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Studies on Inflammability of Hydrogen. IV.  
Influence of Hydrogen Selenide on the Limits  
of Inflammability of Hydrogen-Air Mixtures.

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**Abstract.**

The effect of hydrogen selenide on the upper limit of inflammability of hydrogen is very similar to that of di-ethyl selenide, except that the lowering effect of the former on the upper limit of inflammability of hydrogen is less than that of the latter.

It is noteworthy that, by the addition of 4 % of hydrogen selenide, the lower limit of inflammability of hydrogen has been raised up to 12 % of hydrogen. This is due to small heat of combustion of hydrogen selenide.

The flame temperature necessary for the activation of hydrogen selenide is  $1750^{\circ}\text{C}$ ., which is equal to that obtained for di-ethyl selenide. But the amount of these selenides required to raise the theoretical flame propagation temperature of hydrogen from the initial value of  $1090^{\circ}\text{C}$ . to  $1750^{\circ}\text{C}$ ., are not the same, namely about 1 % in the case of di-ethyl selenide and about 2 % in hydrogen selenide; that is to say, the amount required depends on the nature of the positive atoms or atom groups combining with the selenium atom. This may be ascribed to the difference in the mean cross sectional

areas of the molecules of the selenides and so to the difference in the probabilities that the molecules of the selenides will collide with the hydrogen molecules activated or being activated.

As the calculated flame propagation temperature of hydrogen sulphide is  $1040^{\circ}\text{C}$ ., it may be also concluded that the flame temperature, at which the molecules of a substance begin to be activated, is a function of the nature of the negative atom in the molecules and is independent of the nature of the positive atom or atom groups in the molecules.

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### Introduction.

As was shown earlier<sup>(1)</sup>, the range of inflammability of hydrogen is narrowed markedly by the addition of di-ethyl selenide, the upper limit being lowered very remarkably. The lower limit is also lowered, though in a slight degree, by the addition of the selenide. This lowering of the lower limit must be ascribed to the large molecular heat of combustion of the selenide, which also burn in the flame of the lower limit mixtures of hydrogen and air. It may, therefore, be expected that if a compound, which has the remarkable [extinctive effect on the hydrogen flame, and whose molecular heat of combustion is very small, is added to hydrogen, the lower limit of inflammability of hydrogen may be raised. The present research has been undertaken to test this point, expecting hydrogen selenide as one of such compounds.

### Experimental.

Hydrogen used in the present research was the same as that used in the first report of this series of the studies<sup>(2)</sup>.

Hydrogen selenide was prepared by the action of aluminium selenide on air-free distilled water. Aluminium selenide was made by mixing 10 parts of metallic aluminium and 45 parts of

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(1) Y. Tanaka and Y. Nagai this report, 24, 265, 1927.

(2) Y. Tanaka and Y. Nagai, this report, 22, 249, 1927.

selenium and heating the mixture in a small flask of pyrex glass. From a small separating funnel B, in Fig. I., distilled water was poured on aluminium selenide in a small flask A. Hydrogen selenide

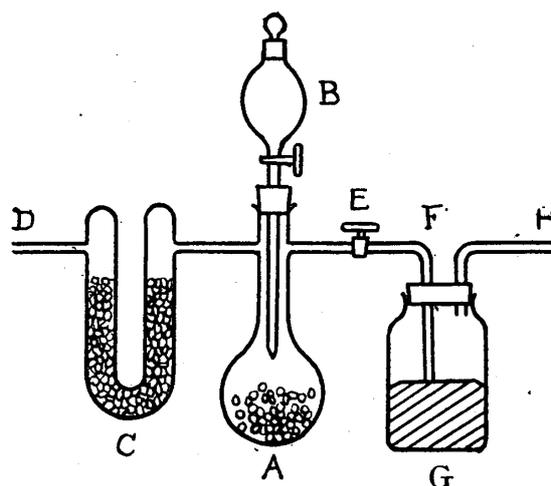


Fig. 1.

generated in A was introduced to the bottle, in which required gaseous mixtures were made, passing through a U-tube C containing calcium chloride. The tube F was dipped into mercury in the bottle G, the excess of hydrogen selenide in the bottle A escaping through the tube H. Every time before hydrogen selenide is prepared, the bottle A and the U-tube C were evacuated, cock E being kept closed, and a few drops of water were poured on aluminium selenide, some hydrogen selenide being generated, which was then pumped out of A and C. These operations were repeated thrice, in order to remove traces of air and the decomposition products of hydrogen selenide, which might be present in A and C. Thus pure and freshly prepared hydrogen selenide was used in each experiment.

