germane, $GeH_4$, which had already been prepared by others, was identified and reserved for future investigation.

The density as gas, the density as liquid, the melting point, and the boiling point of each of these two hydrides were determined, and the tension-temperature curves were plotted. Some of the characteristic chemical properties of digermane and trigermane are described.

After trigermane had been removed by fractionation, a very small amount of a liquid residue remained in the bulb. This residue showed practically no vapor tension at room temperature. Its presence indicates that still higher hydrides in this series probably exist.

ITHACA, NEW YORK

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# CRITICAL POTENTIALS OF HYDROGEN IN THE PRESENCE OF NICKEL CATALYST

BY A. W. GAUGER[1]

RECEIVED DECEMBER 27, 1923

Sabatier's[2] important researches on the catalytic activity of finely divided metals established, among other things, the fact that nickel prepared from the oxide by reduction in hydrogen at temperatures of 300°, or less, is an excellent catalyst for hydrogenation reactions and perhaps the best. Since that time many investigators have studied such reactions in the presence of finely divided nickel and there has been much speculation concerning the mechanism thereof. Nevertheless, we still lack sufficient experimental evidence to know definitely what the role of the catalyst is. However, it has been noted that nickel of the type concerned shows a very marked power to adsorb hydrogen,[3] and the suggestion has been made that the adsorption is chemical in nature, the hydrogen being held on the surface of the metal by chemical forces of either secondary or primary valence,[4] not as molecular but as atomic hydrogen.[5]

One of the theories of catalytic hydrogenation involves, therefore, the adsorption of one or more of the reacting species, reaction between them on the surface, and desorption of the products therefrom. For all practical purposes this theory may be considered identical with the old "intermediate compound" theory, inasmuch as the adsorption is considered to be a chemical rather than a physical phenomenon.[6] Some definite idea of the

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[1] National Research Fellow in Chemistry.

[2] Sabatier-Reid, "Catalysis in Organic Chemistry," D. van Nostrand Co., **1922.**

[3] See Taylor and Burns [THIS JOURNAL, **43,** 1277 (1921)] for references.

[4] Langmuir, *ibid.*, **38,** 2221 (1916).

[5] Langmuir, *ibid.*, **34,** 1310 (1912).

[6] Armstrong and Hilditch, *Proc. Roy. Soc.*, **100A,** 240 (1921). See also note by Professor Bray in the First Report of the Committee on Contact Catalysis [Bancroft, *J. Ind. Eng. Chem.*, **14,** 327 (1922)].

nature of the adsorption of hydrogen by nickel seems, therefore, of fundamental importance in the study of the mechanism of catalytic hydrogenation reactions. Consequently, a study of the ionization and resonance potentials of hydrogen which is adsorbed on a nickel surface was determined upon in the hope of shedding a little light on the mechanism of the adsorption.

The method adopted is similar to that used by Franck and Einsporn[7] in the study of the critical potentials of mercury, by Olson and Glockler[8] in the investigation of the critical potentials of hydrogen, and by Rollefson[9] in determining spectral series in the soft X-ray region. It involves the generation of radiation by electronic bombardment of the substance in question. When this radiation falls upon a platinum plate a photo-electric current is produced and studied as a function of the accelerating potentials applied to the electron producing the radiation. A discontinuity in the rate of increase of the photo-electric current is interpreted as indicating the excitation of characteristic radiation.

## Apparatus

The apparatus used is shown in Fig. 1.

A tungsten filament (1) serves as a source of electrons when heated to incandescence by means of a storage battery. It is kept at a constant positive potential of from 13 to 17 volts during a run. A target (2) consists of a nickel grid which has been activated by dipping in nitric acid and fused nickelous nitrate, then calcining in air at 400°, and finally reducing *in situ* with hydrogen at 300°. It is fastened by nickel wires to the flattened end of a glass tube arranged so as to be cooled by circulating water. The potential on 2 is greater than on 1 and is varied by means of a potential divider and source of electromotive force. A screen of copper wire (3) is kept at zero potential by earthing. Since it is negative to the filament it retards electrons and accelerates positive ions. A screen of copper wire (4) charged positively to 80 volts, attracts electrons and repels positive ions. A screen of platinum wire (5) is kept at zero potential. A platinum disc (6), used as a receiver for the radiation from the target, is connected to a Compton electrometer on which the photo-electric current was measured.

