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Studies on Inflammability of Hydrogen. I.

Influence of Ethyl Bromide on the Limits of Inflammability of Hydrogen-Air Mixtures.

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Abstract.

The mechanism of propagation of flame in a combustible gaseous mixture can be considered as that the molecules of the combustible gas immediately ahead of the flame front are activated by the collision with the swiftly moving molecules in the flame, and the activated molecules thus formed react chemically with oxygen, resulting in combustion and the propagation of the flame. The flame propagated by the upper limit mixture of hydrogen (the mixture of 71.2% of hydrogen and 28.8% of air) is calculated by the authors to have the temperature of 1090°C. Therefore, when the temperature of flame reaches to 1090°C., the hydrogen molecules in the layer immediately ahead ot the flame front are activated by the mechanism stated, at the rate just sufficient to cause the propagation of the flame.

In the presence of a small amount of ethyl bromide in hydrogen-air mixture, the energy of the hydrogen molecules which are activated or being activated is transmitted to the molecules of ethyl bromide on colliding with each other, the former returning to the inactive molecules. Moreover, the swiftly moving molecules in the flame, to which the activation of hydrogen is due, may also lose their energy on colliding with the bromide molecules. Thus the number of activated molecules of hydrogen is reduced markedly, and consequently the higher flame temperature is required for the propagation of flame, resulting in the lowering of the upper limit of inflammability of hydrogen. The more bromide added, the higher flame temperature is necessary to propagate flame, until the flame temperature of 1550°C. is reached, where the bromide is also activated to burn and its extinctive effect on the hydrogen flame is stopped.

The experimental results are tablated and fully discussed. It was found that the range of inflammability of hydrogen containing 1.3% of ethyl bromide is 9–51%, about 2/3 of that of hydrogen and the density of the mixture is 0.113 (the density of air is taken as unity), which is little larger than that of hydrogen (H=0.069), but smaller than of helium (He=0.138). Thus it seems possible to make hydrogen less dangerous without much increasing its density for the aeronautic purpose.

Introduction.

In an investigation[1] of the effect of ethyl bromide on the limits of inflammability of ethyl ether and hydrocarbon, it has been shown that the theoretical flame propagation temperature of the bromide is higher than those of ethyl ether and hydrocarbon, and that, when mixed in the limit mixtures of the latter combustibles, the bromide prevents the combustion of ethyl ether and hydrocarbon, resulting in narrowing the range of inflammability of the combustibles, until a flame temperature is reached, at which the bromide is also markedly activated to burn and its preventing action toward the combustion of ethyl ether and hydrocarbon is choked.

The theoretical flame propagation temperatures of hydrogen calculated from the lower and the upper limits of inflammability in air are, according to A. G. White[2], 765° and 875°C. respectively. These are considerably below 1450°C. of the theoretical

(1) Y. Nagai, Jour. Soc. Chem. Ind., Japan, **92**, 451, 1926.
(2) A. G. White, Jour. Chem. Soc., 2387, 1924.

flame propagation temperature of ethyl ether. If, therefore, the halide prevents also the combustion of hydrogen, the range of inflammability of the latter must be narrowed more exceedingly by the addition of the halide than in the case of ethyl ether and the hydrocarbon. The experimental results of the present research show that this reasoning holds good and, by the addition of as small as 0.7% of ethyl bromide, the range of inflammability of hydrogen is narrowed from 8.89—71.2% of hydrogen to 8—52%. Such remarkable extinctive effect of the bromide on the hydrogen flames is important for the usage of hydrogen in the balloons and the airships and for other industrial purposes. Work is now in progress on the action of various classes of compounds upon the limits of inflammability of hydrogen.

Experimental.

Hydrogen used in the present research was obtained by the electrolysis of water and dehydrated with potassium hydroxide. It was about 99% pure.

Ethyl bromide was highly purified by the treatment with concentrated sulphuric acid at 0°C., followed by washing with water. It was dehydrated over calcium chloride and fractionated with Hempel still-head, the fraction collected boiling within 0.1° of the boiling point of the pure bromide. It had d_4^{15} of 1.4700.

