amalgams were colloidal, as suggested by Paranjpe and Joshi,[11] one would not expect such reproducibility.

Summary

1. Galvanic cells have been studied in which the reaction is the transfer of potassium from an amalgam of higher concentration to one of lower concentration. The e. m. f. of such cells has been determined as a function of temperature and concentration of the amalgam.
2. The partial molal free energy, heat and entropy of the potassium and mercury have been calculated.
3. The solubility of potassium in mercury has been determined from 0–50°.
4. The free energy and heat of formation of the compound KHg_{12} and the heat of solution of this compound have been determined.
5. The significance of these data is discussed.

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[11] Paranjpe and Joshi, *J. Phys. Chem.*, **36**, 2474 (1932); Bent, *ibid.*, **37**, 431 (1933).

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Kinetics of Gas Explosions. IV. Ozone Explosions Induced by Hydrogen[1,2]

BY BERNARD LEWIS[3]

Introduction

The influence of hydrogen on the thermal decomposition of ozone was studied by Belton, Griffith and McKeown.[4] They found that two reactions occurred simultaneously, the decomposition of ozone and the formation of water. The addition of hydrogen to ozone increased the specific rate of ozone decomposition. For example, their bimolecular velocity constant of ozone decomposition increased sixfold when 156 mm. of hydrogen was added to a mixture of 70 mm. of ozone and 650 mm. of oxygen. The velocity constant for the formation of water by the assumed reaction $H_2 + O_3 = H_2O + O_2$ increased less rapidly, it being only threefold on increasing the hydrogen pressure from 33 mm. to 156 mm. in a similar mixture. The amount of hydrogen converted to water was small in comparison with the ozone decomposed. The available data published by these authors indicate that the percentage of hydrogen converted (measured when most of the ozone had decomposed) depends much more on the ozone concentration than on the hydrogen concentration. It increases

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Parts I, II, III, with W. Feitknecht, THIS JOURNAL, **53**, 2910 (1931); **54**, 1784, 3185 (1932).

[3] Physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[4] Belton, Griffith and McKeown, *J. Chem. Soc.*, **128**, 3153 (1926).

a little with increasing initial ozone concentration. The effect of increasing the temperature is to increase the percentage conversion of hydrogen. Thus at 78° it amounted to about 7% in a mixture 38 mm. of ozone, 230 mm. of hydrogen, 450 mm. of oxygen, while at 100° it was about 9.5% in a mixture 35 mm. of ozone, 145 mm. of hydrogen and 500 mm. of oxygen. Our own results agree reasonably well with these values, the percentage conversion of hydrogen being about 7 to 8% in a mixture 50 mm. of ozone, 90 mm. of hydrogen and about 3 mm. of oxygen at 85°.

It is the purpose of this paper to present some rather striking results which indicate that the reaction mechanism of the process is much more complicated than Belton, Griffith and McKeown assumed, that the enhanced rate of ozone decomposition in the presence of hydrogen is due to the initiation of a chain reaction through the medium of hydrogen atoms.

Apparatus and Procedure

Details of the experimental arrangement are given in Part I of this series. In these experiments pure ozone (98–99%) was used. Electrolytic hydrogen was purified by passing it through a layer of charcoal cooled to liquid air temperature. The rise in pressure due to reaction was measured with a quartz spiral manometer. The method of preparing the gases ensured such a purity that the ozone alone or ozone in the presence of hydrogen was extremely stable at room temperatures, there being no appreciable rise in pressure over a period of several hours. Spherical glass reaction vessels of about 200 cc. capacity were used.

The formation of water involves no pressure change, but since the amount of hydrogen converted is small, the rise in pressure represents, as a first approximation, the ozone decomposed.

Results

It was found that the addition of hydrogen to pure ozone at 85° has an enormous effect on the rate at which the pressure increases. For a given ozone pressure (50 mm.), $\Delta p/\Delta t$ is practically proportional to the hydrogen pressure, for relatively low pressures of the latter. Above 50 mm. of hydrogen the rate increases very rapidly, the normal rate of ozone decomposition increasing by hundreds of times for about 70–75 mm. of hydrogen. At about 80 mm. of hydrogen an explosion occurs. Table I shows the time required for the pressure to increase the first 8 mm. for increasing amounts of hydrogen added to 50 mm. of ozone.

TABLE I

INFLUENCE OF HYDROGEN ON THE RATE OF PRESSURE INCREASE (OZONE PRESSURE, 50 MM.)

Pressure of hydrogen, mm.	None	10.1	30.5	50.0	80.0
Time in minutes for Δp = 8 mm.	120	29	11	5.25	Explosion

The pressure of hydrogen necessary to cause explosion increases as the pressure of ozone decreases. Thus, for 40 mm. of ozone the pressure of hydrogen necessary to explode the mixture at 85° is 100 mm.; for 50 mm.

of ozone it is 80 mm. Presumably there is some lower limit of ozone pressure and hydrogen pressure below which no explosion is possible.

