ION–MOLECULAR REACTIONS IN GASES

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INTRODUCTION

Over the last few years there has been an ever-increasing interest in gas phase reactions of ions with molecules. This problem is closely related to the chemistry of high energy reactions in which the primary acts are induced by imparting to molecules, quanta of energies ranging from unity to some several tens of electron-volts.

Radiation chemistry, the chemistry of electric discharge reactions including rather dense plasma, the chemistry of high and ultra-high temperatures as well as photochemistry, are all components of the chemistry of high energy reactions, especially so when examined with respect to the elementary steps involved.

The question as to what is going to occur if an ion collides with a neutral particle is not new. It arose from the first enquiry into the processes occurring in gas discharge tubes. It became evident soon enough that the operation of gas devices used in nuclear physics is closely related to collisions of this kind.

One "physical" problem has had a completely "chemical" aspect for a considerable time. This is the problem of controlling the composition of ions from a hydrogen ion source; the reaction

\[ \text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \]  

(1)

is known to play an important part in the processes responsible for this reaction.

This ion–molecular reaction attracted the attention of physicists some 25 years ago and proved to be the touchstone for the activated complex problem.2

Naturally chemists have also been concerned for some time with the importance of gas phase ion reactions. The first essential steps in this direction were made in radiation chemistry and were due to Lind.3

The first experimental direct determination of ionic reactions in radiation chemistry was also carried out long ago. Two such methods will be mentioned here: that of measuring critical electron energies corresponding to the onset of chemical conversions in the system4 and the ion extraction method discussed in a number of Essex's works.5

However, it is striking that although ionic reactions were studied under macroscopic conditions, at high pressures, systematic direct investigations of elementary ion–molecular reactions were not undertaken either within
the nineteen-twenties and -thirties, or in the -forties. Yet the importance of such studies should have been evident from the experiments of Bonhoeffer and Harteck which were concerned with elementary radical reactions. This is the more puzzling since mass spectrometry was already in use at that time and physicists had, in fact, made the first observations on ion–molecular reactions; these were reaction (1) and

\[ \text{H}_2\text{O}^+ + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{OH} \]

studied in 1940 by Tate et al. (However, some confusion was introduced by the appearance potential of \( \text{H}_3\text{O}^+ \), which was erroneously determined as higher than the ionization potential of water.)

The first attempts to apply mass spectrometric investigations to chemistry seem to have been made in 1936, by Eltenton and Vassiliev in Kondratiev's laboratory at the Institute of Chemical Physics. These investigators attempted to find out what were the ionic processes occurring in electrolysis of organic substances from \( \text{CO} \) and \( \text{H}_2 \), and of ammonia from \( \text{N}_2 \) and \( \text{H}_2 \). By gradually increasing the pressure in the mass spectrometer ion source and measuring the appearance potentials they obtained the reactions

\[ \text{N}_2^+ + \text{H}_2 \longrightarrow \text{N}_2\text{H}^+ + \text{H} \]  
\[ \text{CO}^+ + \text{H}_2 \longrightarrow \text{COH}^+ + \text{H} \]

But leaving history aside, let us consider the present state of affairs and the recent works. Systematic work in the given field has been carried out for about 10 years in a number of laboratories by scientists of many countries, chiefly by Stevenson, Field, Franklin and Lampe, and Hamill in U.S.A., by our laboratory in Moscow, by Lindholm in Sweden, by Henglein in Germany, by Čermac and Hermán in Czechoslovakia, and by a number of other investigators. Finally, I should like to draw attention to the survey of works on ion–molecular reactions published recently by Stevenson and Schissler, in the chapter "Mass Spectrometry and Radiation Chemistry" of the collected works edited by Haissinsky.

I presume that my audience will agree that it would be more reasonable for me to deal in greater length with the work of our own laboratory, rather than to aim at a full survey of the available literature. In order to bring about a more lively discussion I propose to dwell on problems which are not yet completely elucidated.

**MASS SPECTROMETRIC INVESTIGATIONS OF ION–MOLECULAR REACTIONS**

The methods for investigating ion–molecular reactions fall into two basic classes: the first involves the generation of primary ions by electron irradiation, or sometimes by light, within the same chamber in which these ions collide with molecules. We shall define it as *internal* ionization. The second
class involves ions obtained from an external source and introduced into the collision chamber as a separated or non-separated beam. Let us call this the external ionization method.

**The internal ionization method**

A characteristic scheme of internal ionization is shown in Figure 1. An electron beam of pre-determined form is directed into the space between plates I and II, i.e. into the reaction zone. Some of the primary ions succeed in colliding with molecules in the space between plates I and II; the primary and secondary ions are repelled from the reaction zone by the electric field either arising from the potential difference between plates I and II, or from that between plates III and II. Upon passing through the exit slit of plate III the ions are markedly accelerated and then subjected to mass-spectrometric analysis.

![Diagram of the internal ionization method](image)

The primary task of the internal ionization method is the identification of the ion–molecular process as such. This problem is solved more-or-less similarly in all studies. The secondary nature of the ions and the neutral initial products are determined from the secondary and primary ion currents as a function of the partial pressure of the components of the mixture in the collision chamber. Primary ions taking part in the ion–molecular reaction are identified by the appearance potential of secondary ions. Thus, sufficiently accurate determination of ion potentials is of prime importance. The method for quasi-monokinetization developed by Fox has been developed in our laboratory to an automatic procedure by modulation of the electron-retarding potential and resonance amplification of the ion current at the frequency of this modulation.

Curves obtained in this way for the appearance of primary and secondary ions in various processes investigated by us are shown in Figure 2. It may be seen that H$_3$O$^+$ ions are actually obtained from H$_2$O$^+$, and the C$_2$H$_5$OH$^+$ ions via C$_2$H$_5$OH$^+$. In many cases, the high background of some primary ions with the same mass number hinders the detection of secondary ions. A high-resolution spectrometer is very desirable in this case. For instance, the CH$_5^+$ ion observed in our laboratory in the reaction

$$\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$$

(5)
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has the same mass number as the $^{13}\text{CH}_4^+$ and $^{18}\text{OH}^+$ ions, present in the vacuum background. To provide confirmation of the appearance of $\text{CH}_5^+$, we used in interpreting the multiplet associated with 17 atomic mass units (amu), a mass spectrometer of high resolution, designed by Alexeevskii at the Institute of Physical Problems in Moscow. This multiplet obtained under conditions when traces of ammonia were introduced into the mass spectrometer besides methane and traces of water, can be seen in Figure 3.

The above refers to methods for identification of ion–molecular reactions. The determination of rate constants will be considered separately.

The current methods devised for this problem include one of continuous repulsion developed in the U.S.A. by Stevenson and co-workers and Field, Franklin and Lampe, the pulse method devised in our laboratory, and the increased-pressure method (Melton and co-workers, Saporoshchenko and Field).

The method of continuous repulsion—This method is widely used because of its relative simplicity. A fixed potential difference is maintained between plates I and II (Figure I) during measurements. The pressures in the collision chamber are $10^{-5}$ to $10^{-3}$ mm Hg, and only a fraction, $10^{-1}$ to $10^{-3}$, of all ions has a chance of colliding with a gas molecule before leaving the chamber.
The main problem in this case will be the determination of the relation between the phenomenological cross-section \( Q \) in equation

\[
I_2 = I_1 N Q
\]

where \( I_2 \) is the current of secondary ions, \( I_1 \) that of primary ions, \( N \) the concentration of molecules taking part in the secondary process, and \( L \) the primary ion path in the collision chamber, and the reaction rate constant \( k \), corresponding to thermal equilibrium in ion and molecular reaction rates. This is usually of interest to chemists. \( Q \) will naturally depend on \( L \) and the field intensity in chamber \( E \), and it appears that the derivation of a substantiated theoretical equation for calculating \( k \) (and the true microscopic cross-section \( \sigma \)) from the \( Q \) value obtained is often a complicated and a far-from-solved problem. Thus, it would be natural to approach the determination of \( k \) under conditions when ions and molecules are in thermal equilibrium.

