Adsorption and Recombination of Hydrogen Atoms on Glass Surfaces

Part 1.—Method of Study and the Mechanism of Recombination at 77 and 273 K

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The mechanisms by which hydrogen atoms recombine on the surface of a 1 dm^3 Pyrex glass bulb have been studied by following the changes in pressure during and after dissociation of molecular hydrogen at an incandescent tungsten filament. Experiments were conducted in a system capable of ultra high vacuum using hydrogen pressures in the range 10^{-5}-10^{-3} N m^{-2}.

At 77 K, recombination occurred mainly as a result of collisions between gas phase atoms and adsorbed atoms (the Eley–Rideal process), with virtually no contribution from the recombination of adatoms (the Langmuir–Hinshelwood process). With the glass surface at 273 K, a weakly bound state of atomic hydrogen could be maintained on the surface only in the presence of gas phase hydrogen atoms. This weakly bound state constituted $\approx$ 3-10 % of the total adsorbed atomic hydrogen but was of considerable significance, being the major participant in both the Eley–Rideal and Langmuir–Hinshelwood processes occurring at this temperature.

The mechanism of hydrogen atom recombination on glass and silica surfaces is not understood in any detail. Direct experimental evidence of the nature and relative importance of the individual steps in the process is lacking. At a deeper level, there is an inadequate knowledge of the surface and of the adsorbed states of hydrogen taking part in the recombination.

The study of surface catalysed recombination in the past has been focused almost exclusively on the measurement of recombination rate as determined by the disappearance of atoms from the gas phase.[1] Results have been expressed in terms of a single parameter, the recombination coefficient γ, defined as the probability that an atom recombined on encountering the surface. The dependence of this recombination coefficient on gas phase atom concentration and temperature has been used to discuss the mechanism of the reaction. Several investigations of the recombination of hydrogen atoms on glass or silica have been made [2-6] over a number of years, the most extensive being that of Wood and Wise.[4] Values of the recombination coefficient obtained by different groups have been in general agreement, except those reported by Pospelova and Myasnikov [5] above room temperature which do differ substantially from the results of other workers.

Wood and Wise reported almost identical results for both Pyrex glass and quartz above 250 K. The recombination coefficient for glass was found to vary in a complex manner with temperature within the range 10^{-5}-10^{-2} between 77 and 1125 K. Over a wide temperature range the reaction was reported as first order with respect to gaseous atoms, but at both high and low temperature limits a change to second order kinetics was observed.

Two fundamentally different mechanisms have been proposed to explain the general phenomenon of atom recombination at surfaces.[1] The Eley–Rideal

mechanism involves a direct collision of an atom coming from the gas phase with either a mobile or immobile adatom, whereas the Langmuir–Hinshelwood mechanism involves an encounter between two adatoms both of which are presumably mobile. An analysis of recombination coefficients in terms of these two mechanisms can be ambiguous if little is known about the adsorbed phase. At high surface coverage the Eley–Rideal mechanism exhibits first order kinetics and the Langmuir–Hinshelwood mechanism zero order kinetics in the gaseous atom concentration. However, at low coverages when the surface density of adatoms is proportional to the gas phase atom concentrations, both mechanisms give second order kinetics. As the adatoms play such a crucial role in determining both the rate and kinetics of recombination, the nature of the adsorbed phase and the adsorption energies of the adatoms are most relevant to a complete understanding of recombination.

Experimental evidence suggests that hydrogen atoms on glass exist in one of at least two states.[7, 8] According to de Boer and van Steenis, the adsorbed phase can be visualised as a strongly bound layer of hydrogen (binding energy $\approx 184 \text{ kJ mol}^{-1}$) with an overlayer of weakly bound atoms (binding energy $\approx 10 \text{ kJ mol}^{-1}$) present only at temperatures well below room temperature. More recent evidence suggests that this weakly bound layer can be further subdivided into two different states of adsorbed hydrogen atoms.[9]

Wood and Wise,[4] using the model of de Boer and van Steenis, together with their transition state calculations for both Eley–Rideal and Langmuir–Hinshelwood mechanisms based on the above adsorption energies, have been able to reproduce quite closely their own experimental recombination coefficients over the whole range of temperature. Gelb and Kim[10] have, however, criticised the transition state calculations used by Wood and Wise and by applying a collision theory to just the Eley–Rideal mechanism have obtained similar agreement with experiment using the same two-layer model. It is clear from the various theoretical considerations that a single parameter (γ) is not adequate for characterising the mechanism and that techniques other than the measurement of steady state recombination rates must be employed if an understanding of catalysed recombination is to be fully realised.

Molecular hydrogen can be readily dissociated at an incandescent filament. The early experiments of Langmuir[11] showed that the atomic hydrogen produced was rapidly adsorbed by the glass walls of the vacuum system, resulting in a drop in pressure. This drop in pressure was later used by Hickmott[12] to measure the rate of dissociation occurring at the filament. Both Langmuir[11] and Hickmott[8] have reported, as dissociation proceeded, a progressive reduction in the efficiency of the glass in taking hydrogen from the gas phase. Hickmott attributed this so called " fatigue " effect to the recombination of atoms at the surface of the glass as the adatom concentration built up and he proceeded to make a simple analysis on this basis. Unfortunately, as we shall show, Hickmott's vacuum system was badly designed for studying the recombination in detail. We have developed his technique and have been examining both the adsorption and recombination of atomic hydrogen on glass simultaneously under pre-steady state surface conditions. We report here the general features we observe for the recombination at 77 and 273 K.

