[CONTRIBUTION FROM PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Dependence of Methane–Oxygen Low-Pressure Explosion Limit on Nature of Reaction Vessel Surface[1]

BY H. H. STORCH[2]

Neumann and Serbinov[3] present some data on the lower limit for $CH_4 + O_2$ explosions in a quartz vessel. They find induction periods of the order of ten to twenty minutes in the temperature range 630–700°. From their data only two points could be obtained at constant temperature for the construction of a curve showing the position of the limits as a function of the O_2/CH_4 ratio. It was also considered possible that their lower limits might be in error due to the rather long induction period during which an appreciable quantity of the mixture may have reacted before explosion occurred. It was therefore decided to repeat and extend these experiments.[3]

It was found possible to reduce the induction period to about three minutes by treating the quartz vessel with concentrated aqueous hydrofluoric acid. Instead of visual observation of the explosions, the apparatus was arranged so that after a measured time interval the gas mixture could be expanded rapidly to about ten times its volume into an evacuated flask at room temperature, and then circulated through a bulb containing potash fragments before the final pressure (in a space of volume equal to that of the reaction vessel) was observed. From the final pressure datum and a knowledge of the relative volumes and temperatures involved, the percentage conversion of the methane–oxygen mixture to carbon dioxide and water was calculated. Upon plotting the percentage conversions (in equal time intervals) against the initial pressures, a very abrupt change in slope of the curve (such that it became practically parallel to the rate axis) was interpreted as an explosion. It was found that the lower-limit pressure changed by almost 100% depending upon the time of contact of the hydrofluoric acid (aqueous at room temperature) with the quartz. This is shown in Table I.

TABLE I

DEPENDENCE OF LOWER LIMIT ON TIME OF HYDROFLUORIC ACID TREATMENT

Temperature, °C.	642	642
Time of contact of HF, minutes	20	150
O_2/CH_4 ratio	2.0	2.0
Lower limit, mm.	33.5, 38.5	18.0, 22.0

The two data in the fourth row correspond to two separate treatments with hydrofluoric acid of equal contact times. It is apparent that even when the latter is kept constant, the limits are not reproducible within less than about 5 mm. The individual data using the same surface over a short period of time were reproducible to about 0.5 mm. If, however, as much as two days elapsed before a given limit was checked, the reproducibility was very poor. This is shown in Table II.

TABLE II

VARIATION OF LOWER LIMIT WITH AGE OF HYDROFLUORIC ACID TREATED QUARTZ SURFACE

Temp., °C.	O_2/CH_4 ratio	Age of surface, hours	Lower limit, mm. Hg
Surface No. 1, temperature 602°			
	2.4	24	27.0
	2.4	68	21.0
	2.4	108	22.0
	2.4	352	23.5
	2.0	112	27.0
	2.0	304	30.0
Surface No. 2			
642	2.4	24	10.0
642	2.0	27	10.0
602	2.4	40	26.0
602	2.4	64	23.0

The first two data for surface No. 2 indicate the same limit for both 2.0 and 2.4 O_2/CH_4 ratios. These are normally separated by about 5 mm. (see third and fifth rows for surface No. 1), hence surface No. 2 changed rapidly during the three hours necessary to obtain the second datum. From the experiments with surface No. 1 it is apparent that surface chain-breaking activity decreases during the first three days and then increases. Between about the tenth and twentieth days the change is rather slow, that is, <0.5 mm. At the end of this period only a very rapid rate of reaction is observed without any abrupt changes in slope of the pressure rate curves. Occasionally after prolonged evacuation (for about twenty-four hours) an explosion is ob-

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[2] Principal physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Neumann and Serbinov, *Physik. Z. der Sowjetunion*, **4**, 433 (1933).

tained, but immediately after it has occurred only the rapid reaction and no explosions are observed.

Three other types of surfaces were investigated, namely, (1) a silver mirror deposited on the inside of the quartz vessel; (2) the quartz surface rinsed with 1 *M* potassium chloride; (3) the quartz surface rinsed with 1 *M* aluminum nitrate.

