Lower Flammability Limits of Hydrogen Sulfide and Carbon Disulfide Mixtures

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The lower flammability limits for mixtures of hydrogen sulfide, carbon disulfide, and air have been measured for upward propagation at 25° C. and atmospheric pressure. Over most of the range of H_2S and CS_2 concentrations positive deviations from Le Chatelier's formula are obtained.

SMALL amounts of certain compounds, including H_2S, significantly raise the lower flammability limit (downward propagation) of CS_2–air mixtures over a small range of high CS_2 to H_2S ratios (*4*). No data in the literature, though, covers the full range of H_2S, CS_2, and air concentrations.

The purpose of this work was to investigate lower flammability limits (upward propagation) over the entire range of H_2S, CS_2, and air concentrations.

EXPERIMENTAL

The apparatus used in determining the lower limits of flammability for H_2S–CS_2–air mixtures (Figure 1), is a modified version of the Bureau of Mines apparatus (*1*). The H_2S was obtained from the Matheson Co., Inc. and used without further purification. The CS_2 used was reagent grade, redistilled under vacuum.

The desired mixture is tested in a borosilicate glass tube (*a*) 122 cm. long, 5.7-cm. O.D., with a wall thickness of 0.24 cm. Its lower end, which has a ground glass edge, is closed by a slightly lubricated flat surface of a large rubber stopper which contains two metal electrodes, with a 2-mm. spark gap, connected to a 5000-volt transformer.

In a typical experiment, the rubber stopper is held against the open end of the tube and the apparatus is evacuated by a vacuum pump through line (*b*), which contains a calcium chloride drying tube (*c*). Hydrogen sulfide is admitted by opening the needle valve on a standard H_2S lecture bottle (*d*). Pure CS_2 vapor is obtained as follows: The vapor space above liquid CS_2 in a flask is evacuated with the vacuum pump through stopcock (*e*), causing the CS_2 to boil and to purge the vapor space of all air. Stopcock (*e*) is then closed and the system is allowed to equilibrate so that the vapor space contains pure CS_2 at its vapor pressure at room temperature. CS_2 can then be admitted to the tube through stopcock (*f*). The desired amounts of H_2S and CS_2 are introduced by noting the pressure drop on the manometer (*g*) through a magnifying sight glass. For example, to test a mixture containing 4% H_2S the prevailing barometric pressure is multiplied by 0.04. This gives the pressure drop which corresponds to a 4% mixture.

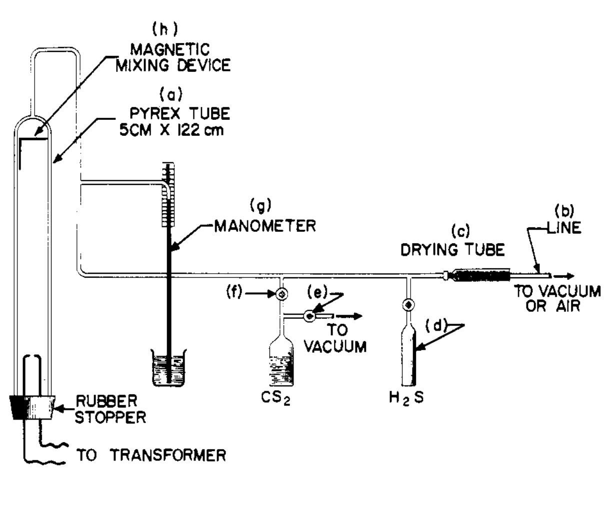

Figure 1. Experimental apparatus

The accuracy of this method was determined by taking gas samples after mixing and analyzing them by gas chromatography and infrared spectrophotometry. To determine the concentration of CS_2, two standard gases (1%, 0.5%) were obtained from the Matheson Co., Inc. and used to calculate the absorptivity coefficient of CS_2 at 2180 cm.$^{-1}$. A 1-meter infrared gas cell was incorporated into the experimental apparatus such that during mixing the gases would flow through it. The concentration of CS_2 in the experimental apparatus was calculated using Beer's Law and the previously determined absorptivity coefficient. The concentration of H_2S was determined by gas chromatography (*3*). Table I shows the results of these analyses and confirms the validity of the experimental method used to prepare the gas mixtures.

