
0.05593	0.0191	87.1	1.174	1.135
0.05808	0.0203	87.0	1.207	1.168
0.06010	0.0191	84.8	1.217	1.185
0.06204	0.0224	85.8	1.201	1.167
0.06406	0.0228	86.1	1.162	1.126
0.06604	0.0218	86.6	1.108	1.070
0.06809	0.0238	87.0	1.050	1.011
0.07006	0.0267	86.9	0.991	0.952
0.07204	0.0284	87.0	0.904	0.864
4. Gas velocity=6 fps				
0.05807	0.0190	86.1	1.192	1.156
0.06003	0.0203	86.2	1.208	1.171
0.06200	0.0192	85.6	1.223	1.186
0.06402	0.0212	84.9	1.186	1.153
0.06601	0.0225	85.4	1.129	1.095
0.06800	0.0238	86.0	1.092	1.056
0.07003	0.0260	86.1	1.027	0.991
0.07198	0.0287	86.3	0.943	0.906
B. 0.2% CH ₃ Br added to air				
1. Gas velocity=3 fps				
0.05406	0.0217	74.5	1.109	1.110
0.05601	0.0202	74.8	1.121	1.120
0.05803	0.0201	75.2	1.126	1.125
0.05998	0.0181	75.2	1.120	1.120
0.06206	0.0207	75.5	1.115	1.113
0.06402	0.0221	75.3	1.049	1.048
0.06599	0.0236	76.0	0.983	0.980
0.06794	0.0251	75.6	0.890	0.889
0.07000	0.0279	75.2	0.787	0.786
0.07202	0.0328	75.1	0.706	0.706
2. Gas velocity=4 fps				
0.05394	0.0203	77.7	1.053	1.044
0.05591	0.0182	75.8	1.088	1.085
0.05794	0.0182	75.8	1.105	1.103
0.05996	0.0183	75.9	1.106	1.103
0.06197	0.0203	76.1	1.092	1.088
0.06391	0.0205	76.4	1.038	1.033
0.06594	0.0220	76.9	0.966	0.960
0.06787	0.0237	77.2	0.899	0.892
0.06994	0.0272	77.4	0.859	0.851
0.07197	0.0295	79.5	0.778	0.764
3. Gas velocity=5 fps				
0.05600	0.0190	77.2	1.091	1.084
0.05800	0.0178	77.5	1.098	1.090
0.05998	0.0198	76.7	1.115	1.110
0.06199	0.0200	76.6	1.122	1.117
0.06396	0.0207	76.6	1.102	1.097
0.06597	0.0218	76.8	1.043	1.037
0.06801	0.0230	76.9	0.995	0.989
0.06999	0.0258	77.1	0.912	0.906
0.07198	0.0278	77.2	0.882	0.874

TABLE 3. *Effect of some variables on flame speed—Continued*

Wt CH ₄	Reaction zone thickness	Gas temperature	Flame speed	Flame speed corrected to 75° F
Wt air+CH ₃ Br				
4. Gas velocity = 6 fps				
0.05798	<i>in.</i> 0.0195	°F 77.8	<i>fps</i> 1.112	<i>ps</i> 1.103
.05994	.0212	77.8	1.126	1.117
.06199	.0207	78.7	1.139	1.127
.06397	.0207	76.2	1.087	1.083
.06597	.0230	76.7	1.064	1.058
.06804	.0247	77.2	.996	.989
.06995	.0278	77.6	.931	.922
.07197	.0295	77.8	.844	.836

C. 0.3% CH₃Br added to air

1. Gas velocity = 3 fps

0.05391	<i>in.</i> 0.0237	°F 80.6	<i>fps</i> 1.004	<i>ps</i> 0.985
.05602	.0253	80.0	1.029	1.013
.05799	.0220	79.6	1.044	1.029
.06019	.0234	79.8	1.001	.985
.06210	.0258	80.3	.956	.939
.06414	.0237	80.4	.892	.874
.06610	.0258	80.2	.817	.800
.06810	.0295	80.6	.747	.729
.06997	.0349	79.2	.701	.687
.07196	.0395	79.3	.631	.617

2. Gas velocity = 4 fps

0.05390	0.0203	78.3	0.984	0.973
.05594	.0200	77.3	1.016	1.008
.05796	.0190	76.5	1.013	1.008
.05996	.0228	76.7	1.024	1.019
.06193	.0217	77.1	1.036	1.029
.06393	.0252	78.3	.965	.954
.06596	.0240	79.1	.909	.896
.06794	.0260	78.9	.839	.827
.07002	.0299	77.9	.778	.769
.07196	.0297	77.2	.729	.722