In the temperature range 602–642°, and at pressures from 25 to 60 mm. of $1CH_4 + 2.4O_2$, the silver surface did not induce any explosions and the reaction rate was considerably slower than with hydrofluoric acid treated quartz. Under the same conditions of temperature and O_2/CH_4 ratio, the potassium chloride treated surface did not induce any explosions up to 110 mm. pressure, the reaction rate being greater than, but of the same order as, that in hydrofluoric acid-treated quartz. The alumina surface induced explosions in about the same pressure and temperature ranges as the hydrofluoric acid-treated quartz, but the surface aged very much more rapidly so that after twenty-four hours no explosions could be obtained.

It is perhaps of interest to note that with untreated quartz, Neumann and Serbinov[3] could obtain no explosions at temperatures below about 630°, whereas in the above experiments with hydrofluoric acid-treated quartz explosions were readily obtained at 602°. Another interesting fact is that neither the author nor Neumann and Serbinov[3] could obtain any explosions for O_2/CH_4 ratios appreciably less than 2.0.

It is apparent from the above experiments that any attempt to quantitatively check the diffusion theory[4] of low-pressure explosions of methane–oxygen mixtures must be preceded by the discovery of a surface which is accurately reproducible, and which does not age too rapidly.

The author has appreciated many helpful discussions with Dr. L. S. Kassel.

Summary

Experiments on the low-pressure explosion limits of methane–oxygen mixtures using various surfaces of reaction vessel show that these limiting pressures vary widely with the type of surface employed.

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[4] Kassel and Storch, This Journal, **57**, 672 (1935).

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[CONTRIBUTION FROM THE NONMETALLIC MINERALS EXPERIMENT STATION OF THE U. S. BUREAU OF MINES, DEPARTMENT OF THE INTERIOR, RUTGERS UNIVERSITY]

The Optical Properties of Certain Salts in the System $(NH_4)_2SO_4$–$CaSO_4$–H_2O[1]

BY ALTON GABRIEL[2]

During investigations of the system $(NH_4)_2SO_4$–$CaSO_4$–H_2O, D'Ans and Schreiner[3] and Bell and Taber[4] obtained certain double salts of ammonium sulfate and calcium sulfate. The optical properties of two of them, ammonium pentacalcium sulfate and ammonium dicalcium sulfate, apparently have never been determined, while Merz, Hardesty and Hendricks[5] have published some optical data on the third salt, ammonium calcium sulfate.

In a more recent investigation of this system Hill and Yanick[6] prepared the three salts mentioned above and kindly permitted the writer to make an optical examination of them. The results are recorded in the following section.

Optical Properties

The colorless monoclinic crystals of the double salt ammonium pentacalcium sulfate monohydrate ($(NH_4)_2SO_4 \cdot 5CaSO_4 \cdot H_2O$) correspond in habit to those of the potassium pentacalcium sulfate monohydrate described by Krüll and Vetter.[7] They are rather long unit prisms with base pinacoids. Pyramidal faces usually are developed. The crystals habitually lie on a prism face (110). (Fig. 1.)

As observed perpendicular to the plane 100, the prism shows a medium birefringence and parallel extinction. This view yields a nearly symmetrical interference figure of the obtuse bisectrix type. The plane of the optic axes lies

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[2] Assistant chemist-petrographer, Nonmetallic Minerals Experiment Station, U. S. Bureau of Mines, Rutgers University, New Brunswick, N. J.

[3] D'Ans and Schreiner, *Z. anorg. Chem.*, **62**, 139–144 (1909).

[4] Bell and Taber, *J. Phys. Chem.*, **11**, 492 (1907).

[5] Merz, Hardesty and Hendricks, This Journal, **55**, 3571 (1933).

[6] Hill and Yanick, *ibid.*, **57**, 645 (1935).

[7] Krüll and Vetter, *Z. Krist.*, **86**, 389 (1933).