EXPERIMENTAL

Experiments were performed in an all glass ultra high vacuum system, pumped by mercury diffusion pumps, capable of attaining a base pressure of 10^{-7}-10^{-8} N m^{-2} after baking to 600 K. The system is shown schematically in fig. 1. Hydrogen was dissociated on a tungsten filament f situated at the centre of a 1 dm^3 Pyrex glass bulb. The filament was

spot welded onto 2 mm tungsten rods which were covered over most of their length with glass, so as to avoid any substantial interaction of atomic hydrogen with cold tungsten. A glass disc was sealed onto the rods below the feed-through, maintaining as closely as possible the continuity of the glass sphere. Hydrogen could enter or leave the cell through a 4 mm hole in the glass wall.
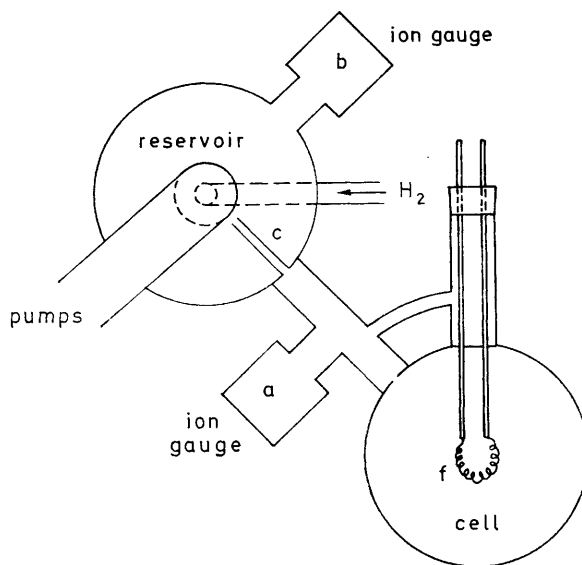

FIG. 1.—Schematic diagram of apparatus used for adsorption/recombination studies of hydrogen atoms on glass.

Hydrogen (BOC X grade) was admitted to the reservoir *via* a heated palladium thimble, the steady state pressure being maintained by control of the thimble temperature or by adjustment of ground glass valves situated above the diffusion pump traps.

Dissociation at the filament led to a drop in pressure in the cell. The hydrogen flow between the cell and reservoir through the narrow tube, c, the conductance of which could be calculated from the geometry, was monitored using ionisation gauges fitted with thoria coated iridium filaments. These filaments were operated to give an electron emission of $5 \mu A$, using a regulator described by Chapman,[13] to prevent hydrogen pumping by the gauges. The ion current from gauge a was measured using a Keithley 417 picoammeter: that from gauge b by a Keithley 602C electrometer. The gauges were calibrated against a McLeod gauge in the range 10^{-3}-10^{-1} N m^{-2}: pressures lower than this were determined by extrapolation of the linear ion current–pressure relationship.

The atomisation filament comprised a coiled length of 0.2 mm diameter tungsten wire. This was lightly etched electrolytically in dilute sodium hydroxide solution in much the same way as the one used by Hickmott.[8] When in the vacuum system, the filament was aged by heating to $\approx$ 2500 K for several hours in a vacuum of $\approx 1 \times 10^{-7}$ N m^{-2}. Prior to each experiment the filament was heated to 2200 K for $\approx$ 3 h under the same conditions to ensure a reproducible dissociation of hydrogen comparable with the results of other workers. To prevent significant evaporation of tungsten and deposits forming on the glass surface, the filament was never heated to temperatures > 2500 K. Even so, after about 12 months operation using the same filament, the surface of the cell did show slight signs of darkening which was presumably a result of evaporated tungsten. This darkening did not appear to have any influence on the results obtained, a finding which is consistent with Langmuir's [11b] observation that a deposit formed by evaporation from a palladium filament did not affect the adsorption of atomic hydrogen on glass.

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Before admitting the hydrogen, the filament temperature was adjusted to 1100 K. At this temperature there was no appreciable dissociation of hydrogen and, at the same time, little adsorption on the filament. To bring about dissociation, the filament was switched to a stabilised d.c. power supply previously adjusted to give the required temperature. The temperature against voltage characteristics of the filament were determined with the aid of an optical pyrometer.

RESULTS AND DISCUSSION

Hydrogen flows through the narrow conductance tube when there is a pressure differential between the cell and reservoir. If hydrogen is being absorbed by the walls of the cell, then the pressure in the cell is lower than in the reservoir and gas flows into the cell. Conversely, desorption of hydrogen leads to a higher pressure in the cell and a gas flow in the direction of the reservoir. In our experiments, since free molecular flow conditions prevail, the pressure differential Δp is a direct measure of the rate F at which gas is flowing from or to the cell for, according to Clausing,[14] $F = C\Delta p$ where $C = ZA/(1+3L/8r)$ provided $L \gg r$; A is the cross-sectional area of the tube, L is its length and r its radius and Z is the collision number as given by the Hertz-Knudsen relationship. The conductivity tube had the dimensions $L = 49.5$ mm, $r = 1.9$ mm (average) giving $L/r = 26.1$ and a value of C equal to 1.01×10^{17} molecules s^{-1} (N m^{-2})$^{-1}$.
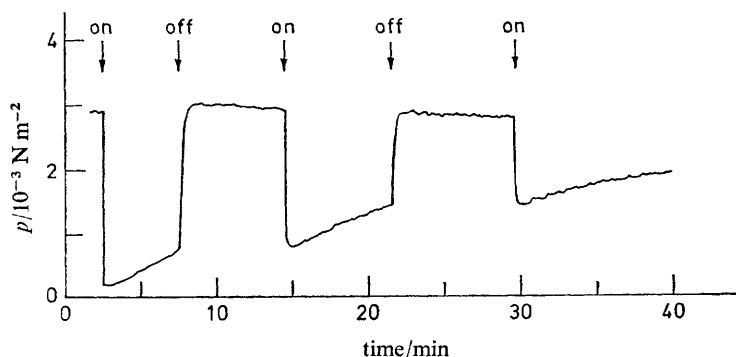

FIG. 2.—Pressure changes in the reaction cell during dissociation of hydrogen. Cell wall at 77 K. The terms " on " and " off " refer to points at which dissociation was started and stopped, respectively. Filament temperature during dissociation = 1616 K.