3. Gas velocity = 5 fps

0.05804	0.0210	77.4	1.055	1.047
.06000	.0222	76.6	1.045	1.040
.06211	.0207	77.5	1.037	1.029
.06410	.0215	76.2	1.013	1.009
.06613	.0242	76.8	.959	.953
.06807	.0270	77.2	.913	.906
.07006	.0300	77.0	.847	.840
.07203	.0350	76.5	.757	.752

4. Gas velocity = 6 fps

0.06196	0.0232	77.8	1.015	1.006
.06418	.0247	77.4	.981	.974
.06607	.0272	78.9	.955	.942
.06804	.0283	77.3	.884	.877
.07006	.0300	77.4	.833	.825
.07198	.0345	77.8	.749	.740

D. 0.4% CH₃Br added to air

1. Gas velocity = 3 fps

0.05391	<i>in.</i> 0.0203	°F 72.5	<i>fps</i> 0.930	<i>ps</i> 0.938
.05593	.0207	73.9	.941	.945
.05795	.0209	75.0	.942	.942
.05993	.0218	75.4	.918	.917
.06194	.0225	75.8	.872	.869
.06393	.0248	74.6	.811	.812
.06596	.0270	72.7	.745	.752
.06790	.0315	72.9	.708	.701
.06988	.0372	74.6	.628	.623
.07195	.0408	75.3	.576	.575

TABLE 3. *Effect of some variables on flame speed—Continued*

Wt CH ₄	Reaction zone thickness	Gas temperature	Flame speed	Flame speed corrected to 75° F
Wt air+CH ₃ Br				
2. Gas velocity = 4 fps				
0.05395	<i>in.</i> 0.0228	°F 74.8	<i>fps</i> 0.895	<i>ps</i> 0.896
.05591	.0227	75.1	.958	.958
.05790	.0205	75.2	.945	.944
.05995	.0217	74.8	.935	.936
.06193	.0237	74.7	.916	.917
.06395	.0248	74.7	.877	.878
.06600	.0280	74.7	.804	.805
.06798	.0303	74.8	.770	.771
.07000	.0360	75.2	.677	.676
.07196	.0397	75.4	.628	.627

3. Gas velocity = 5 fps

0.05795	0.0225	75.3	0.959	0.958
.05978	.0227	75.3	.957	.957
.06177	.0237	74.8	.967	.967
.06375	.0258	73.2	.934	.940
.06578	.0272	74.5	.872	.873
.06775	.0300	75.2	.822	.821
.06978	.0340	75.1	.730	.730
.07175	.0393	74.2	.672	.674

4. Gas velocity = 6 fps

0.06202	0.0233	84.6	0.972	0.941
.06399	.0248	82.8	.971	.945
.06598	.0260	83.0	.934	.908
.06801	.0297	81.0	.843	.823
.07001	.0325	81.6	.778	.757
.07204	.0380	82.9	.741	.716

E. 0.5% CH₃Br added to air

1. Gas velocity = 3 fps

0.05399	<i>in.</i> 0.0248	°F 80.1	<i>fps</i> 0.830	<i>ps</i> 0.814
.05602	.0235	79.7	.844	.829
.05802	.0233	79.9	.858	.842
.06003	.0238	76.8	.849	.843
.06200	.0240	77.6	.826	.818
.06397	.0250	78.3	.801	.790
.06596	.0265	78.6	.773	.761
.06797	.0282	78.6	.769	.757
.07001	.0328	80.0	.734	.718
.07204	.0370	79.6	.629	.614

2. Gas velocity = 4 fps

0.06000	0.0230	78.7	0.876	0.864
.06192	.0232	79.3	.871	.856
.06396	.0252	79.7	.844	.829
.06594	.0278	80.0	.811	.794
.06798	.0307	80.5	.761	.743
.07002	.0330	80.7	.706	.688
.07194	.0387	81.0	.633	.614

3. Gas velocity = 5 fps

0.06196	0.0275	75.0	0.867	0.867
.06398	.0275	75.4	.841	.840
.06593	.0311	74.6	.813	.814
.06793	.0325	75.5	.719	.718
.06994	.0377	75.6	.682	.679
.07199	.0422	75.6	.604	.603

4. Gas velocity = 6 fps

0.06599	0.0293	76.4	0.795	0.790
.06801	.0323	75.5	.735	.733
.06999	.0362	76.0	.684	.681
.07200	.0415	75.8	.603	.601

5. Conclusions

Small amounts of methyl bromide added to methane-air mixtures have a large effect on the flame speed. Maximum flame speed is reduced proportionately to the amount of methyl bromide added. Flame speed of rich mixtures is much more reduced than that of lean mixtures. Reaction zone thickness is increased by the presence of methyl bromide.

6. References

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(Paper 67A1-196)

Publications of the National Bureau of Standards*

Selected Abstracts

Reliability of a system in which spare parts deteriorate in storage. G. H. Weiss, *J. Research NBS 66B (Math. and Math. Phys.) No. 4, 157 (Oct.–Dec. 1962).* 75 cents.

