solid containing a trace of sodium chloride. A pure sample, prepared by five recrystallizations from 80% ethanol, was a white crystalline solid with a waxy luster.

(c) **N,N′-Dibenzylethylenediaminedipropionic Acid.**—The residue was dissolved in a minimum amount of hot distilled water and acidified with an equal volume of 12 *N* hydrochloric acid. A white solid separated upon long standing in the cold. This solid was dissolved in distilled water, and the *p*H was adjusted to 4.2. The aqueous solution was distilled to dryness under reduced pressure, the residue was extracted with hot absolute ethanol, and the filtered extract was distilled to dryness. The residue was warmed in 200 ml. of hot redistilled acetone and was allowed to stand in the cold. The acid which separated was purified by recrystallizing the impure acid four times from 90% ethanol and was isolated as a white crystalline solid.

(d) **Acid Hydrolysis of N,N′-Dioctyl-ethylenediaminedipropionitrile.**—Upon alkalizing the acid hydrolysate obtained from the N,N′-dioctylethylenediaminedipropionitrile, the monohydrate of N,N′-dioctylethylenediamine was recovered. Its melting point (44-46°) showed no depression when mixed with an authentic sample of the diamine. The amount recovered represented 80% of the starting material. Manipulation of the residual solution in various ways yielded only a viscous residue, from which no solid material could be crystallized either by strong acidification or by use of various solvents.

N,N′-Dialkylethylenediaminedipropionic Acids. (Method 2). General Procedure.—To 0.1 mole of the stirred dialkylethylenediamine, 0.2 mole of sodium β-chloropropionate dissolved in 200 ml. of water was added, and the mixture was refluxed 12 hours. The solution was then made strongly alkaline and distilled to dryness under reduced pressure. The residue was then refluxed with two 500-ml. portions of ethyl ether for one hour, in order to remove any unreacted diamine. After decantation, the residue was dissolved in a minimum amount of hot distilled water, and the solution was acidified with 12 *N* HCl to a *p*H of 2. Long standing in the cold resulted in the precipitation of a white solid. The free acids were purified by adjusting the *p*H of an aqueous solution of this solid to the value at the isoelectric point, distilling the solution to dryness under reduced pressure, and recrystallizing the residues from suitable solvents in the manner described under method 1.

Titration Method.—Fifty to one hundred mg. of purified amino acid dissolved in 50-100 ml. of water was titrated with sodium hydroxide. The titration was repeated in the presence of equimolar cupric sulfate and in the presence of 15-molar excess of calcium chloride. The *p*H was measured with a glass electrode according to standard practice.

Absorption Spectra Method.—Stock solutions of 0.01 *M* disodium salts of the dipropionic acid derivatives were prepared. A stock solution of 0.001 *M* copper complex was then prepared from the standard solution of the disodium salt and 0.01 *M* cupric chloride. The concentration of the complex solution was then varied by dilution so that the values of the per cent. of transmission at the regions of maximum absorption were within the range of 10 to 80%. Absorption measurements were carried out in the ultraviolet region (220-350 mμ) with a Beckman quartz spectrophotometer, model DU, in quartz cells. Similar measurements were carried out on solutions of cupric chloride and of the disodium salts of the amino acids at the same concentration as those containing the copper complexes.

Acknowledgment.—The authors are indebted to F. C. Bersworth, of Framingham, Massachusetts, for financial support. The choice of topic was made with his coöperation and the work was aided by his advice.

Summary

The preparation of ethylenediaminetetrapropionic acid, N,N′-ethylenediaminedipropionic acid, and a number of N,N′-dialkylethylenediaminedipropionic acids by hydrolysis of the nitriles and by reaction of the corresponding amine with β-chloropropionic acid is described. Potentiometric and spectrophotometric data indicate chelation with cupric ion but little or no chelation with calcium ion, except in the case of N,N′-dicyclohexylethylenediaminedipropionic acid, which showed no appreciable chelation with either ion.

