

wood-Lindemann¹⁸ theory of unimolecular reactions which give strong consideration to the number of internal degrees of freedom in the configuration of the activated complex. We hope to give this matter more careful scrutiny in further investigations applying the

(17) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, Cambridge, 1939, pp. 524-527.

(18) C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, Oxford, 1947, pp. 79-83.

capacity flow reactor to high temperature gas phase reactions.

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ENERGY ACCOMMODATION IN EXOTHERMIC HETEROGENEOUS CATALYTIC REACTIONS¹

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The steady-state flux of mass and of energy at a solid catalytic surface due to heterogeneous recombination of hydrogen atoms were evaluated by a combination of e.p.r. and calorimetric techniques. The catalytic surfaces employed were filaments of nickel, platinum, and tungsten. In general, only a fraction of the energy of atom recombination was found to be accommodated by the catalyst. The results suggest an upper limit to the energy flux which a solid can accept. This is interpreted to be governed by the lattice force constant of the catalyst which may be the rate-limiting factor in certain exothermic catalytic processes.

Introduction

Recent observations² of the heat flux to metal filaments exposed to a hydrogen discharge of fixed intensity indicated that, of the total energy liberated by the surface-recombining hydrogen atoms, only a fraction was dissipated as heat in the catalyst. The remainder was apparently carried away by desorbing hydrogen molecules formed by heterogeneous atom recombination. Other investigators³ have reported the appearance of electronically excited nitrogen molecules in the proximity of a catalytic surface exposed to nitrogen atoms.

From this qualitative evidence, it appears likely that the efficiency of energy transfer within the crystal lattice of a catalyst may play a fundamental role in exothermic heterogeneous processes. Indeed, the activity of various solid materials for atom recombination has been correlated^{2,4} with the Debye characteristic temperature of the catalyst which, to a first approximation, is a measure of the lattice force constant and hence determines the upper frequency limit at which heat may be transferred through the lattice by spontaneous phonon emission. To investigate this problem further, we have made quantitative measurements of the fraction of available reaction energy imparted to a catalytic surface on which hydrogen atoms are recombining.

Experimental

I. Method.—The objective of our experiment was to measure simultaneously the steady-state mass and energy flux at the catalytic surface due to heterogeneous atom recombination. From such data, the reaction energy accommodation coefficient for the surface was computed, *i.e.*, the fraction of available energy transferred to the solid. Atomic hydrogen possesses a net electron magnetic moment; hence, electron paramagnetic resonance (e.p.r.) spectroscopy was selected as a method for evaluating the flux of atoms flowing through a tube toward a catalytic surface.

(1) This work was supported by Project Squid, Office of Naval Research, Department of the Navy.

(2) B. J. Wood and H. Wise, *J. Phys. Chem.*, **65**, 1976 (1961).

(3) R. R. Reeves, G. Mannella, and P. Harteck, *J. Chem. Phys.*, **32**, 946 (1960); *Can. J. Chem.*, **38**, 1648 (1960).

(4) H. Wise and W. A. Rosser, "Ninth (International) Symposium on Combustion," Cornell University, Ithaca, N. Y., 1962.

The power input to the surface attributable to the exothermicity associated with heterogeneous atom recombination was determined calorimetrically.²

II. Apparatus.—In essence, the experimental apparatus consisted of a tube through which hydrogen gas at a reduced pressure was pumped. At one region in the tube the gas was partially dissociated in a radiofrequency (RF) discharge. Downstream from the discharge an e.p.r. cavity was located, and immediately downstream from the cavity a catalytic filament was situated.

The vacuum system (Fig. 1) was fabricated from Pyrex glass with the exception of a fused quartz section through the e.p.r. cavity. This tube had an outside diameter of 10 mm. and a wall thickness of approximately 0.75 mm. Prior to insertion in the vacuum system, the tube was washed with concentrated nitric acid, followed by thorough rinsing with ethanol and then with distilled water.

Atoms were produced² in a 17 mc./sec. electrodeless discharge. Atom concentration was varied by adjusting the RF input to the discharge. The total pressure in the system was controlled by varying the gas input rate through an adjustable leak, a Granville-Phillips valve.