As the pressure in the reservoir remains approximately constant, changes in pressure in the cell reflect the processes taking place therein. Fig. 2 and 3 illustrate such changes in pressure during two typical experiments. During the run illustrated by fig. 2, the cell was maintained at 77 K after being previously baked at 583 K for ≈ 14 h. For the run shown in fig. 3, the cell wall was at 273 K following a similar bake. In both cases, the pressure in the cell fell as a result of hydrogen adsorption on the walls when the temperature of the filament was raised from 1100 to 1660 K. The minimum pressure p_m recorded by the gauge was reached in ≈ 10 s, but 90 % of the drop occurred within the first 2 s. At both surface temperatures this sharp initial drop was followed by a gradual pressure increase. In general, the rate of the pressure increase varied from one run to another depending on such factors as the initial hydrogen pressure, the filament temperature used for dissociation and the pretreatment of the glass cell. A higher temperature bakeout, for instance, led to a more gradual increase. If dissociation was stopped by switching the filament back

to 1100 K, the pressure rose rapidly to a level that was higher than that in the reservoir. At 77 K the pressure difference was only slight, being no more than a few percent of the total pressure at 10^{-3} N m^{-2} and this was maintained constant with no observable reduction for many minutes. The initial rise of pressure at 273 K was noticeably larger than at 77 K and the magnitude of this increase was also very dependent on how much dissociation had previously taken place. The pressure then reduced quite rapidly following the sharp initial increase, over a period of ≈ 5 min to a level comparable to that observed at 77 K, *i.e.*, the pressure in the cell was just slightly greater than that in the reservoir. Using the methods described later, it can be estimated that this change in pressure observed at 273 K, after turning the dissociation filament down, is a result of 3-10 % of the adsorbed hydrogen leaving the surface.
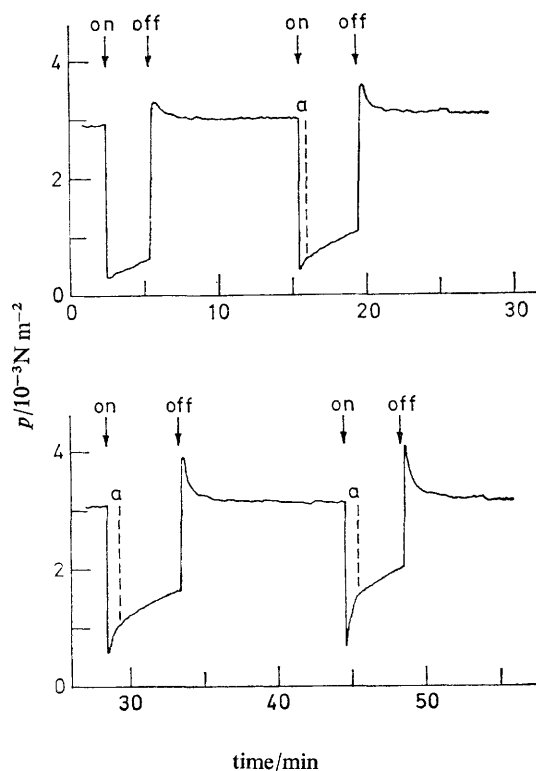

FIG. 3.—Pressure changes in the reaction cell during dissociation of hydrogen. Cell wall at 273 K. The terms " on " and " off " refer to points at which dissociation was started and stopped, respectively. Filament temperature during dissociation = 1616 K.

Dissociation could be recommenced by switching the filament back to the higher temperature. Again marked differences were observed in the pressure profiles at the two surface temperatures. At 77 K, the pressure dropped to the level it had previously reached just before dissociation was stopped. The pressure then continued to rise slowly as before while the dissociation continued. The interruption of dissociation, therefore, caused no marked effect on the gradual rise in pressure. At 273 K, however, the pressure dropped immediately to a value only slightly higher than the minimum p_m reached at the start of the experiment. The pressure then rose in two

distinct stages. The first stage [curve (a) in fig. 3] was rapid and appeared to be associated with replacing that hydrogen lost during the interval when dissociation was not occurring. This could be shown by switching the filament back to 1100 K once this first stage of the pressure rise was complete. The pressure profile then indicated about the same amount (3-10 %) of hydrogen leaving the surface as was observed before. The second stage of the pressure rise was much more gradual and, as at 77 K, was apparently a continuation of the slow rise taking place during the previous dissociation period. These effects could be repeated by a continued cyclic process between the higher and lower filament temperatures, but became more pronounced (at 273 K) with the total amount of hydrogen adsorbed.