The problem considered is that of determining the failure statistics for a system consisting of a single part and n spares, in which it is assumed that that failure occurs at different rates in use and in storage. The resulting equations can be solved explicitly when both types of failures follow a Poisson law. Otherwise algorithms are given for the calculation of the failure probabilities.

Laguerre expansions for successive generations of a renewal process. G. H. Weiss, *J. Research NBS 66B (Math. and Math. Phys.) No. 4, 165 (Oct.–Dec. 1962).* 75 cents.

It is shown that the coefficients in the Laguerre expansions for successive generations in a renewal process are related by an algebraic convolution. Thus the calculations are easily mechanized for computation.

An application of information theory to the analysis of contingency tables, with a table of $2n \ln n$, $n=1(1)10,000$. S. Kullback, M. Kupperman, and H. H. Ku, *J. Research NBS 66B (Math. and Math. Phys.) No. 4, 217 (Oct.–Dec. 1962).* 75 cents.

In this paper we present a number of useful tests for contingency tables in conjunction with a useful table to assist in the necessary computations. A consistent and simple approach based on the notions of information theory is used in developing the various test procedures and the results are analyzed in the form of analysis-of-information tables. Beginning with tests of hypotheses for a one-way table, tests of hypotheses of specified probabilities, independence, conditional independence, homogeneity of classifications, symmetry, and interaction are developed or indicated for contingency tables of two, three, four, and higher order classifications. Extension of these procedures to certain tests for Markov chains is indicated. Worked examples are given throughout the paper. A table of $2n \ln n$ for $n=1(1) 10,000$ is appended for use in computation.

Use of surface refractivity in the empirical prediction of total atmospheric refraction. W. R. Iliff and J. M. Holt, *J. Research NBS 67D (Radio Prop.) No. 1 31 (Jan.–Feb. 1963).* 70 cents.

The use of a 1.9-cm radio sextant capable of precise tracking of the sun has produced accurate measurements of total atmospheric microwave refraction. These data are used to verify the high correlation of such refraction with surface refractivity for low altitude angles. The values of the correlation coefficients obtained vary from 92.2 percent at 16 degrees to 98 percent at 2 degrees. An empirical predictor is developed, based on this correlation, which satisfactorily accounts for the observed refraction. The mathematical form of the predictor is given, and suggestions are made for its use.

Composition of reflection and transmission formulae. J. Heading, *J. Research NBS 67D (Radio Prop.) No. 1 65 (Jan.–Feb. 1963).* 70 cents.

An integral equation for the electric field in a continuously stratified ionized medium is derived; this is then manipulated to yield equations for the reflection and transmission coefficients, at the same time being susceptible to physical interpretation. The equations are solved by successive approximations, the first terms being a Fresnel-type coefficients. Various applications of the results are discussed.

Titheridge coefficients for the polynomial method of deducing electron density profiles from inograms. A. R. Long and J. O. Thomas, *J. Research NBS 67D (Radio Prop.) No. 1 79 (Jan.–Feb. 1963).* 70 cents.

Sets of Titheridge polynomial coefficients suitable for the conversion into electron density profiles of smooth virtual height frequency curves, such as those observed regularly at night, are presented for a series of values of the magnetic dip angle and gyrofrequency. These magnetic conditions have been chosen so that the coefficients are suitable for the analysis, to a reasonable degree of accuracy, of ordinary and extraordinary ray records obtained anywhere in the world.

The coefficients may be used for the analysis of topside-sounder data to a first order of accuracy if the plasma frequency at the satellite is small.

Chemistry of cement. Proceedings of the Fourth International Symposium, Washington, 1960. *NBS Mono. 43, Vol. I (Aug. 31, 1962), \$5.75; Vol. II (Sept. 27, 1962), \$5.50.* The two volumes are available at \$11.25 a set.

This two-volume Monograph contains the complete texts of all papers given at the Fourth International Symposium on the Chemistry of Cement, held in Washington, D.C., October 2–7, 1960. The publication represents one of the most complete reference works available on the subject, and presents the latest information in most of the fields of cement chemistry research. Topics covered, divided according to session titles: Volume I, Chemistry of clinker, chemistry of hydration of cement compounds, and chemistry of hydration of portland cement; Volume II, Properties of cement paste and concrete destructive processes in concrete, chemical additions and admixtures, and special cements.

