

## LETTERS TO THE EDITOR

## ASTRONOMY

## Volcanic Phenomena on the Moon

THE ejection of gas from the central peak of the Alphonsus crater on the Moon observed on November 3, 1958, as well as the subsequent observations of the activity of this crater on October 23, 1959, have indicated that there are volcanic processes taking place on the Moon. It was established that molecular carbon was among the gases ejected. In cases of developed volcanic activity, such sporadic processes should be accompanied by a relatively steady ejection of gases of the fumarole emission type: indeed, observations made in November and December, 1961, showed the presence of such a fumarole field inside the Moon's Aristarchus crater.

So far back as 1955, when I was engaged in searching for luminescent effects on the surface of the Moon, I found that the broad Fraunhofer lines in the violet part of the spectrum of the Aristarchus crater seemed much narrower than in the solar spectrum. This indicated the existence of a luminescent glow in the Aristarchus crater, a glow which overlapped the contour lines. The luminescent effect in the Aristarchus crater was best observed after full Moon, when the Sun stood high over the crater. However, during the same phase of the Moon, seen in different months, the brightness of the glow was not at all the same. These fluctuations in brightness did not indicate any connexion with solar activity. Therefore, the question arose: Were they not caused by the changes in the activity of the crater itself? Such an explanation would prove correct if a substantial part of the emissions observed were caused not by the luminescence of the hard rock on the lunar surface, but by the luminescence of the emissions of gas from the crater. In order to solve this problem a special series of spectral observations of the Aristarchus crater was made with the 50-in. reflector of the Crimean Astro-Physical Observatory.

These observations were carried out in 1961 with the aid of a low-dispersion spectrograph with about 150 Å/min near the  $H_\alpha$  line. The spectrum pictures were taken with a high slit, which made it possible to carry out the photometric treatment by comparing the spectrum of the detail under investigation with the spectrum of the surroundings.

On November 30, 1961, the Moon was in its last quarter. The spectrograms of the Aristarchus crater and its surroundings were obtained on the nights of November 26, 28 and 30 and December 2 and 3, 1961. During these nights quite a large number of spectrograms of the details of the Aristarchus and Herodotus craters were obtained together with the spectrograms of the crevices, neighbouring small craters and other details of the relief.

A series of emission lines could be seen only on the spectrograms taken on the nights of November 26 and 28 and on the two spectrograms of December 3. These could be discerned right in the centre of the Aristarchus crater even without any photometric measurements. The spectrum lines were obtained under exceptionally favourable atmospheric conditions. Apparently the area on which the emission lines appeared was not more than several square kilometres.

The group of emission lines observed in the centre of the Aristarchus crater stood out sharply at the red end of the spectrum. The length of waves of this border-line amounted to 4634 Å with an error of 1 Å. The whole

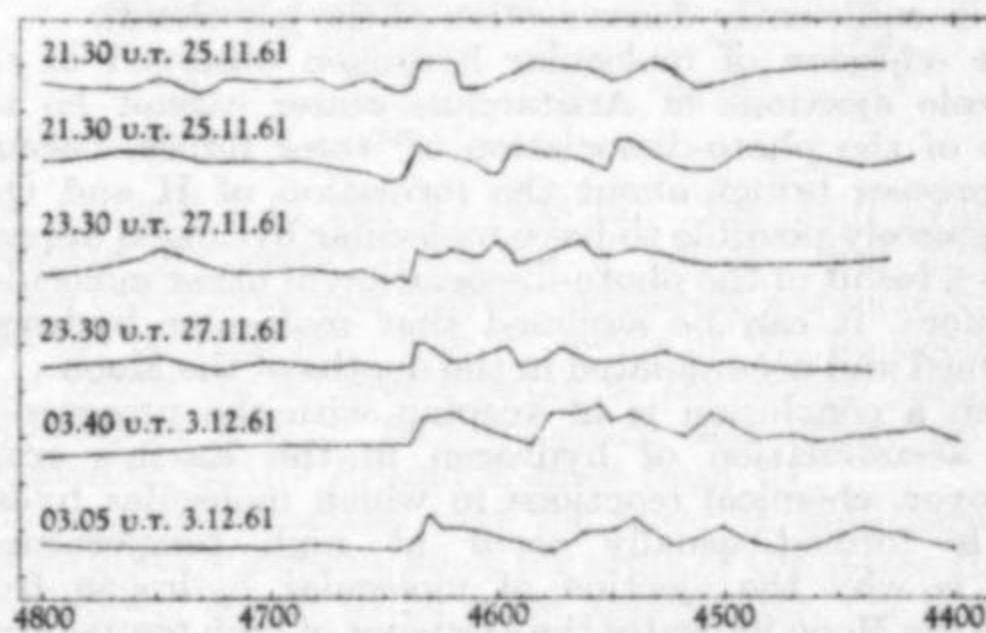


Fig. 1. Additional emission in the blue part of the spectra from the Aristarchus spectra. One division on the vertical scale equals 0.10 log<sub>10</sub> of the background intensity

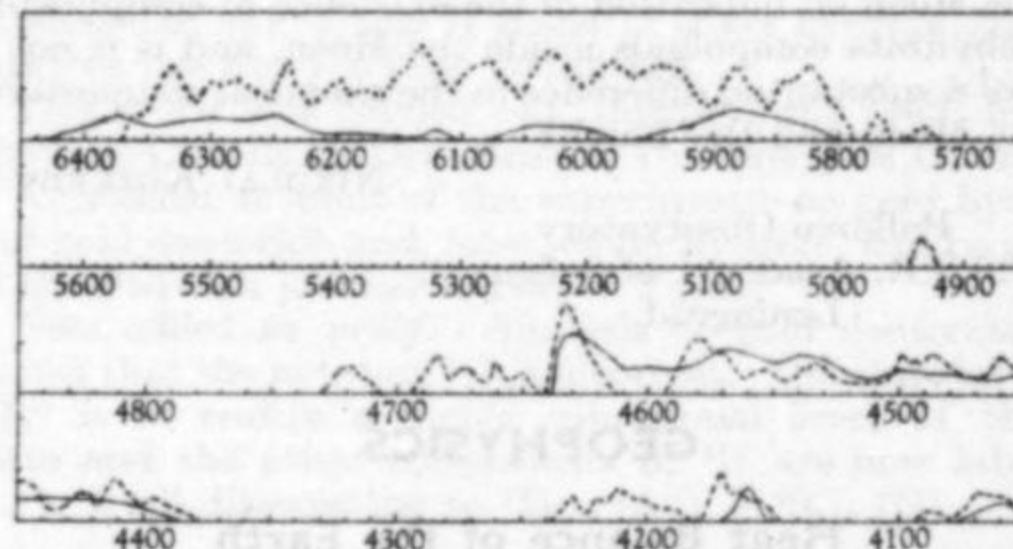


Fig. 2. Emission from Aristarchus compared with the emission of the hydrogen molecule (---) having the same dispersion

group of lines stretches up to 4390 Å, and has a series of maxima. These data definitely establish that the emissions observed are of a gaseous nature. An important confirmation of such a conclusion is provided by the fact that on the photographs, taken on December 3, emission lines somewhat project into the spectrum of the shadow cast by the eastern side of the Aristarchus wall. Hence, one can conclude that the source of emission rises to a certain height over the surface of the crater. It is quite possible that the emissions observed close to the last quarter of the Moon are not accidental, and that the ejection of the gases is made easier by the fact that the Sun's rays heat the crater surface.

The so-called secondary spectrum of hydrogen, that is, the spectrum of the hydrogen molecule, is a most complicated one, and its brightest lines are concentrated in two sections: the orange-red and the dark-blue. The dark-blue section of emission of molecular hydrogen begins with a particularly bright line of the singlet system of hydrogen fumes, with the wave-length exactly equal to 4634 Å. It is because of this line that in cases of lower dispersion the blue section of the hydrogen spectrum looks like a broad strip with a red fringe clearly standing out. The comparison of this strip with that in the Aristarchus crater is convincing proof that there is an emission of molecular hydrogen in the crater.

It is significant that the photometric measurements aided the discovery of a weak emission in the orange-red section of the spectrum in the Aristarchus crater, actually in the same area where there is intensive emission of hydrogen molecules (these are mainly triple lines of orthohydrogen). Usually, in laboratory experiments

a spectrum of atomic hydrogen accompanies the secondary spectrum of hydrogen. However, as regards the Aristarchus crater, specially made measurements did not show any difference between the lines of atomic hydrogen and the way these lines appear in the solar spectrum. This result can most likely be explained by the difficulty of excitation of hydrogen atoms, and also by the fact that these atoms, formed as a result of photo-dissociation, usually leave the area under observation very quickly (that is, sufficiently dense section of the gas cloud).

The emission of molecular hydrogen observed in the fumarole ejections of Aristarchus crater cannot be the result of the photo-dissociation of water fumes, because this process brings about the formation of H and OH. It is scarcely possible to have molecular hydrogen appearing as a result of the photo-dissociation of other molecules. Therefore, it can be assumed that molecular hydrogen is formed and accumulated in the depths of the Moon.

Such a conclusion is in keeping with the presence of local accumulation of hydrogen in the Earth's crust. Moreover, chemical reactions in which molecular hydrogen is formed usually occur at high temperatures. That is why the ejection of molecular hydrogen from inside the Moon indicates the existence of high temperature inside our natural satellite, just as inside the Earth.

The observations made also raise the following question: Are not the emissions of carbon and hydrogen observed on the Moon an indication of the existence of complicated carbohydrate compounds inside the Moon, and is it not a sign of a substantial difference in the chemical composition of the Moon and the Earth?