The catalytic filament was located downstream from the e.p.r. cavity, but the physical dimensions of the cavity limited the minimum distance between its center and the filament to 16 tube radii. Hydrogen atom recombination on the walls of the quartz tube⁵ causes a loss of atoms between the e.p.r. cavity and the filament, under the flow conditions prevailing in our experiments, which was estimated from a theoretical analysis.⁶ In addition, the atom concentration profile within the quartz tube was verified experimentally by positioning the quartz tube so that the e.p.r. cavity and its attendant magnet, mounted on a wheeled carriage, could be moved back and forth horizontally along the tube (Fig. 1). In this manner the longitudinal concentration gradient of atoms in the tube was evaluated (Fig. 2).

III. Catalysts.—The catalytic surface, in the form of a coiled filament, was supported on 16 gage glass-insulated copper wires and was attached to a glass-encapsulated iron armature so that its longitudinal position in the quartz tube could be adjusted from outside the tube with a magnet. Details of the measurement of the rate of heat input attributable to atom recombination on the filament surface are given in an earlier publication.² Surface areas were calculated from the measured dimensions of the wires. Average surface temperatures were computed from the measured values of filament resistance, the filament dimensions, and values of resistivity reported in the literature for the various metals.²

(5) B. J. Wood and H. Wise, *J. Phys. Chem.*, **66**, 1049 (1962).

(6) H. Wise and C. M. Ablow, *J. Chem. Phys.*, **35**, 10 (1961).

IV. E.p.r. Spectrometry.—E.p.r. spectrometry has been employed by several investigators⁷⁻¹¹ to measure the concentrations of gaseous atomic species by observing the intensity of their paramagnetic resonance absorption. The principal problem associated with the use of this method for such purposes is the derivation of a relationship between the indicated resonance absorption intensity of the species and the actual number of the species in the e.p.r. cavity. Since the fine structure and the theory of the e.p.r. spectrum of molecular oxygen have been examined and developed in detail,¹² we chose to employ molecular oxygen as a calibration standard. That is, the concentration of atomic species in the cavity was evaluated by comparing the resonance absorption of the atoms with the absorption of a known pressure of oxygen molecules for a fixed set of geometric and instrumental parameters.

In our experiments a Varian Model V4502 e.p.r. spectrometer with a six-inch magnet was employed. This instrument utilizes a 100 kc./sec. field modulation unit with a multipurpose microwave cavity whose Q is approximately 7000. Microwave energy absorption by a species with an unpaired electron is due to transitions between Zeeman energy levels, and occurs when the species is placed in a magnetic field H and an alternating electric field of frequency ν such that $h\nu = gBH$, where g is the spectroscopic splitting factor, h is Planck's constant, and B is the Bohr magneton 0.92732×10^{-20} erg gauss⁻¹. The Varian spectrometer is operated as a fixed frequency instrument ($\nu \cong 9.4$ kMc./sec.) in which the magnetic field is varied to attain the resonance condition. The derivative of the absorption of the paramagnetic species is detected, amplified, and recorded. The recorded signal is proportional to the derivative of the imaginary part of the complex susceptibility with respect to the magnetic field, $d\chi''/dH$. The total number of unpaired electron spins in the cavity is proportional to the integrated intensity $\int \chi'' dH$. Using the development of Krongelb and Strandberg³ we may write expressions for the number density of oxygen molecules and hydrogen atoms in terms of their integrated intensities. Thus

$$N_{O_2} = \frac{4kT}{\hbar\omega\pi} \times \frac{Z}{f_{\pm}g_{\text{eff}}B} \times \frac{\int \chi''_{O_2} dH}{[4|(JM|_{\mu_x}|J'M')|^2 \exp(-E_{JM}/kT)]} \quad (1)$$

and

$$N_H = \frac{2(2I+1)(6kT) \int \chi''_H dH}{\hbar\omega\pi gBS(S+1)f_+} \quad (2)$$

where

N_{O_2} and N_H are, respectively, the no. of oxygen molecules and hydrogen atoms per cm.³

$\hbar = h/2\pi$

$\nu = 2\pi\nu$

k is the Boltzmann constant

T is the temperature in °K.