BERKELEY, CALIF. RECEIVED FEBRUARY 25, 1950

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

First and Second Pressure Limits of Explosion of Diborane–Oxygen Mixtures[1]

BY FRASER P. PRICE

Introduction

The ease of ignition of the lower hydrides of boron, sometimes spontaneous and frequently with violent results, has long been known.[2] It was only recently, however, that improved methods for their preparation[3] made them available in sufficient quantity to undertake investigation of their reactions with oxygen.

This paper is the first of a series describing their behavior when mixed with oxygen under a variety of conditions. Diborane was chosen for the initial investigation because it was felt that its reactions would be simplest.

It is reported that diborane reacts with oxygen according to the equation[2]

$$B_2H_6 + 3O_2 \longrightarrow 2H_3BO_3$$

However, when diborane is ignited in air there is always a persistent odor characteristic of boron hydrides. Thus it is very probable that in the heat of an explosion some of the diborane is converted to higher, more stable, hydrides, and that the stoichiometry of the explosions discussed below does not correspond to the above equation

Experimental

Materials.—Diborane was obtained from Mine Safety Appliance Company, Pittsburgh, Pennsylvania, and was purified on the day of use by three successive cycles of freezing in liquid nitrogen, pumping and thawing. Analysis using the mass spectrometer indicated a purity of better than 99% before purification.

---

[1] This work done under contract with U. S. Army Ordnance.

[2] Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[3] Schlesinger, *et al.*, in press; Elliott, Boldebuck and Roedel, in press.

Oxygen, nitrogen and hydrogen were obtained from the General Electric Schenectady Works, and all were used directly from the tanks. The tank pressures were always above 1800 p. s. i. to ensure low moisture content of these gases.

Apparatus.—A vacuum line of conventional design was used in this investigation. Attached to the manifold were inlets for the various gases, a mixing bulb, a freezeout, appropriate gages and manometers and a flame arrestor through which the explosive gas mixtures were bled into the reaction bulbs. The arrestor could be by-passed to evacuate the reaction bulbs. A Cenco Hyvac pump was the only source of vacuum used as it was feared that the inclusion of a diffusion pump and its trap might permit accumulation of dangerously large quantities of the hydrides.

The entire apparatus was mounted in a hood and shielded by a plywood panel with small plexiglass viewing windows in it. The stopcocks were turned by brass rods projecting through the panel as did the handle of the automobile jack used to raise the dewar containing liquid nitrogen around the freezeout. The gages and manometer were mounted on the front of the plywood panel and were shielded with plexiglass. The mixing bulb wherein the diborane and other gases were mixed was of 500-cc. capacity and contained a stainless steel wool bat which enclosed a slug of mild steel. This bat, which served as a stirrer, was rotated by an externally mounted Alnico magnet attached to the shaft of a variable speed motor. The flame arrestor consisted of a small mercury-filled trap, the inlet tube of which had its end immersed in mercury and closed by a sintered glass disc. Thus when gas was admitted to the hot evacuated explosion bulb, the pressure of the explosion would push the mercury back up against the sintered glass plug and shut off the supply of fresh incoming gas, thus interrupting the propagation of the flame. This flame arrestor worked very satisfactorily. Out of several hundred explosions only once did the flame propagate back into the vacuum line. The explosion bulbs were squat cylinders of Pyrex glass, usually 43 mm. i.d. and 45 mm. length of straight portion. The ends were approximately hemispherical. In the experiments to test the effect of vessel size, smaller, but geometrically similar, bulbs were used. The following procedure was used for cleaning the bulbs: (a) rinse with distilled water, (b) fill with cleaning solution and immerse one hour in boiling water, (c) rinse six times with distilled water, (d) fill with concd. C. P. nitric acid and immerse in boiling water one hour, (e) rinse six times with distilled water, (f) dry at 110° in air overnight, (g) pump at least 0.5 hour before using. It was found necessary to follow this schedule to get reproducible results.