Tables of Eisenstein functions. Vibrational contributions to the thermodynamic functions. J. Hilsenrath and G. G. Ziegler, *NBS Mono. 49 (July 12, 1962) \$2.75.*

Tables are presented for the contribution of a harmonic oscillator to the free energy function, enthalpy function, entropy, and heat capacity of gases. Dimensionless values of the Planck-Einstein functions are given as a function of $x=hc/kT$ for $x=0.0010(.0001) 0.1500(.001) 4.000(.01) 10.00(.2) 16.0$. A second table which gives the contributions in cal/mole °K directly as a function of frequency μ , and temperature T , was computed using the values 1.43880 for the second radiation constant hc/k , and 1.98717 for the universal gas constant R . The arguments for the latter table are spaced at 10 wave number intervals from 100 cm^{-1} to 4000 cm^{-1} .

Bibliography on atomic transition probabilities. B. M. Glennon and W. Wiese, *NBS Mono. 50 (Aug. 1, 1962) 35 cents.*

A bibliography on atomic transition probabilities is presented. The papers are arranged according to elements and stages of ionization, and the method employed and class of transitions are indicated behind each reference. Only articles on discrete transitions, both permitted and forbidden, are listed. Also included is a supplementary list of papers dealing with transition probabilities from a general point of view, a table showing the availability of numerical material on the individual atoms and ions, and a table of conversion factors.

Experimental transition probabilities for spectral lines of seventy elements. C. H. Corliss and W. R. Bozman, *NBS Mono. 53 (July 20, 1962) \$4.25.*

Relative intensities of 39,000 spectral lines with wavelengths between 2000 and 9000 angstroms have been determined on a uniform energy scale for seventy elements. The light source was an arc between copper electrodes to which a single element was added in the ratio of one atom of element to

1000 atoms of copper. The temperature of the arc was determined, by comparison of the observed intensities with published relative gf -values, to be $5100 \pm 110^\circ\text{K}$. The degree of ionization of eleven elements in the arc was determined by comparison of intensities in spectra of neutral and ionized atoms with known absolute gf -values. With the aid of Saha's ionization equation, the electron density in the arc was found to be $2.4 \times 10^{14} \text{cm}^{-3}$. The ionization of seventy elements separately added to the arc was then calculated with Saha's equation. A correction was made for diffusion of atoms from the arc stream. With this information, relative values of gf on a uniform scale can be computed for the 25,000 lines which have been classified. By calibration with known absolute gf -values, the scale is put on an absolute basis. Absolute transition probabilities for 25,000 lines of 112 spectra have been calculated in this way and the results are tabulated by spectrum. The wavelength in angstroms, energy levels to the nearest kaysr, gA in 10^8 per second, gf , and the log gf are given for each line.

Systems of electrical units, F. B. Silsbee, *NBS Mono.* 56 (Sept. 20, 1962) 30 cents.

The various systems of measurement, with their respective sets of units, used in the literature on electricity and magnetism are described in detail. Their historical development is summarized. The manner in which each is derived from either of the two alternative points of view of the experimentalist and the theoretician is compared and contrasted. The desirability of recognizing both points of view in international standardization, particularly when discussing rationalization, is pointed out. The present status of the absolute measurements on which all electrical units are based is reported, and tables are included for the conversion of equations and numerical values from one system to another.

A tabulation of the thermodynamic properties of normal hydrogen from low temperatures to 540°R and from 10 to 1500 psia, Supplement A (British units), J. W. Dean, *NBS Tech. Note* 120A (June 1962) 45 cents.

Pressure, volume, temperature, internal energy, enthalpy, and entropy of normal hydrogen gas have been tabulated along isobars in 2°R temperature steps. The range covered is from the saturation temperature to 540°R and from a pressure of 10 to 1500 psia. The source of data is Research Paper 1932 of the National Bureau of Standards Journal Of Research. The method is described by which the data presented in Research Paper 1932 is reduced to properties directly useful for engineering calculations. A method is also described for estimating the effects of ortho-para compositions upon the tabulated properties.

Tabular values are presented in the dimensional units of the British system. The tabulations are also available in the dimensional units of the metric system as technical Note No. 120.

The thermodynamic properties of helium from 3 to 300°K between 0.5 and 100 atmospheres, D. B. Mann, *NBS Tech. Note* 154 (Jan. 1962) 50 cents.

The specific volume, enthalpy, entropy, and internal energy values of helium are presented in tabular form as functions of pressure and temperature.

Data are tabulated in one degree Kelvin increments for forty isobars between 0.5 atmospheres and 100 atmospheres. A comparison with previously published data is made where applicable.

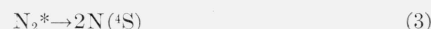
An expression is presented which represents the pressure-density-temperature surface based on previously published data.

The tabulation is presented in the dimensional units of the metric system, but is also available in the dimensional units of the British system (Supplement A).

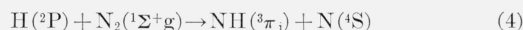
Photosensitized reaction between hydrogen (^2P) atoms and molecular nitrogen, I. Tanaka and J. R. McNesby, *J. Chem. Phys.* 36, No. 12, 3170-3173 (June 15, 1962).