E_{JM} is the energy of a given transition

f_{\pm} and f_+ are the filling factors associated with the respective transitions

Z is the partition sum $\sum J \exp(-E_{JM}/kT)$

$g_{\text{eff}} = d\nu/dH$

M and J are, respectively, the magnetic and total angular momentum quantum numbers, and

$|(JM|_{\mu_x}|J'M')|^2$ is the absolute square of the matrix element for all transitions such that $\Delta M = \pm 1$, where μ_x is the magnetic field operator that causes spin transitions

I is the spin of the proton

S is the spin quantum number (in the case of H we use this notation which is distinct from J in O_2 matrix elements).

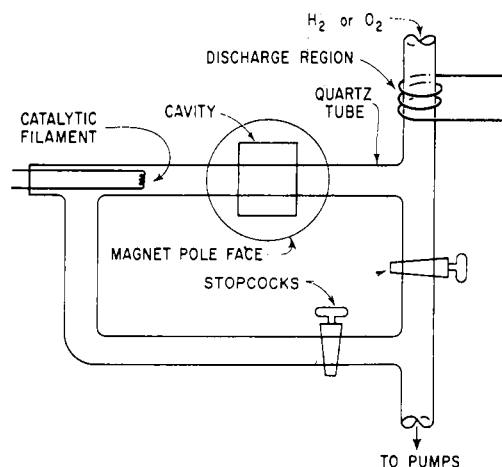


Fig. 1.—Schematic diagram of apparatus.

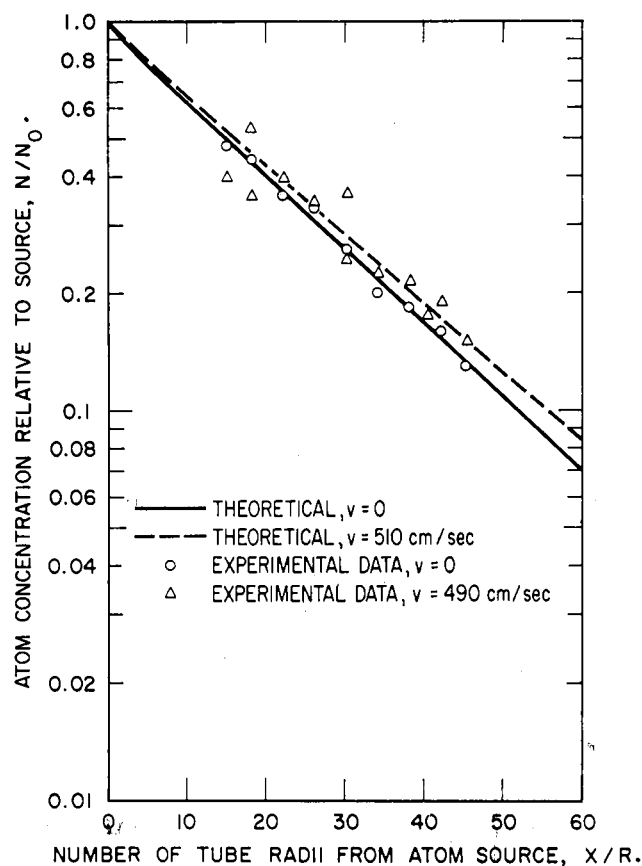


Fig. 2.—Theoretical⁶ and experimental hydrogen atom concentration gradients in quartz tube of radius $R = 0.425$ cm., with tungsten filament located at $x/R = 60$, and total pressure $P = 41 \mu$. Theoretical curves calculated on the basis of $\gamma = 2 \times 10^{-3}$ and $\gamma' = 0.05$.