The temperature of the explosion bulb was maintained by a lagged, electrically heated aluminum cylinder 4 inches in diameter and 16 inches long through which a 2-inch coaxial hole was bored. The axis of the cylinder was vertical and the bulbs were mounted approximately in the center with their inlet tubes coming out the bottom. This oven was used only in the determination of the first explosion limit. In the investigation of the second limit it was necessary to admit gas to the explosion bulb prior to raising the temperature rapidly. For this determination a small silicone oil-filled thermostat of one-gallon capacity was mounted on a scissor-type automobile jack so that it could be raised around the gas filled bulb in about ten seconds. The temperature was regulated in both cases to ±1° by Bristol Controller Model 478LH.

A recording manometer, described elsewhere[4] made plots of the pressure in the explosion bulb against time. A G. E. Light Sensitive Cell of the selenium type was mounted so as to register the light coming from the flame arrestor into which the flame invariably flashed back. The photocell was connected to the recorder so that a pip was produced on the time-pressure trace at the instant of explosion.

Procedure.—Gas mixtures were made up by admitting the desired pressure of B_2H_6, purified as described above, to the mixing bulb and then admitting oxygen or other gases until the desired composition had been attained, assuming no back diffusion out of the bulb. The total pressure was usually about 500 mm. This mixture was then stirred for at least ten minutes. More than 100 such mixtures were made up, some standing for eight hours, and no spontaneous ignition was ever observed. Furthermore, there was no indication of reaction of these mixtures at room temperature as judged by the reproducibility of explosion limits and the absence of solid deposits in the mixing bulb. Subsequent experience with larger vessels in some other work indicates, however, that under certain conditions these mixtures will explode spontaneously at room temperature.

Where it was desired to keep the ratio of B_2H_6 to O_2 constant, but vary a third constituent, the procedure was to make serial dilutions of the original mixture with the third gas. This could be done knowing the volumes of the line and the mixing bulb, and hence the amount of the original mixture used up.

Determination of the first explosion limit was made by admitting about 50 mm. of the gas mixture to the line and slowly bleeding it into the hot evacuated explosion bulb until explosion took place. The time-pressure trace on the recorder chart with the pip from the photocell gave the explosion pressure. Since the explosion products occupied less volume than the reactants, after explosion took place fresh gas mixture could enter the hot bulb again and produce another explosion and the cycle repeat itself several times. This phenomenon occurring above 175° produced a jagged sawtooth trace on the pressure-time record, with sometimes as many as 30 successive explosions. Attempts were made to analyze these traces, but were without success.

The second explosion limits were determined by admitting about 50 mm. of the mixture to the cold evacuated bulb and then raising the hot thermostat around it. After 1.5 minutes the bulb was slowly evacuated until explosion occurred. The recording equipment was the same as described above. The time of 1.5 minutes heat was used, as test runs with nitrogen alone in the bulb showed no further change of pressure after about one minute. Heating for five minutes and longer produced mixtures which would not explode on evacuation, probably due to decomposition of the hydride.

Results and Discussion

First Explosion Limit.—The effects of varying temperature, and composition, are presented in Table I.

The explosion pressures are all the average of at least four determinations and have an error of ±0.5 mm.

The results presented in Table I indicated so great an insensitivity to the variables that it was suspected that the ignition started in the inlet tube to the bulbs. However, cooling the inlets by passing water through copper tubing wrapped around them failed to change the results. Therefore, the reaction must start in the hot bulbs. The stoichiometric mixture (25% B_2H_6) was investigated most thoroughly (Line A, Fig. 1), and it was found that the lowest temperature at which ignition took place was between 130 and 135°. Since it had previously been found that preheated impinging streams of B_2H_6 and O_2 did not ignite until their temperature reached 132°,[5] it was thought that perhaps the ignition temperature of the first pressure limit of between 130 and 135° was of some significance. However, subsequent

---

[4] Price and Zemany, *Rev. Sci. Inst.*, **21**, 261 (1950).

[5] D. T. Hurd, private communication.

