gen wir, indem wir uns auch das Hydratwasser an den Haftstellen festgehalten denken, und zwar für jedes Ion der Art i α_i Wassermoleküle. Beim Austausch eines Ions 2 gegen ein Ion 1 werden somit gleichzeitig

$$\alpha = \alpha_1 - \alpha_2 \qquad (15)$$

Moleküle Wasser ausgetauscht. Am System $Na^{\cdot} - H^{\cdot}$ fanden wir im stationären Zustand $\alpha = 2{,}85$. Mit dem früher gemessenen Wert[3] $D_q/D_s = 1{,}35$ ergibt sich $f = 0{,}63$.

Die in dieser Arbeit beschriebenen Versuche wurden von Herrn Dipl.-Phys. LINKOHR (Quellungsversuche), den Herren W. FRANKE (stationäre Diffusion) und D. FIEDERER (nichtstationäre Diffusion) durchgeführt. Dem Fonds der Chemie danken wir für die Bereitstellung von Mitteln, die uns die Durchführung der Experimente ermöglicht haben, und der Erstgenannte für die Gewährung eines Stipendiums. Den Bayerwerken AG, Leverkusen, sind wir für die Überlassung des Austauschermaterials zu Dank verpflichtet. Unseren besonderen Dank sprechen wir noch Herrn Dr. P. MÜLLER für seine eingehende Diskussion und Verbesserungsvorschläge aus.

Chemical Reaction Kinematics

VIII. Cross Sections of some D-atom Transfer Reactions in the Energy Range 1–100 eV

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A Bendix time of flight mass spectrometer has been modified to enable the determination of some ion-molecule reaction cross sections in the energy range 1 — 100 eV.

In the reactions studied

$$X^+ + D_2 \rightarrow XD^+ + D$$

where X may be Ar, N_2 or CO, the results obtained agree with the predictions of the polarization theory in the range below 10 eV despite the fact that no intermediate complex is formed at these energies. Between about 10 — 50 eV where spectator stripping occurs the cross section follows an approximate E^{-1} dependence. Above these energies the results are consistent with a transition to a region in which knock-on processes predominate and where an impulse approximation treatment would be valid.

The determination of accurate cross sections for ion-molecule reactions is of considerable importance, particularly in the energy region 1 – 100 eV where several different theoretical models have been proposed. Although previous investigations[1–7] have covered various parts of this energy range, no previous study has examined the complete range and it was in an attempt to do this that the present experiments were undertaken.

Experimental

The apparatus is shown in Fig. 1 a. Ions are produced in pulses from an Atlas AN4 ion source, accelerated to 100 eV and then passed through a multielectrode decelerating lens system with circular slit geometry based on the design of LINDHOLM[8]. The ion beam emerging from this lens system enters a collision chamber (length 1.7 cm) in which the entrance and exit slits are 1 mm and 3 mm diam., respectively. This geometry ensures the detection of all products scattered through relatively large angles in the laboratory system (± 5° in the most unfavorable case). The ions emerging from the collision chamber pass into the grid system of a Bendix ion source from behind, the original solid backing plate having been replaced by a standard Bendix mesh. Time of flight analysis follows in the normal way.

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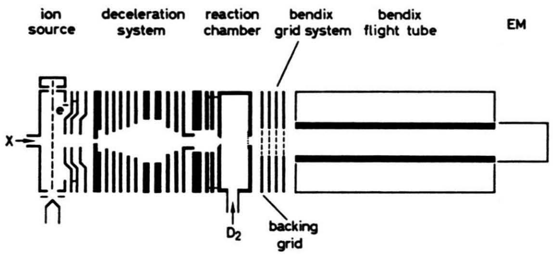

Fig. 1 a. Schematic diagram of the apparatus (not to scale).

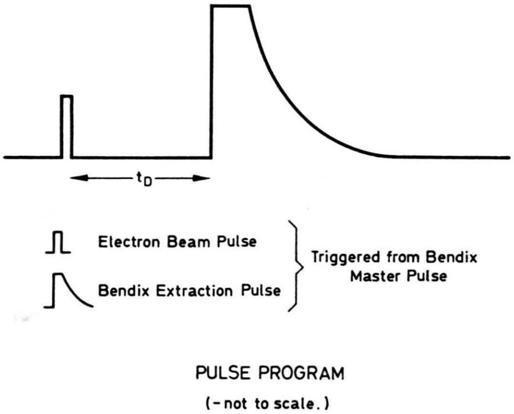

Fig. 1 b. Pulse program. The pulse repetition rate is 10^4 cycles/sec.

The pulse program is shown in Fig. 1 b. The delay time, t_D, must be such that ions entering the Bendix source coincide with the application of the Bendix extraction pulse which exerts a very strong time-focusing effect. For the reactions studied both primary and secondary ions arrive at the Bendix source at approximately the same time.