Dividing equation 1 by 2 we obtain

$$\frac{N_H}{N_{O_2}} = \frac{3f_{\pm}g_{\text{eff}}(2I+1)}{f_+gZ} \times \frac{[4|(JM|_{\mu_x}|J'M')|^2 \exp(-E_{JM}/kT)]}{[S(S+1)]} \times \frac{\int \chi''_H dH}{\int \chi''_{O_2} dH} \quad (3)$$

For atomic hydrogen $I = 1/2$ and $S = 1/2$. The partition sum Z for oxygen may be approximated by its classical value $3kT/2B'$, $= 217$, where B' , a conversion constant for molecular oxygen, $= 43102$ Mc./sec. Also, the ratio of filling factors, $f_{\pm}/f_+ = 1$ since the dimensions and geometry of the cavity and quartz tube are the same for both gases. The g -value for hydrogen atoms is

- (7) T. M. Shaw, *J. Chem. Phys.*, **30**, 1366 (1959).
- (8) S. Krongelb and M. W. P. Strandberg, *ibid.*, **31**, 1788 (1961).
- (9) D. S. Hacker, S. A. Marshall, and M. Steinberg, *ibid.*, **35**, 1788 (1961).
- (10) C. A. Barth, A. F. Hildebrandt, and M. Patapoff, *Discussions Faraday Soc.*, **33**, (1962).
- (11) T. C. Marshall, *Phys. Fluids*, **5**, 743 (1962).
- (12) M. Tinkham and M. W. P. Strandberg, *Phys. Rev.*, **97**, 937 (1955).

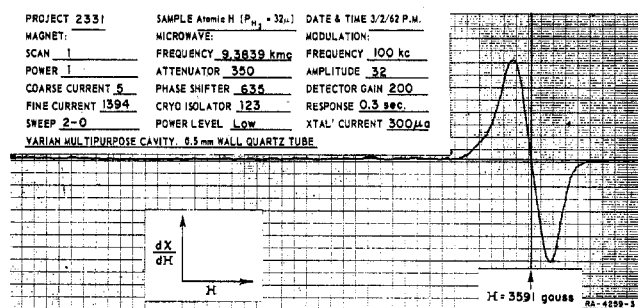


Fig. 3.—Upper paramagnetic resonance absorption line of atomic hydrogen. The integrated intensity of this line indicates an atomic concentration of 3.95×10^{14} atoms/cm.³.

the same as for a free electron, 2.0023. The quantity in brackets in the numerator is termed the "calculated intensity" by Tinkham and Strandberg¹² and has been evaluated by them for a large number of oxygen resonance absorption lines. We chose the line arising from the transition $K = J = 1, \Delta M = -1 \rightarrow 0$ which appears at $H = 5583.8$ gauss and $\nu = 9.47675$ kMc./sec. The calculated intensity¹² for this line is 0.741 and the value of g_{eff} is 1.96.

Inserting the appropriate numerical values of these parameters in eq. 3 we obtain

$$N_H = 2.68 \times 10^{-2} N_{O_2} \frac{\int \chi''_{HD} dH}{\int \chi''_{O_2} dH} \quad (4)$$

or

$$N_H = 8.65 \times 10^{14} P_{O_2} \frac{\int \chi''_{HD} dH}{\int \chi''_{O_2} dH} \quad (5)$$

where P_{O_2} is the pressure of oxygen in mm.

For experiments of the type employed in our study, the integrated intensity of the resonance absorption line, $\int \chi'' dH$, may be evaluated from the experimental data by reducing the function to the form of a first moment of the absorption. The first moment of the derivative function $d\chi''/dH$, as defined, may be integrated by parts to give

$$\int_{-\infty}^{+\infty} H(d\chi''/dH)dH = H\chi'' \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \chi'' dH \quad (6)$$

If $d\chi''/dH$ is of such order that the function is Lorentzian in shape, then the integrated quantity $H\chi'' \Big|_{-\infty}^{+\infty}$ in eq. 6 becomes zero, and the intensity may be readily evaluated by numerical integration

$$\int_{-\infty}^{+\infty} H(d\chi''/dH)dH = \lim_{\Delta H \rightarrow 0} \sum_{-\infty}^{+\infty} H(d\chi''/dH)\Delta H \quad (7)$$

The values of integrated intensity obtained by use of eq. 7 are meaningful even though the line shape may be distorted by over-modulation.¹³ In our work, however, a fixed modulation amplitude was selected empirically such that the recorded signals were not over-modulated and this value was used for all of our experiments.