The reaction between $\text{H}(^2\text{P})$ atoms and molecular nitrogen has been studied. $\text{H}(^2\text{P})$ atoms were produced by irradiating ground state $\text{H}(^2\text{S})$ atoms, generated in a microwave discharge, with Lyman alpha radiation at 1216\AA (ca. 10^{14} - 10^{15} quanta sec^{-1}). The interaction of $\text{H}(^2\text{P})$ atoms with N_2 produces

ammonia but not hydrazine. Two alternative mechanisms of the primary reaction are proposed. The first involves transfer of electronic energy.



The second possibility is a chemical mechanism involving atom transfer.



Ammonia is formed either by reaction of N with H or by reaction of NH with H or H_2 .

Effect of particle size on low-temperature heat capacities, A. C. Victor, *J. Chem. Phys.* 36, No. 10, 2812-2813 (May 15, 1962).

A new model is proposed to account for the particle size effect in low temperature heat capacities. As a first approximation a continuum approach is used. The model gives excellent agreement with sodium chloride data. Moderate success is also obtained with magnesium oxide and beryllium oxide.

Effect of molecular oxygen on the emission spectra of atomic oxygen-acetylene flames, S. L. N. G. Krishnamachari and H. P. Broida, *J. Chem. Phys.* 34, 1709-1711 (1961).

Studies have been made of the emission (3000 to 6000 Å) obtained from low pressure atomic oxygen-acetylene flames diluted with varying amounts of molecular oxygen and molecular nitrogen. Added molecular oxygen greatly increased the OH emission while reducing CH and C_2 emission. It also had an effect on the rotational intensity distribution of OH and on the vibrational intensity distribution of C_2 . Nitrogen addition greatly reduced the rotational and vibrational "temperatures" and decreased C_2 emission relative to the other emitters.

The structure of the vibrational-rotational bands of an asymmetric rotor, H. C. Allen, Jr., *Phil. Trans. Roy. Soc. London, Ser. B. Math. and Phys. Sci.* 253, No. 1030, 335-357 (Apr. 27, 1961).

The structure of A- and C-type vibrational-rotational bands of an asymmetric rotor is related to the band types of the two limiting symmetric rotors. The effect of the degree of asymmetry and the change in the effective inertial constants between the two vibrational states on the band structure is shown. The type of information which can be obtained from the analysis of these two types of band is pointed out.

Real representations of coordinate rotations, U. Fano, *J. Math. Phys.* 1, No. 5, 417-423 (Sept.-Oct. 1960).

Since irreducible tensorial sets that represent observables are of integral degree, their transformations under coordinate rotations have real representations. Real representations, with rows and columns classified by eigenvalues of the commuting operators J_x^2 and $\exp(i\pi J_y)$, are given explicitly, so that complex functions of rotation angles need not be used. The addition of angular momenta is worked out for sets in the real representation such as the sets of real orbital wave functions. Applications to the theory of angular distributions are discussed.

Structural and internal state variables in the description of scalar rate processes in fluids, R. E. Nettleton, *Phys. Fluids* 4, 1488 (1961).

Arguments are presented to show that the internal energy per molecule in a macroscopically small volume element of an infinite liquid should remain constant, in first approximation, during a sudden fluctuation in liquid structure at constant density and temperature. This result is shown to be consistent with a formulation of non-equilibrium thermodynamics in which the departures of structural parameters from their local equilibrium values appear as thermodynamic variables and in which there is no relaxing structural specific heat. However, it is shown that such a relaxing specific

heat must appear in the thermodynamic treatment of thermal variables, which give the populations of internal vibrational-rotational states; and a new non-equilibrium thermodynamics of thermal relaxation, extending the earlier work of Meixner to include inertial effects, is formulated in such a way as to be consistent with this fact. The new formulation, which replaces a previous theory now shown to be valid only for structural variables, is based on the Pauli equation, generalized to include second-order time-derivatives. It is shown, on plausible assumptions about the molecular transition probabilities, that one can calculate all the rate constants and relaxation times introduced to describe inertial effects, as well as the thermodynamic forces.

Quantum-mechanical calculation of harmonic oscillator transition probabilities in a one-dimensional impulsive collision. K. E. Shuler and R. W. Zwanzig, *J. Chem. Phys.* **33**, No. 6, 1778-1784 (Dec. 1960).