The other parts of the apparatus and the method of experiment were the same as in the previous investigation<sup>(1)</sup>, except that the

(1) Y. Tanaka and Y. Nagai, this report, 22, 249, 1927.

both ends of the firing tube were kept closed when electric spark was passed for the ignition of the gas, with the purpose of avoiding poisonous gases escaping into the room. All limits were determined in a glass tube of 5 cm. in diameter and 65 cm. long, in which gaseous mixtures were ignited from the top by electric spark.

The temperatures of the gaseous mixtures before ignition were  $23 \pm 3^\circ\text{C}$ .

The experimental results are shown in the following table:—

Mole per cent. of hydrogen selenide in limit-mixtures.	Mole per cent. of hydrogen in limit-mixtures.	
	Lower limit.	Upper limit.
0	8.8	71
1.00	10.5	55
2.00	11.0	44
3.00	11.5	41
4.00	12.0	38.5
5.0	—	36.5
6.0	11.0	—

These results are shown graphically in Fig. II, where the curves *abc* and *def* give the upper and the lower limits of inflammability respectively. From the figure it can be seen that the influence of hydrogen selenide on the upper limit of inflammability of hydrogen is very similar to that of di-ethyl selenide, described in the previous paper, except that the lowering effect of hydrogen selenide on the upper limit of hydrogen is less than that of di-ethyl selenide, and consequently the same discussion can also be given in this case.

The equation of the straight line *bc* is

$$\frac{n_1}{49} + \frac{n_2}{19} = 1,$$

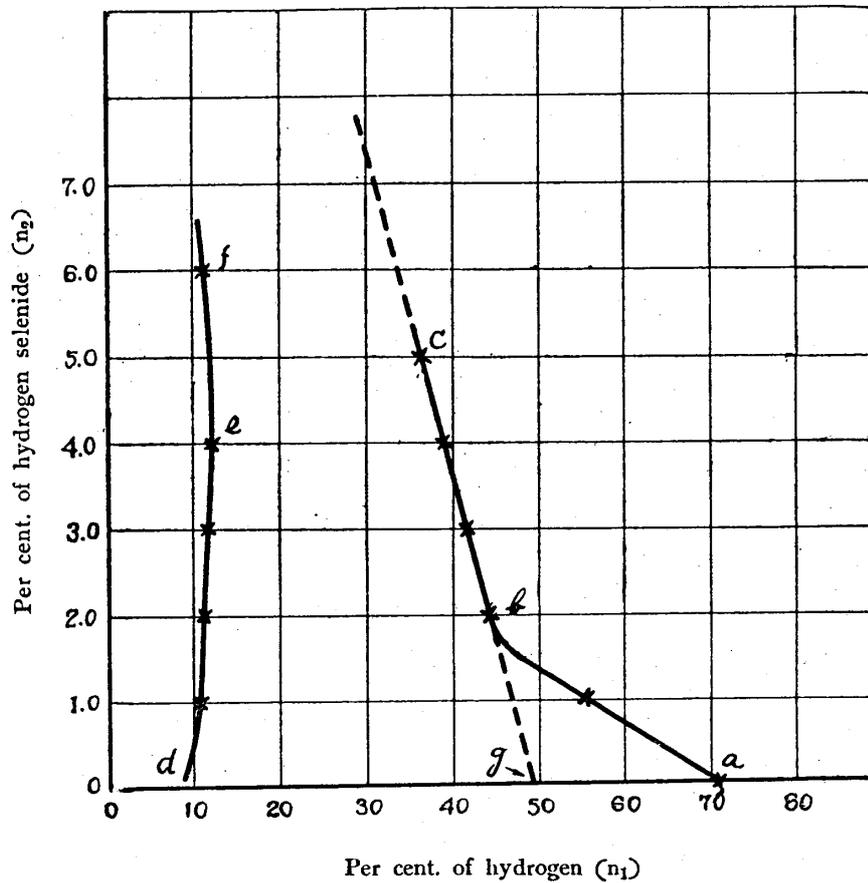


Fig. II.