**The pulse method**—The pulse method permits, in principle, the realization of the above conditions. The electric beam is switched on as a pulse for a very short time \( t_i \), shorter than that of the thermal motion of the ion through the collision chamber. After this, there is a delay \( t_d \) during which equipotential conditions are maintained in the chamber (as in the \( t_i \) period). The potential difference is then supplied in pulses \( t_r \) repelling the ions. Under conditions of uniform ionization and similar repulsion for all points of the ionization zone, the \( I_C^+ / I_A^+ \) ratio of ion currents formed by reaction

\[
A^+ + B \longrightarrow C^+ + D \tag{6}
\]

will be

\[
\frac{I_C^+}{I_A^+} = \frac{kN}{\beta} \sqrt{m_2} \exp \left( \frac{\beta}{\sqrt{m_1}} - \frac{\beta}{\sqrt{m_2}} \right) t_2 \times \\
\left\{ 1 - \frac{\sqrt{m_1}}{\sqrt{m_1} - \sqrt{m_2}} \exp \left( - \frac{\beta}{\sqrt{m_1}} t_i \right) + \frac{\sqrt{m_2}}{\sqrt{m_1} - \sqrt{m_2}} \exp \left( - \frac{\beta}{\sqrt{m_2}} t_i \right) \right\} \\
+ \frac{\sqrt{m_1}}{\sqrt{m_1} - \sqrt{m_2}} \left[ \exp \left( - \frac{\beta}{\sqrt{m_2}} t_r - 1 \right) \right], \tag{ii}
\]

where \( N \) is the concentration of \( B \), \( m_1 \) the mass of \( A^+ \), \( m_2 \) the mass of \( C^+ \), and

\[
\beta = \sqrt{\frac{8\pi k T}{d}} \tag{iii}
\]

here \( d \) is the distance from the site of ion appearance to the ionization chamber wall.

With \( t_i \ll t_d \) and \( \frac{\beta}{\sqrt{m_2}} t_d \ll 1 \) \tag{iv}

we obtain

\[
\frac{I_C^+}{I_A^+} = F(t_i t_r) + kN t_d \tag{v}
\]

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where \( F(t_i, t_r) \) is a certain function of the ionization time \( t_i \) and repelling time \( t_r \).

By varying the delay time \( t_d \) and measuring \( \frac{I^-}{I^+} \) as a function of \( t_d \), it is possible to find \( k \), if \( N \) is known. Equation (v) holds for \( t_d \) values corresponding to conditions when ions do not succeed in reaching the wall or leaving the chamber. Thus the method is quite similar to usual kinetic investigations: the degree of conversion is determined as a function of time elapsed from the onset of the reaction. Whereas routine kinetics deal with hours, minutes and seconds, in the case given, \( t_d = 3 \) to \( 20 \) microseconds. More explicit analysis shows that for \( m_1 \approx m_2 \) equation (v) will be valid also when condition

\[
\frac{3}{\sqrt{m_2}} t_d \ll 1
\]

is unfulfilled, and, in this case, the method appears to be especially convenient.

The observed linear dependence of \( I_{CH_4^-}/I_{CH_4^+} \) on \( t_d \) for the reaction

\[
CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3
\]

is shown in Figure 4. The linear dependence is evident and, consequently,

\[
k = \frac{\tan \alpha}{N}
\]

where \( \alpha \) is the slope of the straight line.

Figure 4. The \( I_{CH_4^-}/I_{CH_4^+} \) ratio as a function of the reaction time when using the pulse method.

Another possibility given by the pulse method is that of considerably increasing the \( I_{CH_4^-}/I_{CH_4^+} \) ratio by taking a sufficiently high \( t_d \) value and \( m_G > m_A \). This has recently been done in our laboratory\(^{24} \). High \( I_{CH_4^-}/I_{CH_4^+} \) ratios would be
important in the identification of any secondary process, especially when the secondary ion is identical to one of the primary ions present in the chamber. This condition will always arise in investigations of charge exchange processes by the internal ionization method. For instance, in studying the reaction

$$\text{Xe}^+ + \text{CH}_4 \rightarrow \text{Xe} + \text{CH}_4^+ \quad (7)$$

secondary ions would have to be detected on a strong background of primary \(\text{CH}_4^+\). By using the pulse method, we succeeded in increasing the \(\text{CH}_4^+_{\text{sec}}/\text{CH}_4^+_{\text{prim}}\) ratio by two orders, as compared with the ratio obtained by the method of continuous repulsion.

The increased-pressure method—By increasing the pressure in the ionization chamber up to about \(10^{-1}\) to \(5 \times 10^{-1}\) mm Hg, it becomes possible to observe, along with secondary processes, "tertiary" and higher processes, i.e. to obtain conditions approaching those for real systems.

The basic methodological improvement consists of using more powerful pumping systems and increasing the degree of differential pumping for the source and analyser regions. Both \(\alpha\)-particles and ordinary electrons of several tens eV were used for ionization. The repelling field seemed to be the same as in the continuous repulsion method. Since even at the highest pressures (0.3 to 0.5 mm Hg\(^{29,30}\) used, a certain fraction of the primary ions still leaves the chamber without colliding, it may be inferred that the experimental conditions reported are far from those required for thermal equilibrium between ions and molecules. Simultaneous application of the high-pressure method and of some variant of the pulse method would probably prove to be of great interest.

The external ionization method

The external ionization method has already been used by physicists for investigating collisions between fast ions and atoms and, in some cases, simple molecules\(^{31-34}\). Lindholm\(^{35-37}\) was the first to apply it fundamentally when studying collisions between ions and multi-atomic molecules; it has also been used in our laboratory in recent years\(^{38-42}\) (Figure 5). Two

![Diagram of the external ionization method](image)

\textit{Figure 5. Diagram of the external ionization method}

features of this method will be noted. As the secondary ions were always repelled normally to the primary ion beam, the recorded portion of the secondary ions that have obtained kinetic energy was always lower than that of the slow secondary ions. This permits a distinction between
resonance and non-resonance processes. However, it will be borne in mind that a certain small portion of the secondary ions possessing super-thermal kinetic energy $E_k$ will nevertheless be repelled, and special experiments or, at least, calculations of the effective repulsion for ions of various $E_k$ values would be of value.

The second feature of the external ionization method is the difficulty encountered in passing to relatively slow primary ions. This is the necessity of ensuring an adequate geometry of the beam of slow ions. Moreover, this beam should not contain electrons abstracted from the edges of electrodes in the ion retarding system. In practice this method is good for ions retarded to 30–10 eV only.

**RESULTS OF MASS SPECTROMETRIC INVESTIGATIONS ON ELEMENTARY ION–MOLECULAR REACTIONS**

Classification of reactions

In classifying ion–molecular reactions by the results obtained, and not by the reaction mechanism, these reactions would fall into two types: (1) transfer and rearrangement of heavy particles, and (2) charge exchange (i.e. electron transfer) with or without dissociation.

The observed and more-or-less studied reactions of type 1 are summarized in *Table 1*, and those of type 2 in *Table 2*.

<table>
<thead>
<tr>
<th>Class of reactions</th>
<th>Investigators</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Positive ion–molecular reactions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H atom transfer</td>
<td>Elleton, Talrose, Frankevieh</td>
<td>$\text{N}_2^+ + \text{H}_2 \rightarrow \text{N}_2\text{H}^+$ + H</td>
</tr>
<tr>
<td>RH + M$^+$ → R + MH$^+$</td>
<td></td>
<td>$\text{H}_2^+ + \text{H}_2 \text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}$</td>
</tr>
<tr>
<td>Proton transfer</td>
<td></td>
<td>$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{H}$</td>
</tr>
<tr>
<td>“Combined” transfer</td>
<td>Smyth, Field, Lampe, Pottie, Barker, Barker, Hogness, Harkness</td>
<td>$\text{C}_3\text{H}_4^+ + n^{-}\text{C}<em>9\text{H}</em>{12} \rightarrow n^{-}\text{C}_3\text{H}_4^+ + \text{C}_3\text{H}_6$</td>
</tr>
<tr>
<td>RH$^+$ + RH → RH$^+_2$ + R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$^-$ transfer</td>
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<td></td>
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<tr>
<td>$\text{RH}^+ + \text{R}_2\text{H} \rightarrow \text{R}_3\text{H} + \text{R}_2^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transfer of heavy atoms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M$^+$ + XY → MX$^+$ + Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transfer of heavy ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M + XY$^+$ → MX$^+$ + Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Combined” transfer of heavy atoms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X$^+_2 + X_4^- \rightarrow X_2^+ + X$</td>
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<td></td>
</tr>
<tr>
<td>Rearrangement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB$^+$ + CD → AC$^+$ + BD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Association</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M$^+$ + M → M$^+_2$</td>
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<td></td>
</tr>
<tr>
<td><strong>Negative ion–molecular reactions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutral transfer</td>
<td>Muschlitz, Henglein, Muccini</td>
<td>$\text{H}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$</td>
</tr>
<tr>
<td>A$^-$ + XY → AY$^-$ + X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rearrangement</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Strictly speaking, secondary ions will obtain a certain kinetic energy as a result of the resonance process as well, since an appreciable “impelling” interaction between the ion and induced dipole occurs at very high impact parameters.
Table 2. Charge exchange reactions