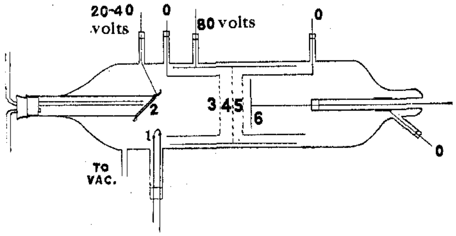

Fig. 1.—Apparatus for determining ionization and resonance potentials.

Hydrogen was prepared by electrolysis of concd. sodium hydroxide solution and purified by passage over heated platinized asbestos and phosphorus pentoxide.

## Method of Operation

After reduction of the nickel target the tube is baked at 400° and evacuated by a mercury vapor pump until a pressure of $10^{-5}$ mm. of mercury

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[7] Franck and Einsporn, *Z. Physik*, **2,** 18 (1920).

[8] Olson and Glockler, *Proc. Nat. Acad. Sci.*, **9,** 122 (1923).

[9] Rollefson, *Phys. Rev.*, **23,** 35 (1924).

may be maintained overnight. A liquid-air trap is inserted in the line just next the tube to freeze mercury vapor.

The voltage on the filament (1) is then fixed, the wire heated to incandescence and a positive voltage greater than that on the filament is placed on the target (2). Electrons are given off by the filament and accelerated toward the target. Collision with the latter induces secondary radiation which exerts a photo-electric action on the plate (6). The plate loses electrons and becomes charged positively, causing a deflection of the electrometer. This deflection increases regularly with the increase in accelerating voltage until resonance or ionization occurs. At these points breaks appear on the curve.

A blank run on the nickel target before hydrogen was admitted showed no appreciable deflection under an accelerating voltage of as high as 30 volts.

The filament was heated and hydrogen admitted to a pressure of approximately 10 mm. of mercury and allowed to remain for five minutes, after which the pumps were started. When the pressure reached $10^{-4}$ mm. of mercury the run was started. The voltage on the target was raised in 0.5–1.0 volt steps and the corresponding deflections were read on the electrometer. The accelerating voltages were plotted against the corresponding electrometer deflections and the breaks read off from the discontinuous curve drawn through the resulting points.

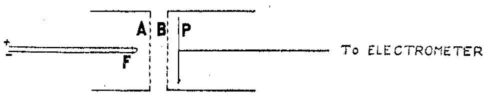

Fig. 2.—Electrode arrangement for determining initial electron velocities.

To determine the correction for the initial velocity of the electrons from the filament as well as for any contact potentials, a similar tube was constructed of gauze catalyst as shown in Fig. 2.

F is the tungsten filament source of electrons and is maintained at a definite positive potential. A is a nickel catalyst gauze prepared as in the case of the ionization experiments and is maintained at a positive potential slightly higher than F. B is a similar nickel gauze but is charged negatively. P is a platinum plate connected to the Compton electrometer.

The potentials on F and A are fixed, the filament is heated and hydrogen admitted in the same manner as in the ionization experiments. The negative potential on B is then raised until electrons are just stopped from reaching P. A–F will be the accelerated voltage. If the electrons had no initial velocity a negative voltage equal to A–F would stop them. The negative voltage required was 0.2 volt greater, indicating a correction of 0.2 volt to be subtracted from the values for the critical potentials.

Nine runs were made, the results of which are shown in Table I. A typical accelerating voltage-electrometer deflection curve is shown in Fig. 3.