RATES FOR ADSORPTION AND RECOMBINATION OF HYDROGEN ATOMS

It can reasonably be argued that the rise in pressure in the cell during dissociation is a result of hydrogen atom recombination at the wall. Glass is known to be an efficient recombination catalyst for hydrogen atoms and as the adsorbed hydrogen builds up on the surface then the possibility of recombination, returning hydrogen back to the gas phase, must increase. The alternative explanation, that the filament becomes progressively less able to dissociate hydrogen as the experiment proceeds, seems extremely unlikely. The differences observed in the pressure changes at the two-cell temperatures are difficult to explain on the basis of some process taking place at the filament. In any case, the " fatigue " effect has not been observed when hydrogen atom traps such as MoO_3 have been used.[15, 16]

On the assumption then that the " fatigue " effect is solely a result of recombination, it can be shown that hydrogen atom adsorption and recombination can be studied in a quantitative way if both the rate of hydrogen uptake by the wall and the simultaneous rate of hydrogen dissociation at the filament can be determined from the changes in pressure.

At a time t during a dissociation period, the rate [$R(t)$] at which the number of hydrogen atoms on the surface changes is given by the difference between the rate at which the atoms stick to the surface [$R_A(t)$] and the rate of recombination. The kinetics of the two recombination processes are fundamentally different so it is important to distinguish between them. If $R_{ER}(t)$ is the rate of recombination by the Eley–Rideal process and $R_{LH}(t)$ the rate of recombination by the Langmuir–Hinshelwood process, then

$$R(t) = R_A(r) - R_{ER}(t) - R_{LH}(t). \tag{1}$$

As the processes of dissociation at the filament and reaction at the wall are fast compared with the change in pressure in the cell, a steady state concentration of gaseous hydrogen atoms must be set up rapidly, under which condition the rate of formation of atoms equals the rate of removal. Atoms are removed from the gas phase by adsorption and recombination, but the only recombination process that is directly active in this respect is the Eley–Rideal process. Therefore

$$R_f(t) = R_A(t) + R_{ER}(t). \tag{2}$$

Combining eqn (1) and (2), we have

$$R_f(t) + R(t) = 2R_A(t) - R_{LH}(t) \tag{3}$$

$$R_f(t) - R(t) = 2R_{ER}(t) + R_{LH}(t). \tag{4}$$

RATE OF HYDROGEN UPTAKE BY THE WALL

The rate of hydrogen uptake by the wall $[R(t)]$ is related to the flow of gas $[F(t)]$ between the reservoir and cell and the change in pressure in the cell. The change in the number of gas molecules (n_g) per unit time in the volume V, defined as the total volume of the vacuum system on the cell side of the conductance tube, is the difference between the rate at which the molecules are flowing through the conductance tube and the rate at which they are being removed (as atoms) by the cell wall. Thus

$$\frac{dn_g}{dt}(t) = C\Delta p(t) - R(t) \tag{5}$$

where $F(t) = C\Delta p(t)$ and $\Delta p(t)$ is the pressure differential between the cell and reservoir.

With the ideal gas relationship, eqn (5) becomes

$$\frac{dp}{dt}(t) = \frac{RT}{6.02 \times 10^{23}V}[C\Delta p(t) - R(t)] \tag{6}$$

where R is the gas constant and T the temperature of the gas. Rearranging this equation,

$$R(t) = C\Delta p(t) - \frac{6.02 \times 10^{23}V}{RT}\left[\frac{dp}{dt}(t)\right]$$

$$= C\left[\Delta p(t) - \frac{1}{\alpha}\frac{dp}{dt}(t)\right] \tag{7}$$

where

$$\alpha = \frac{RTC}{6.02 \times 10^{23}V}. \tag{8}$$

Estimates of Δp and dp/dt can be obtained from the pressure records of the experiment. The volume V is not readily determined because it includes the volume of the gauge and sidearms as well as that of the cell. More important, the temperature T is not uniform throughout the gas since the gauge is above room temperature and the cell is immersed in a constant temperature bath which may be as low as 77 K. Therefore α is not nearly as well defined as would appear from eqn (8). Although α is impossible to calculate accurately, it can fortunately be obtained by a simple experiment.

Before any atomic hydrogen is generated, the pressure in the cell is equal to that in the reservoir. Using the ground glass valve, a change in the reservoir pressure can be achieved "instantaneously" giving a higher or lower steady state value in 2 or 3 s. Due to the restricted flow of gas through c, the pressure in the cell rises or falls more slowly than that in the reservoir and only becomes equal to it again after approximately 1 min. If molecular hydrogen does not interact significantly with the cell wall, $R(t) = 0$ and eqn (7) becomes

$$\frac{1}{\alpha}\frac{dp}{dt}(t) = \Delta p(t) = p_s - p(t). \tag{9}$$

This equation can be integrated to give

$$\ln\frac{p_s - p(t)}{p_s - p(0)} = \alpha t \tag{10}$$

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where $p(t)$ is the cell pressure at a time t after adjusting the glass valve, $p(0)$ is the initial pressure in the cell and p_s the steady pressure in the reservoir, in this case after adjusting the valve. The constant α can then be determined from a plot of