<table>
<thead>
<tr>
<th>Class of reactions</th>
<th>Investigators</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Positive ions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resonance charge exchange without fragmentation</td>
<td>Klemann</td>
<td>$H_2^+ + H_2 \rightarrow H_2 + H_2^+$</td>
</tr>
<tr>
<td></td>
<td>(Rosen)</td>
<td></td>
</tr>
<tr>
<td>Resonance charge exchange with fragmentation</td>
<td>Lindholm</td>
<td>$N^+ + CH_4 \rightarrow N + CH_4^+ + H$</td>
</tr>
<tr>
<td>Non-resonance charge exchange without fragmentation</td>
<td>Lindholm</td>
<td>$P^+ + H_2O \rightarrow P + H_2O^+$</td>
</tr>
<tr>
<td></td>
<td>Markin</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Talrose</td>
<td></td>
</tr>
<tr>
<td>Non-resonance charge exchange with fragmentation</td>
<td>Lavrovskaya</td>
<td>$Xe^+ + C_4H_4 \rightarrow Xe + CH_4^+ + CH_4$</td>
</tr>
<tr>
<td>Resonance charge exchange without fragmentation</td>
<td>Dukelskii</td>
<td>$O_2^- + O_2 \rightarrow O_2 + O_2^-$</td>
</tr>
<tr>
<td>(Nature of transfer undetermined)</td>
<td>Zandberg</td>
<td>$SO_2 + C_6H_4NO_2^- \rightarrow SO_2^- + C_6H_4NO_2$</td>
</tr>
<tr>
<td></td>
<td>Henglein</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Muccini</td>
<td></td>
</tr>
</tbody>
</table>

**Negative ions**

**Constants and temperature dependences**

The cross-sections $\sigma$ of known processes are within the range of $10^{-13}$ to $10^{-18}$ cm$^2$, and rate constants for temperatures of 400 to 500°K within $10^{-9}$ to $10^{-13}$ cm$^3$/molecule sec. Consequently, the upper limits of observed $\sigma$ and $k$ values are about 1–2 orders higher than the usual gas-kinetic values. It will be noted that this holds both for type 1 and type 2 processes. Lower limits depend upon the apparatus used; for a number of reasons, slow processes are more difficult to observe by the mass spectrometric method. Information on the temperature dependence of $k$ is still scanty and refers to type 1 processes.

Stevenson and Schissler$^{16}$ found that no temperature dependence of the rate of transfer of hydrogen atoms from hydrogen molecules to simple ions. On the other hand, the same investigators$^{15}$ and Frankevich with the author$^{53}$ found that there is a slight decrease in $\sigma$ with temperature, similar to the $1/\sqrt{T}$ function which is found for certain other reactions of hydrogen transfer.

Along with a great number of observed processes characterized by high $k$ values, these data provide confirmation of the fact that ion–molecular reactions, at least atom- and hydrogen-ion transfer, proceed without true activation energy.

Whether this holds for other non-resonance ion–molecular processes, is not quite clear. There seems to be only one example (obtained from studies other than mass spectrometry) of an ion–molecular reaction having a true
activation energy (\(~ 7 \text{ kcal/mole}\)). (It was investigated by Pshezhetzky and Dmitriev\(^{54}\).)

\[
\text{N}_2^+ + \text{O}_2 \longrightarrow \text{NO}^+ + \text{NO} \tag{8}
\]

This reaction is seen to be one of rearrangement. At the same time, the rearrangement reaction investigated by Stevenson and Schissler\(^{15}\)

\[
\text{CH}_3^+ + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_6^+ + \text{H}_2 \tag{9}
\]
proceeds without appreciable activation energy.

**Energy transfer**

To understand the mechanism of ion–molecular processes, as well as any other elementary act, it would be necessary to obtain data on the importance and various conversions of energy occurring in this process.

![Figure 6. The currents of CH$_4$ and CH$_3$ ions formed in a methane–xenon mixture as a function of Xe pressure](image)

The effect of excitation energy—This effect was studied by Czechoslovakian scientists\(^{55}\) for the transfer of heavy atoms; they made use of electron excitation reactions only.

It appeared that the reactions observed:

\[
\text{N}_2^+ + \text{N}_2 \longrightarrow \text{N}_2^+ + \text{N} \tag{10}
\]
\[
\text{O}_2^+ + \text{O}_2 \longrightarrow \text{O}_3^+ + \text{O} \tag{11}
\]

involve electron excited ions \(\text{N}_2^+(\text{B}^2\Sigma^+_u)\) (and \(\text{O}_2^+(2\Pi_4)\)). The phenomenological yield of secondary ions in these processes at pressures in the collision chamber amounting to \(10^{-5}–10^{-4} \text{ mm Hg}\) appears to be several orders lower than with non-excited particles, as the majority of excited ions succeeds in emitting light before colliding with the molecule. This is apparently the reason why there is no information on the part played by excitation in reactions involving ions participating simultaneously in secondary processes in a non-excited state. The secondary reactions involving non-excited ions would mask the reactions of the few ions left excited at the time of collision.

The effect of electron-excitation energy on processes of ion–molecular resonance charge exchange was studied very explicitly by Lindholm, who
used the method of external ionization\textsuperscript{35-37}. His basic conclusion was that to obtain the ionizing vertical transfer, the molecule would require the sum of the ionization energy and the energy of electron excitation of an incident ion. The molecular ion formed will decompose (or not) depending upon its structure and the excitation imparted to it. For example

\begin{align*}
\text{Kr}^+(2\text{P}_1) + \text{H}_2\text{S} &\rightarrow \text{S}^+ + \text{H}_2 + \text{Kr} \quad (12) \\
\text{Kr}^+(2\text{P}_1) + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{O}^+ + \text{Kr} \quad (13)
\end{align*}

The part played in charge exchange by slow excited ions was studied using the internal ionization method (Hamill and co-workers\textsuperscript{56}), the increased-pressure method (Melton\textsuperscript{30}) and, lately, the pulse method (our laboratory\textsuperscript{24}).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.png}
\caption{The currents of C\textsubscript{2}H\textsubscript{4}+, C\textsubscript{4}H\textsubscript{2}+ and C\textsubscript{2}H\textsubscript{3}+ ions formed in an ethylene-xenon mixture as a function of Xe pressure}
\end{figure}

Charge exchange involving the excited \(\text{Kr}^+(2\text{P}_1)\) ion

\[ \text{Kr}^+ + \text{CH}_4 \rightarrow \text{Kr} + \text{CH}_3^+ + \text{H} \quad (14) \]

was observed by the latter method. The excited state of the \(\text{Kr}^+(2\text{P}_1)\) ion is \(\sim 0.6\) eV above the ground state and sufficient to make the reaction (14) exothermic by 0.2 eV. Fox \textit{et al.}\textsuperscript{57} showed that excited ions \(\text{Kr}^+(2\text{P}_1)\) and \(\text{Xe}^+(2\text{P}_1)\) are formed in appreciable amounts in the ionization of Kr and Xe by electron impact. The excitation energy for the \(\text{Xe}^+(2\text{P}_1)\) ion is 1.34 eV. This energy appears to be sufficient for making the processes

\begin{align*}
\text{Xe}^+ + \text{CH}_4 &\rightarrow \text{Xe} + \text{CH}_4^+ \quad (15) \\
\text{Xe}^+ + \text{C}_2\text{H}_4 &\rightarrow \text{Xe} + \text{C}_2\text{H}_2^+ + \text{H}_2 \quad (16)
\end{align*}

by 0.44 and 0.04 eV exothermic respectively. Meisels\textsuperscript{58} based his suggestion about the probability of process (15) on results of experiments concerned with radiolysis of methane sensitized with xenon. We have, indeed, observed processes (15) and (16) by means of the pulse ionization method. The dependence of secondary ion currents on the pressure of inert gas is shown in Figures 6 and 7\textsuperscript{†}.

\textsuperscript{†} All current values are given with respect to the Ne\textsuperscript{+} current; small amounts of Ne were added as standard.
Transfer of translational energy—Certain data on interconversion of the energy of translational motion of an ion and a molecule, and the internal energy in the course of the reaction, are already available. There is little information, however, on reactions involving transfer of heavy particles. Frankevieh and the author\(^{41}\) found that an increase up to 15 eV in the kinetic energy of \(\text{C}_2\text{H}_4^+\) ions does not result in reaction

\[
\text{C}_2\text{H}_4^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_3
\]  (17)

which is only 0.9 eV endothermic taking place.

On the other hand, Herzberg and co-workers\(^{59}\) have recently observed an endothermic process

\[
\text{H}_2^+ + \text{He} \rightarrow \text{HeH}^+ + \text{H}
\]  (18)

and suggested that it may proceed at the expense of the translational energy.

It will be noted below that certain results for polyatomic systems obtained by the continuous repulsion method may also be treated as due to transfer of translational into excitational energy.

