$\Sigma_j^{\dagger}\sigma_{i,j}^{\phantom{\dagger}}n^{\dagger}<<(a_i^{\phantom{\dagger}}+r_i^{\phantom{\dagger}})/v$ , we have  $\tau$  =  $1/q_i^{\star}v$ . The autoionization of the N<sup>+4</sup> ions was observed at ion velocities v ( 4 - 12)  $\times$  10<sup>8</sup> cm/sec, i.e., at energies from ~1 to 10 MeV. For all these energies  $\tau$  = (5.5 ± 2) x 10<sup>-8</sup> sec. Approximately the same value of the lifetime,  $\tau$  =  $(4 \pm 2) \times 10^{-8} \text{ sec}$ , was obtained for  $0^{+5}$  (at  $v = 8 \times 10^{8} \text{ cm/sec}$ ).

In all cases the quantity  $\Delta \Phi_{i+1} \sim \alpha_i a_i / (a_i + r_i)$  was of the order of 1%. From this we get the estimate  $\alpha_{\rm i} \gtrsim$  1% for the fraction of the ions which are in autoionized states with the lifetimes indicated above. When the target thickness is increased from  $\sim\!\!2$  to 20  $\mu g/cm^2$  the number of such ions remains essentially the same, since  $\triangle \Phi_{i+1}$  increases in this case by only 20% (for  $v = 8 \times 10^8$  cm/sec). Practically no such ions were produced in a gas target ~10<sup>15</sup> atoms/cm2 thick, placed along the path of the beam in place of the celluloid film.

The lifetime of the excited states subject to autoionization decay is usually  $10^{-13}$  -10-14 sec [4]. However, for negative helium ions He and for lithium atoms there are known metastable autoionization states  $(1s2s2p)^4P_{5/2}$  with lifetimes  $\tau \approx 10^{-3}$  sec for He<sup>-</sup> ions and  $\tau \approx 5 \times 10^{-6}$  for lithium atoms [5,6]. The metastable autoionization states of the lithiumlike nitrogen and oxygen atoms, observed by us, apparently belong to the same type of states with maximum possible values of the total angular and spin momenta.

Inasmuch as there should be many more excited states of ions with lower lifetimes than metastable states with  $\tau \approx 10^{-8}$  sec, it follows from the obtained results that immediately after leaving the solid target an appreciable fraction of the fast multiply-charged ions loses an electron and its charge increases as a result of autoionization.

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- N. Bohr and I. Lindhard, Danske Mat-Fys. medd. 28, 7 (1954).
- V. S. Nikolaev, UFN 85, 679 (1965), Soviet Phys. Uspekhi 8, 269 (1965).
  V. S. Nikolaev, I. S. Dmitriev, L. N. Fateeva, and Ya. A. Teplova, JETP 40, 989 (1961), [3] Soviet Phys. JETP 13, 695 (1961).
- E. H. S. Burhop, The Auger Effect and Other Radiationless Transitions, Camb. Univ. Press, [4]
- [5] [6] J. Pietenpol, Phys. Rev. Lett. 7, 64 (1961).
- P. Feldman and R. Novick, ibid. 11, 278 (1963).

## DIRECT ATOMIC-MOLECULAR OR IONIC-MOLECULAR REACTIONS

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Several experiments have been recently performed [1-4] on ion-molecular reactions of the type A + BC  $\rightarrow$  AB + C (A = atom or ion, BC = diatomic molecule or ion), and have cast light on the energy dependence of the absolute cross sections of these reactions. These experiments pertain to a relative-motion energy close to 10 eV, for which the theories based on the use of the intermediate-state concept (see [5-6]) should not be valid. It is therefore advisable to consider an alternative mechanism for such reactions, based on the model of direct interactions between the incident particles A and bound particles B and C, without formation of an intermediate state.