To avoid problems associated with microwave power saturation of the observed electron spin transitions, the Varian low power microwave bridge was used. The microwave power incident on the sample in the cavity varied between 2.0 and 20 milliwatts. In practice, the power required to saturate the sample was determined by observing e.p.r. signal intensity as a function of incident power, then reducing the power level below saturated values.

As a rule, measurements were made with fixed settings of incident power and signal amplifier gain. In several experiments, where these parameters were varied, corrections were made by means of an empirical calibration of these respective functions with samples of molecular oxygen at known pressures.

Lines were identified by measuring the magnetic field H at resonance with a proton fluxmeter. The molecular oxygen

resonance line of interest appeared at $H = 5454$ gauss and $\nu = 9.2565$ kMc./sec., which corresponds to the line reported by Tinkham and Strandberg¹² at $H = 5584$ gauss and $\nu = 9.4768$ kMc./sec. The hydrogen atom e.p.r. spectrum¹⁴ consists of two absorption lines of equal intensity separated by 506.8 gauss and centered on either side of $g = 2$ ($H = 3338$ gauss, $\nu = 9.3839$ kMc./sec.). The upper line is shown in Fig. 3.

V. Gases.—Ordinary grade compressed oxygen was employed. The manufacturer's stated purity was 99.5–99.8 volume % O_2 .

Matheson pre-purified grade hydrogen was passed through a De-oxo unit to remove traces of O_2 . In some experiments the gas was bubbled through water at room temperature prior to its introduction into the vacuum system. (It has been demonstrated that traces of water vapor enhance the quantity of hydrogen atoms in the vicinity of an electrodeless discharge.¹⁵) The minimum detectable concentration of hydrogen atoms by e.p.r. spectrometry in our apparatus was approximately 1×10^{13} atoms/cm.³.

Results

Considering both convective flow and diffusion, the total flux of atoms to the filament, Φ , is given by

$$\Phi = \Phi_{diff} + \Phi_{conv} \quad (8)$$

For first-order kinetics of heterogeneous atom removal the diffusive term is related to the atom-concentration gradient at the catalytic surface, located at a fixed position $x = L$, by¹⁶

$$\Phi_{diff} = -D_{12} (\partial N / \partial x)_L = \frac{\gamma' c N}{4D_{12}[1 - (\gamma'/2)]} \quad (9)$$

where D_{12} is the binary diffusion coefficient of hydrogen atoms through the molecular gas, c , the mean atomic velocity, γ' , the recombination coefficient defined as the fraction of incident atoms which recombine, and N , the hydrogen atom density.

The effective contribution of the convective term to atom recombination on the solid is given by

$$\Phi_r = \gamma' \Phi_{conv} = \gamma' v N \quad (10)$$

where v is the linear velocity of the flowing gas. Consequently the effective total flux of recombining atoms is

$$\Phi_s = \gamma' N \left\{ \frac{c}{2(2 - \gamma')} + v \right\} \quad (11)$$

For the case of hydrogen atoms the magnitude of the convective flow term in eq. 11 is of the order of 1% of that of the diffusive flow term at the pumping speeds encountered in our experiments. The contribution of bulk flow to Φ_s was therefore neglected in our calculations. Experimental evaluation of the atom concentration gradients in the tube under conditions of both convective-diffusive flow and diffusive flow only demonstrated that neglect of the convective flow term in eq. 11 was justified (Fig. 2).

The steady-state heterogeneous recombination process may be described in terms of an energy balance

$$w/A = \Phi_s \beta Q \quad (12)$$

where w is the net power input to the filament due to heterogeneous atom recombination, A is the geometric surface area of the filament, Q is the heat of recombination of hydrogen atoms = 8.5×10^{-20} cal./atom, and β the reaction energy accommodation coefficient. Sub-

(14) N. F. Ramsey, "Molecular Beams," Oxford University Press, London, 1956, p. 246.

(15) F. Kaufman and F. P. Del Greco, *J. Chem. Phys.*, **35**, 1895 (1961).