With charge exchange processes the conversion of kinetic to internal energy and *vice versa* for vertical transitions is known to be greatly hindered. Appreciable cross-sections for non-resonance processes would appear only at relative motion energies corresponding to the Massey criterion

\[
\frac{a|\Delta E|}{hv} \sim 1 \tag{vii}
\]

where \(a\) is the cross diameter of colliding particles, \(E\) is a resonance defect, \(v\) is the rate of relative motion of particles. On the other hand, it was noted many years ago\(^{60,61}\) that when the potential curves for initial and final systems intersect, the cross-section for a corresponding electron process may be considerable; an appreciable activation energy may be observed in this case, but the process may proceed also at lower rates of particles.

For instance, Hasted and co-workers\(^{62}\) found that in the low-energy range the cross-sections for charge exchange processes \(\text{A}^+ + \text{Kr}, \text{Ne}^+ + \text{A}, \text{C}^+ + \text{Kr}\) are many times higher than would be expected from the criterion of (8). Similar results were obtained by Bydin and Bukhteev\(^{63}\) for the ionization of fast atoms of alkali metals in collisions with \(\text{H}_2, \text{D}_2, \text{N}_2\) and \(\text{O}_2\). Examples of considerable deviation from the Massey criterion were already known for atomic systems.

Finally Magee\(^{64}\) suggests that when the particles are not too fast, charge exchange may occur *via* an intermediate complex of a lifetime exceeding one vibrational period. The reaction would then proceed in the same way, as in heavy particle transfer, and the conversion of rotational to internal energy would seem to be markedly favoured.

It should be stated at once that the available experimental data, those obtained both by Lindholm and in our laboratory, are not yet adequate for settling this problem. The main reason for this seems to lie in the fact that the geometry used involves a secondary beam normal to the primary one. This geometry permits good recording of very slow secondary ions
only. Whereas when a second ion appears by a non-resonance reaction of a very fast primary ion with a thermal molecule, as is the case in using the external ionization method, the translational energy of the majority of secondary ions will be considerable and the portion repelled (\( \eta \)) small.

In our device, for example, when an ion and a molecule of identical masses collide at an energy of 300 eV to form identical-mass particles via an intermediate complex, \( \eta \) will amount to 5 per cent of the repelled thermal ions. As a result, resonance processes may be observed but non-resonance processes appear to be considerably masked. However, the \( \eta \) value appears to be sufficiently high for identification of certain non-resonance processes, both by Lindholm's and our apparatus.

\[ \text{Figure 8. The intensity distribution in the mass spectrum of Xe}^+ - \text{C}_2\text{H}_4 \text{ charge exchange products as a function of the kinetic energy of Xe}^+ \text{ ions} \]

For instance, along with ion–molecular charge exchange, independent of the translational energy of the particles and their consequent resonant properties, it is sometimes possible to record inverse cases. The dependence of the spectrum for products of charge exchange Xe\(^+\) + C\(_2\)H\(_4\) upon the kinetic energy of Xe\(^+\) (obtained in our laboratory) is given as an example in Figure 8. It may be seen that for sufficiently endothermic processes, such as

\[
\text{Xe}^+ + \text{C}_2\text{H}_4 \rightarrow \text{Xe} + \text{CH}_2^+ + \text{CH}_2 - \begin{cases} 7.14 \text{ eV} \ (2P_3^o) \\ 6.8 \text{ eV} \ (2P_3^o) \end{cases}
\]  

(19)

there is an energy threshold, practically similar to that calculated from energy and momentum conservation, and the excitation function of this process shows an increase immediately after the threshold, considerably more steep than that implied by the quasi-adiabatic Massey hypothesis.

On the other hand, it would be of interest to consider an example of the pulse method application to this problem. It was shown\(^{66}\) that the spectrum for charge exchange between argon and methane, and between krypton
and ethylene does not change in passing from the method of external ionization by ions of 300 eV to the pulse method of internal ionization, i.e. to thermal ions. Corresponding mass spectra of charge exchange products are shown in Table 3. Consequently, for a very broad range of energies, we seem to be concerned in this case with a resonance mechanism only.

Table 3. Charge exchange reaction products for fast and thermal primary ions

<table>
<thead>
<tr>
<th>Ions</th>
<th>Energy</th>
<th>Thermal</th>
<th>300 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar⁺ + CH₄</td>
<td></td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>CH₃⁺ + CH₄</td>
<td>0.83</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>CH₂⁺ + CH₄</td>
<td>0.17</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Kr⁺ + C₂H₄</td>
<td></td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>C₆H₅⁺ + C₂H₄</td>
<td>0.60</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>C₂H₅⁺ + C₂H₆</td>
<td>0.40</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>C₂H₇⁺ + C₂H₆</td>
<td></td>
<td>0.002</td>
<td></td>
</tr>
</tbody>
</table>

The mechanism and theory of ion-molecular processes

Let us now try to conceive the mechanism of chemical conversions that may take place in collisions of ions with molecules (Figure 9). Processes necessitating relatively high energies (impact ionization, dissociation, etc.) will be disregarded throughout this paper.

First of all it is necessary to distinguish between two mechanisms: the resonance ("long-range") mechanism and that involving the formation of an intermediate complex.

Of prime importance is the fact that the first mechanism will result in charge exchange only (or perhaps in resonance excitation transfer), while the second may involve the transfer of heavy particles as well. The predominant mode of the intermediate complex decomposition will be determined by its structure and excitation level. There is every reason to believe that
ION-MOLECULAR REACTIONS IN GASES

Qualitatively this scheme is true. Indeed, the resonance mechanism has been repeatedly observed in very different systems. Direct experimental studies of the mechanism involving an intermediate complex have been less explicit. However, a number of direct experiments providing evidence for the formation of such complexes may be cited. For saturated molecules with a relatively small number of atoms such evidence was obtained in the experiments of Frankevieh and the author\textsuperscript{53,67} which were concerned with the distribution of ions with respect to translational energies in reactions

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$ \hspace{1cm} (1)

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$$ \hspace{1cm} (20)

$$H_2O^+ + H_2O \rightarrow H_3O^+ + HO$$ \hspace{1cm} (2)

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$$ \hspace{1cm} (5)

It appeared that this distribution was near to that expected on the assumption that energy distribution is uniform over all degrees of freedom for the final products.

Hamill and Pottie\textsuperscript{47} succeeded in detecting the complex ions formed in a reaction involving multi-atomic particles

$$C_3H_2I^+ + C_3H_7I \rightarrow (C_3H_7I)_2^+$$ \hspace{1cm} (21)

and which involved a lifetime of $\sim 10^{-6}$ sec. Using the pressure increase method, Field\textsuperscript{29} detected the complexes

$$C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+$$ \hspace{1cm} (22)

$$C_2H_3^+ + C_2H_4 \rightarrow C_4H_7^+$$ \hspace{1cm} (23)

$$C_2H_2^+ + C_2H_4 \rightarrow C_4H_6^+$$ \hspace{1cm} (24)

and found their half-lives to be $(0.2$ to $1) \times 10^{-7}$ sec.

Thus, the ion–molecular problem should be concerned with at least two problems. Firstly, it is necessary to know the method of calculating cross-sections for the resonance process and for the complex formation. Most important, at the given stage, seems to be the determination of their ratio and its dependence on the rate of relative motion of the particles. Secondly, a theory for calculating absolute and relative rates of decomposition of the intermediate complexes by various modes is necessary.

How does the question stand with respect to the first problem? There exists a theory of resonance charge exchange. It gives a relation for the cross-section\textsuperscript{68}

$$\sigma = 2\pi \int_0^\infty P(R_0) R_0 dR_0$$ \hspace{1cm} (viii)

where

$$P(R_0) = \sin^2 \left[ \frac{1}{\hbar V} F(R_0) \right]$$

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$R_0$ is the impact parameter, and $v$ the relative motion rate. However, this theory does not account for the possible formation of a complex.

On the other hand, the existing theory of complex formation which is concerned, with certain restrictions, with non-polar molecules does not account for possible resonance charge exchange. According to Stevenson and Gioumousis this theory, based on the classical work of Langevin gives an expression for $\sigma$

$$\sigma = \frac{2\pi e}{v} \sqrt{\frac{\alpha}{\mu}} \tag{ix}$$

where $\alpha$ is the polarizability of the neutral particle, $\mu$ is the reduced mass, $v$ is the rate of relative motion of an ion and a molecule.

The rate constant of an ion–molecular reaction calculated by the activated complex method ($k_T$ is the theoretical $k$ value, $\kappa$ the transmission coefficient of the transient state theory) may in a certain sense be considered as the rate of an intermediate complex formation.