$$\ln \{[p_s - p(t)]/[p_s - p(0)]\} \text{ against } t.$$

The results of such experiments are shown in fig. 4. At 273 K, the plot is linear and independent of whether the gas flows into or out of the cell. At 77 K, however, there does appear to be some significant difference between the two directions of flow. As we are only interested in the flow characteristics of the system this unexplained difference in α is not important. The form of eqn (9) and (10) is retained so the rate at which the hydrogen adatom concentration is changing during an adsorption/recombination run at 77 K can be determined provided the experimental value of α appropriate to the direction of flow is used. The linearity of the plots is good evidence that there is no interaction of the molecular hydrogen with the walls of the vacuum system, even at 77 K.
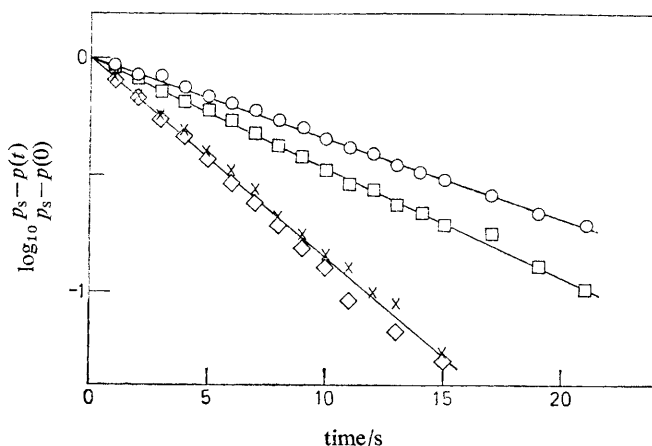

FIG. 4.—Flow characteristics of molecular hydrogen between reservoir and cell. Cell temperature 77 K; $\bigcirc$, flow from reservoir to cell; $\square$, flow from cell to reservoir. Cell temperature 273 K; $\times$, flow from reservoir to cell; $\diamondsuit$, flow from cell to reservoir.

DISSOCIATION OF HYDROGEN

There is general agreement that hydrogen is dissociated at the surface of a hot tungsten filament and that adsorption of atomic hydrogen on the walls of the vacuum system, or on a more efficient atom trap such as MoO_3, leads to a fall in the pressure. There has, however, been much controversy over how directly this fall in pressure relates to the rate of dissociation. Langmuir[11] calculated the rate of dissociation from both the fall in pressure of hydrogen and the heat loss from the filament as a consequence of dissociation but, because of the " fatigue " effect observed with glass surfaces, found the heat loss method to be more reliable. Bryce,[15] using MoO_3 as an atom trap, claimed that his results yielded rates which were 200 times greater than those found by Langmuir. More recently, Moore and Unterwald[17] have even proposed that solution of molecular hydrogen in the tungsten filament at high temperatures could be responsible for the major part of the fall in pressure, but experiments reported by Frauenfelder[18] would seem to refute this suggestion. Results of Anderson and Ritchie[19] suggest that some surfaces may adsorb forms of

" thermally activated " hydrogen other than the dissociated gas, *i.e.*, molecules with large translational rotational or vibrational energies. Anderson, Ritchie and Roberts,[20] having considered the various work done on the dissociation of hydrogen on tungsten, have reconciled the results of Langmuir and Bryce showing there to be in fact no discrepancy. These early results also appear to be in agreement with the more careful determinations of Brennan and Fletcher [16] and Hickmott [12] at lower pressures. Therefore, in those cases where glass or MoO_3 have been used as atom traps, the method for determining the disssociation rates using the fall in pressure has been justified.

At the commencement of each run, the glass surface is free of hydrogen atoms and so the only process that can occur is adsorption. Eqn (1) and (2) give

$$R(0) = R_f(0) = R_A(0). \tag{11}$$

However, since the filament is unlikely to reach an equilibrium temperature within the first few seconds, any measurement at $t = 0$ is really quite meaningless. At the minimum reading on the cell gauge (p_m), which is reached after about 10 s, equilibrium of the filament and steady state conditions in the gas should be achieved. At the same time recombination is generally insignificant. The usefulness of choosing p_m as a reference point for determining the rate of atomisation lies in the direct relationship that can be applied between $F(t)$ and $R_f(t)$ at this pressure since $dp/dt = 0$. The rate of formation of atomic hydrogen is then given by $C(p_s - p_m)$, corresponding to a cell pressure p'_m. The difference between the pressure as measured on the gauge and the actual pressure of the cell arises from the effect of thermal transpiration, which is a direct consequence of the cell temperature being different from that of the gauge. Using the approximate relationship that $p'_m/p_m = \sqrt{(T/298)}$ (T is the temperature of the cell bath and 298 K is assumed to be the temperature of the gas in the vicinity of the gauge) the dependence of the rate of formation of hydrogen atoms on pressure (p'_m) is shown in fig. 5 for a series of runs at both 273 and 77 K. The points cover a range of pressure from $\approx 1 \times 10^{-5}$ to 4×10^{-4} N m^{-2} and the three filament temperatures indicated. The close agreement with Hickmott's results [12] (dashed line) at 1600 K is probably fortuitous owing to errors in gauge calibration, differences in material quality and, in our case, no correction for temperature gradient at the filament ends. Differences in the rate of dissociation at the two cell temperatures arise from the greater collision rate of hydrogen molecules with the tungsten filament at 273 K compared with 77 K. However, even when this is taken into account there is still some discrepancy in the rates at the two temperatures. Our evidence suggests that this effect is genuine and is associated with a sticking coefficient for molecular hydrogen on tungsten which is dependent on gas temperature but not on the surface temperature. This will be discussed in a separate publication.

We have shown the linear relationship between the rate of formation of atoms and pressure to be correct for a limited range of pressure. Because of the design of our system, more rapid changes of pressure resulting from a significant recombination in the region of p_m prevented us from extending these measurements to pressures in excess of 4×10^{-4} N m^{-2}. However, Hickmott [12] has shown, for the same range of filament temperatures, the linear relationship to be valid for pressures greater than 10^{-3} N m^{-2} with the cell at 298 K.