TABLE I

SUMMARY OF BREAKS IN ACCELERATING VOLTAGE-ELECTROMETER DEFLECTION CURVES

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | .... | .... | .... | 16.6 | .... | 20.6 | .... |
| | 10.7 | 12.2 | 13.5 | 16.6 | .... | 20.6 | 22.6 |
| | 10.3 | 12.2 | 13.4 | 16.5 | 17.9 | 20.6 | 22.2 |
| | .... | .... | .... | 16.1 | 18.0 | 20.8 | .... |
| | 10.1 | .... | 13.4 | 16.1 | 18.2 | 20.1 | 23.3 |
| | 10.8 | .... | 13.3 | 16.1 | 18.2 | 20.6 | .... |
| | 10.7 | 12.0 | 14.2 | 16.5 | 18.4 | 20.0 | 22.2 |
| | 10.3 | 11.5 | 13.2 | 16.2 | 18.3 | 20.3 | .... |
| | 10.2 | 11.9 | 14.0 | 16.7 | .... | .... | .... |
| Av. | 10.4 | 12.0 | 13.6 | 16.4 | 18.2 | 20.5 | 22.6 |

The following interpretation is placed upon the breaks obtained, the figures being the averages shown in Table I: 10.4, resonance of one atom of hydrogen; 12.0, the second line of the Lyman series (hydrogen atom); 13.6, ionization of the atom (alternative, dissociation of the molecule plus resonance of one atom); 16.4, dissociation of the molecule plus ionization of one atom; 18.2, dissociation of nickel-hydrogen complex plus ionization of a hydrogen atom; 20.5, resonance of two atoms of hydrogen; 22.6, molecular ionization.

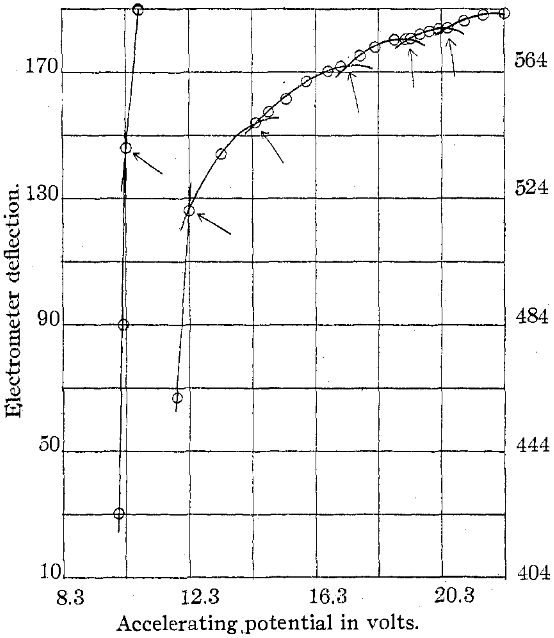

Fig. 3.

An alternative interpretation of the 18.2 volt point is possible, namely, that it represents dissociation of the molecule plus ionization of one atom plus the first line of the Balmer series ($3.2 + 13.5 + 1.5 = 18.2$ volts). This presupposes the presence of sufficient excited atoms.

The critical potentials of hydrogen have been determined by many experimenters with a variety of results.[10,7,8]

A discussion of the various values for the critical potentials is not within the scope of this paper. It will be sufficient to compare the agreement between the values determined by the writer and a few of those recently determined by others. These are given in Table II.