A similar relation may be obtained without using the transition state theory. $\kappa$ will then have the significance of a collision “efficiency” coefficient only. Correlation of the solution for the continuous repulsion method (obtained from Boltzmann’s equation) with relations (10), (9) and (1), taken from the work of reference, gives an expression permitting the determination of $\kappa$ from known values of $Q$, $E$ and $l$, i.e.

$$\kappa = \frac{Q}{2\pi e} \sqrt{\frac{M}{\alpha}} \sqrt{\frac{eEl}{2m_1}} \tag{xi}$$

The first condition for the validity of this calculation is the proportionality of the $I_2/I_1$ ratio to the $\sqrt{\frac{l}{E}}$ value, or, what amounts to the same thing, the inverse proportionality of $Q$ to $\sqrt{E}l$. Indeed, this relation was obtained by Gutbier and Stevenson and Schissler for a number of reactions between simple ions and molecular hydrogen. Moreover, in some cases $\kappa$ appeared to be close to unity. On the other hand, as shown by Stevenson and Schissler and, particularly, by Field, Franklin and Lampe, the dependence of $I_2/I_1$ upon $E$ appears to be more pronounced in more complex systems, i.e. it lies somewhere between $1/\sqrt{E}$ and $1/E$. Field, Franklin and Lampe succeeded in deriving an equation for this dependence

$$\frac{I_2}{I_1} = \mathcal{N} \frac{600\pi \kappa \sqrt{2kT}}{E} \sqrt{\frac{m_1 + m_N}{m_N}} \arcsinh \left( \frac{eEl}{150kT} \right) \tag{xii}$$

where $m_N$ is the neutral particle mass, and $k$ is the Boltzmann constant.

† Hamill gave at the Congress an example of such a theory for polar molecules.
Field, Franklin and Lampe also use equation (xii) for determining the $\kappa$ value, and for the cases they investigated it appears to lie between 0.5 and 1. It will be noted, however, that this equation was obtained as a result of a somewhat rash replacement of one of the three translational partition functions in the initial equation of Eyring et al. by the effective temperature

$$\frac{l}{2k} = \frac{l}{2k} T + \frac{e^2E^2q^2}{2m} \quad (xiii)$$

Why the theory of Stevenson and Gioumousis should be used for simpler systems, and that of Field, Franklin and Lampe for more complex cases, is not clear.

Though there is a large gap between the resonance charge exchange theory and that for the complex formation, attempts should be made to determine how these processes compete. This should be done by comparing experimental results for various processes. For instance, Field, Franklin and Lampe noted that the rate constant decreases in the order

$$CD_t^+ + CH_4 \longrightarrow CD_4H^+ + CH_3 \quad (25)$$
$$CD_t^+ + C_2H_6 \longrightarrow CD_4H^+ + C_2H_5 \quad (26)$$
$$CD_t^+ + C_3H_8 \longrightarrow CD_4H^+ + C_3H_7 \quad (27)$$
$$CD_t^+ + iC_4H_10 \longrightarrow CD_4H^+ + iC_4H_9 \quad (28)$$

while the polarizability increases. Stevenson stated in a private communication that the reactions of type

$$Kr^+ + H_2 \longrightarrow KrH^+ + H \quad (29)$$

appear to take place, while the exothermic reaction

$$Kr + H_2^+ \longrightarrow KrH^+ + H \quad (30)$$

is not observed. Indeed, the competing role of charge exchange may be supposed to be obvious in all these cases. However, a number of inverse cases may also be cited.

Thus, charge exchange with thermal Ar ions

$$Ar^+ + H_2 \longrightarrow Ar + H_2^+ \quad (31)$$

was observed in our laboratory along with reaction

$$Ar^+ + H_2 \longrightarrow Ar_2H^+ + H \quad (32)$$

The pulse method was used and the cross-sections for these reactions were comparable. However, according to Stevenson and co-workers, the rate constant of reaction (31) is high and corresponds to $\kappa = 1$.

The same seems to be true for reactions

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \quad (5)$$
$$H_2^+ + H_2 \longrightarrow H_3^+ + H \quad (1)$$
though charge exchange at thermal energies was not investigated here. On the other hand, the reaction rate

$$\text{Kr}^+ + \text{H}_2 \rightarrow \text{KrH}^+ + \text{H} \quad (30)$$

is not high ($\kappa = 0.3$)\textsuperscript{16,17} though charge exchange between $\text{H}_2$ and $\text{Kr}^+$ ($^2\text{P}_1$), as well as $\text{Kr}^+$ ($^2\text{P}_\frac{1}{2}$), is very endothermic.

In making these comparisons it should be borne in mind that in discussing the competition with resonance charge exchange we are referring to the intermediate complex formation step and, consequently, to the first problem of the ion–molecular theory. Whereas in discussing the competition with non-resonance charge exchange, we usually pass to the second step and, thus, to the second theoretical problem, namely the relative probability of various intermediate complex decomposition modes.

What is the position with respect to the second problem, that of the decomposition of complexes? Field, Franklin and Lampe\textsuperscript{20} suggested that it may be solved by means of the theory for the decomposition of excited ions, developed earlier by Eyring and co-workers\textsuperscript{71} for dissociative ionization by electron impact, and based on the concept of random distribution of the excitation energy among all the vibrational and rotational degrees of freedom. A great similarity was observed, in particular, between the spectra of decomposition products in reactions (22), (23) and

$$\text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_2 \rightarrow [\text{C}_4\text{H}_4]^+ \quad (33)$$

and those for the products of dissociative ionization of 1-butene, 1,2-butadiene and vinylacetylene.

It must be emphasized that the quasi-equilibrium theory should be used in this case no less cautiously than in the interpretation of mass-spectra involving large molecules, as the main postulate for energy distribution in an excited ion is far from being always fulfilled, as has been shown, for example, by Tunitzky\textsuperscript{72,73}. However, for complexes that are not so large (and probably not too small), the use of this theory, at least for semi-quantitative treatment, may prove justifiable (see also references 45 and 47).

It will be noted that in investigating the complex decomposition by the continuous repulsion method, and especially by the external ionization method, no allowance was made for the considerable additional excitation of the complex by the imparted energy of the relative ion–molecule motions. The fact that this excitation may affect the decomposition mode seems to be obvious. Less exothermic modes, including that of inverse decomposition, will become more probable. When this is taken into account, our approximate equation of the secondary ions current takes the rather cumbersome form

$$\frac{I_2}{I_1} = NK \frac{V^m}{L} \int_{z=0}^{L} \left( cEz \right)^{n-1} \left[ 1 - \frac{(\delta E z)^n}{(\delta E z + E^* - \epsilon_i)^n} \right] \text{d}z \quad (xiv)$$

where $\delta$ is the portion of kinetic energy converted into the internal energy of the complex, $E^*$ is the energy released by complex formation, and $\epsilon_i$ is the activation energy for decomposition of the complex by the $i$-th mode.
This equation supports, in particular, a more marked dependence of $I_2/I_1$ on $E$, rather than on $1/\sqrt{E}$.

Moreover, with increase in translational energy, the portion converted into excitation energy, as consistent with energy and momentum conservation, would become such that the complex lifetime would decrease to the duration of one vibrational period and the complex will simply cease to form. Using the repulsion method we shall have, in this case,

$$
\frac{I_2}{I_1} = k_T N \sqrt{2mE_{t(ex)}} \frac{1}{eE}
$$

where $E_{t(ex)}$ is the translational energy value above which the complex is not formed. Here, $I_2/I_1 \sim 1/E$.

Thus, a possible approach to the problem of strong dependences of phenomenological cross-sections on particle rates may depart from the translational–excitational energy conservation concept.

It would be of interest to undertake systematic experiments within a range of rather high translational energies and attempt to apply the external ionization method that would emphasize the relations of interest.

Thus, the treatment of an ion–molecular elementary act as consisting of two steps, that of activated complex formation competing with the resonance charge exchange, and that of the complex decomposition, seems to be justifiable and permits the definition of possible ways of approaching experimental and theoretical problems.

The attention paid in this lecture to uncertain and unsolved problems of the ion–molecular reactions theory should not be considered as evidence for complete lack of clear understanding in this field. On the contrary, during the relatively few years of extensive investigations on this topic we seem to have acquired more knowledge than that available in the classical kinetic studies of neutral particles. Indeed, a precise qualitative picture of the reaction mechanism, knowledge of the activation energy (or, as a rule, of its absence), of the conformity of theoretical and experimental reaction rate constants, with an accuracy to within a factor of 2–3, etc., might be considered as a great success in any kinetic investigations.