The quantum mechanical vibrational transition probabilities $P_{i \rightarrow f}(\epsilon)$ for harmonic oscillators, undergoing impulsive hard sphere collisions along the line of centers with an incident atom with relative kinetic energy ϵ , have been computed by a machine (IBM-704) solution of the relevant Schrödinger equation. Curves for $P_{i \rightarrow f}(\epsilon)$ over a range of ϵ are presented for initial (i) and final (f) vibrational oscillator states $i, f=0, 1, 2$ and 3. It is shown that this model of an inelastic collision gives rise to appreciable vibrational transitions $v(i) \rightarrow v(f)$ with $|\Delta v| > 1$ (in addition to the $|\Delta v|=1$ transitions) in contrast to the Landau-Teller-Herzfeld adiabatic, 1st order perturbation treatment which permits only transitions for which $|\Delta v|=1$. The implication of this result is discussed in relation to the dissociation of diatomic molecules and to the adsorption of atoms on solids. Averaged transition probabilities $\bar{P}_{i \rightarrow f}(T)$ are computed for an incident beam of particles with a Maxwellian velocity distribution. It is pointed out that such averaged transition probabilities may give a misleading impression of the efficiency of translational-vibrational energy transfer if the $P_{i \rightarrow f}(\epsilon)$ show a resonance type of behavior, i.e. a strong order of magnitude dependence of $P_{i \rightarrow f}(\epsilon)$ on ϵ over a small interval of ϵ .

The vapor pressure of 20 °K equilibrium hydrogen. L. C. Weber, Jr., D. E. Diller, H. M. Roder, and R. D. Goodwin, *Cryogenics* **3**, 236-238 (June 1962).

The vapor pressure of 20 °K equilibrium hydrogen has been measured between the normal boiling point and the critical point. The data are represented analytically for purposes of smoothing and interpolation, and the results are compared with earlier work.

The densities of saturated liquid hydrogen. R. D. Goodwin, D. E. Diller, H. M. Roder, and L. A. Weber, *Cryogenics* **2**, 81-83 (Dec. 1961).

Densities of para hydrogen from 17° to 32 °K are obtained by extrapolating newly determined compressed liquid isotherms to corresponding vapor pressures. Results are combined with earlier data for the range 14° to 20 °K and compared with normal hydrogen by means of density-temperature relationships.

Reference tables for 40% iridium-60% rhodium versus iridium thermocouples. G. F. Blackburn and F. R. Caldwell, *Book, Temperature, Its Measurement and Control in Science and Industry* **3**, Pl. 2, 151-175 (Reinhold Publ. Corp., New York, N.Y., 1962).

In a program to establish reference tables for several alloys of iridium and rhodium against iridium, the work has been completed on 40% iridium-60% rhodium. Tables have been prepared giving emfs for temperatures in degrees Fahrenheit from 32 °F to 3800 °F and in degrees Celsius (centigrade) from 0 °C to 2100 °C, and temperatures in these units with emf in millivolts as the argument. They are based on the average emfs measured on eight thermocouples, made from three lots of wire obtained in 1955, 1958 and 1960.

Measurements at temperatures 32 °F to 2500 °F were made in a platinum-wound furnace of conventional design, using a Pt-10% Rh vs Pt thermocouple to measure temperature. From 1950 °F to 3800 °F (thus overlapping the upper end of the lower range), the furnace used was an iridium block

heated by electric induction. Blackbody conditions prevailed in the cavity in which the test thermocouple was inserted, and enabled measurement of the temperature with an optical pyrometer.

Rate of vaporization of refractory substances. J. J. Diamond, J. Efimenko, R. F. Hampson, and R. F. Walker, (*Proc. 4th Intern. Symp. Reactivity of Solids*), *Book, Reactivity of Solids*, ed., J. H. de Bower et al., p. 725 (Elsevier Publ. Co., Amsterdam, The Netherlands, 1961).

The more important factors affecting the rate of vaporization of solid systems are summarized. Techniques for measuring the rates of vaporization of refractory substances at temperatures in the 1600-3000 °C range are briefly described. The techniques pertain to measurements both in vacuum and in the presence of foreign gases. Some of the factors and the experimental techniques are illustrated by brief reference to studies of the vaporization of platinum and aluminum oxide.

Young's modulus of single crystal corundum from 77 °K to 850 °K. J. B. Wachtman, Jr., W. E. Tefft, and D. G. Lam, Jr., *Book, Mechanical Properties of Engineering Ceramics*, p. 221-223 (Interscience Publ. Inc., New York N.Y., 1961).

An equation is proposed to represent the temperature dependence of Young's modulus. This equation fits data on some corundum single crystals very well.

The dynamic compressibility of a rubber-sulfur vulcanizate and its relation to free volume. J. E. McKinney, H. V. Belcher, and R. S. Marvin, *Trans. Soc. Rheology* **4**, 347-362 (1960).

The dynamic bulk compliance of natural rubber=12% sulfur was measured for varying static pressure (0 to 1000 bar), temperature (-30 to +70 °C), and frequency (50 to 1000 cps). The data can be represented by reduced frequency or temperature plots, assuming viscosity is proportional to $\exp(1/\phi)$, a fractional free volume which is a linear function of temperature and pressure. The temperature-frequency reduction fits the "universal" WLF constants, and the temperature-pressure reduction term is practically the same as that found by Singh and Holle for polyisobutylene.