A very interesting effect was observed. If the reaction rate is measured for several successive runs using a similar but fresh mixture after evacuating for about five minutes between each run, the reaction rate increases in each succeeding experiment. With each experiment the reaction vessel becomes more active. If a mixture just above the explosion limit is admitted to an inactive vessel, it does not explode until several such experiments are carried out in the vessel. If the mixture is below the explosion limit the rate reaches a constant maximum value. This effect is illustrated in the following table in which the time is given for Δp to reach a certain value for several runs starting in an inactive vessel with a mixture below the explosion limit.

TABLE II

EFFECT OF PREVIOUS EXPERIMENTS ON THE RATE OF PRESSURE INCREASE

Ozone pressure, 50 mm. Hydrogen pressure, 50 mm.

Experiment	1	2	3	4
Time in minutes for Δp = 10.5 mm	13	8.2	7.3	7.2

The activity acquired by the vessel after the above treatment lasts for several hours, and even after twenty hours the vessel still shows small evidences of it. The vessel can be deactivated by heating and pumping with a mercury vapor pump for some time.

It is believed that the increased activity of the vessel is due to the formation during the reaction of some substance which is adsorbed on the wall and which facilitates the process. This substance may be water or some active radical or atom. While it was found, in agreement with Warburg,[5] that the presence of water increases the rate of decomposition of ozone, this effect is very much smaller than that encountered in the above phenomenon. The following experiment shows that water is not the cause of the enhanced activity of the vessel. A vessel was activated to the explosion point by running several experiments with a mixture 50 mm. of ozone and 90 mm. of hydrogen. During an explosion all the hydrogen is burned to water. The products of the explosion were allowed to remain in the vessel for about thirty hours, after which they were pumped out quickly, leaving a layer of water on the wall. If the activity were due to water, a similar explosive mixture might be expected to explode. Instead, a reaction occurred comparable in rate with that to be expected in an inactive vessel.

It was suspected that the cause of the activity was the adsorption on the walls of hydrogen atoms formed during the reaction. This was shown to be very probable by the following set of experiments. The inactive vessel was pumped out for some time, hydrogen admitted to a pressure of about

(5) Warburg, *Sitzb. preuss. Akad. Wiss.*, 644 (1913).

0.5 mm. to 1 mm. and a discharge passed through the gas for about fifteen minutes at room temperature. A mixture of 50 mm. of ozone, 80 mm. of hydrogen, was admitted to the vessel, which was still at room temperature. The reaction which occurred was negligibly small. (Similarly, the reaction is inappreciable at room temperature in a very active vessel, made active by first running several experiments at 85°.) The vessel was pumped out, heated to 85°, and three hours later received a similar mixture. The mixture exploded promptly. Thus, even after this time the vessel was sufficiently active to explode the mixture, which without the previous sparking treatment would have reacted non-explosively. It may be concluded that hydrogen atoms formed during the discharge, likewise during a reaction, are adsorbed on the wall in some active form which is responsible for the enhanced activity of the vessel.

That the activity is not attributable to oxygen atoms is shown by the fact that the explosion of pure ozone alone (ignition by local heating with a flame) in an inactive vessel, during which many oxygen atoms are formed, does not alter the activity of the vessel appreciably.

Discussion

It is proposed that the adsorbed active hydrogen facilitates the starting at the walls of reaction chains which then spread out into the gas phase.[6] The following mechanism may be suggested as being consistent with the known facts.

At the outset, a certain number of oxygen atoms are formed during the normal thermal decomposition of ozone.

$$O_3 \longrightarrow O_2 + O \tag{1}$$

Hydrogen atoms may be generated as follows

$$O + H_2 = OH + H\ (+1\ \text{Kcal.}) \tag{2}$$

The velocity of formation of hydrogen atoms for a given ozone concentration would be proportional to the hydrogen concentration. The hydrogen atoms now react with ozone relatively easily giving rise to active OH radicals which in turn react with ozone, regenerating hydrogen atoms; *i. e.*

$$H + O_3 = OH^* + O_2^*\ (+78\ \text{Kcal.}) \tag{3}$$

$$OH^* + O_3 = 2O_2 + H\ (-10\ \text{Kcal.}) \tag{4}$$

where the * indicates an energy-rich molecule. The initial presence on the walls of active hydrogen (supposedly behaving as atomic hydrogen), as in the activated vessel described above, would enable reactions 3 and 4 to proceed therefrom without waiting for the hydrogen concentration to build up through reaction 2. If a sufficient number of reaction 3 is started in unit time the gas will heat up and accelerate all four reactions.

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(6) A similar phenomenon was reported by Farkas, Haber and Harteck [*Z. Elektrochem.*, **36**, 711 (1930)] in the explosion of hydrogen and oxygen. If the vessel had been prepared by exploding a mixture of hydrogen and oxygen with a spark at 420°, a second and similar mixture admitted to the evacuated vessel a minute or two later exploded spontaneously. This effect was attributed to the adsorption on the walls of an active product, presumably hydrogen atoms.