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## GEOPHYSICS

### Heat Balance of the Earth

FROM the values of the mean thermal conductivity and temperature gradient observed over the surface of the Earth we deduce the net loss of heat by conduction (the geothermal flux). To suppose that this loss represents the only sink in the heat balance of the Earth is to accept a very severe constraint on geophysical theories. Thus it is widely assumed that naturally radioactive elements must be confined effectively to the surface layer of the Earth accessible to our probing. The latest application of the constraint appears in Stacey's criticism<sup>1</sup> of Runcorn's theory<sup>2</sup> of the growth of the Earth's core. In accepting the constraint but not Stacey's criticism, Runcorn<sup>3</sup> turns to a radical modification of the widely accepted thermal history of the Earth. Whatever the merit of the respective arguments, it is worth noting that the constraint which forms the basis of the controversy may be considerably weakened.

It has been pointed out by Bass and Schrödinger<sup>4</sup>, and confirmed by subsequent discussions<sup>5,6</sup>, that the present experimental knowledge of electromagnetism is entirely compatible with the existence of a rest mass of the photon not exceeding the order of  $10^{-47}$  g. In particular, the longitudinal waves and photons arising from this modification of the conventional electromagnetic theory would interact with matter too weakly to be detected in the laboratory. On the other hand, celestial bodies massive enough to be at least semi-opaque to longitudinal radiation would emit a good deal more energy than could be registered by instruments placed around their surface. The efficacy of this concealed cooling mechanism has been calculated<sup>7</sup> for the case of the Earth with a result permitting a plausible distribution of radioactive elements throughout its volume. A comparison of that calculation with Stacey's figures<sup>1</sup> shows that the heat sink provided

by the photon mass is also ample to accommodate all the heat involved in the present argument.

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- <sup>1</sup> Stacey, F. D., *Nature*, **197**, 582 (1963).
- <sup>2</sup> Runcorn, S. K., *Nature*, **195**, 1248 (1962).
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- <sup>5</sup> Bass, L., and Schrödinger, E., Supp. *Nuovo Cimento*, **4**, 825 (1956).
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## PHYSICS

### A Fundamental Extension of Einstein's Diffusion - Mobility Relationship

DIFFUSION is a fundamental process, possessed by molecular, atomic and sub-atomic particles. The process is associated with a density gradient, and is independent of particle charge.

About half a century ago, Einstein's work<sup>1</sup> on diffusion led to a fundamental relation between the diffusion and mobility of charged particles. The equation, named after Einstein, has proved to be of significant importance in semi-conductor physics<sup>2</sup>. Einstein's equation is:

$$D = \left( \frac{kT}{q} \right) \mu \quad (1)$$

where  $D$  is the diffusion constant for the particles, and  $\mu$  is their mobility,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $q$  is the magnitude of the particle charge.

The Einstein equation suggests some intimate compatibility between the drift and diffusion processes. The purpose of this communication is to describe some fundamental consequences of this compatibility.

It is well known that in a pure drift process each free positively charged particle would have an average motion along the electric field. The motion is a result of a drift force. It is also well known that in a pure diffusion process a charged or neutral free particle would have a net motion against the particle density gradient. In view of these properties, and the compatibility between the diffusion and drift suggested by Einstein's equation, it seems reasonable to assume the following:

Every particle involved in a diffusion process, on the average, would be acted on by a force. Let this force be called the particle diffusion force. We shall next calculate an expression for this quantity.

Consider a three-dimensional region, in which there is a large number of positive, equally-charged, microscopic, mobile particles. Let the only processes in this region be the diffusion and drift. Suppose that at a particular point,  $P$ , the two processes were in equilibrium. Thus, at  $P$ , the current density  $J$ , due to the combined drift and diffusion actions, may be described<sup>3</sup> by:

$$J = q(n\mu\varepsilon - D\nabla n) = 0 \quad (2)$$

Here  $n$  is the density of the particles, and  $\varepsilon$  is the electric field intensity.

Because of the equilibrium at  $P$ , the sum of the assumed particle diffusion force,  $f_D$ , and the particle drift force,  $f_\varepsilon$ , must be zero. Thus:

$$f_D + f_\varepsilon = 0 \quad (3)$$

It is well known, however, that:

$$f_\varepsilon = q\varepsilon \quad (4)$$

Therefore, from (2) and (4), it follows that:

$$f_\varepsilon - \left( \frac{qD}{\mu} \right) \nabla n = 0 \quad (5)$$

Comparison of (3) and (5) shows that:

$$\mathbf{f}_D = - \left( \frac{qD}{\mu} \right) \frac{\nabla n}{n} \quad (6)$$

Substituting the Einstein equation into (6), we get:

$$\mathbf{f}_D = - (kT) \frac{\nabla n}{n} \quad (7)$$

The assumed particle diffusion force  $\mathbf{f}_D$ , as expressed in equation (7), does not depend on the particle charge, and conceivably would hold true whether or not there were other processes, if the Einstein relation were satisfied. The answer appears to be consistent with the fundamental property of diffusion that it is independent of the particle charge.

We shall next calculate the average energy  $W_D$ , gained by a particle, diffusing from a point  $A$  of high concentration  $n_a$ , to a point  $B$  of low concentration  $n_b$ . This energy would be:

$$W_D = \int_A^B \mathbf{f}_D \cdot d\mathbf{s} \quad (8)$$

where  $s$  is the particle path.

In view of equations (7), and (8), we have:

$$W_D = (kT) \ln \left( \frac{n_a}{n_b} \right) \quad (9)$$

which is independent of the path. This energy is the amount gained from the diffusion process alone.

The concept of a particle diffusion force suggested in this communication does not seem to be inconsistent with the well-established laws of Nature. In fact, the collective contribution of the particle diffusion force would, in some cases, give rise to the osmotic pressure discussed in Einstein's original paper<sup>1</sup>. Furthermore, osmotic pressure effects are well-known observations.

Many processes and phenomena in the life, natural, and engineering sciences involve the diffusion process. It is probable that the particle diffusion force, and gained energy, might be useful, if not essential, for a better understanding of some of these processes and phenomena, wherever they may be, if the Einstein equation holds.

I thank Dr. C. W. Schultz for his comments.

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<sup>1</sup> Einstein, A., *Ann. Physik*, **17**, 549 (1905).

<sup>2</sup> Shockley, W., *Electrons and Holes in Semiconductors*, 299 (D. Van Nostrand Co., Inc., New York, 1950).

<sup>3</sup> See ref. 2.

### Absorption Spectrum of Gold Hydride in the Ultra-violet

THE absorption spectrum of gold hydride has been photographed in the region 2200–2900 Å.

Gold hydride has two known excited states,  $A^1\Sigma^+$  at 27,340 cm<sup>-1</sup> and  $B^1\Sigma^+$  at 38,230 cm<sup>-1</sup> above the ground-state  $X^1\Sigma^+$ . Transitions from several vibrational levels of  $A$  and from  $B(v'=0)$  to  $X$  have been observed in emission<sup>1,2</sup>. The 1–0 transition of  $B$ – $X$  has been observed in absorption<sup>3</sup>.

In the region 2200–2900 Å eleven bands were found, all shaded towards the red. Of these the band farthest to the ultra-violet (head at 43,846 cm<sup>-1</sup>) was too weak and diffuse to be analysed, but it is too complex to be a  $^1\Sigma^-$  transition. The bands are given in Table 1.

The  $B$  state dissociates very probably to  $^2D_{5/2}$  (Au) +  $^2S_{1/2}$  (H) and the  $A$  state (10,890 cm<sup>-1</sup> below  $B$ ) to  $^2D_{5/2}$  (Au) +  $^2S_{1/2}$  (H), where  $^2D_{5/2}$  is 12,270 cm<sup>-1</sup> below  $^2D_{3/2}$  and 9,160 cm<sup>-1</sup> above the  $^2S_{1/2}$  ground state of gold.

The  $C^1\Sigma^+ - X^1\Sigma^+$  transition shows broad lines increasing roughly linearly with  $J$  (width at  $J = 10 \sim 2$  cm<sup>-1</sup>). This indicates a predissociation of  $C$ , probably by an unstable  $\Pi$ -state.

The  $^3\Pi$  state is inverted and the constants given are for  $^3\Pi_1$ . A  $^3\Pi - ^1\Sigma$  transition should have 5 branches in Hund's

Table 1

No.	$v_0$ (cm <sup>-1</sup> )	$v' - v''$	Transition
1	35,425.3	1–2	$B$ – $X$
2	36,013.1	0–1	$B$ – $X$
3	36,821.2	2–2	$B$ – $X$
4	38,231.8	0–0	$B$ – $X$
5	38,953.4	2–1	$B$ – $X$
6	39,776.2	1–0	$B$ – $X$
7	40,104.2	0–1	$a^3H_g - X^1\Sigma^+$
8	41,172.1	2–0	$B$ – $X$
9	42,323.0	0–0	$a^3\Pi_g - X^1\Sigma^+$
10	43,105.5	0–0	$C^1\Sigma^+ - X^1\Sigma^+$

Preliminary constants (cm <sup>-1</sup> ):			
$B_g$ or $B_h$	$a$	$\omega_e$	$\omega_{gZg}$
$B^1\Sigma^+$	5.849	0.187	1,693.1
$a^3H_g$	5.464		
$C^1\Sigma^+$	5.79		

case (a) and 9 in Hund's case (b). For gold hydride 5 branches are observed at low  $J$  values. For higher  $J$  values extra branches appear, indicating a transition from case (a) to case (b). The  $0^+$  levels of  $^3\Pi_g$  lie about 100 cm<sup>-1</sup> below the  $0^-$  levels owing to the strong perturbing influence of  $C^1\Sigma^+$ . This influence also shows up as a broadening of the  $R$ - and  $P$ -lines from  $^3\Pi_g$ .

It may be remarked that the notation used here may not be quite adequate, since for some of the states Hund's coupling (c) seems to be more appropriate. It is hoped that projected experiments with gold deuteride will elucidate further the problem.