where  $n_1$  is the concentration of hydrogen in per cent. and  $n_2$  is that of hydrogen selenide in the limit-mixtures. Therefore, if the upper limits of hydrogen and hydrogen selenide are taken as 49 per cent. and 19 per cent., respectively, Le Chatelier's rule holds well in the upper limit mixtures containing more than about two per cent. of hydrogen selenide.

By the addition of four per cent. of hydrogen selenide, the lower limit of inflammability of hydrogen is raised up to 12 per cent. of hydrogen, as expected. But further addition of the selenide lowers the limit slightly.

### Discussion of results.

The above experimental results can be explained along the same line of reasoning as those given in the previous reports.<sup>(1)</sup> Namely the theoretical flame temperature, at which the molecules of hydrogen selenide begin to be activated to burn, is  $1750^{\circ}\text{C}$ ., as mentioned below. If the small amount of the compound is added to the limit-mixtures of hydrogen, the energy of activation of the molecules of hydrogen activated or being activated is transmitted to the molecules of the selenide and thus the combustion of hydrogen is retarded, resulting the lowering the upper limit and the rising of the lower limit of inflammability of hydrogen. The lowering of the lower limit by the addition of di-ethyl selenide seems to be due to the comparatively large molecular heat of combustion of the latter compound, causing the high temperature of the flame propagated by the lower limit-mixture. It is therefore highly probable that the rising of the lower limit is due to small heat of combustion of hydrogen selenide added.

In the upper limit-mixtures containing more than two per cent. of hydrogen selenide, hydrogen behaves as if it had the same theoretical flame propagation temperature of  $1750^{\circ}\text{C}$ . as the selenide, and consequently Le Chatelier's rule holds well in those mixtures, the upper limit of hydrogen lowering along a straight line *bc*. In the lower limit mixtures containing a large amount of the selenide, the heat generated by the combustion of the latter compound becomes large and so the lower limit of hydrogen lowers along a curve *ef*.

The flame temperature of the mixtures represented by the straight line *bc* is the temperature necessary to activate the molecules of hydrogen selenide. Calculating the flame temperature of

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(1) Y. Tanaka and Y. Nagai, this report, **22**, 249, 1927; **23**, 259, 1927; **24**, 265, 1927.

the mixture represented by  $g$  (the mixture of 49 per cent. of hydrogen and 51 per cent. of air), which is the intersecting point of the straight line  $bc$  and the abscissa, the authors obtained the value of  $1750^{\circ}\text{C}$ . Therefore the calculated flame temperature necessary for the activation of the hydrogen selenide is  $1750^{\circ}\text{C}$ ., which is equal to that obtained for di-ethyl selenide<sup>(1)</sup>. Hydrogen sulphide begins to be activated at the calculated flame temperature of  $1040^{\circ}\text{C}$ <sup>(2)</sup>. It may, therefore, be concluded that the flame temperature, at which the molecules of a substance begin to be activated, is a function of the nature of the negative atom in the molecule of the substance and is independent of the nature of the positive atom or atom groups in the molecule.

Although both of the selenides have thus the same theoretical flame propagation temperature, the amount of them required to raise the theoretical flame propagation temperature of hydrogen from the initial value of  $1090^{\circ}\text{C}$ . to  $1750^{\circ}\text{C}$ ., is not the same, namely about one per cent. in the case of di-ethyl selenide and about two per cent. in hydrogen selenide; that is to say, the amount required depends on the nature of the positive atoms or atom groups combining with the selenium atom. This may be ascribed to the difference in the mean cross sectional areas of the selenides and so to the difference in the probabilities that the molecules of the selenides will collide with the hydrogen molecules activated or being activated.

### Summary.

- (1) The effect of hydrogen selenide on the limits of inflammability of hydrogen was investigated and the results was discussed.
- (2) By the addition of a small amount of hydrogen selenide

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(1) Y. Tanaka and Y. Nagai, this report, **24**, 265, 1927.

