

Microwave Discharge Production of Hydrogen Atoms. Control of Hydrogen Atom Quantity Produced

BØRGE BAK and JOHN RASTRUP-ANDERSEN

Chemical Laboratory of the University of Copenhagen, Copenhagen, Denmark

Production of hydrogen (and deuterium) atoms by a microwave discharge is described. Three different methods of estimating the quantity of atoms produced have been tested. A hotwire detector, a thermometric detector, and a 'chemical', luminescent detector. Application of each of the three types of indicator is useful in various phases of experimental work.

As is well-known, hydrogen atoms have very frequently been produced in a so-called Wood's tube¹ (from its inventor) in which a stream of molecular hydrogen passes metallic electrodes. In an electrodic discharge, dissociation occurs to an appreciable extent.

Experience has, however, shown such production to be unreliable, one main reason being that somehow or other metal dust particles are soon scattered in almost every part of the equipment. As this happens, the yield of hydrogen atoms decreases very rapidly because metals catalyze the recombination of hydrogen atoms to molecules. This is why an electrodeless discharge of the type which can be arranged by means of microwaves, is advantageous *a priori*.

Of course, other factors are operative in helping the hydrogen atoms to recombine. While recombination cannot occur in a simple two-body collision (because of energy), the *walls* of the container may assist. Already Wood discovered that he could make the container walls less effective as a recombination catalyst by 'poisoning' them with syrupous phosphoric acid or other compounds. If this precaution is not taken, the walls slowly 'dry out' in the vacuum usually applied. A *dry* glass surface seems rather effective as a hydrogen combiner. Phosphoric acid *etc.* thus serves as a source of loosely bound water. Evidently, constant admixing of water vapor may serve as well in many cases since the inevitable production of the OH radical from H₂O will do no harm in cases where the reaction zone is well separated from the production zone, so that the reaction $H + OH \rightarrow H_2O$ annihilates all OH radicals before the reaction zone has been reached. In all our experiments we have,

therefore, used moist hydrogen or deuterium, produced by letting the gas at atmospheric pressure bubble through water at room temperature, the water vapor content thereby being of the order of 3–4 %. If the temperature of the water, through which H_2 (or D_2) was bubbled, was lowered to $1^\circ C$, a marked decrease in hydrogen atom yield was noted.

THE PRODUCTION OF HYDROGEN OR DEUTERIUM ATOMS

Commercial tank hydrogen (free of CO and halogens) or D_2 (produced by electrolysis of $D_2O + NaOD$) was passed through a commercial De-oxo unit * (for removal of oxygen) and a washbottle with water at atmospheric pressure into a capillary tube (length 10 cm, i.d. 0.18 mm), backed up by the rest of the equipment, consisting of 17 mm i.d. tubing, wider flasks, traps *etc.* and a Leybold D2 vacuum pump (capacity $2 m^3$ per hour at the pressure of 0.1–1 mm Hg applied here). The hydrogen pressure was read on a silicon oil manometer.

Quartz tubing was used at the place where molecular hydrogen was passed through a microwave cavity because of its dielectric properties, superior to those of ordinary glass and Pyrexglass, the microwave input through a glass wall being smaller (although by no means negligible). The cylindrically shaped microwave cavity, made of brass, (dimensions: 75 mm of diameter, 75 mm of length, with a central hole at both ends, 25 mm wide) was coupled to a Q.K.62 magnetron (forced-air cooled) by means of a coaxial connexion with two perpendicular tuning stubs (Fig. 1). Forced-air was continuously blown into the cavity through one of the two central openings. Matching of the magnetron-cavity system was ensured by means of the tuning stubs and adjusted to maximum brilliance of the discharge, the starting of which was performed by a Tesla-coil leak detector. Final matching of magnetron and cavity, resulting in maximum production of hydrogen atoms, was obtained by use of a hot-

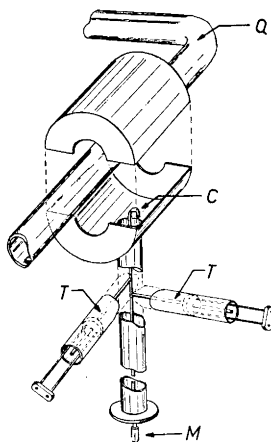


Fig. 1. Microwave discharge arrangement. Q = quartz tube for streaming gas; C = coupling loop; T = tuning stub; M = magnetron connector.

* Engelhard Industries Ltd., Baker Platinum Div., High Holborn, London W.C.I.

wire hydrogen atom detector to be described in a later paragraph. The Q.K.62 Raytheon magnetron was powered by a 1250 V d.c. power-supply, capable of yielding 100 mA. The actual current was 80–90 mA. The magnetron filament current was 3.3 A, the voltage 6.2 V.