As the cell pressure rises during a run as a result of recombination, it should be possible to calculate the rate of dissociation at a time t, $[R_f(t)]$, from the equation

$$R_f(t) = R_f(0) \times p(t)/p_m \tag{12}$$

on the basis of the linear relationship. In estimating $R_f(t)$, it has been found more

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satisfactory to treat each run on an individual basis and relate $R_f(t)$ to the initial value $R_f(0)$ for that particular run rather than to the mean value for the series shown by one of the continuous lines in fig. 5. The scatter that is evident in this figure appears to arise from slight differences in the condition of the tungsten surface associated with the pretreatment procedure.
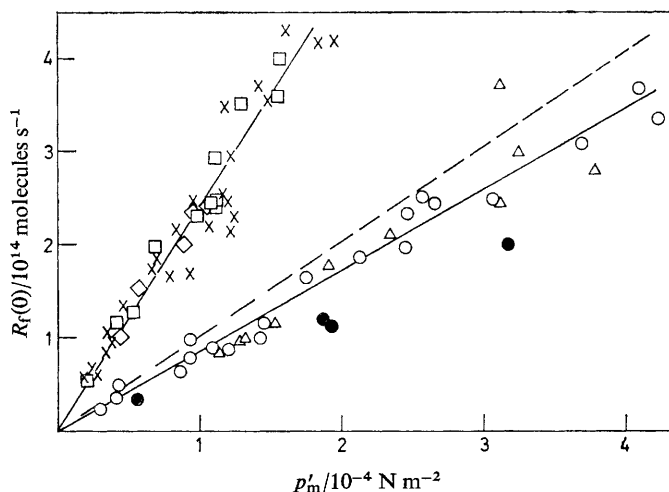
FIG. 5.—Rate of dissociation of hydrogen as a function of pressure. Filament temperature 1848 K ; ×, cell temperature = 77 K ; ○, cell temperature = 273 K. Filament temperature 1616 K ; □, cell temperature = 77 K ; △, cell temperature = 273 K. Filament temperature 1522 K ; ◇, cell temperature = 77 K ; ●, cell temperature = 273 K. (- - -) Hickmott's results for filament temperature 1600 K, cell temperature = 298 K.

During dissociation, gas in the cell is composed of both molecular and atomic hydrogen. The steady state partial pressure of atomic hydrogen depends on the relative efficiency of adsorption and recombination compared with atom formation. We have assumed, in relating the rate of formation of the atoms to the gas pressure, that p'_m is due just to molecular hydrogen with no contribution from the atoms present. A maximum of 5-10 % of atoms escape from the cell during a run. Any error in taking p'_m to represent the partial pressure of hydrogen molecules is likely to be small, since most of these atoms will anyway be trapped by the wall of the tube leading to the gauge.

CALCULATION OF CHANGES IN SURFACE COVERAGE

To obtain kinetic information from the rates determined above, it is necessary to know the amount of hydrogen adsorbed on the glass surface. This can be obtained by numerical integration of the rate of uptake by the wall with respect to time

$$n_A = \int_{t_1}^{t_2} R(t)\,dt + a[p(t_2) - p(t_1)] \tag{13}$$

where n_A is the change in the number of atoms adsorbed between times t_1 and t_2. The term $a[p(t_2) - p(t_1)]$ is a small correction which takes into account the amount of gas taken up from or given to the cell volume, as a result of the change in pressure, as distinct from that passing through the conductance tube. This correction is only

of real significance when the change of coverage is small and $p(t_2) - p(t_1)$ large. According to eqn (7)

$$\int_{t_1}^{t_2} R(t)\, dt = \int_{t_1}^{t_2} C\Delta p\, dt + \frac{1}{\alpha} \int_{p(t_1)}^{p(t_2)} dp = \int_{t_1}^{t_2} C[p_s - p(t)]\, dt + \frac{1}{\alpha}[p(t_2) - p(t_1)] \quad (14)$$

so that n_A can also be determined directly by numerical integration of the flow rate between the cell and reservoir.

RECOMBINATION AT 273 K

The pressure changes in fig. 3 show clearly that each time dissociation is stopped during an experiment hydrogen continues to desorb from the surface for a period of several minutes. The quantity removed is, however, very much less than the accumulated amount on the glass, being $\approx$ 3-10 % of the total. The variation in the rate of removal of hydrogen, as calculated from $C\Delta p(t)$ (also shown) using eqn (7) is given in fig. 6. The importance of the term $(1/\alpha)(dp/dt)$, especially during the first few seconds after dissociation ceases, is shown by the difference in $R(t)$ and $C\Delta p(t)$.
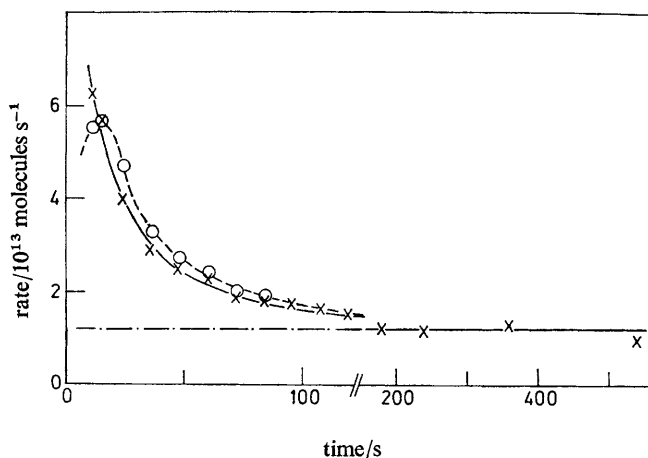

FIG. 6.—Recombination of hydrogen at 273 K in the absence of dissociation; ○, hydrogen flow between cell and reservoir (2nd cycle, fig. 3); ×, calculated values for the rate or recombination. (— · — ·) Estimated recombination from the more strongly bound state.