The energy of the primary ions is determined by the application of a retarding potential to the backing grid in the absence of the extraction pulse. Determination of the ion energy at low ion energies presents something of a problem since retarding field methods may involve a contact potential effect. In our case the decelerating lens system and collision chamber are graphitised and the retarding net is of Ni-mesh.

Our ion intensity versus retarding potential curves are of the same form as those obtained by GIESE [3] and we have also used the point of inflection as a measure of the ion energy. We realise however that a comparatively small but constant error in the ion energy determination could lead to somewhat different results at low energies.

The gas pressure in the collision chamber was measured directly using a McLeod gauge. Owing to the comparatively small pressure to be determined (typically 10^{-3} mm Hg), the error on this value is about 10%.

Results and Discussion

The following reactions were studied

$$Ar^+ + D_2 \rightarrow ArD^+ + D \quad (1)$$

$$N_2{}^+ + D_2 \rightarrow N_2D^+ + D \quad (2)$$

$$CO^+ + D_2 \rightarrow COD^+ + D \quad (3)$$

and the measured excitation functions are shown in Figs. 2 a, b, c, together with the results of other workers and the absolute variation predicted by a consideration of polarization interaction [9]. The polarization values are only shown over the energy range in which they might be expected to have some validity. Previous discussions with reference to the polarization theory of the range above about 10 eV where the cross section predicted from the polarization theory is smaller than the gaskinetic cross section, would seem to be meaningless.

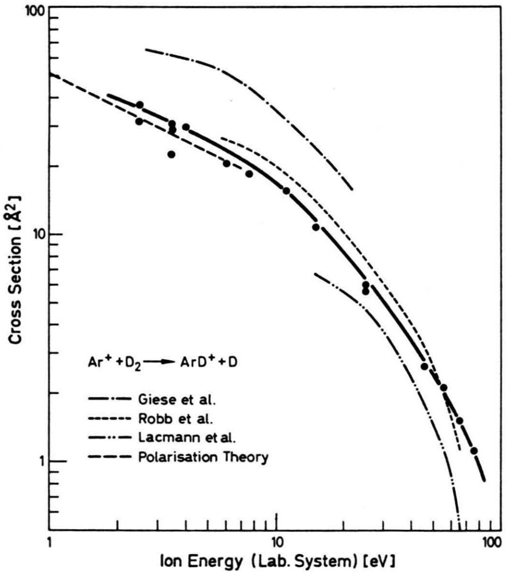

Fig. 2 a. Variation of the cross section with energy for the reaction $Ar^+ + D_2 \rightarrow ArD^+ + D$. Our results are shown in heavy type.

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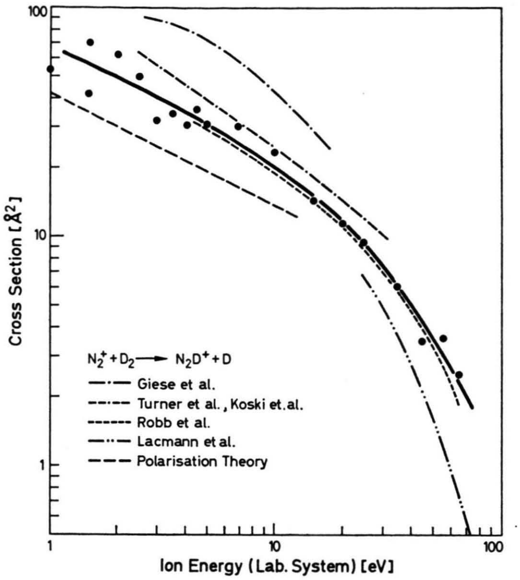

Fig. 2 b. Variation of the cross section with energy for the reaction $N_2^+ + D_2 \rightarrow N_2D^+ + D$. Our results are shown in heavy type.

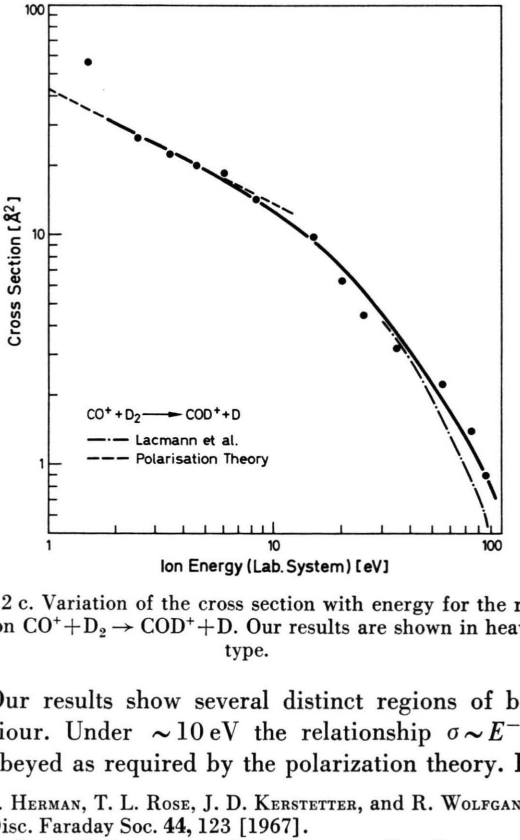

Fig. 2 c. Variation of the cross section with energy for the reaction $CO^+ + D_2 \rightarrow COD^+ + D$. Our results are shown in heavy type.