Under suitable conditions an explosion results. More hydrogen atoms may be formed by means of the following step coupled with reaction 2.

$$O_2^* + O_3 = 2O_2 + O\ (-25\ \text{Kcal.}) \tag{5}$$

The oxygen atoms may also decompose ozone, giving rise to another chain of reactions, the nature of which is not entirely clear[7] but which may be written for the time being simply as

$$O + O_3 = 2O_2^*\ (+\ 93\ \text{Kcal.}) \tag{6}$$
$$O_2^* + O_3 = 2O_2 + O\ (-25\ \text{Kcal.}) \tag{7}$$

The mechanism of the formation of water from hydrogen and oxygen is still in a state of uncertainty. So far these experiments throw no additional light on the subject. The Bonhoeffer–Haber[8] mechanism would indicate the following step

$$OH + H_2 = H_2O + H\ (+\ 14\ \text{Kcal.}) \tag{8}$$

The efficiency of this reaction at 85° is quite low,[9] but with the energy attached to the OH^* radical emerging from reaction 3, reaction 8 would be expected to occur fairly frequently, although OH radicals from reaction 2 would be comparatively ineffective. With reaction 3 removing hydrogen atoms rather easily and the existence of a competition for OH between reactions 4 and 8, it should be difficult to complete the Bonhoeffer–Haber chain, especially while the ozone concentration is appreciable. It is apparent that the amount of hydrogen converted to water should be low in comparison with the ozone decomposed. which is in agreement with the experiment. Of course, the reaction

$$O_2^* + H_2 = H_2O + O\ (-\ 1\ \text{Kcal.}) \tag{9}$$

is not impossible. A quantitative study of the amount of hydrogen and ozone converted from point to point in a given run might contribute valuable information toward elucidating the mechanism of the burning of hydrogen. This involves elaborate technique and has not been attempted so far.

If the formation of water occurs through the medium of hydrogen peroxide, it might be argued that the enhanced decomposition of ozone is also due to this molecule. It is, however, difficult to understand how a regenerative chain could be set up under these conditions to account for the high rate of ozone decomposition. The point could be tested experimentally by mixing hydrogen peroxide and ozone and if a reaction occurs determining whether more ozone decomposes than corresponds to the equation $O_3 + H_2O_2 = H_2O + 2O_2$.

Summary

Experiments were carried out at 85° to determine the influence of hydrogen on the thermal decomposition of ozone. With addition of hydrogen, the rate of decomposition increases enormously up to the point of

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[7] Bernard Lewis, *J. Phys. Chem.*, **37**, 533 (1933).

[8] Bonhoeffer and Haber, *ibid.*, **137A**, 227 (1928); Haber, *Z. angew. Chem.*, **42**, 745 (1930).

[9] Von Elbe and Lewis, THIS JOURNAL, **54**, 552 (1932).

explosion, which occurs under suitable pressure conditions. Thus 50 mm. of ozone requires 80 mm. of hydrogen, while 40 mm. of ozone requires 100 mm. of hydrogen to cause the mixture to explode at 85°. The amount of hydrogen converted to water in the non-explosive reaction is only a fraction of the ozone decomposed.

An ordinary glass vessel becomes activated during the course of a reaction. In each succeeding reaction the vessel exhibits increased activity. The criterion for activity is the rate of reaction. Thus, an explosive limit mixture will not explode until several runs are carried out in the vessel first, while with a non-explosive mixture the reaction rate increases in each succeeding experiment until a constant value is reached. The activity lasts for several hours. Experiments were performed which indicate that the activity is due to the formation, during the reaction, of hydrogen atoms which are adsorbed on the walls. A mechanism of the process is suggested by which hydrogen atoms take part in a chain of reactions accounting for the bulk of the enhanced decomposition of ozone, *i. e.*, $H + O_3 = OH^* + O_2^*$ and $OH^* + O_3 = 2O_2 + H$, where * represents a molecule rich in energy.

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A Note on the Heat of Sorption of Water Vapor by Massive Gold

BY ELLIOTT PIERCE BARRETT

A paper by Barry and Barrett[1] describes the methods used and the results obtained in a study of the heat of sorption of water vapor by massive gold in a saturated atmosphere. It is the purpose of this communication to point out that the relationship between heat of sorption and weight of vapor sorbed obtained from that investigation is similar to that found by other investigators working with quite different systems.

In the joint paper to which reference has been made, it was shown that for water vapor and gold, the integral heat of sorption, H, at any time, t, measured from the beginning of sorption, is given by the relation

$$\log H = a - b/t^c \qquad (1)$$

where a, b and c are empirical constants. An analogous equation

$$\log W = a' - b'/t^{c'} \qquad (2)$$

was shown to describe the increment in weight, W, of the gold which accompanied the liberation of heat and which was assumed to measure the quantity of water vapor sorbed by the gold.

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(1) Barry and Barrett, THIS JOURNAL, **55**, 3088 (1933).