Absorption spectra of silver hydride have also been taken for wave-lengths below 2700 Å. These show the existence of new  $\Sigma$  and  $\Pi$  states of silver hydride, but the analysis has not yet been completed.

This work was carried out, during June 1962, in the Physical Chemistry Department, University of Oxford.

A detailed account of the experiments on gold hydride and gold deuteride and, later, silver hydride, will be given in the Swedish journal *Arkiv för Fysik*.

Note added in proof. Analysis of gold deuteride has shown that the notation  $^3\Pi$  is incorrect. The state labelled  $^3\Pi_g^+$  is in reality a higher vibrational level of the  $B$  state and the other components of  $^3\Pi$  are now labelled  $0^-, 1, 2$ , all dissociating to  $^2D_{5/2}$  (Au) +  $^2S_{1/2}$  (H).

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<sup>2</sup> Imanishi, S., *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **31**, 247 (1937).

<sup>3</sup> Hulthén, E., and Zumstein, R. V., *Phys. Rev.*, **28**, 13 (1926).

### Electron Spin Resonance in Neutron-irradiated Diamond

RECENT work has shown that the nature of the electron spin resonance spectrum observed in irradiated diamond depends on the type and amount of irradiation. Faulkner and Lormer<sup>1</sup> used comparatively heavy doses of 2-MeV electrons (up to  $8 \times 10^{19}$  electron cm<sup>-2</sup>) and distinguished four systems, all of which show a  $g$ -value which is isotropic and equal to the free-spin value within 0.2 per cent: (a) a single line of width about 5 gauss; (b) a system of 24 lines with symmetry axes near the  $<221>$  directions, and a  $D$ -value of 0.14 cm<sup>-1</sup>; (c) a system of 6 lines with symmetry axes along the  $<100>$  directions and a  $D$ -value of 0.14 cm<sup>-1</sup>; (d) a broad absorption with a half-power width of about 70 gauss, showing a complicated anisotropic structure.

Baldwin<sup>2</sup>, using a much lower effective dose ( $9 \times 10^{17}$  electron cm<sup>-2</sup> at 0.75 MeV), observed only the system (a), which was shown to be composed of at least three superimposed lines.

Here we give the results of room-temperature measurements at 9 kMc/s on four specimens of type IIa diamond which have been subjected to irradiation with fast neutrons at a temperature of about 50°C in the National Institute for Research in Nuclear Science irradiation facility in the Atomic Weapons Research Establishment Herald reactor. We find that the features of the spectrum

can be classified under the headings of the (b), (c) and (d) systems given here.

The main feature of the spectrum is a broad absorption centred at  $g = 2.00$ , with a half-power width (obtained by numerical integration of the recorded derivative curves) of about 80 gauss. This line shows a weak anisotropic structure in the two less heavily irradiated specimens, but appears smooth in the other specimens; the line has very long tails and its shape is not Lorentzian. There is no evidence of a dependence of the half-power line width on irradiation dose, the measured values all being equal within  $\pm 5$  per cent; however, the details of the central part of the derivative curve show a dependence on dose, so that the separation between points of maximum slope is not a reliable indication of the width of the absorption. Because of the resemblance of this absorption to the (d) system in electron-irradiated specimens, we assume that it has a similar origin and have classified it under the same heading.

The (b) and (c) systems were identified without difficulty; they were broadened by about 20 gauss in the most heavily irradiated specimens. As in the case of the most heavily electron-irradiated specimens, the (a) system could not be distinguished.

The integrated intensities of systems (b), (c) and (d) were compared with the integrated intensity of the absorption line in a specimen of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in order to determine the number of magnetic centres in each system. The results, calculated on the assumption that  $S=1$  for the diamond centres, are given in Table 1. We estimate that these figures are correct within a factor of 2 for the (b) system, a factor of 1.5 for the (c) system and  $\pm 20$  per cent for the (d) system.

Specimen	Dose $n^{\circ} \text{cm}^{-2}$	Magnetic centres $S=1 \text{ cm}^{-3}$		
		(b)	(c)	(d)
D215	$3 \times 10^{17}$	$3 \times 10^{17}$	$5 \times 10^{18}$	$1.9 \times 10^{19}$
D92	$3 \times 10^{18}$	$3 \times 10^{18}$	$8 \times 10^{18}$	$9 \times 10^{18}$
D16	$9 \times 10^{18}$	$1.5 \times 10^{19}$	$5 \times 10^{19}$	$3.1 \times 10^{20}$
D218	$1 \times 10^{19}$	$3 \times 10^{19}$	$6 \times 10^{19}$	$3.1 \times 10^{20}$

The dose figures refer to fast neutron flux as measured by the  $^{58}\text{Ni}(n,p)^{58}\text{Co}$  foil threshold detector.

It appears from Table 1 that the intensities of the (b) and (c) systems remain below a value corresponding to  $10^{19}$  magnetic centres  $\text{cm}^{-3}$ , while the intensity of system (d) rises to 30 times this value. Furthermore, there is no evidence of any constant ratio between the intensities of the three systems.

It is interesting to compare these results with the earlier measurements reported by Griffiths, Owen and Ward<sup>3</sup>. These workers observed an increase in the width of the central absorption with increasing neutron dose from 20 to 70 gauss; however, most of their specimens were much less heavily irradiated than ours, and we suggest that the observed central line was in fact an absorption of type (d) superimposed on a line of type (a). It was seen in the electron-irradiated specimens that system (d) increases regularly with dose while the (a) line reaches a limiting intensity, so that in the most heavily irradiated specimens the width of the central absorption is that of the (d) system only. We did not identify the  $<110>$  system described by Griffiths *et al.*, and we suggest that this was probably a product of annealing.

It has recently been suggested by Harris, Owen and Windsor<sup>4</sup> that in neutron-irradiated diamond the absorption systems which we refer to as (c) and (d) are due to damage centres which are present in roughly equal numbers, the (d) system being due to vacancies and the (c) system being due to interstitial carbon atoms which are not all in a paramagnetic state. The work reported here appears to contradict this hypothesis, because in the first three specimens the (d) system grew in intensity with increasing neutron dose while the (c) system did not; furthermore, annealing experiments (to be fully reported later) show that by suitable heat-treatment after irradia-

tion one can prepare a specimen which does not show the (b) or the (c) systems, but which shows a substantial (d) system. On the other hand, the present results are not inconsistent with the hypothesis put forward by Faulkner and Lomer<sup>1</sup> that the basic unit responsible for the (d) system is the vacancy-interstitial pair with  $S=1$ , and that the anisotropic structure is due to interactions between the components of such pairs. The differences between the spectra induced by neutron and by electron irradiation would be due to the fact that neutron irradiation produces localized regions of high defect concentration, so that the structure of the (d) absorption is smeared out by magnetic interactions between pairs.

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<sup>3</sup> Griffiths, J. H. E., Owen, J., and Ward, I. M., *Rep. Bristol Conf. (London, Phys. Soc.)*, 81 (1955); *Nature*, **173**, 439 (1954).

<sup>4</sup> Harris, E. A., Owen, J., and Windsor, C., *Bull. Amer. Phys. Soc.*, **8**, 252 (1963).

### Spontaneous Dissolution of Metals in Polar Electrolytes

WHEN a solid metal is dipped into a polar electrolyte, a spontaneous transient pulse of net current, carried across the interface by metal ions, generates a potential difference  $\Delta V$  between the solid and the bulk of the liquid. It is then either offset by an opposite electron current (gas evolution) or, if the bulk of the electrolyte contains some concentration  $c_m(\infty)$  of the metal ions to begin with, the familiar dissolution-deposition equilibrium supported by  $\Delta V$  (which is calculated from  $c_m(\infty)$  according to Nernst<sup>1</sup>) may be established across the interface.

Beginning with the latter equilibrium, suppose that we gradually replace metal ions in the bulk by hydrogen ions carrying equivalent charges. If that equilibrium persisted for any  $c_m(\infty)$ , we could generate arbitrarily large  $\Delta V$ 's by continuing the replacement process. The replacement of the last few metal ions per c.c. of the bulk can scarcely cause  $\Delta V$  to grow to infinity. Some situation resembling equilibrium must gradually replace the familiar picture as  $c_m(\infty)$  is reduced, since noble metals are stable in many infinite electrolytes initially containing none of their ions (regardless even of convection). Starting from this last case we therefore seek an interface interaction (not based on deposition or gas evolution) which aids dissolution for only a brief period after dipping. The height of the potential barrier separating the bound metal ion from its solvated state must be temporarily much reduced as compared with the real potential,  $V_0$ , separating the bound ion from *vacuo*. The barrier is probably lowered by thermal collisions of suitably oriented groups of solvent dipoles with the interface<sup>2</sup>. In macroscopic terms we may suppose that the electrostatic binding energy,  $V_0$ , of the outermost ions of the solid is reduced by the dielectric action of the electrolyte to  $V_0/\epsilon$ , provided that we can attach to the dielectric constant  $\epsilon$  values which correspond to the underlying microscopic mechanism. In any event,  $\epsilon_0 \sim 80 \geq \epsilon \geq \epsilon_\infty \sim 3$  for dilute aqueous solutions, the upper limit  $\epsilon_0$  arising from orientational, distortional and optical polarizability, the lower limit only from the latter two.