Col. 1 gives the values calculated on the basis of the Bohr-Sommerfeld theory of the structure of the hydrogen atom.[11] The figures correspond to the first, second and convergence lines of the Lyman series. The ionization voltage is determined by the limit of the series, namely, by Rydberg's number, $R = 109{,}677$ cm.$^{-1}$ The other voltages are determined by the other lines of the series calculated from the formula ($\nu =$ wave number), $\nu = R\left(\frac{1}{1^2} - \frac{1}{k^2}\right)$, where $k = 2$ or 3. Thus the resonance voltage is determined by the base line of the series, namely, $\nu = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 3/4\ R$, and the second line by the equation, $\nu = R\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = 8/9\ R$. These may be converted into volts by the following relationship, $eV = h\nu = h \times c/\lambda$, where $e$ is the charge on electron $= 1.59 \times 10^{-20}$ e.m.u.; $V$ is the voltage in e.m.u.; $V \times 10^8 =$ volts (practical units); $\nu$ is the frequency of radiation; $\lambda$ is the wave length in cm.; $h$ is Planck's constant $= 6.55 \times 10^{-27}$ erg. sec. Then volts $\times\ \lambda$ (Å.) $= \frac{h \times c}{e} = 12{,}346$, and volts $= \frac{12{,}346}{\lambda \text{ (Å.)}}$, where the voltage is in practical units and wave length in Ångström units.

The ionization potential is given by the expression: volts $= 12{,}346 \times \nu \times 10^{-8} = 12{,}346 \times R \times 10^{-8} = 1.234 \times 10.968 = 13.53$. Since the other frequencies are $3/4\ R$ and $8/9\ R$, respectively, the corresponding

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[10] (a) Franck, Knipping and Krüger, *Verh. deutsch. physik. Ges.*, **21,** 728 (1919). (b) Davis and Goucher, *Phys. Rev.*, [2] **10,** 101 (1917). (c) Found, *ibid.*, **16,** 41 (1920). (d) Mohler and Foote, *Bur. Standards, Sci. Paper,* **400,** 669 (1920); *J. Opt. Soc. Am.*, **4,** 49 (1920). (e) Horton and Davies, *Proc. Roy. Soc.*, **97A,** 1 (1920); *Phil. Mag.*, **46,** 872 (1923). (f) Krüger, *Ann. Physik,* **64,** 288 (1921). (g) Bishop, *Phys. Rev.*, **10,** 244 (1917). (h) Compton and Olmstead, *ibid.*, **17,** 45 (1921). (i) Mohler, Foote and Kurth, *ibid.*, **19,** 414 (1922). (j) Boucher, *ibid.*, **19,** 189 (1922). (k) Olmstead, *ibid.*, **20,** 613 (1922). (l) Duffendack, *ibid.*, **20,** 665 (1922). (m) Franck, *Z. Physik,* **11,** 155 (1922). (n) Mackay, *Phil. Mag.*, **46,** 828 (1923). (o) Olmstead and Compton, *Phys. Rev.*, **22,** 559 (1923).

[11] Sommerfeld (trans. by Brose), "Atomic Structure and Spectral Lines," Methuen and Co., Ltd., London, **1923.**

voltages will be: $3/4\ R = 3/4 \times 13.53 = 10.15$ volts; $8/9\ R = 8/9 \times 13.53 = 12.03$ volts. Col. 2 gives the average values observed by the author, and the other columns give the values reported by other experimenters.

TABLE II

CALCULATED AND OBSERVED CRITICAL POTENTIALS OF VARIOUS INVESTIGATORS

| Calculated | Observed | Olson and Glockler[8] | Horton and Davies[10e] | Mackay[10n] | Franck[10m] | Olmstead[10o] |
|---|---|---|---|---|---|---|
| 10.15 | 10.4 | .... | 10.2 | .... | .... | 10.15 |
| 12.03 | 12.0 | 11.98 | 11.9 | .... | .... | 12.05 |
| .... | .... | .... | 12.6[a] | .... | .... | .... |
| 13.53 | 13.6 | .... | 13.5 | .... | .... | 13.54 |
| .... | 16.4 | .... | 15.9 | 15.8 | 16.4 | 16.0 |
| .... | 18.2 | .... | .... | .... | .... | .... |
| .... | 20.5 | .... | .... | .... | .... | .... |
| .... | 22.6 | .... | 22.8 | .... | .... | .... |

[a] Horton and Davies interpret the 12.6 volt point as dissociation of the molecule plus resonance of one atom, and the 13.5 volt point as ionization of one atom.