However, we should strive for a broadening of our ideas in this field for two reasons. First, ion–molecular reactions, due to their large cross-sections and to the possible use of the mass spectrometric technique, seem to be the only kinetic means yet available of carrying out investigations by the single-collision method, as is the practice in nuclear physics. The application of this technique would make possible the accumulation of evidence on the nature of elementary acts to a degree undreamed of in normal kinetic studies of neutral particles. At the same time, it is possible that many features of ion–molecular reactions are displayed by other reactions as well. Perhaps insufficient attention is paid to the formation of relatively long-lived complexes in reactions involving neutral particles. Perhaps by assuming the possible formation of such a complex in many reactions obeying Polanyi's rule, some new light might be thrown upon this rule.

†Conclusions in part similar to those given here have been arrived at by Moran and Hamill.

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The second reason for perfecting ion–molecular investigations is the need for rate constant values considerably more precise than those required in neutral particle kinetics, as the difference in rate constants of various exothermic ion–molecular reactions is considerably smaller than with exothermic reactions involving neutral particles. However, these small differences are those accounting for the modes of complex reactions involving ion–molecular elementary steps.

THE APPLICATION OF DATA ON ELEMENTARY ION-MOLECULAR REACTIONS IN VARIOUS FIELDS OF THERMODYNAMICS AND GAS PHASE KINETICS

Let us now make certain necessarily brief statements as to the part played by elementary ion–molecular reactions in various fields of thermodynamics and gas phase kinetics, and discuss the conclusions arrived at, as well as the possible methodological applications of these conclusions.

Application of results on ion–molecular reactions in investigating heats of formation and bond energies

Investigations on elementary ion–molecular reactions resulted in the development of a new method for determining these fundamental thermochemical values, namely the ion-impact method.

Reaction rate constants not lower than $10^{-12}$ to $10^{-13}$ cm³/sec may be determined using single-collision methods. The mere possibility of observing a reaction involving very slow ions shows that it proceeds without activation energy (to within 2–3 kcal/mole) and, consequently, may be considered as exothermic or thermoneutral.

This makes possible the derivation of corresponding thermochemical inequalities for heats of formation and bond energies. For example, Frankevich and the author⁴³ found that process

$$H_2O + H_s^+ \rightarrow H_2O^+ + HS$$

is observable; this means that the proton affinity of water is

$$S_{H_2O} \geq D(H - SH) + E_i(H) - E_i(H_2S) = 167 \text{ kcal/mole}$$

$E_i$ is the ionization potential and $D$ the bond energy.

Several laboratories have used this method to determine limiting values for proton affinities and energies of H atom abstraction for a number of cases.

In using this method for H and H⁺ transfer, we further postulated⁴³ that a reaction unobservable in a mass-spectrometer may be considered as endothermic. Such an extension of the method’s principle was, of course, of an empirical nature. It was based on the fact that it appeared to be justified in about 70 reactions investigated, with the exception of rare cases when the transfer reaction was not observed, but a competing reaction between the same particles occurred. This problem became a subject of discussion⁹,²⁰,⁷⁴–⁷⁸, arising in part through misunderstanding, and the only thing that need be said at present is that while the “first part” of the method is unquestionably

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adequate for all cases, the "second" should be used cautiously and, at the very least, requires strong evidence for the absence of competing reactions.

Thus, Frankevich and the author\textsuperscript{43} estimated the upper limit for proton affinity of water on the basis of the fact that processes

\begin{align*}
\text{H}_2\text{O} + \text{NH}_3^+ & \rightarrow \text{H}_3\text{O}^+ + \text{NH}_2 \\
\text{H}_2\text{O} + \text{C}_2\text{H}_2^+ & \rightarrow \text{H}_3\text{O}^+ + \text{C}_2\text{H} \quad (35) \quad (36)
\end{align*}

were unobservable and, consequently, that

\begin{align*}
S_{\text{H}_2\text{O}} & < D(\text{NH}_2 - \text{H}) + E_i(\text{H}) - E_i(\text{NH}_3) = 184 \text{ kcal/mole} \\
S_{\text{H}_2\text{O}} & < D(\text{C}_2\text{H} - \text{H}) + E_i(\text{H}) - E_i(\text{C}_2\text{H}_2) = 171 \text{ kcal/mole}
\end{align*}

In the latter case secondary ions of a mass above 26 amu, which could have been produced by a competing reaction of \text{H}_2\text{O} with \text{C}_2\text{H}_2^+, were also undetectable. (The H atom transfer reaction \text{H}_2\text{O} + \text{C}_2\text{H}_2^+ \rightarrow \text{OH} + \text{C}_2\text{H}_2^+ is 31 kcal/mole endothermic.) Charge exchange involving slow ions is excluded in both cases being endothermic.

Of interest are the proton affinity values for water and alcohols obtained by Frankevich and the author\textsuperscript{43,77} using the ion impact method (Table 4). A systematic decrease in these values by 20 kcal/mole, as compared with the most reliable values obtained by indirect methods, will be noted\textsuperscript{78}.

<table>
<thead>
<tr>
<th>Reactions for upper and lower limits</th>
<th>Limiting values</th>
<th>$\delta$</th>
<th>Calculated from data on the crystal lattice energy, without allowing for hydrogen bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{H}_2\text{O} + \text{H}_3\text{S}^+ \rightarrow \text{H}_3\text{O}^+ + \text{HS}</td>
<td>&gt; 167, &lt; 171</td>
<td>169 $\pm$ 2</td>
<td>188.6</td>
</tr>
<tr>
<td>\text{H}_2\text{O} + \text{C}_2\text{H}_2^+ \rightarrow \text{H}_3\text{O}^+ + \text{C}_2\text{H}</td>
<td>$\geq 177$</td>
<td>180 $\pm$ 3</td>
<td>209</td>
</tr>
<tr>
<td>\text{CH}_3\text{OH} + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{OH}_2^+ + \text{OH}</td>
<td>$&lt; 183$</td>
<td>$\geq 185$</td>
<td>216.5</td>
</tr>
<tr>
<td>\text{CH}_3\text{OH} + \text{NH}_3^+ \rightarrow \text{CH}_3\text{OH}_2^+ + \text{NH}_2</td>
<td>$&lt; 202$</td>
<td>194 $\pm$ 9</td>
<td>216.5</td>
</tr>
</tbody>
</table>

Sokolov and co-workers suggested later\textsuperscript{79} that by allowing for the hydrogen bond energy of an ionic crystal involving \text{H}_3\text{O}^+ ions, the proton affinity of water will also be decreased by 18 kcal/mole compared with the results of ref. 78.

Speaking of "onium" ions it will be of interest to note that up to now the \text{CH}_3^+ ion discovered 10 years ago by Lyubimova and the author\textsuperscript{12} was the only product ever observed of proton addition to a saturated hydrocarbon. An explanation for this might lie in the suggestion of Frankevich and the author\textsuperscript{74,80} that the proton affinity of methane homologues is lower than that of methane (114-129 kcal/mole), which is, of course, astonishing, or it might lie in the idea of Lampe and Field\textsuperscript{81} that all reactions used for obtaining \text{C}_2\text{H}_2^+ proceed by some competing and more probable ways. Lampe and Field infer the proton affinity of ethane from the reaction

\begin{align*}
\text{CH}_3^+ + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H}_2 \\
\text{475}
\end{align*}
which would proceed via the excited $C_2H_4^+$ complex. On the basis of the fact that the heat of complex formation is somewhere between the heats of formation of initial and end products, they found that

$$244 > \Delta H_f(C_2H_4^+) > 224 \text{ kcal/mole}$$

and

$$101 < S(C_2H_6) < 121 \text{ kcal/mole}$$

Finally, it may be emphasized that a very important and useful feature of the ion impact method is the possibility it offers of estimating the proton affinity of saturated compounds; this cannot be measured by other direct experimental methods.

**Charge exchange as a means of ionization in analytic mass spectrometry**

The analytical mass spectrometry of multi-atomic molecules is often confronted with the requirement that ionization be produced without, or almost without, dissociative ionization.

A most popular method meeting this requirement is that of ionization with low-voltage electrons (Eltenton82) (see also refs. 83 and 84). At the same time attempts have been made to devise other methods for obtaining "single-line" and "few-line" spectra, such as the methods of photoionization85,86 and ionization in a strong electric field87. The charge exchange method is also promising in this respect. Lindholm89 discussed the possible application of resonance charge transfer. The author88,89 noted that the great number of multi-atomic ion levels, and also the ready conversion of translational into excitational energy in charge exchange involving multi-atomic molecules, favours the use of the charge exchange method for obtaining "few-line" mass spectra; the bombarding ion should be selected here on the simple principle that

$$E_{di} > E_n \geq E_i$$
where $E_i$ is the ionization potential of the molecule, and $E_{di}$ the potential of dissociative ionization yielding the ion to be avoided. We suggested the use of this method for mass spectrometric detection of free radicals when dissociative ionization is particularly undesirable.