We report here the results of theoretical calculations based on the following assumptions: (i) the interaction potential V is additive in the reference system of particles A, B, and C, i.e.,  $V = V_{AB}(\vec{\rho}_{AB}) + V_{BC}(\vec{\rho}_{BC}) + V_{AC}(\vec{\rho}_{AC})$ , (ii) the effective time  $\tau \sim R/v$  of the paired interaction between particle A and particle B or C (R = effective interaction radius of the particles, v = their relative velocity) is small compared with the period of the molecular oscillations, i.e.,  $\tau\omega_{BC} < 1$ . This requirement is satisfied starting with a relative-motion energy of several electron volts (if one of the colliding particles is light). The foregoing conditions allow us to use the impulse approximation for the calculation of these reactions, on the basis of which the operator T in the matrix element  $(\Psi_f, T \Psi_i)$  of the process in question  $(\Psi_i$  and  $\Psi_f$  are the wave functions of the initial and final states of the system in the laboratory frame) can be represented in the form  $T = t_{AC}$ , where  $t_{AC}$  is the operator of elastic scattering of particles A and C.

The cross section  $d^2\sigma/d\varepsilon d\theta_C$  for the production of a bound state AB with energy  $\varepsilon$  and emission of a particle C into a solid-angle element  $d\theta_C$  can be represented (see [7]) in the form of an average over the state  $\phi_{BC}$  of the initial molecule BC (in its c.m.s.). For the direct knock-on process (operator T =  $t_{AC}$ ) we thus obtain (using a system of units in which n=1)

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\epsilon\,\mathrm{d}\theta_\mathrm{C}} = (\phi_{\mathrm{BC}}, \mathcal{I}\phi_{\mathrm{BC}}), \quad \mathcal{I} = \frac{1}{2\pi} \quad \frac{^{\mathrm{m}}_{\mathrm{A}}^{\mathrm{m}}_{\mathrm{C}}}{\mu_{\mathrm{AC}}^2} \quad \frac{^{\mathrm{k}}_{\mathrm{C}}}{^{\mathrm{k}}_{\mathrm{A}}} \quad \int_{-\infty}^{\infty} \exp(-\mathrm{i}\epsilon t) \, F_{\mathrm{AC}}^{*} \exp(\mathrm{i}H_{\mathrm{AB}}^{\dagger}t) \, F_{\mathrm{AC}} \exp(-\mathrm{i}H_{\mathrm{BC}}t) \, \mathrm{d}t, \quad (1)$$

where  $H_{AB}^{\dagger} = H_{AB} + \vec{\kappa} \cdot \vec{p}/\mu_{AB} + R$ ,  $H_{AB}$  and  $H_{BC}$  are the Hamiltonians of molecules AB and BC,  $R = \kappa^2/2\mu_{AB}$ ,  $\vec{\kappa} = m_B(\vec{k}_A - \vec{k}_C)/m_A + m_B$ ,  $\vec{k}_A$  and  $\vec{k}_C$  are the momenta of the incident particle A and the knocked-out atom C,  $m_A$ ,  $m_B$ ,  $m_C$ ,  $\mu_{AB}$ ,  $\mu_{BC}$ ,  $\mu_{AC}$  are the masses and reduced masses of the corresponding particles, and  $F_{AC}$  is the elastic-scattering amplitude of particles A and C. Calculation based on formula (1) for the case when the molecule BC is in the vibrational ground state, and the amplitude  $F_{AC}$  corresponds to solid-sphere interaction, leads to the following expression for the total cross section of the process A + B = AB + C:

$$\sigma(E_{A}) = \frac{\sigma_{AC}}{2E_{m}} \int_{0}^{Df} \langle \operatorname{erfS}_{2} - \operatorname{erfS}_{1} \rangle d\epsilon, \quad S_{1,2} = \frac{\Delta V + R_{1,2} - \epsilon}{\gamma_{1,2}^{2}}, \qquad (2)$$

where

$$\begin{split} &\sigma_{AC} = \frac{4\pi}{|F_{AC}|^2}, \quad E_m = \frac{4m_A m_B m_C E_A}{(m_A + m_C)^2 (m_A + m_B)}, \quad E_A = \text{energy of incident particle,} \\ &R_{1,2} = (k_A \mp k_C)^2 m_B / 2m_A (m_A + m_B), \qquad \triangle V = V_{AB} (\vec{\rho}_O + 2F_{AC} \frac{\vec{k}_C}{k_C}) + D_f, \end{split}$$

