

stable particles in reactions (1) is supported also by the fact that the efficiency curve for  $\text{HeLi}^+$  ion is practically identical with the electron excitation curve for metastable helium atoms which was obtained in a quite different way from secondary electron emission due to the arrival of separated metastable atoms at a metal surface<sup>10</sup> (Fig. 2).

The reaction cross-section may be at present only roughly estimated. Taking the mean path of the excited particle in the reaction zone  $\approx 0.25$  cm and the ratio of the corresponding excitation and ionization cross-sections (in the maximum of the excitation function) for argon  $Q_e/Q_i \approx 0.1$ , the cross-sections for formation of  $\text{ArNa}^+$ ,  $\text{ArK}^+$  and  $\text{ArCs}^+$  are  $1.5 \times 10^{-15}$  cm<sup>2</sup>,  $2 \times 10^{-15}$  cm<sup>2</sup> and  $5 \times 10^{-15}$  cm<sup>2</sup>, respectively. These results indicate that reactions (1) may effectively compete with ionization processes (2) for which a cross-section of the order of the gas kinetic cross-section may be expected.

It can be concluded that the formation of molecular ions in reactions with excited neutrals is a rather common process. Further investigation of these reactions promises to discover new ionic species, the knowledge of which may be of value in the aforementioned fields. Moreover, the formation of molecular ions may serve as a mean for the detection of excited molecular states. For example, if the molecular beam of metastable particles is used and the kinetic energy of the electron released in reaction (1) is measured, there may be obtained useful data on the energy levels of metastable biatomic and polyatomic molecules, data on the shape of excitation curves for intercombination transitions and an estimate of the bond strengths in new, unusual ions. Preliminary experiments in these directions have been commenced.

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### Equilibrium Coverage of Copper by Chemisorbed Hydrogen

SEVERAL instances have been given in the literature<sup>1-3</sup> in which copper will catalyse the *para-ortho* hydrogen conversion. This process requires the chemisorption of hydrogen, regardless of the reaction mechanism which may be prevailing.

Recently<sup>4</sup> the chemisorption of hydrogen by copper has been examined calorimetrically and volumetrically and the equilibrium surface coverage was found to be at a value of  $\theta = 0.15$ , where the heat of adsorption was determined as 10 kcal/mole.

Confirmation of these values has been obtained in the course of a study of the kinetics of the *para-ortho* hydrogen conversion on evaporated metal films. It has been shown previously<sup>5</sup> that an investigation of the pressure dependency of the *para-ortho* hydrogen conversion enables a determination of the heat of adsorption to be made. In this manner the heat of adsorption of hydrogen on copper at equilibrium coverage was found to be 8.0 kcal/mole.

The Stevenson equation<sup>5</sup> has been used<sup>6</sup> to calculate a value for the heat of adsorption of hydrogen on copper, giving a value at zero surface coverage of  $\Delta H_{\theta=0} = 25.6$  kcal/mole. An experimental value of 28.0

kcal/mole has been reported<sup>6</sup> for silica-supported copper. The dipole moment of the hydrogen-copper bond may be calculated from the electronegativities of the elements as 0.73 Debye units, using Sanderson's<sup>7</sup> value for the electronegativity of hydrogen and calculating that for copper<sup>8</sup> from the work function as given by Michaelson<sup>8</sup>.

The fall in the heat of adsorption with increasing surface coverage is related to the change in work function by the following equation<sup>9</sup>:

$$\delta(\Delta H) = e \Delta V \quad (1)$$

where  $e$  is the electronic charge and  $\Delta V$  the change in work function. The change in work function may be related to the surface coverage in the following manner:

$$\Delta V = 4\pi\sigma\mu\theta \quad (2)$$

where  $\sigma$  is the number of surface sites per cm<sup>2</sup> and  $\mu$  the dipole moment of the bond.

In the present case values of  $\Delta H$  at equilibrium coverage of 10 kcal/mole and 8 kcal/mole were available, and the change in work function was calculated from equation 1. This value was substituted in equation 2 to obtain a value for the equilibrium surface coverage,  $\theta$ . A value of  $\sigma$  for the 111 plane of copper was used. These calculations give, respectively, values of  $\theta = 0.17$  and  $\theta = 0.15$ , which may be compared with the previously reported value of  $\theta = 0.15$ .

The calculations assume no change in the dipole moment of the copper-hydrogen bond with increasing surface coverage. This seems reasonable as the surface of copper is sparsely populated and has been shown to be correct for hydrogen chemisorbed on nickel<sup>10</sup>.

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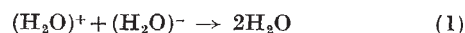
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### Behaviour of Polarons produced by the Action of Ionizing Radiation in Aqueous Media

It has been suggested<sup>1,2</sup> that the action of, for example,  $\gamma$ -rays on water leads primarily to the formation of radiation-produced electrons and the corresponding positive holes and that these electrons, and possibly also the holes, become self-trapped in the polar medium, water, leading to what should be regarded as 'polarons', in the sense of Landau, as discussed by Mott<sup>3</sup> and Pekar<sup>4</sup>. Afterwards, some definite experimental evidence was produced for the negative polaron<sup>5,6</sup>. This was based on its chemical reactions and reactivity, which in many cases (for example, with  $\text{CO}_2$ , leading to the formation of the  $\text{CO}_2^-$  radical ion<sup>6</sup>) were found to be different from hydrogen atoms which are known to be present in irradiated aqueous solutions under certain conditions. The chemical evidence concerning negative polarons has now been corroborated by the recent work using the methods of pulse radiolysis<sup>7</sup>. In pure water, the majority of the positive and negative polarons,  $(\text{H}_2\text{O})^+$  and  $(\text{H}_2\text{O})^-$ , annihilate each other according to:



On the other hand, as suggested previously<sup>1,2</sup>, the interaction of two polarons of the same species ('bipolarons') can lead to the 'molecular yield' processes. In the case of