CONTROL OF ATOM PRODUCTION

A. Hot-wire detector

Hot-wire detectors for the control of hydrogen atom production have been constructed by numerous investigators¹. The present construction owes most of its features to T. M. Shaw who has published a most valuable report on studies of microwave gas discharges². The use of some sort of hydrogen atom detector seems indispensable, although often neglected, since probably no equipment can be constructed yielding a constant production of hydrogen atoms because of uncontrollable contamination with dust that may include metal particles. Shaw's three-dimensional hot-wire detector was replaced by us by a simpler two-dimensional construction which seemed equally effective and less difficult to prepare and to handle (Fig. 2). The detector was placed at the location in the equipment where we expected the hydrogen atoms to react, *i.e.* 18 cm from the microwave discharge. Electrically, the detector formed one of four arms of a bridge (Fig. 3), the same arm including an ammeter (1000 mA full scale) for measurement of the detector current I_D . Also, the voltage across the detector wire could be measured (detector voltage V_D). When the bridge is balanced, the resistance of the hot-wire detector attains a reference value (R_1 of Fig. 3). The current across the bridge (and through the detector) is variable by means of R_4 (Fig. 3).

In one experiment, undissociated molecular hydrogen, at the pressure and temperature to be used under hydrogen atom production, passed the detector, suitably heated to a light-read glow (700–800°C) by I_D , in this case denoted by I_D^0 , the corresponding voltage drop being V_D^0 . Now, the microwave discharge was started. This caused the temperature of the detector to rise because of the recombining hydrogen atoms. Therefore, the bridge current was lowered, until balance was again obtained at current I_D^x and voltage V_D^x . Obviously, the recombination of hydrogen produced

$$I_D^0 V_D^0 - I_D^x V_D^x \text{ watts.}$$

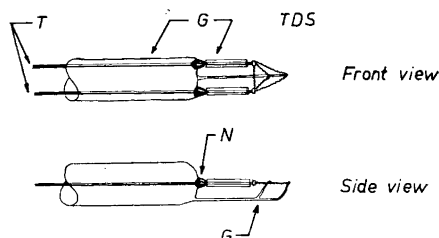


Fig. 2. Hot-wire detector. T = tungsten rod; TDS = tungsten double spirals (filaments from 75 watts electric bulbs (220 V)); G = glass; N = Nonex beads.

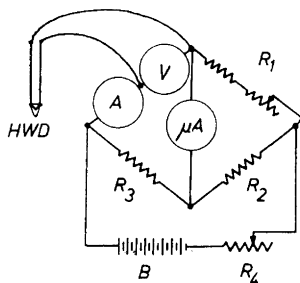


Fig. 3. Balanced bridge A = ammeter (1 A., full scale); V = voltmeter (25 V, full scale); μA = microammeter (-50 to $50 \mu A$); $R_1 = 52 \Omega$ plus 10Ω variable; $R_2 = R_3 = 100 \Omega$; $R_4 = 50 \Omega$; HWD = hot-wire detector; B = battery (30 V.).

In a typical example, $I_D^0 = 0.362$ A, $V_D^0 = 11.0$ V (3.99 watt) and $I_D^x = 0.254$ A, $V_D^x = 7.7$ V (1.95 watt). Difference, 2.04 watt. In this experiment, the molecular hydrogen input ($p = 0.3$ mm Hg) was 0.140 ml/sec, or 5.86×10^{-6} moles/sec. Complete dissociation would produce 11.72×10^{-6} atoms/sec. At their recombination, they would liberate $\frac{1}{2} \times 11.72 \times 10^{-6} \times 1.03 \times 10^5$ cal. or 2.52 watts. This means that at 18 cm from the microwave discharge, 80% of the hydrogen still existed as atoms. If the above-mentioned 18 cm distance was increased to 25 cm, the yield decreased to 65%. In view of this it is, therefore, quite probable, that our hot-wire detector gives a fair measure of the quantity of atomic hydrogen. It was impracticable for us to arrange an experiment with a distance *smaller* than 18 cm because a bend on the quartz tubing had deliberately been introduced in order to prevent the radiation from the microwave zone to reach the point where the quantity of hydrogen atoms is measured and where the atoms are scheduled to react with other compounds.

B. Effect of pressure and temperature changes

Doubling of the molecular hydrogen input and pressure ($p = 0.6$ mm Hg) to 0.280 ml/sec gave $I_D^0 V_D^0 - I_D^x V_D^x = 2.35$ watts, the yield now having decreased to 37%.

Heating of the quartz tube (to 200°C) in a 5 cm zone between the generator and the detector caused a very serious decrease in yield (to about one-half). This may be in disharmony with Shaw's findings². However, while the walls of our tubing were not 'poisoned' (moist hydrogen or deuterium being used instead), Shaw treated his equipment with GE Dri-Film SC77 ($(\text{CH}_3)_2\text{SiCl}_2 + \text{CH}_3\text{SiCl}_3$), which might account for the fact that the hydrogen atom yield, obtained by Shaw, was rather independent of heating of the tube following the discharge zone. A film of adsorbed water, 'poisoning' our tubing at 25°C , obviously partly evaporates at higher temperatures. This latter circumstance, on the other hand, gives the possibility of constructing a variable hydrogen atom 'attenuator', permitting the investigator to vary his hydrogen atom production in a very useful way without change of molecular hydrogen input.