The apparatus and the method of experiments are the same as in the previous investigation(1), all limits being determined in a glass tube of 5 cm. in diameter and 65 cm. long, in which the combustible mixtures were ignited from the top by electric spark, both ends of the tube being opened before the ignition. The temperature of the gaseous mixtures before the ignition were $17 \pm 3° C$,

The experimental results are shown in the following table:—

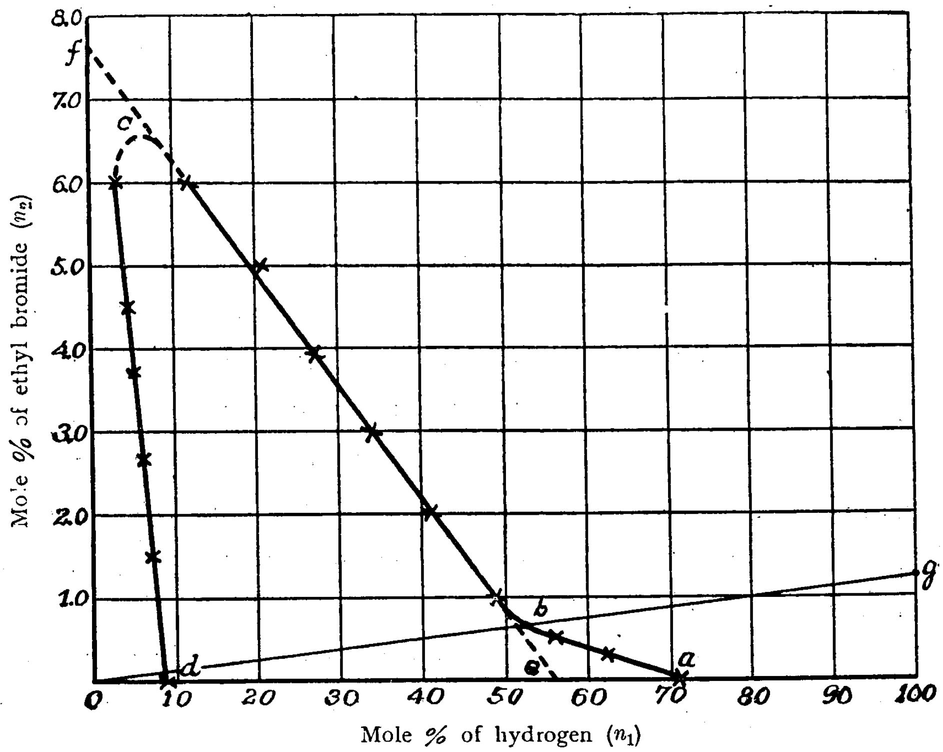
(1) Y. Tanaka, Y. Nagai and K. Akiyama, this report, **21**, 235, 1927.

Mole per cent. of ethyl bromide in limit mixtures.	Mole per cent. of hydrogen in limit mixtures.	
	Lower limit.	Upper limit.
0.00	8.89	71.2
0.25	—	62
0.50	—	56
1.00	—	49
1.50	7.2	—
2.00	—	41
2.70	6.2	—
3.00	—	34
3.75	5.3	—
3.90	—	27
4.50	4.7	—
5.00	—	21
6.00	3.5	12
6.6	Flame could not propagate in mixtures containing 4.5, 5.5 and 6.1% of hydrogen.	

These results are shown diagrammatically in the following figure.

The curves *abc* and *dc* represent the upper and lower limits respectively. Consequently an area *abcd* represent the compositions of inflammable mixtures of hydrogen and air containing various amount of ethyl bromide.

The addition of a small amount of ethyl bromide to the mixtures of hydrogen and air results in exceedingly narrowing the range of inflammability of the mixture, the upper limits being more remarkably effected than the lower limits.