Absorption spectrum of CF₂ trapped in an argon matrix. A. M. Bass and D. E. Mann, *J. Chem. Phys.* **36**, No. 12, 3501-3502 (June 15, 1962).

The products of a discharge through a mixture of C₄F₈ and argon were condensed on a liquid-helium cooled surface. The absorption spectrum of the condensate shows a series of broad bands in the region 2300 to 2700 Å, and appears to correspond to the spectrum of the CF₂ radical.

Thermocouple materials. F. R. Caldwell, *Book, Temperature, Its Measurement and Control in Science and Industry* **3**, Pl. 2, 81-134 (Reinhold Publ. Corp., New York, N.Y., 1962).

Thermocouple materials are considered that are used primarily as immersion temperature sensors in the range from 0 °C up. Included are the conventional thermocouples that have survived since the beginnings of the art of thermoelectric temperature measurement, newer noble metal thermocouples, and thermocouples of refractory metals for use in the extreme range for immersed sensors. Because of the wide use and increasing popularity of ceramic-packed thermocouples in metal sheaths, they are included.

Limitations of the thermocouple wires are given as to range, stability, environment included atmosphere, magnitude of thermoelectric emf, and accuracy of commercially available materials of standard and extra quality. In addition, properties of the separate elements that are pertinent to the selection or use of thermocouples have been compiled.

In the case of the ceramic-packed thermocouples the following properties are presented: temperature range of the sheath, mechanical properties of the sheath, kinds of packed insulation, resistance between thermocouple wires and between wires and sheath, minimum bending radius of the packed stock, gas-tightness of the packed insulation, and types of measuring junctions available, i.e. grounded, ungrounded, bare, totally enclosed, stagnation mounting, etc.

Thermal radiation standards and measurements of the Radiometry Section at the National Bureau of Standards, A. G. Maki, (*Proc. conf. Radiative Transfer from Solid Materials, Boston, Mass., Dec. 12-13, 1960*), Book, *Radiative Transfer from Solid Materials*, ed., H. H. Blau, Jr., and H. Fischer, Sec. III, p. 135-141 (The Macmillan Co., New York, N.Y., 1962).

A discussion was given of two aspects of the work of the Radiometry Section at the National Bureau of Standards. Two standards of thermal radiation were described and the method of their calibration detailed. The latter half of this paper will include a description of some work currently being carried on with the aim of obtaining the normal spectral emissivity of gold, aluminum, and platinum in the infrared.

The ammonia beam maser as a standard of frequency, J. A. Barnes, D. W. Allan, and A. E. Wainwright, *IRE Trans. Instrumentation* **1-11**, 26-30 (June 1962).

It has been suggested that an error in tuning of the resonant cavity in an ammonia beam maser could be detected by observing a frequency shift of the maser with the application of a magnetic field. Following this suggestion, an oscillatory magnetic field was applied to the NBS double beam maser and a low noise phase demodulator was constructed to detect any phase modulation present in the maser signal. With this equipment, a servo-loop was completed to constantly control the tuning of the maser's resonant cavity. Not only did this result in the elimination of the most critical parameter of the maser's frequency dependence, but improvement of the frequency dependence upon other parameters was also observed.

The radiative formation and destruction of negative ions, L. M. Branscomb, *Proc. Fifth Intern. Conf. Ionization Phenomena in Gases, Munich, Germany, I, 1-18* (North Holland Publ. Co., Amsterdam, The Netherlands, 1961).

Recent advances in our understanding of the formation and destruction of negative ions by radiative processes are reviewed. Photodetachment spectra of four atomic ions, H^- , O^- , S^- and C^- have been studied experimentally in crossed beams. Agreement between theory and experiment on H^- is now excellent, except in the threshold region, where the theoretical values are about 10% low, presumably because of neglect of polarization effects. The C^- spectrum is consistent with that expected for a C^+S ground state, about 1.25 eV below the continuum, and a weakly bound metastable (presumably 2D) state which gives rise to a weak absorption on the infrared side of the 1.25 volt threshold. Metastable states of other atomic ions are predicted. Radiative attachment cross sections and rate coefficients are discussed. The difficulties in interpretation of molecular photodetachment spectra are emphasized.

Group theory and crystal field theory, C. M. Herzfeld and P. H. E. Meijer, *Book, Solid State Physics* **12**, 1-91 (Academic Press, Inc., New York, N.Y., 1961).

A survey of the principal group theoretical principles and methods used in crystal field theory.

Ferroelectricity in the compound $Bi_4Ti_3O_{12}$ P. H. Fang and C. R. Robbins, *Phys. Rev.* **126**, No. 3, 892 (May 1962).