C. Thermometric detector

Already Bonhöffer¹ demonstrated the usefulness of a metal-coated thermometer as a detector. We have studied this matter in somewhat greater detail because of the simplicity of the principle. The following procedure for coating the thermometer bulb with a thin layer of silver gave fully reproducible results. The bulb of an ordinary 350°C thermometer (length of the bulb 10 mm, diameter 5 mm) was ground by emery cloth. The matt surface thus produced was treated by hot chromic acid-sulphuric acid mixture, washed thoroughly with distilled water, immersed in alcohol for a few seconds and thereafter immersed in 0.1 N aqueous AgNO₃. After wetting, the bulb was dried in a stream of hot air, while the thermometer was rotated. It is important that no AgNO₃ reaches the thermometer stem. 3–4 times, a fresh droplet of AgNO₃ was added and the water evaporated. No further addition of AgNO₃ was necessary, as shown by our experiments.

When a thermometer so prepared is placed in the equipment instead of the hot-wire detector, and immersed in a stream of atomic hydrogen, AgNO₃ is rapidly reduced to metallic silver, which sticks extremely well to the bulb. In a stream of hydrogen atoms, such as the first one described under paragraph A of this paper, the equilibrium temperature obtained after 10–15 min) is as much as 300°C. Since this detector type is easy to make, easy to place in a side-arm of almost any type of equipment, and easy to insert and withdraw (magnetically) without braking the vacuum or interrupting an experiment, this high thermometer reading deserves attention. We have, for example, found it useful to place a thermometer after the zone of a chemical reaction. The initiation and the termination of a chemical reaction between hydrogen atoms and a reagent was simply indicated by a pronounced drop and rise in temperature. Table 1 shows a series of experiments in which the hot-wire detector and a given thermometric detector were compared.

Table 1. Comparison of hot-wire and thermometric detector.

Moles H ₂ /sec × 10 ⁵	0.586	0.732	0.878	1.024	1.170
$I_D^o V_D^o - I_D^x V_D^x$ watts	2.04	2.19	2.25	2.32	2.35
Temperature reading	308°	317°	319°	312°	307°

In these five experiments, approximately a constant quantity of hydrogen atoms is produced (as shown by the wattage) in spite of the increasing molecular hydrogen input. To a fair degree, the thermometer reading is also constant. On several occasions we have observed that inferior atomic output (for example, due to impurities left-over from chemical reactions, or because of incorrect matching of the magnetron) is easily and unequivocally indicated by the thermometer, provided that the thermometer is correctly stored between uses, for example, by withdrawal to a side-arm of the equipment, the bulb being removed 8–10 cm from the zone of the hydrogen atoms.

D. Chemical detection

In a paper by Vance and Bauman³ it is stated that at a specified concentration of CCl_4 vapor, the reaction between hydrogen atoms and CCl_4 may be used to determine the concentration of hydrogens actually being produced, since all hydrogen atoms are converted to HCl . The conditions necessary for obtaining this are: a pressure of about 0.8 mm Hg, a temperature of 150–200° and a CCl_4 :H ratio of about 10:1, that is, in the equipment specified in Ref.³.

If CCl_4 vapor was introduced by us through a jet in a small heated zone (215°C) where, from previous experiments, we know that a hydrogen atom yield of about 35% is obtained, the yield of HCl , trapped in 2 successive, liquid nitrogen-cooled traps, turned out to be 7% with respect to hydrogen. In this experiment, the CCl_4 :H ratio was about 9:1, the somewhat undefined pressure of the reaction zone being of the order of 0.4 mm of Hg. Hence, we were unable to reproduce the result of Ref.³. Nevertheless, it is of interest to see what happens at the more easily obtainable room temperature. Here, in experiments, where our hot-wire detector indicated the presence of 64% dissociated hydrogen molecules, an excess of CCl_4 vapor produced only 15% HCl . The reaction zone was clearly visible, because a light-green radiation was emitted. This result was reproducible. Under many circumstances this radiation and the accompanying HCl -production might be used as an indicator of an existing hydrogen atom production, 8–10 times higher than indicated by the amount of HCl formed. The method of Ref.³ has not been listed in the appropriate paragraph II, 8 of Ref.¹.

REFERENCES

1. Steacie, E. W. R. *Atomic and Free Radical Reactions*, Reinhold Publishing Co., N.Y. 1954.
2. Shaw, T. M. *General Electric Techn. Inform.* No R 58, ELM 115, G.E. Microwave Laboratory, Palo Alto, California.
3. Vance, J. E. and Bauman, W. C. *J. Chem. Phys.* 6 (1938) 811.

Received July 8, 1961.