It is also interest to note that the upper limit is lowered markedly along a straight line *ab* up to the content of about 0.7 per cent. of ethyl bromide in limit mixture, beyond which more slowly along another straight line *bc*. It will be noted that Le Chatelier's rule holds well in the upper limit mixtures containing more than about 0.7 per cent. of ethyl bromide, if the upper limits of hydrogen (n_1) and ethyl bromide (n_2) are taken as 56.0 and 7.60 per cent. respectively, as shown in the following equation:

$$\frac{n_1}{56.0}+\frac{n_2}{7.60}=1$$

The point *g* represents a gaseous mixture of 1.3% of ethyl bromide and 98.7% of hydrogen. This gaseous mixture has the range of inflammability of 9—51%, which is about two thirds of that of hydrogen, and its density is 0.113 (density of air is taken as unity), which is little larger than that of hydrogen (density of hydrogen is 0.069) but smaller than that of helium (density of helium is 0.138). Thus, by the addition of a small amount of ethyl bromide, hydrogen becomes less dangerous without much increasing its density.

Discussion of results.

The mechanism of propagation of flame in a combustible gaseous mixture can be considered as such that the molecules of the combustible gas immediately ahead of the flame front are activated by the collision with the swiftly moving molecules in the flame, and the activated molecules thus formed react chemically with oxygen, resulting in combustion and the propagation of the flame.

The flame propagated by the upper limit mixture of hydrogen (the mixture of 71.2% of hydrogen and 28.8% of air) is calculated to have the temperature of 1090°*C*. In this calculation, the values for specific heat at constant pressure, obtained by Holborn and Henning[1], were used for nitrogen, carbon dioxide and steam. The molecular value for oxygen was taken to be equal to that of nitrogen. The purity of hydrogen was assumed, in the calculation, to be 99 per cent., the balance being oxygen. Heat losses from the flame were neglected. Thus, it will be seen that when the temperature of flame reaches to 1090° *C.*, the hydrogen molecules in the layer immediately ahead of the flame front are activated by the mechanism stated at the rate just sufficient to cause the propagation of the flame. In the presence of a small amount of ethyl bromide in hydrogen-air mixture, the activation energy of the molecules which are activated or being activated, is transmitted to the molecules of ethyl bromide on colliding with each other, the former returning to the inactive molecules. Moreover, the swiftly

(1) Holborn and Henning, Ann. Physique, **18**, 739, 1905; **23**, 809, 1907.

moving molecules in the flame, to which the activation of hydrogen is due, may also lose their energy on colliding with the bromide molecules. Thus the number of activated molecules of hydrogen is reduced markedly by the addition of the bromide and consequently the higher flame temperature is required for the propagation of flame, resulting in the lowering of the upper limit of inflammability of hydrogen. Thus the upper limit of hydrogen is lowered along a straight line *ab* by the addition of the bromide. But when the point *b* is reached, corresponding to the addition of about 0.7 per cent. of the bromide, the flame temperature becomes high enough to activate markedly the molecules of the bromide for the combustion, and the extinctive effect of the latter compound on the hydrogen flame is consequently choked at this point. Therefore, for the propagation of the flame in the hydrogen-air mixture containing more than 0.7 per cent. of the bromide, it is only necessary that the flame has the temperature, at which the bromide molecules are activated. In other words, hydrogen in these mixtures has the theoretical flame propagation temperature(1) same as that of the bromide. Therefore Le Chatelier's rule must be closely followed by these mixtures and so the upper limit of hydrogen is lowered along a straight line *bc*. The flame temperature of the mixtures represented by the straight line *bc*, and so also that of the mixture represented by the point *e*, an intersecting point of the straight line *bc* and the absissa, must be the theoretical flame propagation temperature of ethyl bromide, which is calculated by the authors from the composition of the mixture *e* (56.0% of hydrogen and 44.0% of air) to be 1550° *C*.

The point *f* represents a mixture of 7.60% of ethyl bromide and 92.4% of air. This is the "imaginary upper limit of inflam-

(1) The theoretical flame propagation temperature is the calculated temperature of flame, which is required to activate the combustible molecules at the rate just sufficient to cause the propagation of flame.

mability" of ethyl bromide in the hydrogen flames.

Summary.

(1) The influence of ethyl bromide on the limits of inflammability of hydrogen in air was investigated.