A metal ion bound near the interface and oscillating with a frequency,  $\omega$ , subjects the adjacent dielectric to a periodic electrical perturbation causing the solvent dipoles to turn towards it (solvate it) so far as they can follow the rapidly variable field. We are thus led to identify the  $\epsilon$  dividing  $V_0$  with the temperature-dependent  $\epsilon(\omega)$  of Debye's theory<sup>3</sup> of anomalous dispersion in polar liquids:

$$V_0/\epsilon(\omega) = V_0 \frac{1 + (\omega\tau)^2}{\epsilon_s + \epsilon_\infty(\omega\tau)^2} \quad (1)$$

thus obtaining the spectral distribution of the barrier height ( $\tau$  is Debye's well-known viscous relaxation time). If we select an assembly of ions vibrating near the interface as quantized oscillators at a frequency  $\omega$ , consideration of the relevant orders of magnitude shows that the probability,  $P_\omega$ , per ion and unit time of surmounting the barrier may be approximated by the immediately plausible expression:

$$P_\omega = \frac{\omega}{2\pi} e^{-\frac{V_0}{\epsilon(\omega)kT}} \quad (2)$$

To estimate the distribution of ions over frequencies we adapt Debye's model<sup>4</sup> for the calculation of specific heats of solids to the vibrations of the metal layers at the interface. The approximate number of ions vibrating at a unit area of the interface in the frequency band between  $\omega$  and  $\omega + d\omega$  turns out to be  $d\xi = 3N\hbar^3 n^3 \rho A \omega^2 d\omega / k^3 \theta^3 M$ , involving universal constants (Avogadro's  $N$ , Boltzmann's  $k$  and Planck's  $2\pi\hbar$ ), the density  $\rho$  of the metal, its atomic weight  $M$  and the interionic distance  $A$  in its lattice; the Debye characteristic temperature  $\theta$  is connected with the limiting cut-off frequency which is slightly lowered if we allow the dielectric to modify also the shape of the barrier, whereby the refractive index  $n = \epsilon_\infty^{1/2}$  of the solution becomes involved in  $d\xi$ . The total dissolution rate,  $R$   $\text{cm}^{-2}\text{sec}^{-1}$ , is the integral of  $P_\omega d\xi$  over the active frequencies. Since  $k\theta/\hbar \gg 2\pi/\tau$  in typical cases,  $\epsilon \sim \epsilon_\infty$  near the cut-off frequency and thus the integrand is negligible at both integration limits. A good first approximation is:

$$R \approx \left( \frac{3N\hbar^3}{4\pi k^3} \right) \left( \frac{n^3}{\tau^4} \right) \left( \frac{\rho A}{M\theta^3} \right) e^{-\frac{V_0}{\epsilon_s k T}} \quad (3)$$

which represents the maximum rate of spontaneous dissolution. Equation (3) is very sensitive to temperature, explicitly as well as through  $\tau$ ; for silver at 300° K it yields a dissolution current of  $2.6 \times 10^{-4}$  amp  $\text{cm}^{-2}$ . Ultimately polyvalent ions probably cross the barrier in monovalent form and are ionized further by a redox step.

To account for stability of metals when  $c_m(\infty) = 0$  we observe that even slight dissolution generates an interface field  $E$  ( $\epsilon E = 4\pi Q$ ,  $Q$  being the positive diffuse charge per unit area of the interface) so strong that the argument  $\mu E/kT$  of the Langevin function is of the order of unity,  $\mu$  being the dipole moment of the water molecule. Thus saturation of the orientational polarizability reduces  $\epsilon$  to  $\epsilon_\infty$  and  $P_\omega$  to values so small that  $R$  is cut down to values not noticeable over many years. This effect is greater by many orders of magnitude than the direct electrostatic action of  $Q$  on  $R$ . If we suppose for simplicity that full saturation sets in at  $\mu E/kT = 3$  (extending the linear approximation of the Langevin function), we can estimate the quasi-stable charge  $Q$  required to stop dissolution effectively, as well as the time in which the original  $R$  generates it. At 300° K the former is of the order  $5 \times 10^{-6}$  coulomb  $\text{cm}^{-2}$ , probably representing the main part of the zero point charge on stable metals; the latter is of the order  $2 \times 10^{-3}$  sec for silver, indicating the duration of the initial pulse of net current.

A significant test of the present model is obtained when we extend it to continued dissolution with hydrogen gas evolution, due to transitions of conduction electrons tunnelling from the metal to adjacent solvated hydrogen ions. To conserve energy, the ionization energy  $I_H \approx 13.5$  eV of the hydrogen atom gained in the transition must be supplemented by work done by the field  $E$  in transit, in order to supply energy at least equal to the electron work function  $f$  plus the solvation energy,  $W_H \approx 12$  eV, of the hydrogen ion in water. Since the nearest hydrated  $H^+$  is

at a distance from the interface of the order of two molecular radii of water ( $2a \approx 4 \times 10^{-8}$  cm), the work done by  $E$  is about  $2aeE$  and energy conservation requires  $2aeE + I_H \geq f + W_H$ , exceptions being insignificant at the temperatures under consideration. On the other hand, the build-up of  $E$  by dissolution ceases in the model at  $\mu E = 3kT$ , so that spontaneous gas evolution cannot occur if:

$$\frac{6ae}{\mu} < \frac{f + W_H - I_H}{kT} \quad (4)$$

This condition of stability yields  $f > 2.3$  eV at 300° K and  $f > 2.5$  eV at 373° K in water, thus distinguishing very satisfactorily between alkali metals and others. Since stability is not due to thermodynamic equilibrium in equation (4), this condition is not derivable thermodynamically.

When equation (4) is not satisfied, electron transitions keep  $E$  permanently below saturation values and equation (3) may be used to estimate continued dissolution and gas evolution rates in the activation-controlled case. The theory then reproduces the relative reactivities of alkali metals with water. Thus at 373° K we obtain from equation (3) some 30 amp  $\text{cm}^{-2}$  for rubidium, but only  $4 \times 10^{-2}$  amp  $\text{cm}^{-2}$  for lithium, the difference being due notably to the Debye temperatures of these metals. As regards the absolute values of the rates, some corrections may be required for the state of the surface of a rapidly dissolving metal.

A full account of this theory will be given elsewhere.

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## METALLURGY

### L<sub>2</sub> Structure of the Alloy AuAgZn<sub>2</sub>

PROBABLY the most interesting examples of the L<sub>2</sub><sub>1</sub> structure are the copper-based Heusler alloys Cu<sub>2</sub>MnX (X = aluminium, indium or tin), which are ferromagnetic in the ordered state. Recent additions to this structural type are Cu<sub>2</sub>MnSb (ref. 1), which is antiferromagnetic, and Au<sub>2</sub>MnAl (ref. 2), which is ferromagnetic. With the possible exception of Cu<sub>2</sub>MnSb a difficulty common to all these from the point of view of an experimental study of ordering effects in ternary systems is that the L<sub>2</sub><sub>1</sub> structure is stable only at high temperatures. Low-temperature anneals or slow cooling, while though initially increasing the degree of order and enhancing the magnetic properties, finally lead to the breakdown of the structure or the precipitation of a second phase.

Muldawer<sup>3</sup> has briefly reported resistivity measurements characteristic of ordering in the quasi-binary AuCd—AgCd system and the existence of the L<sub>2</sub><sub>1</sub> structure at AuAgCd<sub>2</sub>. Somewhat more favourable atomic scattering factors occur in the analogous AuZn—AgZn system and we have therefore examined an alloy of composition AuAgZn<sub>2</sub>. This may be regarded as a structure formed by the coalescence of B2 β-AuZn and β-AgZn, and conditions are favourable for L<sub>2</sub><sub>1</sub> ordering.

The alloy was prepared *in vacuo* from elements of spectroscopic purity and homogenized for 48 h at 600° C. The loss of weight was negligible. The existence of the L<sub>2</sub><sub>1</sub> structure was confirmed from powder photographs of samples heat-treated at different temperatures and examined with copper Kα-radiation in the quenched condition. At 18° C the unit cell has dimensions of 6.2919 ± 0.0003 Å and 6.2932 ± 0.0003 Å after one week at 280° C and 600° C respectively. There was a slight

change in the visually estimated intensities of the superlattice lines in the two cases and the parameter changes are presumably due to differences in the degree of order. No evidence was obtained of decomposition or the precipitation of a second phase at the lower temperature.

We thank the Council of the Royal Society for a grant-in-aid, and the Department of Scientific and Industrial Research for a maintenance grant for one of us (C. D. P.)

*Note added in proof.* Cu<sub>2</sub>MnAl has recently been shown<sup>4</sup> to partially disorder to a CsCl structure at high temperatures.

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### Superconducting Alloys of the Nb<sub>3</sub>Sn<sub>x</sub>M<sub>1-x</sub> Type

In a report prepared in this Laboratory some of the empirical observations concerning superconductivity which have been proposed in recent years were evaluated and modified using data obtained from the literature<sup>1</sup>. This work suggested that the initial materials to be examined should have the β-tungsten structure, contain an element which itself was a good superconductor, and have an average valence electron-per-atom ratio of approximately 4.75. Since Nb<sub>3</sub>Sn, which has the highest superconducting transition temperature reported, meets the foregoing criteria, the many alloys which can be prepared by partial or total substitution for tin by elements with the same or nearly the same number of valence electrons as tin also will meet these criteria providing they retain the β-tungsten structure. As a consequence, an attempt was made to prepare and examine alloys with the general formula Nb<sub>3</sub>Sn<sub>x</sub>M<sub>1-x</sub>, where M is germanium, silicon, aluminium or antimony, and is in the same group or neighbouring group of the Periodic Table as tin.

In the preparation of all the alloys, powders of the elements of 99 per cent purity were mixed in the desired stoichiometric amounts and ball-milled dry for 0.5 h. The powders then were pressed into pellet form and heated under the following conditions. Alloys in which germanium or silicon was substituted for tin in Nb<sub>3</sub>Sn were heated at 1,750° C for 5.5 h under argon, and those containing antimony or aluminium were sealed first in evacuated silica capsules before heating them to 1,100° C for four days.

Small amounts of the samples were ground and powder X-ray photographs were taken using a 57.3 mm radius Philips X-ray powder camera and high-intensity copper Kα-radiation with settings of 50 kV and 40 m.amp for 3 h. The X-ray patterns were read, indexed, and the cell sizes determined by extrapolation of  $a_0$  versus  $1/2(\cos\theta/\sin\theta + \cos^2\theta/\theta)$  to  $\theta = 90^\circ$  (ref. 2).