If the above interpretation of these experiments is correct it would appear that the energy relations in the system comprising hydrogen and a nickel catalyst are similar to those predicted by theory and experimentally found for atomic hydrogen.[10l] No inferences can be drawn with regard to the amount "dissociated," the thickness of the adsorbed layer, or the mechanism of the adsorption. However, the following reactions offer a satisfactory picture of the latter (Ni:H representing the adsorbed hydrogen).

$$2\mathrm{Ni} + \mathrm{H_2} \rightleftarrows 2\mathrm{Ni{:}H} \quad (1) \qquad 2\mathrm{Ni{:}H} \rightleftarrows 2\mathrm{Ni} + 2\mathrm{H} \quad (2) \qquad 2\mathrm{H} \rightleftarrows \mathrm{H_2} \quad (3)$$

If the reactions in Equilibrium 3 are slow (for which conclusion there is some evidence in R. W. Wood's experiments on the Balmer series[12]) whereas those of Equilibria 1 and 2 are rapid, it is easy to understand the presence of atomic hydrogen at or near the surface of the metal; hence, the breaks at 10.4, 12.0 and 13.6 volts are readily accounted for. The author considers that these experiments shed a little light on the marked activity of nickel catalyst in hydrogenation reactions. The hydrogen is undoubtedly in an "activated" condition, momentarily at least, and is concentrated in such condition at or near the surface of the metal. However, we must not infer that this is the whole story, for probably it is necessary that the other reacting molecules undergo a suitable activation such as through adsorption, etc., before reaction occurs.

The author wishes to express his thanks and appreciation to Dr. G. K. Rollefson for his valuable suggestions and to Mr. W. J. Cummings, laboratory glass blower, for construction of the intricate glass apparatus.

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[12] Wood, *Phil. Mag.*, **44**, 538 (1922).

The work was carried out under a Fellowship of the National Research Council for which the author expresses his gratitude.

## Summary

Seven critical potentials of hydrogen in the presence of nickel catalyst have been determined. Four of these have been attributed to the atom, two to the molecule and one to the nickel-hydrogen complex. The results are considered to indicate the presence of atomic hydrogen in the system, hydrogen-nickel catalyst.

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## NOTE

**The Bifilar Quartz Fiber Manometer.**—In a recent article,[1] I described a form of bifilar quartz fiber micromanometer suitable for adsorption measurements at low pressures. The instrument was separated from the rest of the apparatus by a gold-foil trap, with the object of keeping out mercury vapor, and was cooled with snow in order to prevent errors due to temperature variations. In working with this manometer at still lower pressures, it soon became apparent that the gold trap was quite ineffective. When a plain trap was substituted, and cooled to —25°, the constant "$a$," (reciprocal of time in which the amplitude falls to $1/e$ times its original value in a perfect vacuum) fell from 0.0006 per second to 0.0002 per second, in the case of Gage "B." Further cooling the trap did not further diminish the damping. Variations in the temperature of the gage did not alter the damping. The great diminution of damping previously found to be caused by cooling the gage must therefore have been due simply to the removal of mercury vapor by condensation on the cold walls.

This error in the evaluation of "$a$" cannot have affected the validity of the conclusions drawn in the previous paper, since it merely added a constant quantity to $C$ in all readings; moreover, it is entirely negligible at the higher pressures with which the paper was mainly concerned.

When the gage is used in the lower range, its temperature need not be known. The resistance which a fiber of unit length and velocity experiences in moving through a gas at low pressure is, by Haber and Kerschbaum's[2] Equation 13, $K = \frac{4P\sqrt{M}}{\sqrt{3RT}}D + Z$, where $D$ is the diameter of the fiber, and $Z$ its intrinsic viscous resistance. If, now, such a fiber is calibrated against a Macleod gage at the same temperature, and the temperature of the quartz gage is then changed (the pressure in the Macleod

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[1] Coolidge, THIS JOURNAL, **45**, 1637 (1923).

[2] *Z. Elektrochem.*, **20**, 297 (1914).