(2) By the addition of a small amount of ethyl bromide, the upper limit of hydrogen is lowered markedly up to the content of about 0.7 per cent. of the bromide, beyond which more slowly along a straight line. The lower limit of inflammability of hydrogen is also lowered very slowly by the addition of the bromide. These results are discussed and a theory explaining the extinctive effect of the bromide is described.

(3) The theoretical flame temperature necessary to activate the molecules of ethyl bromide to burn in the hydrogen flames is calculated and found to be 1550°C.

(4) In the upper limit mixtures containing more than about 0.7 per cent. of ethyl bromide, hydrogen behaves as if it had the theoretical flame propagation temperature of 1550°C. and consequently Le Chatelier's rule is closely followed by these mixtures.

(5) The "imaginary upper limit of inflammability" of ethyl bromide in the hydrogen flames is 7.60 per cent.

(6) The density of hydrogen containing 1.3 per cent. of ethyl bromide (density of air is taken as unity) is 0.113 and is smaller than that of helium. The range of inflammability of this mixture is 9—51 per cent., about two thirds of that of hydrogen.

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抄　　錄

水素の燃燒に關する研究（第一報）

水素の燃燒範圍に對する臭化エチルの作用

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氣球及び航空船氣囊用の氣體として現今使用せらるゝものは唯水素あるのみである。不燃性の故を以てヘリウムが以上の目的に最も好適するものと考へられては居るが、其の自然界に於ける生產が少量で且偏在し、隨時到る所に捕集採製することが出來ない憾みがある。是れ今日猶水素が殆ど唯一の氣體として以上の目的に使用せらるる所以である。然るに水素の大なる缺點は極めて燃燒性に富むことである。氣球及び航空船に於て屢々起る災害は是れに基くのである。本研究者は水素の燃燒を防止又は抑制せんと企て、之れは水素の燃燒範圍を縮小することに依て達し得可しと考へた。而して水素に或る適當なる物質を混和し、其の比重を著しく增加せしめずして水素の燃燒の範圍を著しく縮小することを得ば其の目的を達するに近しと考へた。本研究第一報は其の階梯として水素の燃燒研究より水素に臭化エチルを微量に加へたる場合の燃燒範圍に就て研究した結果である。本研究に依り水素に微量の臭化エチルを加へたるものは、其の比重を著しく增加せずして而かも能く其の燃燒範圍は著しく縮小せらるゝことを初めて認むることを得た。以上の現象の基く理論は次の通りである。

水素及び空氣混合氣體中に火焰の傳播するや、火焰中に於て大なる運動エネルギーを有する分子が火焰前面に於ける未活性の水素分子に衝突して之れを活性化せしめ、活性化せられたる水素分子は酸素と衝突して燃燒する。斯くして火焰は傳播するのである。然るに若し水素空氣混合氣體中に臭化エチルの存在する場合には、此の火焰中及び火焰前面の活性化せられたる、又は活性化せられつゝある分子のエネルギーが臭化

ェチルの分子に傳へられ、且又大なる運動エネルギーを有する火焔中の分子も臭化エチル分子と所謂第二種の衝突をして其のエネルギーを失ひ從つて水素分子を活性化する能力を失ひ結局水素の活性分子の數が減少し、火焔の温度を水素のみの場合よりも一層高めなければ火焔の傳播は困難となる。即ち火焔の傳播する爲めには高極限は低下しなければならぬ。而して臭化エチルの添加量の増加に從ひ火焔の傳播に必要なる理論火焔温度は高くなり、即ち火焔傳播高極限は益々低下するのであるが、此の状態は終に臭化エチル分子自身が著しく活性化せらる可き温度に到て止むのである。本研究に於ては水素の理論火焔傳播温度並に水素火焔中に於ける臭化エチルの理論火焔傳播温度をも求めて之れを論じてある。

本研究結果の一例を示せば、水素に1.3%の臭化エチルを加へたものは空氣の比重を1として其の比重が0.113でヘリウムの比重(0.138)よりも小で、而かも其の燃燒範圍は水素の9—71%に對して9—51%であるから、燃燒範圍は約$\frac{2}{3}$に縮小された譯で從て爆發の危險性は著しく減少し得ると考へる。