Both $R(t)$ and $C\Delta p(t)$ fall to a small but constant value $R(\infty)$ after 4-5 min suggesting two contributions to the removal of hydrogen. In the early stages, the major contribution to the rate appears to arise from a state of adsorbed hydrogen which has a low population, is readily desorbed and hence is only weakly bound. The minor contribution, which is maintained constant over a period of 10-20 min, presumably originates from a state which has a larger population and is more strongly bound. The two contributions to the rate are separated by subtraction for it can be shown that the weakly bound state of hydrogen is of major interest and importance and hence a detailed analysis of the rate data for this state is necessary.

The rate of removal of weakly bound hydrogen at a time t is $R(t) - R(\infty)$ for a surface population n_ω equal to

$$\int_t^\infty [R(t) - R(\infty)]\, dt + a[p(\infty) - p(t)].$$

A van't Hoff plot of $\log_{10}[R(t) - R(\infty)]$ against $\log_{10} n_\omega$ is shown in fig. 7 for the hydrogen desorptions observed in fig. 3 during the second (fig. 6) and third cycles. Second order kinetics are apparent at higher n_ω but as the total amount of hydrogen taken up by the surface gets larger, the second order rate constant progressively decreases and the plot assumes some curvature. These effects, as well as the first order kinetics at lower n_ω, are believed to arise as a result of hydrogen atoms which reside, perhaps in pores, below the surface layer.[21]
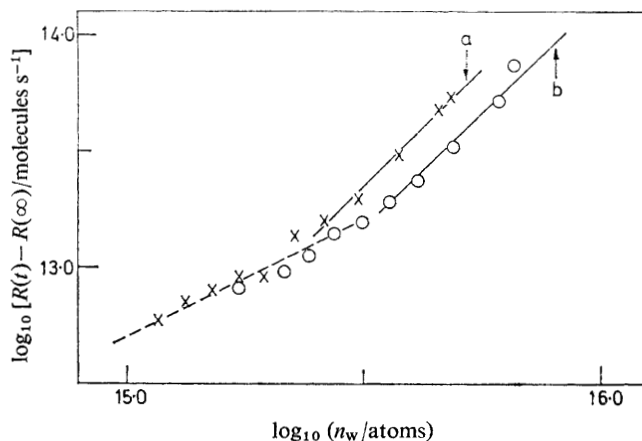

FIG. 7.—$\log_{10}[R(t) - R(\infty)]$ plotted against $\log_{10} n_\omega$ for second ($\times$) and third ($\bigcirc$) cycles of fig. 3. Continuous line, dependence required for second order kinetics; dashed line, dependence required for 1st order kinetics. a and b refer to initial rates at maximum coverage.

The observed second order kinetics would point to hydrogen atom recombination on the surface by a Langmuir–Hinshelwood mechanism determining the rate for hydrogen desorption.

$$R(t) = R_{LH}(t) = k_{LH}[n_\omega(t)]^2.$$

There is, however, an alternative process involving an Eley–Rideal step which also gives rise to a second order rate equation. The possibility of this process is remote but even so it must be considered carefully. The model is as follows.

If the adsorbed state is very weakly bound, as seems most likely, then adatoms could desorb as well as recombine on the surface. Rapid desorption of atoms followed by rapid readsorption within the enclosed volume of the cell could lead to a surface coverage for the weakly bound adatoms which is linearly related to the gaseous atom concentration, if recombination is relatively slow;

$$n_\omega \propto [H].$$

A rate for recombination by the Eley–Rideal mechanism is then given by

$$R_{ER}(t) = k_{ER}n_\omega(t)[H](t) = k[n_\omega(t)]^2.$$

If the symbol τ is used to represent the time that dissociation ceases, $\tau+$ the time immediately before this event and $\tau-$ the time immediately after, then the respective rates of recombination can be derived using the relationships;

$$R_f(\tau+) - R(\tau+) = 2R_{ER}(\tau+) + R_{LH}(\tau+), \tag{15}$$

from eqn (4), and

$$R(\tau-) = R_{ER}(\tau-) + R_{LH}(\tau-). \tag{16}$$

The steady state concentration of hydrogen atoms in the gas phase is set up as a consequence of simultaneous dissociation of hydrogen molecules and adsorption, desorption and recombination of atoms. As dissociation proceeds, this steady state concentration is expected to increase quite substantially. If the model based on the Eley–Rideal step is correct, then once dissociation stops the steady state concentration of atoms must decay slowly, otherwise an Eley–Rideal process could not continue to take place. Therefore, the gaseous hydrogen atom concentrations immediately before and immediately after dissociation stops must be approximately the same. As the adatom concentration also changes very slowly $R_{ER}(\tau+) = R_{ER}(\tau-)$ and $R_{LH}(\tau+) = R_{LH}(\tau-)$. It is then possible to solve eqn (15) and (16) to obtain the relative contributions of the Eley–Rideal and Langmuir–Hinshelwood mechanisms. $R_f(\tau+)$ and $R(\tau+)$ can easily be obtained from the experimental data, but $R(\tau-)$ is more difficult since the rapid pressure changes that occur during the crucial first 10-15 s make it impossible to measure $(1/\alpha)(dp/dt)(\tau-)$. An alternative approach is to extrapolate the van't Hoff plots of fig. 7 since the total amount of weakly bound hydrogen on the surface at time τ can be determined using eqn (14). Even so, this method is not particularly accurate owing to the curvature of these plots.