The transition temperatures of the alloys prepared with the general formula Nb<sub>3</sub>Sn<sub>x</sub>Ge<sub>1-x</sub> were found to vary approximately linearly with composition, falling between the transition temperatures of Nb<sub>3</sub>Sn and Nb<sub>3</sub>Ge (6° K). Since germanium lies in the same group of the periodic table as tin, these alloys all had the same electron-per-atom ratio. When antimony was substituted for tin in Nb<sub>3</sub>Sn, however, the electron-per-atom ratio increased from 4.75 to 5, and the transition temperature of these alloys showed a rapid drop with increasing amounts of substitution.

The substitution of aluminium for tin lowered the electron-per-atom ratio and lowered the transition temperature which, unlike antimony alloys, then reached a maximum with total substitution of aluminium, Nb<sub>3</sub>Al (17.5° K) (ref. 3), indicating that there may be another ideal electron-per-atom ratio for the β-tungsten structure at 4.5 as well as 4.75. While this communication was in preparation, it was learned that Dr. T. Reed of the Lincoln Laboratories has also examined systems which involved the substitution of germanium, aluminium and antimony for tin in Nb<sub>3</sub>Sn (ref. 4), so it was decided to present only the general trends that we had found.

As an extension of our work, the Nb<sub>3</sub>Sn<sub>x</sub>Si<sub>1-x</sub> system was also investigated. It is interesting to note that Nb<sub>3</sub>Si does not adopt the β-tungsten structure as the other Nb<sub>3</sub>M compounds in this work but instead was found to have the ordered Cu<sub>3</sub>Au structure<sup>5</sup>. The largest amount of silicon which could be substituted for tin with retention of the β-tungsten structure is ~50 atomic per cent. Table 1 presents the compositions, cell sizes, and transition temperatures of the phases prepared.

Table 1. DATA FOR Nb<sub>3</sub>Sn<sub>x</sub>Si<sub>1-x</sub> ALLOYS

Alloy	Structure	Cell size (Å)	T <sub>c</sub> °K
Nb <sub>3</sub> Sn	β-tungsten	5.292	17.8
Nb <sub>3</sub> Sn <sub>0.98</sub> Si <sub>0.02</sub>	β-tungsten	5.285	17.8
Nb <sub>3</sub> Sn <sub>0.75</sub> Si <sub>0.25</sub>	β-tungsten	5.263	16.4
Nb <sub>3</sub> Sn <sub>0.75</sub> Si <sub>0.25</sub>	β-tungsten	5.261	13.9
Nb <sub>3</sub> Sn <sub>0.50</sub> Si <sub>0.50</sub>	β-tungsten	5.239	8.3
Nb <sub>3</sub> Sn <sub>0.50</sub> Si <sub>0.50</sub>	β-tungsten	5.235	7.0
Nb <sub>3</sub> Si	ordered Cu <sub>3</sub> Au	4.22	1.5

Since Nb<sub>3</sub>Si and Nb<sub>3</sub>Sn have the same electron-per-atom ratio of 4.75, the drop in transition temperature with increasing amounts of substituted silicon cannot be attributed to a deviation from this favourable ratio for the β-tungsten structure. Instead it may be that substitution of small silicon atoms for much larger tin atoms may decrease the stability of the chain of niobium atoms which runs through the β-tungsten structure until at 50 per cent substitution the structure is no longer retained.

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### RADIATION CHEMISTRY

#### Electron Spin Resonance Investigations of Irradiated Carbohydrates

DURING an examination of the radiation chemistry of cellulose, electron spin resonance measurements were performed on a series of irradiated sugars. Certain novel features of the results which were observed are summarized here. Various carbohydrates have been examined previously by electron spin resonance<sup>1-5</sup>, but no detailed investigation of a series has been reported using comparable conditions of irradiation and measurement.

Irradiations were carried out in a cobalt-60 source at dose rates of  $1.25 \times 10^6$  rads/h in both vacuum and air to total doses of  $10^7$  and  $10^8$  rads. For vacuum irradiations samples were vacuum-dried to constant pressure before being sealed off in ampoules at less than  $10^{-3}$  mm mer-

cury<sup>6</sup>. Spectra were measured at room temperature in a spectrometer of conventional design featuring an electronic field sweep to record the first derivative of the absorption curve in approximately 4 min.

The spectra of the irradiated monosaccharides, disaccharides and polysaccharides (Table 1) were similar and showed little hyperfine structure. The significant feature of the results was the doublet of 15–20 gauss separation exhibited by all compounds with two notable exceptions—lyxose and lactose, which produced four-line spectra. In marked contrast to the remainder of the series the two amorphous polysaccharides, amylose and amylopectin, when irradiated in air, produced only very weak signals. The appearance of satellite peaks or poorly resolved lines in some of the spectra, especially glucose and fucose, rendered absolute interpretations difficult. Both effects may be due to overlapping lines from at least one other radical species. This situation can readily occur with the disaccharides if the primary radiation act ruptures the glycosidic linkage and leaves a predominance of two radical fragments. Chromatographic analysis of all the irradiated disaccharides showed that rupture of the glycosidic linkage occurs<sup>7</sup>.

Table 1. SUMMARY OF ELECTRON SPIN RESONANCE SPECTRA OF IRRADIATED CARBOHYDRATES

Compound	Dose (Mrads)	Atmosphere	No. of lines in derivative	Separation (gauss)	Splitting (gauss)
Amylose	100	Vacuum	2	15	3–5
	100	Air	Very weak	signal at maximum sensitivity	
Amylopectin	100	Vacuum	2	16	3–5
	100	Air	Very weak	signal at maximum sensitivity	
Cellulose	100	Vacuum	2	16 and 33*	5
	100	Air	2	16 and 35*	3–4
Glucose	100	Vacuum	2	16–18	†
	100	Air	2	18	9
Galactose	100	Vacuum	2	18 and 40*	9
	100	Air	2	16 and 32*	3–5
Mannose	100	Vacuum	2	18 and 33*	†
	100	Air	2	17	5–6
Fucose	100	Vacuum	2	17	5–6
	100	Air	2	18	8
Arabinose	100	Vacuum	2	17	5
	100	Vacuum	2	18	5
Sucrose	100	Vacuum	2	18	5
	100	Vacuum	2	18	7
Celloolose	100	Vacuum	2	18	7
	100	Air	2	18	7
Trehalose	100	Vacuum	2	17	†
	100	Air	2	18	4–5
Maltose	100	Vacuum	2	18 and 40*	3–5
	100	Air	2	15 and 34*	†
Melibiose	100	Vacuum	2	15 and 34*	†
	100	Air	2	17	5–6
Lyxose	100	Vacuum	4	16 and 40*	11
	100	Vacuum	4	17 and 33*	6
Lactose	100	Vacuum	4	18 and 36*	6 and 31

\* Second figures refer to separation of outer satellite lines.  
† Splitting cannot be determined because of probable overlapping of lines.

The occurrence of a doublet in most spectra indicates spin-coupling with one proton and suggests that the radical arises from the ejection of a hydrogen atom from C<sub>1</sub> or C<sub>6</sub>. The four-line spectra from lyxose and lactose indicate an interaction with three protons. This situation may occur in the latter if the odd electron is localized predominantly at C<sub>1</sub> and then spin-couples with the three protons from C<sub>4</sub> and C<sub>6</sub>. In like manner, for the lyxose radical existing in either pyranose or furanose forms, the free electron if localized on C<sub>4</sub> may couple with the three protons from C<sub>3</sub> and C<sub>5</sub> to give the observed spectrum.

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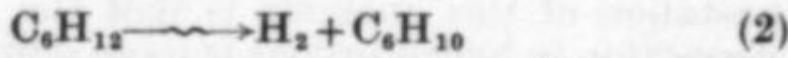
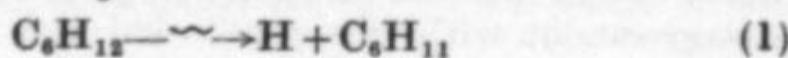
## Spur Reactions in the Radiolysis of Liquid Aliphatic Hydrocarbons

A CONTRAST between the radiation chemistry of water and that of liquid aliphatic hydrocarbons is that, in the former, interpretation of the system is made on the basis of models involving the concepts of tracks and spurs<sup>1</sup>, and that in the latter these concepts are much less frequently invoked<sup>2,3</sup>. ('Hot' atom, unimolecular and 'cage' reactions have been suggested and may occur within a spur, but it is reactions other than these that are primarily discussed here.)

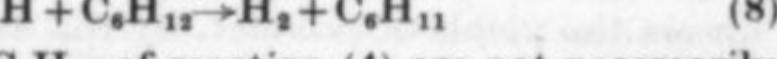
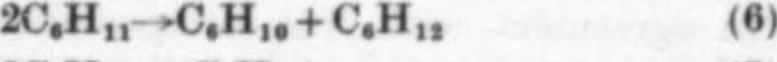
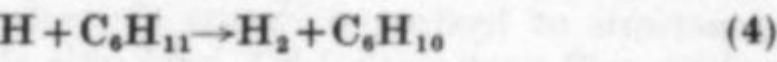
Evidence is accumulating that charged species participate in the radiolysis of water and aqueous solutions but, nevertheless, the application of a simple model in which free radicals are distributed in spurs and tracks has made a considerable contribution to the understanding of these systems. In the radiolysis of liquid hydrocarbons, reactions of excited or charged species may also possibly occur, but it has been pointed out that in these systems complicating ionic effects are less likely to occur, and that the size of spurs would seem to be comparable to that found in aqueous systems<sup>4</sup>. Application of a similar model would therefore seem to be justified.