Our results show several distinct regions of behaviour. Under ~10 eV the relationship $\sigma \sim E^{-1/2}$ is obeyed as required by the polarization theory. In the case of both Ar^+/D_2 and CO^+/D_2 systems agreement with the absolute polarization values is remarkably good. Velocity analysis has shown that these reactions proceed by a stripping mechanism even at energies of about 1 eV [10, 11] but this is not irreconcilable with the above observations since the control of the reaction cross section by an r^{-5} polarization force does not necessarily imply the formation of an intermediate complex. In addition the invocation of polarization forces has been found necessary to explain deviations from pure stripping observed in the velocity spectra below ~10 eV [10].

In the range about 10 – 50 eV, the cross section shows a stronger dependence on incident ion energy with an energy exponent of about – 1. In this range, polarization forces can practically be neglected and the velocity spectra have been shown to agree with what is expected from the spectator stripping model.

A straightforward treatment of these reactions assuming a pure stripping mechanism predicts the occurrence of a "critical energy" above which no product ions can be formed as they would be required to contain more internal energy than their dissociation energy [4]. This however ignores the possibility that the reaction may proceed through other types of mechanism as the energy increases in which the "spectator" atom no longer remains only a spectator. Experimental evidence of deviation from a pure stripping mechanism is found in the occurrence of reactions (2) and (3) at energies well above any predicted critical energy where there is also a shift in the velocity spectrum of the product ions to velocities higher than those calculated for a stripping process [5]. Above 100 eV an "impulse approximation" has been applied to calculating cross sections for "knock-on" processes. In this energy region the reaction may be visualized as a series of two body collisions and polarization and chemical binding forces ignored. A classical treatment by BATES et al. [12] predicts cross sections in the energy range 10^2 to 10^6 eV. The energy dependence of the cross section which this theory predicts is not constant but for reaction (1) varies from about $E^{-2,5}$ at an energy of about 200 eV towards a limiting value of $E^{-5,5}$ at very high energies (~10^5 eV). Quantum mechanical modifications [13] do not seem to alter the results significantly.

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In Fig. 3 theoretical predictions of both the polarization theory and impulse approximation method are shown for reaction (1) over the energy regions in which they are expected to have some validity. The present experimental results can be seen to provide an almost complete "fill-in" of the intermediate region.

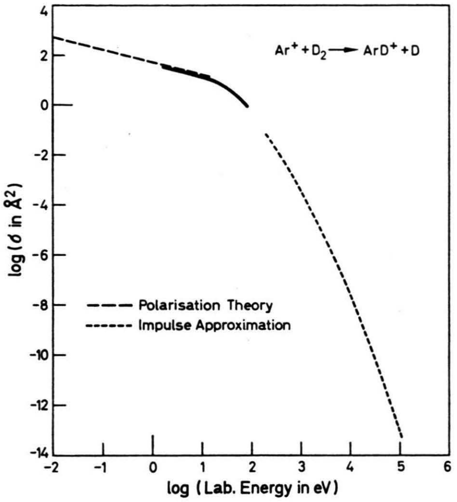

Fig. 3. Theoretical cross section vs. energy variations predicted by the polarization theory and the impulse approximation for the reaction $Ar^+ + D_2 \rightarrow ArD^+ + D$. Our experimental results are shown as a solid line which, for purposes of clarity, has been slightly displaced downwards in the region of the polarization theory.

Our results agree well with previous measurements. Over the common energy range they concur exactly with those obtained by ROBB et al. [1, 2]. The previous cross sections reported from this laboratory over the higher energy part of the range [4, 5] are somewhat lower than the present series reflecting difficulties in determining small secondary ion intensities in the previous measurements.

GIESE's results [3] which are considerably higher than other measurements, are certainly in error owing to the application of an incorrect factor. This factor, required to correct for the number of secondary ions which because of their position of formation and the geometry of the instrument do not reach the second mass spectrometer, was evaluated assuming an isotropic distribution of the secondary ions in the centre-of-mass system. This is now known to be incorrect since these reactions involve a stripping mechanism with forward scattering in the centre-of-mass system. Thus the correction factor and hence the results obtained by its use are too high.

TURNER [6] and KOSKI [7] both report results on reaction (2) which agree well with each other and are, in absolute terms, not greatly different from the present results although they do not show either a clear $E^{-1/2}$ or E^{-1} dependence of cross section on energy.

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