TABLE I

EFFECT OF TEMPERATURE AND COMPOSITION ON FIRST EXPLOSION LIMIT OF B_2H_6–O_2 MIXTURES

43 mm. i. d. bulbs coated with reaction products

% B_2H_6	% O_2	Temp., °C.	$P_{exp.}$, mm.
10.1	89.9	No explosion at 175 or below	
10.1	89.9	200	16.8
10.1	89.9	225	27.1
14.6	85.4	225	21.2
20.3	79.7	150	15.4
20.4	79.6	175	17.8
20.1	79.9	200	15.3
20.0	80.0	225	13.2
20.0	80.0	250	4.8
25.2	74.8	135	16.1
25.0	75.0	150	13.8
25.4	74.4	175	14.8
25.1	74.9	200	15.0
25.3	74.7	225	13.5
25.2	74.8	250	4.9
33.3	66.7	150	13.9
33.4	66.6	175	13.9
33.5	66.5	200	12.4
33.5	66.5	225	14.9
50.0	50.0	No explosion from 150–225	

discovery of a second pressure limit showed that this probably is not true.

The effect of diluting the gas mixture with hydrogen or nitrogen is to raise the explosion pressure slightly. Changing the wall/volume ratio by packing the bulb with $^1/_4$-inch glass tubes or decreasing its size has little effect until the area has markedly increased, when the explosion pressure again rises. These facts, coupled with the relative insensitivity of the limit to temperature and composition, indicate that both chain branching and chain breaking occur on the wall.[6] If both branching and breaking occurred in the gas phase there would never be a wall effect. If either occurred in the gas phase it would have an exponential dependence on temperature. Since a diffusion process to the wall would have a rate that depends on only the square root of the temperature, if one process occurred at the wall and the other in the gas phase, the latter would eventually overwhelm the former. Therefore, it is concluded that both chain branching and chain breaking occur at the wall.

Second Explosion Limit.—The effect of temperature on the second explosion limit of a stoichiometric mixture of B_2H_6 and O_2 is illustrated in Table II and plotted on Line B in Fig. 1.

TABLE II

EFFECT OF TEMPERATURE ON SECOND EXPLOSION LIMIT, 25% B_2H_6–75% O_2

Temp., °C.	155	160	165	170	175
$P_{exp.}$, mm.	11.5	13.5	16.2	16.0	17.5
Temp., °C.	180	185	190	195	200
$P_{exp.}$, mm.	18.2	19.6	20.2	20.2	28.2

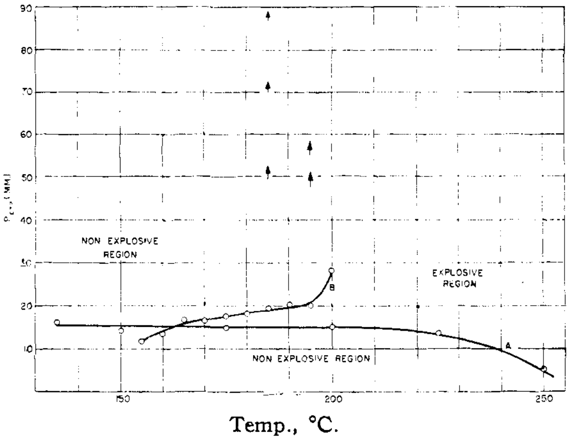

Fig. 1.—First and second explosive limits for 25% B_2H_6–75% O_2 Pyrex bulbs coated with reaction products. Arrows indicate explosion on adding gas.

These results are with two exceptions the average of at least two measurements. The 195° point was the lowest of two trials that did not explode while heating, out of a total of six runs. The 200° point was the only one out of five attempts that did not explode while bringing the system up to temperature. Above 200° all attempts resulted in ignition before temperature had been attained, and below 155° explosion never occurred on evacuation. It will be noted that the second limit falls below the first limit at temperatures below 162°. This point has been checked and it is reproducible. As it is difficult to see how it could be real, it probably is an artifact introduced by the overshooting of the recorder or by the production of some inhibitor by the thermal decomposition of the hydrides. In any event, it introduces an error of only 3 mm. in the pressure at explosion.