 $D_{\underline{i}}$  and  $D_{\underline{f}}$  are the dissociation energies of the molecules BC and AB, and  $\rho_{\underline{O}}$  is the equilibrium distance in the molecule BC. The symbol  $\langle$   $\rangle$  denotes averaging over the orientations of the molecules BC, characterized by the angle between the axis of the molecule and the vector  $\vec{k}_{\underline{C}}$ . If the molecule BC is in a strong excited vibrational state, then formula (1) leads to the expression

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\epsilon\,\mathrm{d}\theta_{\mathrm{C}}} = \frac{\mathrm{^{m}A^{m}C}}{\mathrm{^{m}A^{2}}} \left| F_{\mathrm{AC}} \right|^{2} \frac{\mathrm{^{k}C}}{\mathrm{^{k}A}} \left( \frac{\mathrm{^{\mu}BC^{\omega}BC}}{\mathrm{^{m}D(\rho^{\dagger})}} \frac{1}{\left| \frac{\mathrm{d}}{\mathrm{d}\rho} \left( H_{\mathrm{AB}}^{\dagger} - H_{\mathrm{BC}} \right)_{\rho = \rho^{\dagger}} \right|} \right), \tag{3}$$

where

$$\begin{split} p &= \sqrt{2\mu_{BC}(\epsilon_{1} - D_{1} - V_{BC}(\rho))}, & H_{AB}^{\epsilon} &= \frac{p^{2}}{2\mu_{AB}} + V_{AB}(\rho_{1}) + D_{f} + R + \frac{\vec{\kappa} \cdot \vec{p}}{\mu_{AB}}, \\ (\vec{\rho}_{1} &= \vec{\rho} + 2F_{AC} - \frac{\vec{k}_{C}}{k_{C}}), & H_{BC} &= p^{2}/2\mu_{BC} + V_{BC}(\rho) + D_{1}, \end{split}$$

 $\rho'$  is determined from the condition  $\epsilon$  -  $\epsilon_i$  =  $H_{AB}'$  -  $H_{BC}$ , and  $\epsilon_i$  is the energy of vibrational excitation of the molecules BC. If the energy  $E_A$  is sufficiently large, so that the condition

$$D_{f} - \frac{\mu_{BC}}{\mu_{AB}} \epsilon_{i} - R_{1} < B = \sqrt{4\mu_{AB}} \frac{m_{B} E_{A} \epsilon_{i} / \mu_{BC} (m_{A} + m_{B})}{m_{B} E_{A} \epsilon_{i} / \mu_{BC} (m_{A} + m_{B})}$$

is satisfied, then formula (3) is greatly simplified and the total cross section for the reaction is written in the form

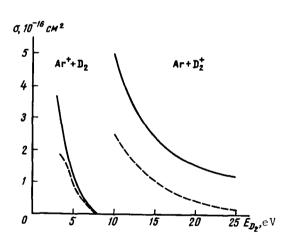
$$\sigma(E_{A}) = \frac{8}{15\sqrt{2}\pi} \sigma_{AC} \frac{\left(D_{f} - \frac{\mu_{BC}}{\mu_{AB}} \epsilon_{i} + B - R_{1}\right)^{5/2}}{E_{m}B^{3/2}}.$$
 (4)

The quantities  $R_{1,2}$  in (2) and (4) are determined from the conservation law

$$\mathbf{E}_{\mathbf{A}} = \frac{\mathbf{k}_{\mathbf{A}}^{2}}{2\mathbf{m}_{\mathbf{A}}} = \frac{\mathbf{k}_{\mathbf{C}}^{2}}{2\mathbf{m}_{\mathbf{C}}} + \frac{\left(\mathbf{k}_{\mathbf{A}} + \mathbf{k}_{\mathbf{C}}\right)^{2}}{2\left(\mathbf{m}_{\mathbf{A}} + \mathbf{m}_{\mathbf{B}}\right)} + \epsilon - \epsilon_{\mathbf{i}} - Q$$

(Q = heat of reaction).