The mass spectra of (a) hydrazine and (b) acetone obtained by Lavrovskaya, Markin and the author$^{89}$ for charge exchange involving NH$_3^+$ ions are shown in Figure 10. The lines for molecular ions are very intensive, while those for fragmentary ions are considerably weaker than in mass spectra of the same substances obtained by ionization with electrons of 60 eV. Consequently, the detection of free radicals in the presence of a large concentration of molecules is easier with "charge exchange" mass spectra. Mass spectra obtained in NH$_3^+$ charge exchange for products of pyrolysis of (a) hydrazine and (b) acetone from a reactor heated to 1,000° and located in the immediate vicinity of the charge exchange chamber, are shown in Figure 11. The conclusion may be drawn from the observations that CH$_3$CO and CH$_3$ radicals are formed in acetone pyrolysis, while that of hydrazine yields N$_2$H$_3$ radicals and, probably, N$_2$H$_2$, N$_2$H, NH$_2$ and NH.

Finally, let us note that charge exchange as a means of ionization seems to have been used for the first time by Dukelskii and Zandberg$^{52}$ in obtaining negative oxygen ions by charge exchange involving Na$^-$, K$^-$, O$^-$, OH$^-$. The radiation chemistry of gases

The part played by ions in the radiation chemistry of gases attracted the attention of Lind as far back as 1920. The investigations carried out last year made possible a rational approach to obtaining a better insight into the part played by ion–molecular reactions in this field.

Let us mention first the determination of the ion–molecular reactions responsible for the over-all process. This is done by analysis of the

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end products of radiolysis, with simultaneous use of some method for predominant generation of a certain type of ions. We may mention here the work on oxidation carried out by Pshezhetzky and Dmitriev\textsuperscript{54} who determined the importance of the reaction

\[ \text{N}_2^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{NO} \]  

(8)

and its activation energy by making simultaneous use of the critical potential method\textsuperscript{4} and kinetic analysis of the reaction rate temperature dependence. We may also mention the work of Lampe\textsuperscript{90} on radiolysis of a mixture of excess inert, or certain other, gases with H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}. Lampe suggested that atomic hydrogen obtained by a reaction of the type

\[ \text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \]  

(32)

was responsible for ethylene hydrogenation under these conditions.

The important mass-spectrometric investigations mentioned above, and those concerned with ions yielded by bombardment of gas with electrons or \( \alpha \)-particles at pressures up to 0.5 mm Hg, should be recalled here.

The lifetimes of intermediate complexes obtained by Field\textsuperscript{29} for ethylene and acetylene (~10\textsuperscript{-7} sec) show the necessity of allowing for the reactions and stabilization of these complexes in working out mechanisms of complex radiation-induced reactions.

Furthermore, studies may be mentioned which attempt to devise reaction schemes and compare the calculated and experimental values of end products (Meisels, Hamill and Williams\textsuperscript{56}, Futrell\textsuperscript{91}, Dorfman and Sauer\textsuperscript{92}, Reinish\textsuperscript{93}, etc). These authors combine the mass spectrometric data obtained, \textit{i.e.} the yield in primary products of radiation-induced reactions, with data, and sometimes hypotheses, on possible secondary reactions involving ions and radicals.

It will be noted that they use substances other than those of Melton's and Field's experiments, namely saturated hydrocarbons, for which the sequence of ion–molecular reactions appears to come to an end at the first or second step, since the next conceivable ion–molecular process will be endothermic and the ion recombination rate will exceed the rates of these processes.

It is important to note that satisfactory results may be obtained by this approach. This would seem to mean that the lifetimes of intermediate complexes in these systems are short. Let us recall that we are concerned with intermediate complexes of two types—the primary excited ions, and ion–molecular complexes. Consequently, both types should persist less than \( 10^{-9} \) to \( 10^{-10} \) sec. This is consistent with the conclusions of Tunitzky and co-workers\textsuperscript{72,73} on very fast decomposition of ions in saturated hydrocarbons.

On the other hand (as stated above) for markedly unsaturated ion–molecular complexes, \( \tau \approx 10^{-7} \) sec, and as to primary excited ions, the question remains still unsettled. The importance of the problem of excited ion lifetimes in radiation chemistry has recently been emphasized by Platzman\textsuperscript{94} and Stevenson\textsuperscript{95}.

The determination of ion lifetimes with respect to unimolecular decay of \( 10^{-8} \) to \( 10^{-10} \) sec, and perhaps to even lower values, is a problem, the
solution of which though difficult to realize, is fundamental for obtaining insight into the mechanism of high-pressure ion–molecular reactions and for the rational application of data obtained by using the single-collision method. The same may be said about measurements of the rates of reactions between molecules and the ions so recently formed. It would also be desirable to extend mass-spectrometric investigations to within the atmosphere-pressure range, the more so as this has already been achieved in investigating the composition of ions in flames.65,66.

There has lately been a revival of interest in the part played by clusters in radiation induced gas phase reactions. This has been due, in part, to the experimental and theoretical studies on cluster formation discussed in the preceding part of this paper. The change in ideas about the part played by clusters is of interest. In the early days of radiation chemistry clusters were considered to be responsible for higher radiation-induced yields, compared with ionic yields, whereas now there is every reason to believe that the occurrence of clusters in ion recombination decreases the probability of dissociation through chemical bonds. This is in part due to a decrease in the free energy of the system as a result of cluster formation. Hence the process

\[
\text{Cluster} \rightarrow \text{XY}^+ + \text{nM} + e = X + Y + nM
\]  

may even appear to be endothermic. It is highly probable that even when there is enough energy the molecules will take up this energy by small portions, and dissociation into X and Y radicals will not occur. (See Magee and Funabashi44.)

Burton97 reports that a decrease in radiolysis yields with a drop in ethane temperature down to the liquefaction point occurs in the gas phase, but under conditions close to the critical state. This he explains by the effect of clusters.

Fiquet-Fayard98 suggested that the higher ion yields in water radiolysis (as compared to the liquid phase) reported by Firestone99 are due to the decomposition reaction,

\[
\text{H}_2\text{O}^+ + e \rightarrow 2\text{H} + \text{OH}
\]

Pshezhetzky and the author100 consider this suggestion as scarcely possible, since at room temperature and pressures of the order of 0·1 mm Hg, the water vapour ions will be present as strongly hydrated hydroxonium; this was shown recently by Knewstub and Tickner101.

It would be of interest to determine the behaviour of the ion-polymers which have been observed mass spectrometrically by Melton and Field at elevated pressures. A simultaneous quantitative analysis of the end-polymers produced in radiolysis would be of considerable help.

**Electric discharge**

Direct investigations dealing with the effect of ion–molecular reactions, and heavy ions in general, on the main discharge characteristics are relatively
few. We may mention the well-known studies of Biondi\textsuperscript{102} on the effect of processes of the type

\begin{align*}
\text{Ar}^* + \text{Ar} &\rightarrow \text{Ar}_2^+ + e \quad (40) \\
\text{Ar}_2^+ + e &\rightarrow \text{Ar}^* + \text{Ar} \quad (41)
\end{align*}

upon the rate of decomposition of the discharge plasma.

Knewstubb and Tickner\textsuperscript{101} of Canada have reported recently on the predominant formation of ions $\text{H}^+ \cdot n\text{H}_2\text{O}(n = 1 \ldots 5)$ under a glow discharge in water at a pressure of 0.34 mm Hg. The question arises whether the part played by minor water admixtures in the formation of free atoms in electric discharge is limited by the decrease in recombination activity at the wall?

The processes:

\begin{align*}
\text{H}_2^+ + \text{H}_2 &\rightarrow \text{H}_3^+ + \text{H} \quad (1) \\
\text{H}_3^+ + e &\rightarrow 3\text{H} \text{ or } \text{H}_2 + \text{H} \quad (42)
\end{align*}

are obviously very important for powerful ion sources in accelerators as main generators of atomic hydrogen which yields, in its turn, atomic ions

\begin{align*}
\text{H} + e &\rightarrow \text{H}^+ + 2e \quad (43)
\end{align*}

(see, in particular, reference 31).

The inhibiting effect of charge exchange $\text{H}^+ + \text{H} = \text{H} + \text{H}^+$ in plasma investigated in connection with nuclear physics is well known\textsuperscript{102}. Finally, the relation between charge exchange and the effect of admixtures upon the work of discharge counters for fast particles\textsuperscript{104} was postulated long ago.

An increase in interest in the direct investigation of ion–molecular reactions and heavy ions in discharges of various types is to be expected.

**Ionospheric processes**

It is a common belief nowadays that the important secondary processes occurring in the ionosphere, and which are to a considerable extent responsible for the attainment of its ionic balance, are, in fact, ion–molecular reactions\textsuperscript{105,106}.