(2) A. G. White, Journ. Chem. Soc., 2392, 1924.

the upper limit of hydrogen is lowered markedly up to the content of about two per cent. of the selenide, beyond which more slowly along a straight line. Lower limit of hydrogen is raised to 12 per cent. by the addition of four per cent. of the selenide, beyond which it is lowered slightly. These results can be explained along the same line of reasoning as that given for the extinctive effect of the di-ethyl selenide and the ethyl bromide described in the previous reports.

(3) The theoretical flame temperature necessary to activate the molecules of hydrogen selenide to burn is  $1750^{\circ}\text{C}$ ., which is the same as that obtained for di-ethyl selenide and is higher than that obtained for hydrogen sulphide. From this it seems that the flame temperature necessary for the activation is a function of the nature of the negative atom in the molecule and is independent of the nature of the positive atoms or atom groups in the molecule.

(4) Although the hydrogen selenide and the di-ethyl selenide have the same theoretical flame propagation temperature, the amount of them, required to raise the theoretical flame propagation temperature of hydrogen from the initial value of  $1090^{\circ}\text{C}$ . to  $1750^{\circ}\text{C}$ ., is not the same, namely about one per cent. in the case of di-ethyl selenide and about two per cent. in the case of hydrogen selenide. That is to say the amount required depends on the nature of the positive atoms or atom groups combining with the selenium atom. This may be ascribed to the difference in the mean cross sectional areas of the selenides and so to the difference in the probabilities that the molecules of the selenides will collide with the hydrogen molecules activated or being activated.

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## 抄 錄

### 水素の燃焼に関する研究 (第四報) 水素の燃焼範圍に對するセレン化水素の作用

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本報は水素の燃焼範圍を縮小せしむる研究の繼續として、セレン化水素の作用に関する研究である。前報迄に發見した抑制劑は、何れも水素燃焼の高極限を低下せしむること極めて著しいのであるが、低極限を高めることが出来ない。殊に二エチルセレンは水素の高極限を極めて顯著に低下せしめるに拘らず、低極限は殆ど之れを高めることが出来ない。其の理由として著者等は、水素の特殊の燃焼の爲めに二エチルセレンも亦燃焼し、其の燃焼熱に依て理論火焰温度を高めるが爲めであることを考へた。此に於て、二エチルセレンと其の化學的構造の類似したもので、而かも燃焼熱の小なるセレン化水素を撰び、之れが水素燃焼の範圍に對して、果して如何なる影響を呈す可きかを研究したのである。本報告は其の結果である。

之れに依るとセレン化水素は、水素燃焼の高極限を著しく低下せしむると同時に、豫想の通り其の低極限を上昇するのである。低極限を上昇せしめた新事實は、本實驗が最初であることに殊に興味を感ずる。

猶セレン化水素の理論火焰傳播温度は  $1750^{\circ}\text{C}$ . で、二エチルセレンの夫れと同じく、硫化水素の夫れよりも著しく高い。依て斯の如き物質が燃焼す可く活性化せられる温度は、負原子の性質に依て定り正原子又は正原子團の性質には無關係である様に思はれる。又二エチルセレンの1%は、水素の理論火焰傳播温度を  $1090^{\circ}\text{C}$ . から  $1750^{\circ}\text{C}$ . まで高むるに充分であるが、セレン化水素は2%で同様の効果を示す。即ち水素の高極限低下の効率は、決して混合氣體中のセレン原子の數のみに依て定まるも

のでは無く、之れと結合せる他の原子又は原子團の性質が關係することが判る。是れはセレン化物分子の平均斷面積の大小に依り、水素の活性分子及び活性化されつゝある分子等が、之れと衝突する Probability に大小を生ずるが爲めであると思はれる。

セレン化水素は水素の燃焼防止劑として實用上には不適當と考へられる多くの點がある。例へば有毒で且稍不安定であるが如き性質は夫れである。従て恐らく實用上の價値は無いが、本研究の結果は更に優良なる水素爆發防止劑の探究に新しき指針を示したものである。