Formulas (1) - (4), obtained on the basis of the direct knock-on model, describe all the main qualitative features of the reactions investigated in [1-4], viz., the rapid decrease of the cross section  $\sigma(E_A)$  with energy  $E_A$  for the reactions  $Ar^+ + H_2 \rightarrow ArH^+ + H$  and  $Ar^+ + D_2 \rightarrow ArD^+ + D$  [4] (formula (2); the much slower decrease of the cross section  $\sigma(E_A)$  for the reaction  $Ar^+ + D_2^+ \rightarrow ArD^+ + D$  [1] (formula 4), attributable to the presence of a strong vibrational excitation of the  $D_2^+$  ions under the conditions



of [1]; and the larger values of the cross sections for the production of ArH<sup>+</sup> compared with the cross sections for the production of ArD<sup>+</sup> in the reactions Ar + HD<sup>+</sup>  $\rightarrow$  ArH<sup>+</sup> + D and Ar + HD<sup>+</sup>  $\rightarrow$  ArD<sup>+</sup> + H [3], which follows from formula (4). An example of a qualitative comparison of theory and experiment for the reactions Ar + D<sub>2</sub>  $\rightarrow$  ArD<sup>+</sup> + D [1] and Ar<sup>+</sup> + D<sub>2</sub>  $\rightarrow$  ArD<sup>+</sup> + D [4] is shown in the figure. The solid lines represent experiment and the dashed ones theory. The parameters of the ions ArD, required for the calculation, were taken from [4,8], and  $\sigma_{AC}$  =

2 x 10<sup>-16</sup> cm<sup>2</sup>.

- [1] C. F. Giese and W. B. Maier, J. Chem. Phys. 39, 739 (1963).
- [2] M. G. Menendez, B. S. Thomas, and T. L. Bailey, ibid. 42, 802 (1965).
- [3] M. A. Berta and W. S. Kosur, J. Amer. Chem. Soc. 86, 5098 (1964).
- [4] A. Hengelein, K. Lackman, and J. Jacobs, Ber. Buns. Ges. 69, 279 (1965).
- [5] G. Gioumousis and D. P. Stevenson, J. Chem. Phys. 29, 294 (1958).
- [6] O. B. Firsov, JETP 42, 1307 (1962), Soviet Phys. JETP 15, 906 (1962).
- [7] G. K. Ivanov and Yu. S. Sayasov, JETP 45, 1456 (1963), Soviet Phys. JETP 18, 1006 (1964).
- [8] T. F. Moran and L. Friedman, J. Chem. Phys. 40, 860 (1964).

JUMP IN VOLUME AND MELTING CURVE OF CESIUM AT PRESSURES UP TO 17,000 kg/cm2

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The lack of a finished theory of melting does not allow us to predict the course of the melting curve and to state whether it has a maximum, whether it approaches some temperature asymptotically, or whether it increases continuously with increasing pressure. This question can be answered only by experiment. Until recently the melting temperature increased continuously with increasing pressure in all experiments. Recently, however, a maximum on the melting curve was observed for several substances [1-6]. Unfortunately, the experiments in which a maximum was observed on the melting curve were carried out in apparatus with a quasihydrostatic medium. The presence of the maximum is therefore subject to doubt and can be attributed to the appearance of a new phase in the solid, a phase that might have been overlooked as a result of the crude nature of the experiment.

Confirmation of the maximum on the melting curve would be provided by measurement of the jump of volume along the melting point. On approaching the maximum, the magnitude of the volume jump should tend to zero, in accord with the Clayperon-Clausius equation. We report below the results of an experiment on the determination of the volume jump in cesium, for which Kennedy [1] observed a maximum on the melting curve.

The apparatus in which the present experiments were carried out, together with the procedure for determining the volume jump, is described in detail in [7]. The experiments were made in a hydrostatic medium (benzene). The volume jump was determined from the break in the continuity of the volume-pressure curve. At the instant of melting the volume was measured at constant pressure, and the magnitude of its change was determined from the deflection of the pointer of a special device. The temperature and pressure along the melting curve were measured simultaneously with the volume jump.

The experimental results are shown in Figs. 1 and 2. The first figure shows the experimental data on the dependence of the volume jump  $\Delta \overline{V}$  on the melting temperature T. The error