Table I. Gas Mixture Analysis

Introduced Into Apparatus, %	Found Experimentally, %
H_2S–4.05	3.97, 3.99
CS_2–0	...
H_2S–2.37	2.40, 2.43
CS_2–1.06	0.97, 1.00
H_2S–0	...
CS_2–0.92	0.85, 0.87

Table II. Lower Flammability Limits of H_2S and CS_2 in Air

Vol. % H_2S	Vol. % CS_2
4.00	0.00
3.85	0.07
3.64	0.17
3.44	0.22
3.33	0.30
3.42	0.44
3.40	0.53
3.32	0.63
3.15	0.75
2.45	1.00
1.44	1.33
0.86	1.52
0.62	1.60
0.40	1.67
0.20	1.63
0.13	1.60
0.06	1.55
0.00	1.43

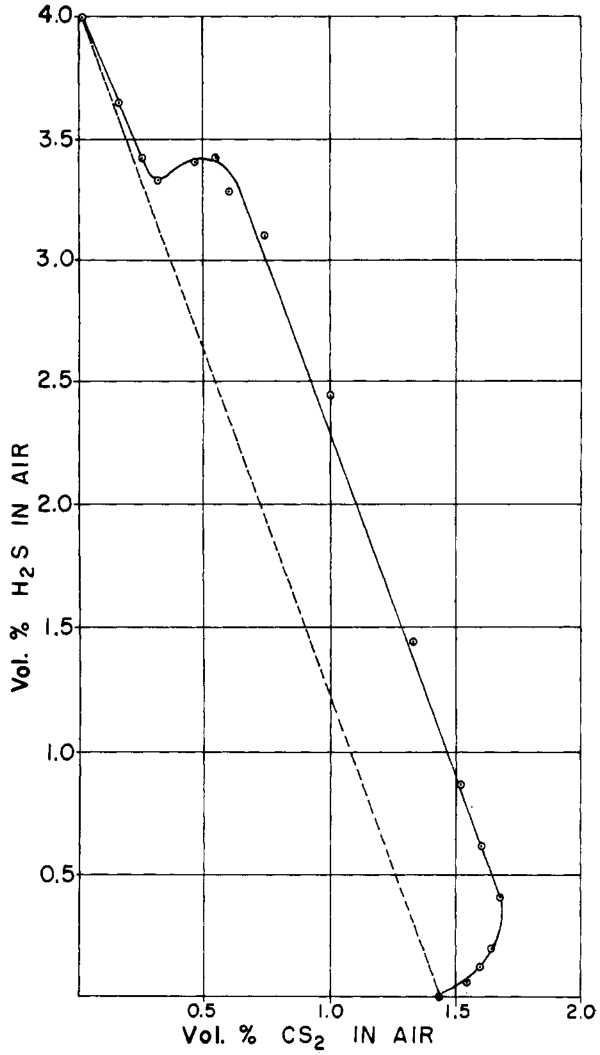

Figure 2. Lower flammability limits of H_2S and CS_2 in air

-------- Theoretical

———— Experimental

When the appropriate quantities of H_2S and CS_2 have been added, dry air is admitted through line (*b*), until about 2 or 3 inches of mercury vacuum remains in the system to hold the rubber stopper in place. The gases are then mixed by means of steel strip (*h*) which is moved up and down by a magnet run along the outside of the tube. The metal strip was run up and down the tube 25 to 30 times to ensure a good gas mixture. Immediately after mixing, line (*b*) was again opened to bring the system to atmospheric pressure so that the rubber stopper would loosen and drop about 2 inches to a supporting clamp. As soon as the stopper loosened, the transformer switch was thrown, giving a spark across the 2-mm. gap. A mixture was considered flammable if the flame traveled uniformly up 80% of the tube.

To find points on the experimental curve, perpendicular lines were drawn to the straight line predicted by Le Chatelier's formula, and points were tried along each line until a limit point on the experimental curve was found.

RESULTS AND DISCUSSION

The results of the room temperature determination of the lower flammability limits of H_2S-CS_2 mixtures in air are given in Table II and shown graphically in Figure 2. Also plotted in Figure 2 is the straight line relationship predicted by Le Chatelier's law (*2*); this straight line connects the two points representing the lower limits of pure H_2S in air and of pure CS_2 in air, which were also determined experimentally and in good agreement with values given in the literature (*5*).

The experimental curve shows a very interesting pattern in its deviation from Le Chatelier's formula. Starting at the point representing pure H_2S and progressively increasing the relative amount of CS_2, the experimental curve follows the theoretical prediction until a critical amount of CS_2 is reached. At this point, the limit curve suddenly increases to a point well above the theoretical line and remains a constant distance from the latter until the amount of H_2S present becomes very small, at which point it curves in to meet the theoretical line at the point representing pure CS_2. In the region of high CS_2 to H_2S ratios and from about 3.35 to 3.42% H_2S there are two lower limits. For 3.35% H_2S, CS_2 can be added until a flammable mixture is formed at 0.26% CS_2. If, however, more CS_2 is added the mixture will again become nonflammable at 0.38% CS_2 and remain so until 0.58% is reached. At the other end, if one starts with 1.5% CS_2 and adds H_2S, the mixture is flammable until 0.05% H_2S is reached. With further addition of H_2S the mixture remains nonflammable until 0.89% is reached.

CONCLUSION

Throughout most of the range of composition the lower limits of flammability from H_2S-CS_2 mixtures in air are higher than would be predicted from the individual limits for the two combustibles. Of particular interest is the observation that even trace amounts of H_2S present in CS_2 air mixtures substantially raise the lower flammability limit.

LITERATURE CITED

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