Some ferroelectric and crystallographical properties of the compound $Bi_4Ti_3O_{12}$ are presented. The compound has a dielectric maximum at 685°C on increasing temperature and at 670°C on decreasing temperature. At these temperatures, temperatures, an endothermic peak and an exothermic peak, respectively, occur. Ferroelectricity was observed along the c axis of the single crystal of this compound.

Linear thermal expansion of aluminum oxide and thorium oxide from 100° to 1100° K, J. B. Wachtman, Jr., T. G. Scuderi, and G. W. Cleek, *J. Am. Ceram. Soc.* **45**, 310-323 (July 1962).

The linear thermal expansion of single crystal and polycrystalline aluminum oxide and polycrystalline thorium oxide was measured from 100° to 1100° K with an interferometric technique. For each substance the results are well described by Grüneisen's equation using a Nernst-Lindemann energy function.

Dielectric loss in "non-polar" polymers, A. J. Curtis, *J. Chem. Phys.* **36**, No. 12, 3500 (June 15, 1962).

Using published values of dipole moments of some saturated hydrocarbons, obtained from microwave spectroscopy, we have shown that the dielectric dispersion and loss observed in hydrocarbon polymers may be reasonably accounted for in large part in terms of asymmetry in structure. These calculations show that it is not necessary to propose impurities, oxidation products such as carbonyl groups, or catalyst fragments to account for much of the dielectric relaxation in these materials. These calculations also predict considerably lower dielectric loss in a completely linear polymer such as polyethylene than in a branched material such as polypropylene.

Mobilities of positive ions in argon, E. C. Beaty, *Proc. Conf. Ionization Phenomena in Gases, Aug. 28-Sept. 1, 1961, Munich, Germany*, p. 183 (North Holland Publ. Co., Amsterdam, The Netherlands, 1962).

Ions of three different mobilities are observed in the afterglow of a pulsed discharge in pure argon. The low field mobilities are: 1.535 ± 0.007 , 1.833 ± 0.008 , 2.60 ± 0.02 (cm^2 volt $^{-1}$ sec $^{-1}$). The lowest value is associated with A^+ . The identities of the other two are uncertain; however, semi-quantitative data are presented which indicate that each of the three are argon ions and are not the products of charge exchange with a contaminant. The ion of intermediate mobility was called A^+ by Munson and Tyndall, and A_2^+ by Hornbeck. The fastest ion was called A_2^+ by Biondi and Chanin.

Infrared spectrum of dideuteroacetylene (C_2D_2), E. D. Tidwell and E. K. Plyler, *J. Opt. Soc. Am.* **52**, No. 6, 656-664 (June 1962).

Thirty bands of C_2D_2 have been observed and measured between 1900 and 3300 cm^{-1} . Twenty of these have been resolved well enough to permit extraction of rotational constants. The Δ_2F values up to J_{35} for three Σ_g ground state bands were averaged and correlated with other data for a more reliable $B_0 = 0.84794 \pm 0.00005$ and $D_0 = 7.85 \times 10^{-7} \pm 0.4 \times 10^{-7}$ where the indicated uncertainties are the probable errors of the coefficients. Better resolution and higher J values have reduced the uncertainty derived from other sources. The l -type doubling constants for v_4^1 and v_5^1 have been obtained from resolved Q branches and split P and R branches; they are $q_4 = .00316$ cm^{-1} and $q_5 = .00314$ cm^{-1} .

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Journal of Research 66B (Math. and Math. Phys.), No. 4 (Oct.-Dec. 1962), 75 cents.

Reliability of a system in which spare parts deteriorate in storage. G. H. Weiss. (See above abstracts.)

Estimation of dispersion parameters. W. A. Thompson, Jr. Laguerre expansions for successive generations of a renewal process. G. H. Weiss. (See above abstracts.)

Bounds on ratios of means. G. T. Cargo and O. Shisha.

A model for the viscoelastic behavior of rubberlike polymers including entanglement effects. R. S. Marvin and H. Oser.

Black box maximization of circular coverage. C. T. Zahn, Jr.

An application of information theory to the analysis of contingency tables, with a table of $2n \ln n$, $n=1(1)10,000$.

S. Kullback, M. Kupperman, and H. H. Ku. See above abstracts.)

Journal of Research 67D (Radio Prop.), No. 1 (Jan.-Feb. 1963), 70 cents.

A lunar theory reasserted—a rebuttal. J. V. Evans.

Point-to-point communication on the moon. L. E. Vogler. HF communication during ionospheric storms. G. E. Hill.

Use of surface refractivity in the empirical prediction of total atmospheric refraction. W. R. Iliff and J. M. Holt. (See above abstracts.)

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- Titheridge coefficients for the polynomial method of deducing electron density profiles from ionograms. A. R. Long and J. O. Thomas. (See above abstracts.)
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