The much greater complexity of products in the radiation chemistry of liquid aliphatic hydrocarbons<sup>5</sup> is an obvious reason why spur and track effects are difficult to find, and this fact also explains why the main effort in these systems has been directed towards the symmetrical hydrocarbons such as cyclohexane and neopentane, where the chemistry is relatively more simple. The following discussion, therefore, refers to cyclohexane and neopentane in particular but the arguments apply in general to liquid aliphatic hydrocarbons.

It is generally stated<sup>6</sup> that the primary reactions that occur on radiolysis of cyclohexane include:



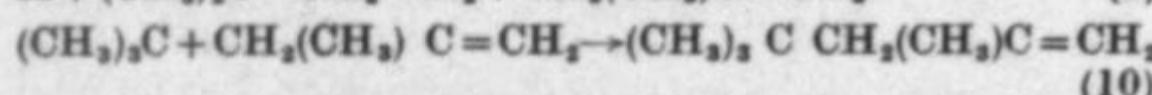
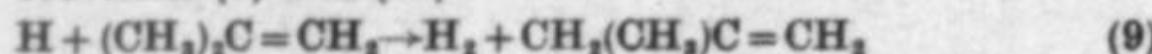
If these reactions occur in a spur there will be a local high concentration of H, C<sub>6</sub>H<sub>11</sub> and C<sub>6</sub>H<sub>10</sub>, and possible spur reactions from reaction of these intermediates will include reactions (3) to (7):



where the H and C<sub>6</sub>H<sub>11</sub> of reaction (4) are not necessarily from the same cyclohexane molecule. If a situation similar to that accepted for water pertains here, the rates of reactions (3), (4), (6) and (7) are probably diffusion-controlled and a fraction of the primary intermediates will disappear by reactions inside the spur, while the remaining fraction diffuses out of the spur and reacts by approximately homogeneous kinetics. The rate constant of reaction (5) has been given<sup>7</sup> as  $K_s \approx 10^9$  litres mole<sup>-1</sup> sec<sup>-1</sup>, a value sufficiently high as not to rule out the reaction as a spur reaction. Because the most probable spur reactions lead to intermediates and products similar to those formed by reactions occurring in the bulk of the liquid, no obvious indication of the occurrence of spur reactions is to be expected from an analysis of the main products of reaction. Evidence for spur reactions, therefore, has to be sought elsewhere, and an examination of (1) minor products of reaction, (2) effect of linear energy transfer (LET) and (3) effect of solutes is presented here.

1. *Minor Products of Reaction.* Detection of minor products is complicated by the fact that primary intermediates may react with accumulating product, often by the reaction that may also be a spur reaction. Thus the fall in the amount of hydrogen per 100 eV absorbed

( $G(H_2)$ ) with increasing dose in cyclohexane<sup>7</sup> and neopentane<sup>8</sup> is attributed to the reaction of hydrogen atoms with accumulating olefin product, and to avoid contributions from such secondary reactions a system must be examined at low conversion. This in turn does not facilitate analysis of minor products, and extrapolation of minor products to zero dose must therefore be carried out with great care. An extensive investigation has been made with neopentane<sup>8</sup>, where there is evidence that hydrogen atoms, *t*-butyl and isobutene are among the primary species. Reaction of hydrogen atoms and isobutene produces mainly *t*-butyl radicals, but approximately 10 per cent of the reaction gives an unexpected but characteristic free radical, the production of which in the radiolysis of neopentane is indicated by the detection of the corresponding C<sub>5</sub> and C<sub>6</sub> recombination products, for example, 2,4,4-trimethyl-1-pentene is produced by reactions (9) and (10):



These products are also produced by secondary reactions, but extrapolation of the yields of product to very low dose indicates that they are present in relatively large amounts for the small amounts of secondary reaction occurring at these low conversions. Thus such products may well be 'initial products'—that is, not produced by reactions of accumulating product—arising from reactions that occur in a spur.

**2. Effect of LET.** It has been shown<sup>9</sup> that if the initial pattern of energy distribution in cyclohexane is similar to that accepted in water, and if reactions (3) and (8) are the only important reactions of H atoms, there should be a marked decrease in  $G(H_2)$  with increase in LET. The observed invariance of  $G(H_2)$  with increase in LET<sup>10</sup> is in disagreement with this conclusion and a suggested interpretation of this anomaly is that the pattern of energy deposition in hydrocarbons is more diffuse than in water<sup>11</sup>.

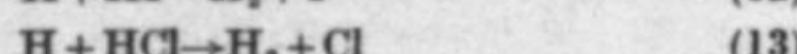
However, other investigations of the effect of increase in LET show that the pattern of energy distribution in hydrocarbons shows similarities to that in water<sup>11</sup>. These disagreements may be resolved if it is accepted that reactions (4) and (5) may also occur. There are then four reactions of hydrogen atoms the relative importance of which will vary with LET, and it is then not difficult to account for the relative invariance of  $G(H_2)$  with LET. In agreement with this interpretation a change in the relative amounts of liquid products with LET is found<sup>12</sup>.

**3. Action of Solutes.** In general, addition of solute lowers the yields of product, by the introduction of competitive scavenging reactions. Thus the fall in  $G(H_2)$  with added solute is attributed<sup>2</sup> to the competition of reaction (11) with reaction (8).



The effect of scavenging solute on the radiolysis of isotopic mixtures of C<sub>6</sub>H<sub>12</sub> and C<sub>6</sub>D<sub>12</sub> should be to reduce substantially the amounts of HD produced by reactions of D and H atoms abstracting H and D atoms respectively from the corresponding cyclohexanes. Experimentally, significant amounts of HD are produced in the presence of scavenger<sup>13</sup>. Spur reactions are less accessible to scavengers, and the persistence of significant amounts of HD could plausibly be attributed to the incomplete suppression by scavenging solute of spur reactions between mixed isotopic species corresponding to reactions (3) and (4).

Other scavenging solutes such as hydrogen iodide and hydrogen chloride react by:



and if no spur reactions occur at low LET, no change in  $G(H_2)$  is expected with added solute. Experimentally, an increase in  $G(H_2)$  of > 1·0 is observed<sup>14-16</sup> for which a

satisfactory explanation has not yet been found<sup>16</sup>. Competition of reactions (12) or (13) with reaction (3), (4), (5) and (8) would give just such an increase in  $G(H_2)$  with added solute, thus providing a simple alternative interpretation.

There are thus several unusual features in the radiation chemistry of liquid aliphatic hydrocarbons which have not yet been satisfactorily explained. The effects discussed above may have other interpretations than the arguments presented here, but it is noteworthy that a number of phenomena may be accounted for by the postulate that spur reactions occur in the radiolysis of liquid aliphatic hydrocarbons.

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### Szilard - Chalmers Reaction on Methyliodide with Simultaneous Extraction during Irradiation

THE distribution of iodine-128 between the organic and inorganic fraction when irradiating methyliodide with thermal neutrons has been examined by many authors<sup>1-6</sup>. It has been shown that when irradiating on a neutron source with a high intensity of accompanying  $\gamma$ -radiation then the organic yield is about 50–60 per cent. On the other hand, while irradiating purified methyliodide on neutron sources with a low  $\gamma$ -radiation background the organic yield was about 100 per cent. When irradiated in the same conditions, but in the presence of very small quantities of elementary iodine, the organic yield rapidly decreased, at concentrations of  $10^{-4}$ – $10^{-3}$  mol/l. It reached the value of organic yield about 50–60 per cent corresponding to the formal experimental conditions.

It has been suggested<sup>7</sup> that an isotopic exchange of pseudo-monomolecular mechanism<sup>8</sup> between elementary iodine and methyliodide is responsible for the raising of the organic yield. The role of exchange is depressed by the presence of elementary iodine in methyliodide without any great difference whether caused by radiolysis or mechanical addition. This statement limits the specific activity of inorganic iodine-128.

In our previous communication<sup>9</sup> we proposed using simultaneous extraction during irradiation as a method for suppressing the undesired influence of exchange reactions on the results of hot atom chemistry processes. For methyliodide we hoped to obtain by this method a decrease in organic yield of iodine-128 without being forced to add any amount of elementary iodine.

Before the output of the horizontal channel of the VVR reactor a paraffin shielding of about 30 cm wall thickness was set up. In the middle of this was placed a 250-ml. flask completely darkened by a black painted cover, which suppressed the role of proteolysis. Further on there was an arrangement which made it possible to mix the liquid content of the flask with a glass propeller connected to an

electric motor giving about 400–500 rotations per min. In place of the irradiation vessel the intensity of neutron flux was in the range  $10^5$ – $10^6$  n/cm<sup>2</sup> sec and that of  $\gamma$ -radiation 5–10 r./h. The low value of accompanying  $\gamma$ -radiation was reached by inserting a bismuth cylinder (diameter nearly the same as the diameter of the horizontal channel and about 70 cm long) in the horizontal channel. Using this apparatus, methyl iodide was irradiated under two different conditions: (1) 50 ml. methyl iodide without stirring during irradiation; 50 ml. of  $10^{-2}$  M Na<sub>2</sub>SO<sub>4</sub> in distilled water was added up to the end of irradiation; (2) 50 ml. of methyl iodide and 50 ml. of  $10^{-2}$  M Na<sub>2</sub>SO<sub>4</sub> in distilled water mixed before irradiation; the liquids were stirred during irradiation. In each experiment the methyl iodide used was purified by standard methods and freshly re-distilled before each irradiation. Irradiation in every case took 2 h. About 2 min (ref. 10) after the end of irradiation the samples were placed in a separation funnel and shaken for 3 min. After separating the layers, equivalent portions of the organic and aqueous fraction were taken in order to measure the radioactivity. This was done in a special measuring vessel under a mica-window Geiger-Müller counter. After introducing the usual corrections on the basis of the relation between the activity in organic fraction and the activities in both fractions (organic + aqueous) the amount of iodine-128 in organic form was estimated. In all cases accomplished under condition (1)  $99 \pm 1$  per cent was estimated; under condition (2)  $50 \pm 1$  per cent in organic form.