In table 1 $R_f(\tau+) - R(\tau+)$ and $R(\tau-)$ are shown for the run illustrated in fig. 3. As solution of eqn (15) and (16) using this data gives large negative values for R_{LH}, the interpretation given above cannot be correct. The condition $n_\omega(\tau+) = n_\omega(\tau-)$ giving $R_{LH}(\tau+) = R_{LH}(\tau-)$ must be valid, otherwise there could be no recombination of any type when dissociation ceases, and so the relationship $R_{ER}(\tau+) = R_{ER}(\tau-)$ must be at fault. For realistic values of R_{LH}, $R_{ER}(\tau+) \neq R_{ER}(\tau-)$ and $R_{ER}(\tau-) \approx 0$. When dissociation is stopped, the steady state concentration of gaseous hydrogen atoms must, therefore, decay rapidly leaving the Langmuir–Hinshelwood mechanism as the sole recombination process.

TABLE 1.—RECOMBINATION DATA IMMEDIATELY BEFORE AND IMMEDIATELY AFTER DISSOCIATION CEASES FOR THE FOUR CYCLES SHOWN IN FIG. 3

total coverage /10^{17} atoms	$R_f(\tau+) - R(\tau+)$ /10^{14} molecules s^{-1}	$R(\tau-)$ /10^{14} molecules s^{-1}
8.3	26.0±1.0	3.6±0.5
16.9	66.0±1.0	6.0±0.7
25.0	58.0±1.2	9.1±2.0
28.8	73.1±1.4	12.2±6.0

The important role of the weakly bound atoms at 273 K can further be seen when dissociation is recommenced after a period sufficient to remove all of these atoms from the surface. As the pressure falls to a value close to the minimum pressure p_m achieved with a " clean " surface at the start of the experiment, the implication is that nearly all of the newly formed atoms are being adsorbed and very few recombined ($R_A \gg R_R$ so that $R_f \approx R_A$). Since $n_\omega = 0$, there is no Langmuir–Hinshelwood contribution to recombination and as a result $R_A \gg R_{ER}$. As it is unlikely that the removal of the weakly bound atoms has significantly enhanced the ability of the surface to adsorb hydrogen atoms from the gas phase, it must be assumed that R_{ER} is effectively zero when n_ω is zero. There is therefore very little recombination involving the hydrogen atoms more strongly bound to the surface. We can conclude that a weakly bound state of atomic hydrogen is of the utmost importance for recombina-

tion on glass, being the major participant in both Eley–Rideal and Langmuir–Hinshelwood mechanisms at 273 K.

One may question why the effects that we observe were not seen or reported by Hickmott.[8] It should be noted that in his fig. 3, the pressure appears to recover very slowly as a result of switching the filament off and rises to a steady level only after $\approx$ 10 min. Such a long rise-time would have undoubtedly masked the sharp desorption effect that we have observed. Although it is not clear from the information provided by Hickmott, this is most likely to have arisen from some design fault in his system, perhaps a gas conductance problem at the hydrogen inlet.

RECOMBINATION AT 77 K

There is no significant recombination observed when dissociation is stopped during experiments at 77 K, implying an absence of a Langmuir–Hinshelwood mechanism either during or after dissociation. Eqn (3) and (4) are reduced to

$$R_f(t) - R(t) = 2R_{ER}(t) \tag{17}$$

$$R_f(t) + R(t) = 2R_A(t). \tag{18}$$

Rates of adsorption and recombination can be evaluated directly during the course of an experiment. Since both rates increase with time as a result of the higher rate of dissociation with increasing pressure, it is more relevant to plot the ratio of the rate of recombination to the rate of adsorption. This is done for a typical run in fig. 8.
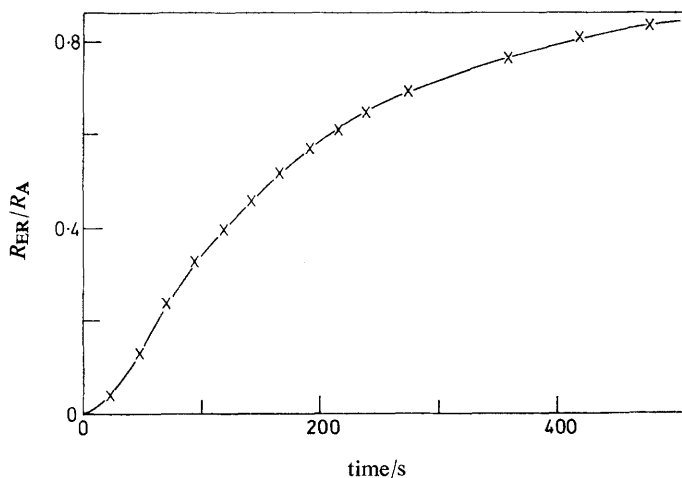

FIG. 8.—Variation in R_{ER}/R_A during run at 77 K. Filament temperature 1616 K.

PROBABILITY OF ADSORPTION AND RECOMBINATION

After adsorbing atomic hydrogen on the walls of the cell, the cell was baked to about 570 K to regenerate the " clean " surface. An approximately quantitative recovery of hydrogen was obtained (95 %) irrespective of whether the surface was originally at 77 or 273 K. During each experiment the only way a hydrogen atom could leave the cell was through the small opening which served to admit the molecular hydrogen. The ratio of the area of this opening to the total area of the cell is 2.42×10^{-4}. Therefore an atom must react at the surface within an average of 10^3

collisions if it is to have no chance of escape into other parts of the system. The average reaction probability for adsorption and recombination throughout each experiment at 77 or 273 K is estimated to be $> 10^{-3}$ because of this.

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