Since a second explosion limit had been found and defined, and since it was known that the ignition temperature of B_2H_6–O_2 mixtures at atmospheric pressure was around 130°, it was expected that as in the case of the hydrogen–oxygen reaction[7] a third limit could be found. Therefore, several experiments were tried wherein the procedure was the same as that in the determination of the second limit, except that after temperature had been attained gas was added instead of removed. At 180° the pressure was raised to 172 mm. without explosion, while at 185° and above addition of gas produced immediate explosion regardless of the pressure of the hot gas already in the bulb. These experiments are indicated by the small vertical arrows on Fig. 1. More experiments were done than are indicated by the arrows, all with the same indeterminate results, even though it was possible to heat 100 mm. of the

---

(6) Lewis and Von Elbe, THIS JOURNAL, **59**, 970 (1937).

(7) Hinshelwood, *et al.*, *Proc. Roy. Soc.* (*London*), **A185**, 369 (1946); Lewis and Von Elbe, *J. Chem. Phys.*, **10**, 366 (1942).

mixture at 190° for 45 minutes with no explosion taking place.

In any event, the explosion *P–T* diagram seems to have a long thin peninsula, the explosion side of which curves sharply up in pressure in the region of 190–200°.

The effect on the second limit of adding B_2H_6, O_2, N_2 and H_2 to a 25% B_2H_6–75% O_2 mixture was next studied. The results are presented in Table III.

TABLE III

EFFECT OF DILUENTS ON SECOND EXPLOSION LIMIT, 43 mm. I. D. BULBS COATED WITH REACTION PRODUCTS 180°

P = partial pressure in mm. of indicated gas at explosion

Added gas	$P_{B_2H_6}$	P_{O_2}	$P_{\text{added gas}}$
None	5.33	15.90	0.00
	4.37	14.94	.00
	3.54	14.00	.00
	10.10	18.70	.00
	9.27	17.20	.00
	6.18	14.50	.00
	6.32	14.90	.00
	3.88	11.95	.00
	5.82	17.52	.00
	3.59	15.40	.00
	2.40	13.41	.00
H_2	5.05	14.15	.00
	5.49	16.31	.00
	4.57	13.56	1.97
	3.74	11.15	4.31
	5.95	17.83	.00
	5.47	16.53	.00
	4.25	12.34	1.01
	4.26	12.37	3.57
	3.49	10.48	4.03
N_2	5.23	16.77	0.00
	4.93	15.05	2.5
	4.80	14.50	4.5
	4.29	13.11	10.2
	3.53	10.65	19.3

These data fit an equation of the type

$$aP_{B_2H_6} + bP_{O_2} + \sum_i c_iP_i + k = 0 \qquad (1)$$

where a, b, c and k are constants and the P's are pressures. The procedure in determining the constants is first to plot the $P_{B_2H_6}$ *vs.* P_{O_2} with no diluent present and determine the slope, $-b/a$. Then maintaining P_{O_2}/P_{B_2} constant (see Table III), plot $P_{B_2H_6}$ *vs.* P_i and obtain c_i/a from the slope. Substitution of values of the correct pressures into equation (1) is sufficient to determine k/a. When this is done, the resulting coefficients are

$$b/a = -0.90 \qquad c_{N_2}/a = -0.16$$
$$c_{H_2}/a = -0.60 \qquad k/a = 9.0$$

The expression for the explosion limit (Eq. 1) represents the state of affairs when rate of chain branching equals rate of chain breaking. It appears in the denominator of a rate equation as the result of the solution of the steady state equations for chain carriers in some mechanism, and the ratios b/a and c_i/a represent ratios of rate constants.