In studying all possible exothermic reactions between $\text{O}^+_2$, $\text{O}^+$, $\text{N}^+_2$, $\text{N}^+$ and $\text{O}_2$, $\text{O}$, $\text{N}_2$, $\text{N}$, Krassovsky\textsuperscript{106} reached the conclusion that the reaction

\begin{align*}
\text{O}^+ + \text{N}_2 &\rightarrow \text{NO}^+ + \text{N} \quad (44)
\end{align*}

plays an important part in the upper ionosphere, where primary ionization is due to $\text{O}^+$. The rate constant of this process is $K_{44} \simeq 10^{-8}$ cm$^3$ sec$^{-1}$ and the heat of reaction $+0.83$ eV.

Determination of the effective recombination coefficient, under the assumption that reaction (44) is of predominant importance, provided an explanation for certain experimental results and led to the conclusion that this coefficient is dependent upon electron concentration.

A more accurate and explicit study of the part played by reaction (44) in the establishment of the ionic balance of the ionosphere was carried out
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by Bagaryatzkii\textsuperscript{107}. The results obtained were consistent with conclusions drawn by Krassovsky\textsuperscript{106}. Bagaryatzkii showed that the \( N_2 \) concentration is the parameter responsible for probable variations in the nature of recombination with increase in altitude. Thus, although above 150 km the electron disappearance rate depends upon dissociative recombination with \( \text{NO}^+ \) (as photorecombination with \( \text{O}^+ \) will be ineffective under all conditions)

\[
\text{NO}^+ + e \rightarrow \text{N} + \text{O} \quad (45)
\]

\( K_{45} \approx 10^{-6} \text{ cm}^3 \text{ sec}^{-1} \)\textsuperscript{107}, yet at high altitudes (and lower \( N_2 \) content) it will be determined by the rate of reaction (44).

It will be noted, however, that the rate constant of reaction (44) may be considerably lower than \( 10^{-8} \text{ cm}^3 \text{ sec}^{-1} \), as established by the work of Bates\textsuperscript{108}.

**Loaded ions in thermal equilibrium: ionization of gases**

Thermal ionization of gases is a process of great interest both from the theoretical and practical standpoints. The main experimental investigations on this topic are concerned with ionization in flames and, to a certain extent, in detonation waves. In the majority of cases, the systems studied are far from equilibrium, at least for neutral particles. However, a fundamental feature of these systems is beyond doubt, i.e. that the degree of gas ionization is higher than that corresponding to the Saha equilibrium equation, under the assumption that the ionization equilibrium is due to abstraction of electrons from neutral particles and recombination of electrons and ions,

\[
\text{M} \rightleftharpoons \text{M}^+ + e \quad (46)
\]

The calculated value for the degree of ionization also appears to be lower than that observed experimentally when the particles considered are free radicals and atoms\textsuperscript{†}, and the high values of their non-equilibrium concentrations in flames are taken into account.

Various suggestions have been made as to the nature of “increased” ionization. The most justifiable for certain systems is the assumption that “loaded” ions, i.e. those possessing more atoms than the neutral particles, favour ionization on energetic grounds. This suggestion received direct confirmation in the recent experiments of Knewstub and Sugden\textsuperscript{95,96}. These authors detected mainly \( \text{H}_3\text{O}^+ \) ions in the flame of hydrogen at a pressure of 1 atm. Thus, it is to be expected that the formation of “loaded” ions may be of importance in thermal gas ionization. However, it will be borne in mind that any process of formation of “loaded” ions from molecules, for instance

\[
2\text{M} \rightleftharpoons \text{M}_2^+ + e \quad (47)
\]

which is energetically more favourable than (46), would, nevertheless, be less favourable from the entropy standpoint.

When the temperature increases and the relative effect of the corresponding reaction heats on the degree of ionization becomes less marked (i.e. with increase in the importance of the entropy factor), process (46), the routine

\textsuperscript{†} i.e. Particles having lower ionization potentials than those for saturated molecules.
equilibrium ionization, will be responsible for the degree of ionization. Thus, the most pressing problem is that of finding out whether this temperature range is attained before or after ionization becomes important in some respect or other.

![Figure 12](image12.png)

**Figure 12.** Equilibrium ionization of $\text{H}_2\text{O}$ vapour: ---- over-all concentration accounting for $\text{H}_3\text{O}^+$ formation; --- without $\text{H}_3\text{O}^+$ formation

Larin and the author$^{109}$ evaluated various ionization equilibria taking into account the formation of "loaded" ions. Mass spectrometric results on the formation of secondary ions were used for obtaining heats of reactions. Calculated data for water, hydrogen and argon are shown in **Figures 12** and 13. The concentration of "loaded" ions from thermal ionization, over a certain temperature range, may be seen to exceed considerably that of all other positive ions and be responsible for the concentration of free electrons and, consequently, for the gas conductivity at the given temperature. The excess of "loaded" ions over the maximum concentration of charged particles amounts to $\sim 3$ orders of magnitude for water at $2,000^\circ\text{K}$, and about $3.5$ orders for argon at $2,500^\circ\text{K}$.

![Figure 13](image13.png)

**Figure 13.** Equilibrium ionization of $\text{H}_2$ and Ar: ---- accounting for $\text{H}_3^+$ formation; --- without accounting for $\text{H}_3^+$

It is interesting to note that in the curve for the over-all concentration of ions in water the ion concentration does not increase with temperature from $3,500$ to $4,500^\circ\text{K}$, and perhaps even decreases. This is accounted for by the effect of neutral dissociation reactions on the formation of $\text{H}_3\text{O}^+$. 482
The calculated equilibrium ionization values, taking into account the formation of $H_3O^+$ ions ($2.5 \times 10^8 \text{l/cm}^3$ at 1 atm and 2,300°K) appear to be close to the value obtained mass spectrometrically by Knewstubb and Sugden\textsuperscript{101} for a hydrogen flame ($10^9 \text{l/cm}^3$).

Another process that occurs in hydrogen/oxygen mixtures, and which is very important in connection with the equilibrium formation of $H_3O^+$, is

\[ H_2 + H_2 + O_2 \rightleftharpoons H_3O^+ + OH \] (48)

Thus, if we consider the combustion of a mixture with the composition investigated, for instance of 98 per cent of oxygen, the resulting equilibrium concentration of $H_3O^+$ will be very close to the experimental value.

As stated before, and as is evident from the curves of *Figure 12*, at sufficiently high temperatures there is no necessity to allow for the concentration of loaded ions in calculating the over-all equilibrium ion concentration. However, the importance of the formation of such ions for states far from equilibrium and, particularly, for the kinetics of the process leading to equilibrium, may be very great. For example, when the pre-exponential factors of the rate constants for reactions

\[ \text{Ar}^* + \text{Ar} = \text{Ar}^+ + \text{Ar} + \text{e} \] (49)
\[ \text{Ar}^* + \text{Ar} = \text{Ar}_2^+ + \text{e} \] (50)

are similar and the activation energies for these reactions are equal to their heats\textsuperscript{†} ($\Delta H_{48} = -15.8 \text{ eV}$; $\Delta H_{49} = -11.49 \text{ eV}$), the ratios of their rates will be $2.3 \times 10^4$ at $T = 5000^\circ\text{K}$ and $1.5 \times 10^2$ at $T = 10,000^\circ\text{K}$. Thus, even at very high temperatures, when ionization is due solely to Ar$^+$, the formation of the latter will proceed via the Ar$_2^+$ formation step.

**Surface ionization and “loaded” ions**

Gomer and Inghram discovered several years ago\textsuperscript{87} that in a strong electric field created close to the surface of a very fine tip, the ionization may proceed with molecules of very high ionization potentials. Beckey and Groth\textsuperscript{110} found recently that the ions emitted from such a source in CH$_3$OH ionization are in fact CH$_3$OH$^+$ ions. Thus it appears that reactions of the type

\[ \text{XH}^+ + \text{YH} = \text{XH}_2^+ + \text{Y} + \text{e} \] (51)

which are thermodynamically more favourable than simple ionization, occur at the surface.

It was found recently at Ionov’s laboratory of the Leningrad Physico-technical Institute\textsuperscript{111} that metallic surfaces heated to relatively low temperatures emit certain heavy ions, apparently of an organic nature (oil-vapour pumps were used in this work). The author believes that this interesting phenomenon can scarcely be explained without invoking certain processes of associative ionization. The endothermic heat of these processes will be even lower because of the electron or radical affinity of the surface.

\*\*\*\*\*\*\*\*\*\*\*\*

\textsuperscript{†} This is true as inverse recombination reactions are not activated.
V. L. TALROSE

To the extent of his capabilities and the time available the author has attempted to emphasize the essential results and trends of recent researches into ion–molecular reaction investigations; it is a fascinating field of chemical kinetics, and is highly favourable for combined studies of elementary and complex reactions.

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