These results are not only in very good agreement with the suggestions described, but they also suggest that the true organic yield of iodine-128 in irradiated methyl iodide caused purely by hot atom processes is 50 per cent.

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## CHEMISTRY

### Temperature-dependent Hyperfine Splitting in a Sterically Hindered Radical

SUBSTITUTED phenoxy radicals derived from 2,6-di-tertiary butyl phenols by lead dioxide oxidation or photolysis are quite stable and particularly suitable for examination by electron spin resonance<sup>1,2</sup>. The experimental results indicate that the spin distribution in the aromatic ring is not very sensitive to alkyl substituents and that a hyperconjugatively coupled methyl-type proton in the 4 position should have a hyperfine coupling constant of about 10 gauss. However, the 2,6-di-tertiary butyl 4-cyclohexyl phenoxy radical has a coupling constant of about 4.5 gauss (at room temperature) for the single  $\alpha$ -proton of the cyclohexyl ring<sup>3</sup>.

It seemed likely that this small hyperfine splitting was due to a steric effect, the  $\alpha$ -proton being constrained to lie near the plane of the aromatic ring. Such a conformation would show a smaller coupling than one where there was free rotation of the cyclohexyl ring, since the coupling for the  $\alpha$ -proton would depend on  $\cos^2\theta$ , where  $\theta$  is the

dihedral angle between the aliphatic C–H bond and the symmetry axis of the 2p orbital on the adjacent aromatic carbon atom<sup>4</sup>. Dreiding models support this hypothesis, the source of hindrance being interaction between the four  $\beta$ -hydrogen atoms of the cyclohexyl ring and those in the 3 or 5 positions in the aromatic ring: the models indicate that these hydrogens could approach to about 1.8 Å.

The hyperfine splitting by the  $\alpha$ -proton has been examined as a function of temperature in hexane, methyl cyclohexane and dodecane solutions, and some results obtained from several different samples are shown in Fig. 1. As well as the hyperfine splitting increasing with temperature there is a small dependence on solvent. The spectra also show resolved splittings of  $1.69 \pm 0.05$  gauss from the 3,5-protons in the aromatic ring and of  $0.48 \pm 0.03$  gauss from the four  $\beta$ -protons in the cyclohexyl ring. No temperature dependence was observed for these splittings. Some should occur for the  $\beta$ -protons but the appropriate value of  $\theta$  for these in the equilibrium position should be rather small and a very slight dependence on temperature is not unreasonable. The dependence of the  $\alpha$ -proton coupling constant on solvent is small but real, the values at 295° K being 4.55, 4.60 and  $4.76 \pm 0.05$  gauss in hexane, methyl cyclohexane and dodecane respectively. This is brought out more clearly in Figs. 2a and b, which show the spectra in hexane and dodecane at 295° K. Fig. 2c illustrates the change which occurs in the spectrum in hexane when the temperature is raised to 341° K and Fig. 2d shows a reconstruction of Fig. 2b in terms of the above coupling constants. The radicals were prepared by flash photolysis<sup>5</sup>. The coupling constants were measured by comparison with the spectrum of Fremy's salt; temperatures were measured with a thermo-couple and are estimated accurate to  $\pm 2^\circ$  K.

These observations support the suggestion that steric hindrance tends to keep the  $\alpha$ -proton in the plane of the

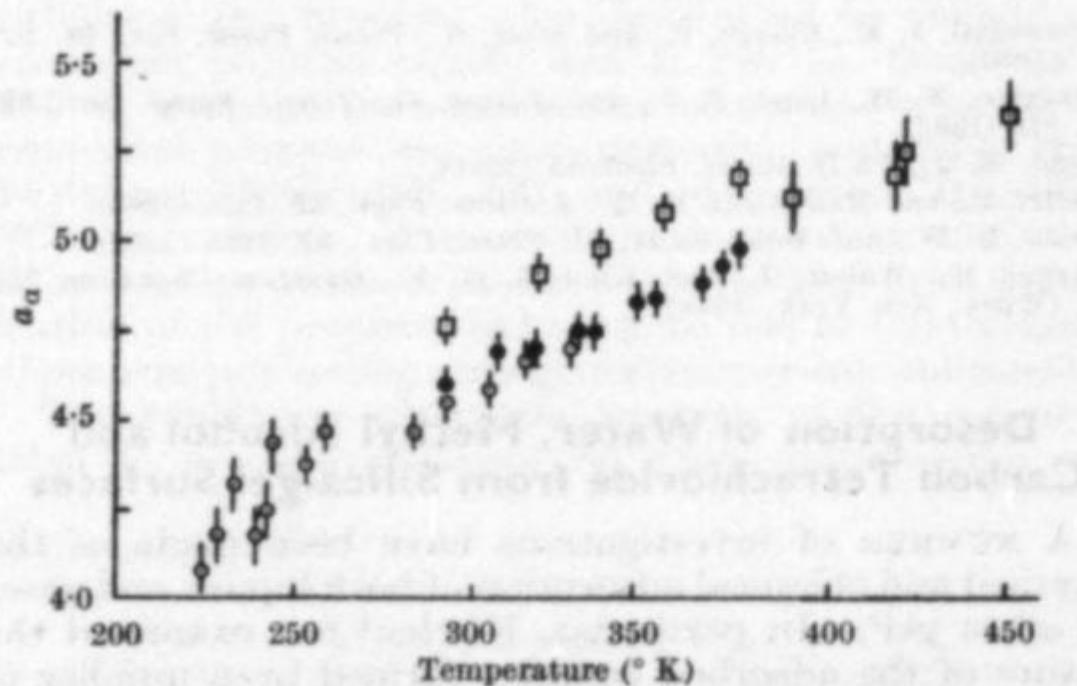


Fig. 1. Variation of  $\alpha$ -proton coupling constant,  $\alpha_a$ , with temperature ( $^\circ$  K); open circles, hexane; filled circles, methyl cyclohexane; squares, dodecane

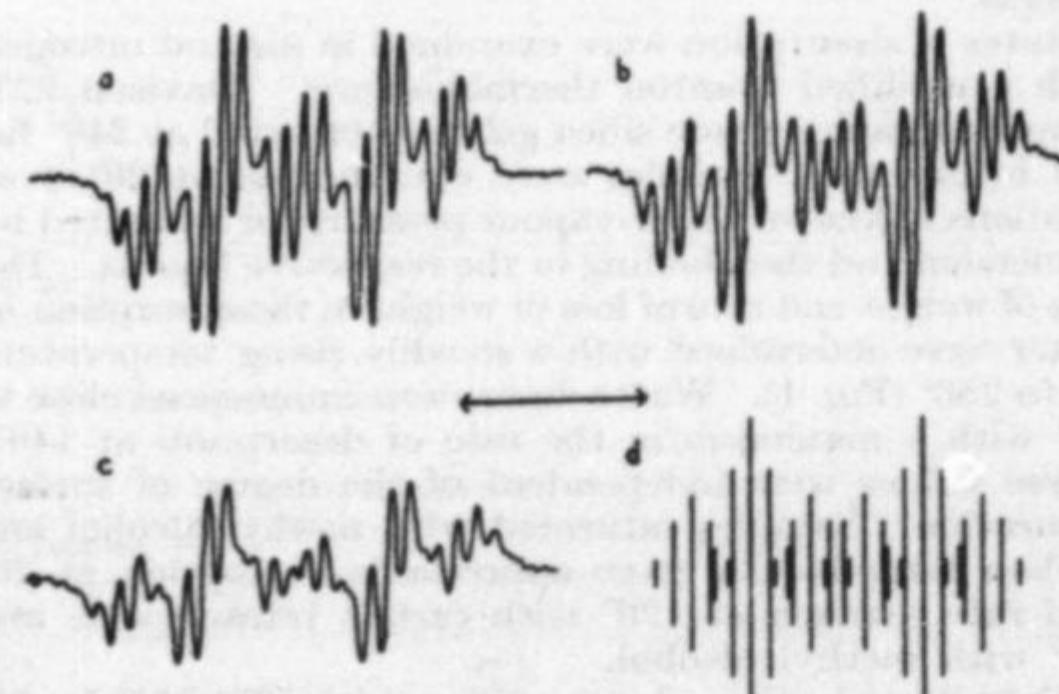


Fig. 2. Electron spin resonance spectra of 2,6-di-tertiary butyl 4-cyclohexyl phenoxy. a, in hexane, 295° K; b, in dodecane, 295° K; c, in hexane, 341° K; d, reconstruction of 295° K dodecane spectrum (2b). The marker indicates 5 gauss

aromatic ring. The proper description of the temperature dependence of the hyperfine coupling in this case requires the evaluation of the quantum mechanical average of  $\cos^2\theta$  over the eigenstates of a torsional oscillator, which are solutions of the Mathieu equation. The problem has been discussed recently by Stone and Maki<sup>5</sup>, who have computed the explicit temperature dependence of the hyperfine splittings in some nitroalkane radicals. Since solutions to the Mathieu equation have not been computed over a sufficient range of energies to cover the problem they have used the usual approximation of considering a harmonic oscillator for states of lower energy than the height of the potential barrier and a free rotator for the higher energy states<sup>5</sup>. However, they do not have a direct comparison between experimental and calculated values. The results presented here show a temperature-dependence of the general type expected.

Stone and Maki<sup>5</sup> do comment that there is a possibility that the solvent may contribute to the potential barrier. Although the effect observed here is small, it may mean that the actual barrier to free rotation within the molecule itself will be difficult to assess. The effect does not seem capable of a simple interpretation in terms of the solvent viscosity, for the hyperfine couplings show an inverse correspondence with the viscosities. It may be the disposition of only one or two solvent molecules around the radical which determines the solvent's contribution to the potential barrier.