Nitrogen cannot enter into the reaction chemically and can only serve as a gas phase chain breaker. Since the ratio of rate constants must be positive, the negative sign of c_{N_2}/a must be associated with a chain breaking process. Therefore, the terms involving the P_{O_2} and P_{H_2} must also represent chain breaking processes because of their negative signs.

The positive sign of the k/a and $P_{B_2H_6}$ terms must mean that these represent the branching processes. If only first or second order processes are considered in the mechanism, then the k/a term represents either spontaneous branching or branching at the wall. If third order processes are considered then this term could result from gas phase bimolecular branching. Several experiments, not reported above, with varying bulb size showed no wall effect. Therefore, the constant term, k/a, represents either spontaneous monomolecular branching or it appears as a result of a bimolecular branching process in a mechanism which has as other third order processes those involving branching with B_2H_6 and those involving breaking with the diluent gases (O_2, and possibly B_2H_6 included). Since third order branching processes are virtually unknown, it is most probable that the k/a term represents spontaneous branching. The positive sign of the B_2H_6 term means that either there is only chain branching resulting from a collision between the chain carrier and B_2H_6, or that there is both chain branching and chain breaking resulting from the same type of collision, depending perhaps on the orientation of collision. This latter state of affairs is the more probable, and the B_2H_6 coefficient probably represents the difference between the branching and breaking rate constants, the former being the larger. Therefore, for some chain carrier, X, the most probable set of reactions is

$$\left.\begin{array}{l} \mathrm{X} + \mathrm{B_2H_6} \longrightarrow \\ \mathrm{X} \qquad\quad\ \longrightarrow \end{array}\right\}\text{Branching} \qquad \begin{array}{r}(2)\\(3)\end{array}$$

$$\left.\begin{array}{l} \mathrm{X} + \mathrm{O_2} \longrightarrow \\ \mathrm{X} + \mathrm{N_2} \longrightarrow \\ \mathrm{X} + \mathrm{H_2} \longrightarrow \end{array}\right\}\text{Breaking} \qquad \begin{array}{r}(4a)\\(4b)\\(4c)\end{array}$$

and possibly

$$\mathrm{X} + \mathrm{B_2H_6} \longrightarrow \qquad (4d)$$

and

$$k_2 > k_{4d}$$

If on the other hand third order processes are considered, both the chain branching, B_2H_6, term and the chain stopping terms would be third order. The latter are most reasonable explained on the basis of a termolecular collision of the type

$$\mathrm{X} + \mathrm{O_2} + \mathrm{M} \longrightarrow \text{break} \qquad (5)$$

where M is any other gas and the O_2 was picked rather than B_2H_6 because in similar reactions this is known to be the case.[8] The branching term

---

[8] Melville, *J. Chem. Phys.*, **2**, 739 (1939).

would be $\{X\}$ $\{O_2\}$ $\{B_2H_6\}$, and could be explained on the basis of a rapid reversible reaction between any two of the above three species followed by a slower chain branching step involving the third.

However, in the light of present knowledge of this reaction, the mechanism outlined in equations 2 to 4 is to be preferred.

Regardless of whether the mechanism involves third order terms or not, from the magnitudes of the coefficient ratios of Equation 1 it can be seen that oxygen is about 1.5 times as effective a chain stopper as hydrogen, and is five times as effective as nitrogen. Further, since there is no correlation with the relative collision frequencies, these effects are probably partially chemical in nature rather than pure energy transfer as in the hydrogen–oxygen reaction.[9]

It should be emphasized that the mechanism proposed above should be considered tentative only. However, in common with most reaction schemes, it explains in a fairly satisfactory manner most of the proved facts. Much more work obviously must be done with such a complex and labile system before a definitive mechanism can be proposed.

Summary

The first and second pressure limits of explosion of B_2H_6–O_2 mixtures have been investigated. The effects of temperature, composition and vessel size have been studied.

The first limit showed little effect of temperature (135–250°) and composition (10% B_2H_6–50% B_2H_6) occurring around 10–15 mm. total pressure. It was concluded that both chain branching and chain breaking processes occur at the wall.