(16) H. Mots and H. Wise, *ibid.*, **32**, 1893 (1960).

(13) K. Halbach, *Phys. Rev.*, **119**, 1230 (1960).

stituting eq. 11 (less the negligible convective flow term) into eq. 12, we obtain

$$\beta = \frac{4w[1 - \gamma'/2]}{NcAQ\gamma'} \quad (13)$$

The values of β obtained in this way from our experimental data are shown in Table I.

TABLE I

EXPERIMENTAL VALUES OF REACTION ENERGY ACCOMMODATION COEFFICIENTS, β , FOR HYDROGEN ATOM RECOMBINATION ON METALS

(Gas temperature = 300°K.)

Catalytic surface (filament)	Filament temp. (°K.)	Range of atom concn. ^b [(atoms/cm. ³) × 10 ⁻¹⁴]	Total gas density [(molecules/cm. ³) × 10 ⁻¹⁴]	γ'^a	β (av.)
Nickel	423	0.15–2.4	51.8	0.20	0.60 ± 0.11
Tungsten	443	.34–7.8	48.5	.07	.79 ± .08
	480	.33–2.9	10.4	.07	.81 ± .05
	773	.69–10.4	10.4	.07	.85 ± .13
Platinum	376	.79–2.2	26.0	.040	.49 ± .07
	378	.66–2.1	28.2	.040	.57 ± .07
	588	.30–1.7	28.2	.079	.25 ± .03
	813	.94–5.6	26.0	.10	.19 ± .02

^a Values of γ' were calculated from data of ref. 2 using most recently reported¹⁷ values of D_{12} . ^b Atom concentrations were evaluated at the e.p.r. cavity and were varied within the indicated range of values at the indicated total gas density by adjusting the RF power input to the discharge.

Discussion

The measured values of β (Table I) seem to strengthen the hypothesis² that the relative efficiency with which this energy can be removed from the reacting system is the key to catalytic efficiency for reactions of this type. To some degree the magnitude of β appears to be inversely related to the value of γ' . This is particularly evident in the case of platinum, which exhibits a variation in recombination coefficient with temperature.² It is of interest to observe that the product $\beta\gamma'$ is constant over the range of filament temperatures measured. From this observation and from eq. 13, we may con-

clude that there exists an upper limit to the energy flux which the solid can accept.

Such an interpretation finds an analogy in the case of collisional energy transfer between a gaseous species and a solid surface in the absence of chemical reaction. Theoretical considerations¹⁸ based on a classical model lead to the conclusion that the transfer of energy, by spontaneous phonon emission into the crystal lattice from the point of impact, becomes less efficient when the kinetic energy of the incident particle lies above a certain level. In a steady state process, therefore, in which the total rate of energy input to the surface exceeds this level, only a fraction of the liberated energy can be accommodated.

The variation in accommodation coefficients among various solids is a function of the lattice force constant of the crystal; the greater the magnitude of this parameter, the smaller the quantity of energy that can be transferred by phonon emission per collision.¹⁹ This fundamental characteristic of a crystal, however, may be altered by the introduction of foreign atoms or ions into the lattice. The dissolution of hydrogen in certain metals, for example, has been demonstrated to profoundly affect such physical properties as metal atom spacing in the lattice²⁰ and possibly the electron-energy distribution. Such lattice changes may be expected to influence phonon transfer and may account for the variation in β with temperature in the case of platinum.

It appears that the hydrogen molecules formed in heterogeneous recombinations are not in thermal equilibrium with the catalyst. Hence, these particles must leave the surface with an excess of energy in the form of internal and/or translational modes. A quantitative evaluation of the energy distribution in such desorbed molecules would be of some importance to studies concerned with energy transfer in the presence of exothermic heterogeneous chemical reaction.

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(18) N. Cabrera, *Discussions Faraday Soc.*, **28**, 16 (1959).

(19) R. W. Zwanzig, *J. Chem. Phys.*, **32**, 1173 (1960).

(20) D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, Illinois, 1948.

(17) S. Weissman and E. A. Mason, *J. Chem. Phys.*, **36**, 794 (1962).