Electron spin resonance spectra were taken on a Varian 100kc spectrometer provided by the Department of Scientific and Industrial Research, whom one of us (R. S. F. H.) thanks for financial support.

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### Desorption of Water, Methyl Alcohol and Carbon Tetrachloride from Silica-gel Surfaces

A NUMBER of investigations have been made of the physical and chemical adsorption of both liquids and gases on silica gel<sup>1</sup>. In particular, Kiselev<sup>2</sup> has examined the nature of the adsorbed complex formed by a number of gases including water and methanol. However, no rate data are available on either the adsorption or desorption process.

Rates of desorption were examined in air and nitrogen with a modified Stanton thermobalance. 'Davison 923' chromatographic grade silica gel was activated at 240° for 2 h before use. Samples were equilibrated at 20° over solutions of known water-vapour pressure<sup>3</sup> or saturated by immersion and then boiling in the respective liquids. The loss of weight and rate of loss of weight in the desorption of water were determined with a steadily rising temperature up to 250° (Fig. 1). Water desorption commenced close to 55° with a maximum in the rate of desorption at 140°. These values were independent of the degree of surface saturation. Samples saturated with methyl alcohol and carbon tetrachloride gave appreciable desorption at 20° and rate maxima at 120° with carbon tetrachloride and 80° with methyl alcohol.

Dehydrated silica gel was prepared in air at 950° for 6 h to remove all physically adsorbed water and all, or almost all, structural water<sup>4</sup>. Ion-exchange was by immersion of 10 g of gel in 100 ml. of 1 M sodium chloride until equilib-

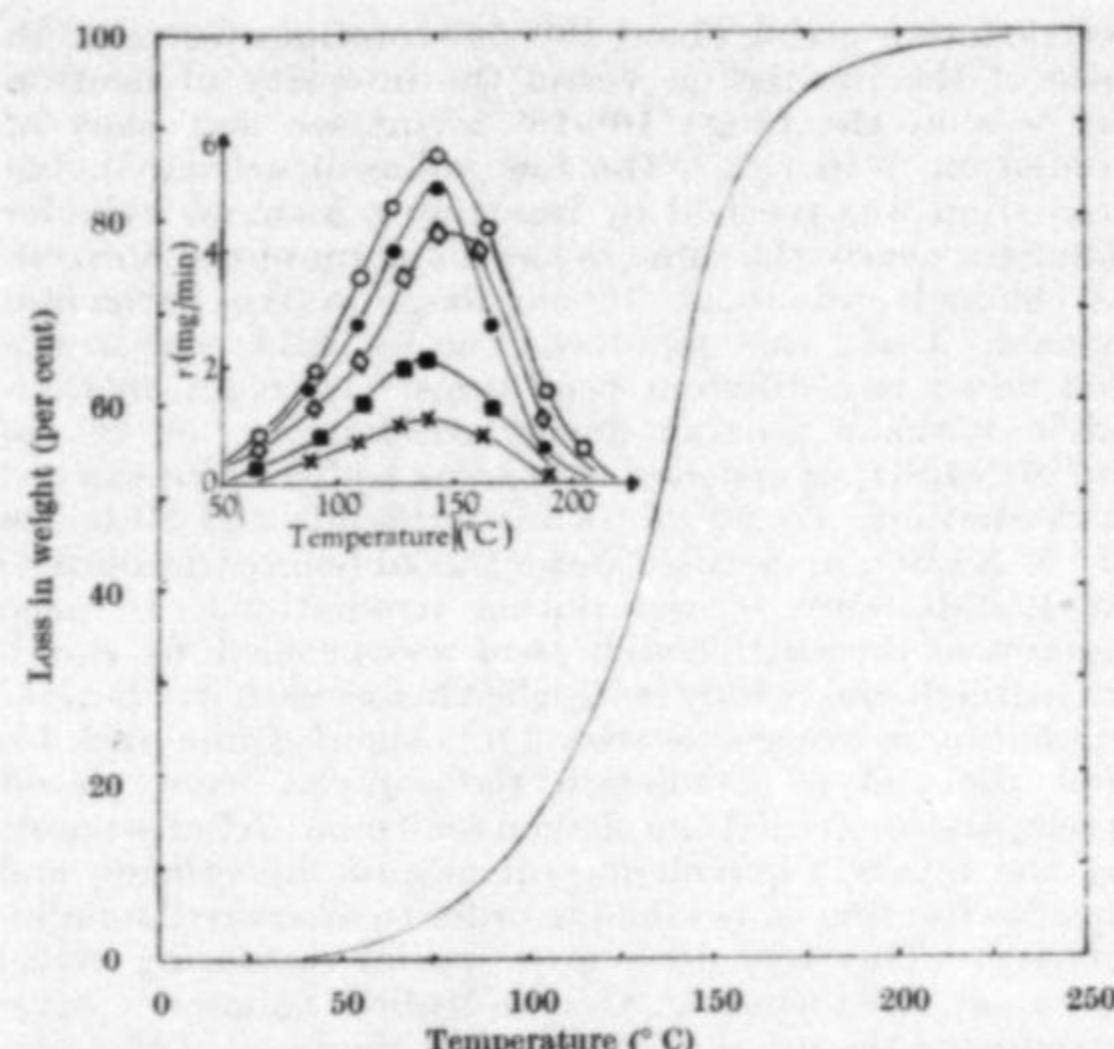


Fig. 1. Loss in weight from water-saturated gel. Inset, rate of loss in weight at different saturation-levels. ○, Saturated; ●, ◇, ■, ×, equilibrated respectively at 100%, 75%, 50% and 25% relative humidity

rium was reached. Analysis showed that the amount of Na<sup>+</sup> ion exchanged was 212 µg ion/g gel, with no measurable amount on a blank original.

Isothermal rates of desorption from saturated surfaces were investigated at a series of temperatures of 60°–212°. For each adsorbent, the maximum weight loss was always reached first with thermally dehydrated samples and last with unmodified samples. Mathematical analysis of these results showed that the rate of desorption for carbon tetrachloride and methyl alcohol was directly proportional to the amount adsorbed on all surfaces; for water the results clearly indicated a rate proportional to the square root of the amount adsorbed. The latter result is shown in Fig. 2, where  $r$ , the rate of desorption, is plotted against  $w^{0.5}$ .

As expected, with each type of gel, water gave the highest and carbon tetrachloride the lowest adsorption capacity. Infra-red spectra showed almost complete disappearance of the hydroxyl peak, at 3,740 cm<sup>-1</sup>, on dehydration while no appreciable change was noted in the spectrum of dehydrated silica gel after adsorption of methanol.

Preliminary results for the activation energy of the desorption of water from surfaces with various degrees of

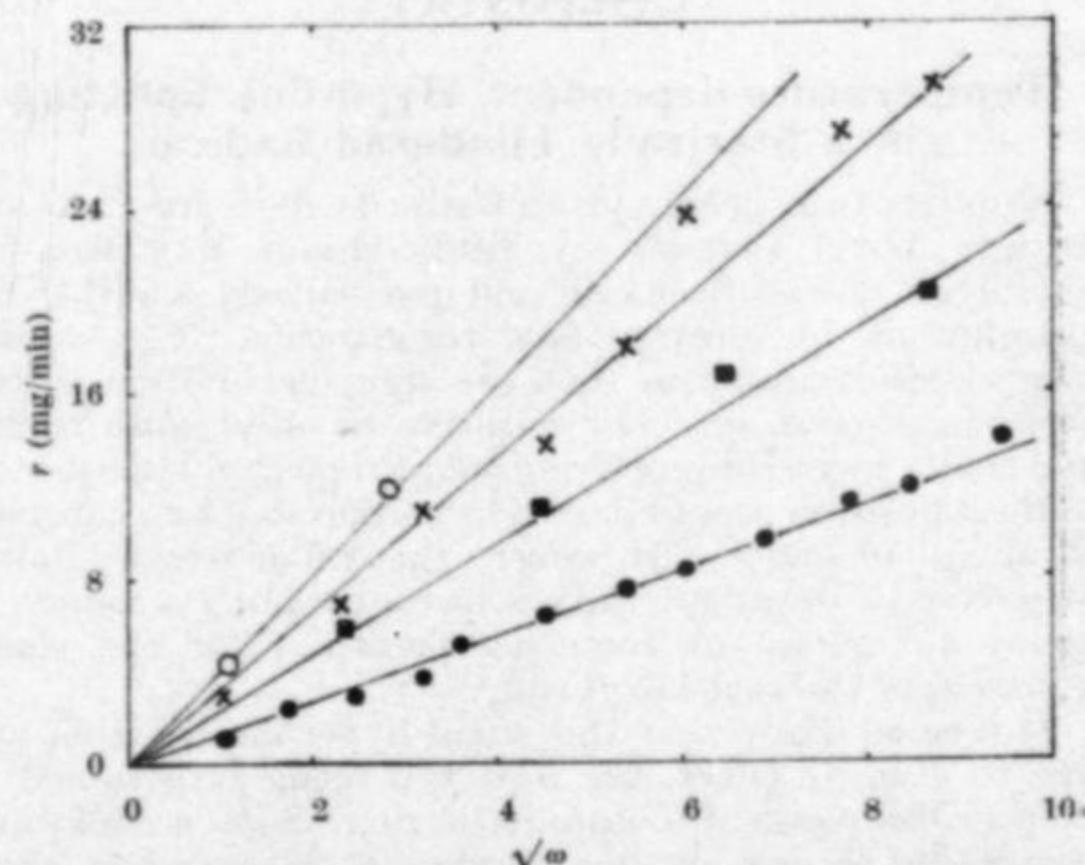


Fig. 2. Rate of desorption of water from saturated surfaces. ○, Ion-exchanged gel at 191°; ×, activated gel at 147°; ■, dehydrated gel at 139°; ●, activated gel at 100°