The second limit of the stoichiometric mixture was studied as a function of temperature. The influence of diluent gases on the second limit was studied at 180°, and showed a marked effect. The limit could be expressed by an equation of the type $aP_{B_2H_6} + bP_{O_2} + \sum_i c_iP_i + k = 0$. It was concluded that here both chain branching and breaking took place in the gas phase.

SCHENECTADY 5, N. Y. RECEIVED MAY 5, 1950

---

[9] Frost and Alyea, THIS JOURNAL, **55**, 3227 (1933): Hinshelwood, *et al.*, *Trans. Faraday Soc.*, **24**, 559 (1928); Hinshelwood, *et al.*, *Proc. Roy. Soc.* (*London*), **122A**, 610 (1929); **124A**, 219 (1929).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, METAL HYDRIDES, INC.]

The Titanium–Hydrogen System and Titanium Hydride. I. Low-Pressure Studies

BY THOMAS R. P. GIBB, JR., AND HENRY W. KRUSCHWITZ, JR.

The titanium–hydrogen system has been investigated by several workers whose results are unfortunately somewhat at variance with one another. The only systematic study of p–t relations is that of Kirschfeld and Sieverts[1,2,3] who report isotherms and isobars over a wide range of temperatures but only for pressures less than 800 mm. It is evident from the fact that the stoichiometric composition, TiH_2, was not closely approached under otherwise favorable conditions that these workers did not use sufficiently pure titanium or hydrogen. The density and lattice constants of various compositions are reported by Biltz[4] and by Hägg[5] whose results are not completely concordant, and the density by Sieverts.[3] Fitzwilliam[6] studied magnetic susceptibility as a function of composition, and Gulbransen and Andrew[7] have found the rate of absorption of hydrogen by titanium to be complex and not easily interpreted. The heat of formation of $TiH_{1.73}$ was measured calorimetrically by Sieverts and Gotta[8] who obtained a value of 31.1 kcal. for the heat of formation. McQuillan,[9] who studied the effect of hydrogen lowering on the α–β transformation temperature of titanium (860–900°), has calculated the heat of solution of hydrogen in the α and β forms of titanium and finds an anomalous positive value in the vicinity of the transformation temperature. Smith[10] compares the titanium- and palladium–hydrogen systems and adduces evidence for their basic similarity. An excellent theoretical interpretation of metal–hydrogen equilibria is given by Barrer,[11] who refers briefly to the Ti–H system.

Discussion

The unique ability of hydrogen to form alloy-like compositions with a number of metals has prompted several investigations of the properties and structures of such systems. Unfortunately early investigators failed for the most part to recognize that traces of impurities in the metal, or more seriously in the hydrogen, inhibit the dissolution of hydrogen.

---

[1] H. Huber, L. Kirschfeld and A. Sievets, *Ber.*, **59B**, 2891 (1926).

[2] L. Kirschfeld and A. Sieverts, *Z. physik. Chem.*, **145**, 227 (1929); *Z. Elektrochem.*, **36**, 123 (1930).

[3] A. Sieverts, *Z. metallkunde. Chem.*, **21**, 37 (1929).

[4] W. Biltz, *Z. anorg. allgem. Chem.*, **174**, 42 (1928).

[5] G. Hägg, *Z. physik. Chem.*, **B11**, 433 (1931).

[6] J. Fitzwilliam, A. Kaufmann and C. Squire, *J. Chem. Phys.*, **9**, 678 (1941).

[7] E. Gulbransen and K. Andrew, *J. Metals*, **1**, No. 10, Trans. 741 (1949).

[8] A. Sieverts and A. Gotta, *Z. anorg. allgem. Chem.*, **199**, 384 (1931).

[9] A. D. McQuillan, *Nature*, **164**, 24 (1949).

[10] D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, Illinois, 1948.

[11] R. M. Barrer, *Discussion Faraday Soc.*, No. 4, 68–81 (1948).