[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Elementary Processes in Radiation Chemistry. I. Some Considerations of Mechanism of Electron Capture[1,2]

BY JOHN L. MAGEE AND MILTON BURTON

1. Introduction

High-energy particles and radiation give up their energy in matter primarily in two ways: by excitation and by ionization. The amount of energy dissipated per ion pair produced from molecules is roughly twice that of the ionization potential. Consequently, the energy is about equally divided to give the two processes. The phenomena of excitation are essentially those of photochemistry—although, in any particular case, of somewhat greater variety. The phenomena of ionization are characteristic of radiation chemistry.

Ensuant on ionization may be decomposition of a metastable positive ion so-produced, or discharge of that ion by a negative entity. These phenomena, and the subsequent chemical processes, were first discussed in some detail by Eyring, Hirschfelder and Taylor (EHT).[3] The EHT mechanism for that fraction of the process in which the ions initially produced are not decomposed is

$$A \longrightarrow A^+ + \epsilon \qquad \text{(I)}$$

$$A^+ + \epsilon \longrightarrow A^* \qquad \text{(IIa)}$$

or

$$A^+ + M^- \longrightarrow A^* + M \qquad \text{(IIb)}$$

$$A^* \begin{cases} \nearrow R + X & \text{(IIIa)} \\ \searrow B + C & \text{(IIIb)} \end{cases}$$

In this scheme, the A^+ ion of reactions (IIa) or (IIb) is recognized as having an average nuclear configuration different from the ion as initially produced in (I); A^* is a resultant excited molecule; M^- is a negative ion which may provide a mechanism for discharge of the positive ion; R and X are free radicals or atoms; B and C are stable molecules.

The EHT mechanism given has been repeatedly reviewed,[4] particularly in reference to the nature and the stability of A^* and the nature of the products produced. However, customarily the details of step (II) as well as of other important ion discharge processes, have not been discussed.

In this paper details of some simple discharge processes involving hydrogen are carefully examined. From such examination, it is found that discharge of an ion can take place under rather limited conditions; that the process may involve an activation energy; and that the mechanism of the discharge process has considerable bearing on the chemical effects of the irradiation.

These processes can be examined semi-quantitatively in the limited case of hydrogen. However, in radiation chemistry the behavior of more complicated molecules is more usually studied. Consequently a qualitative extension of the results to the case of such molecules is attempted and some conclusions are drawn by apparently reasonable analogy.[4a]

In this paper we concern ourselves exclusively with the effects of thermal electrons. Later we expect to consider effects of more energetic electrons. The majority of secondary electrons created by high velocity charged particles is produced with kinetic energy of amount less than that required to produce additional excitation.[5] The high energy recoil electrons will quickly lose their excess energy in various excitation processes. In most systems there will not be electron capture processes having cross sections large enough to capture these electrons before they are thermalized by means of elastic collisions. Thus, we expect usually to have large numbers of thermal electrons in irradiated systems.

Method of Attack on Problem.—Mechanism of the discharge process in any particular case may be seen from examination of pertinent potential energy curves. These curves are quite conventional but our method of consideration requires some explanation. Let us, for example, examine the discharge of the diatomic ion M_2^+ by a thermal electron to give M_2. The conventional potential energy curves are drawn for the systems $M + M^+$ and $M + M$ including all significant excited states. The system M_2^+

---

(1) Presented before the Symposium on Elementary Processes in Reaction Mechanism, Division of Physical and Inorganic Chemistry, San Francisco, California, March 28, 1949.

(2) A contribution from the Radiation Chemistry Project, originally operated under Department of the Navy, Office of Naval Research contract 165 T.O.II, now operated under Atomic Energy Commission contract AT(11-1)-38.

(3) H. Eyring, J. O. Hirschfelder and H. S. Taylor, (a) *J. Chem. Phys.*, **4**, 479 (1936); (b) **4**, 570 (1936).

(4) *Cf.* M. Burton, *J. Phys. Colloid Chem.*, **51**, 786 (1947); **52**, 564 (1948); Proc. Conference on Nuclear Chem., Chem. Institute of Canada, 179 (1947). Note that Essex (*cf.* N. T. Williams and H. Essex, *J. Chem. Phys.*, **16**, 1153 (1948)) repeatedly emphasizes that A^+ may be discharged, for example at the walls in a gaseous system, without further chemical reaction.

(4a) *Note added in proof:* It should be emphasized that this paper is purposely restricted to consideration of the interaction of an electron and an isolated molecule or ion. At pressures of relatively few millimeters, the electron frequently interacts simultaneously with an ion and a molecule because of the long range of coulomb forces. The excited particle produced may be stabilized by radiation as well as by inelastic collision. Alternatively, the type of decomposition process hereafter discussed in this paper occurs; the forms of potential energy curves described and their interpretation apply equally well in this case with the restriction noted that not all captures involve decomposition. The authors would like to thank Professors James Franck and Robert L. Platzman for reading this paper before publication. Professor Franck pointed out that this important process of bimolecular capture had been omitted from discussion—apparently inadvertently.

(5) H. Bethe, "Handbuch der Physik," Vol. 24, part 1, p. 517.

differs from M_2 by one electron but this apparent difficulty is easily removed. Let us add to the system M_2^+ a single electron (in the same box) which has approximately zero kinetic energy (*i. e.*, of the order of kT) when it is far away from M_2^+. Since the added electron is essentially at infinite distance most of the time, it cannot interact appreciably with M_2^+. Thus the shape of the M_2^+ potential energy curve is unaltered. Since the electron is thermal, the total electronic energy of the system is practically unaltered (*i.e.*, $RT \simeq 0.6$ kcal./mole). Thus, we give the usual M_2^+ potential energy curve for the system $M + M^+ + \epsilon$, where the free electron is "at rest" and at infinite distance.

M and M^+ are treated essentially as particles. The electron, however, must be treated as a wave. The positions of the particles during any phase of their approach, or of their vibration, are fixed by the particular point of the potential energy curve under consideration. This statement does not, however, apply to the electron. Because of its wave-like nature there is a certain probability that it will be anywhere in the box, either close to, or remote from, M or M^+ or the pair of them, at any instant. All regions of the box are accessible to the electron, although not necessarily equally accessible.

With this point of view, we can now examine the significance of a crossing of curves for the systems, M_2^+ and M_2. Such a crossing represents a configuration at which transition can occur between them. For example, if the electron (which pervades all the space of the box) is localized near M_2^+ at the instant it is in the configuration of the crossing, it may be captured and transition to the M_2 state may occur if the two states bear the proper symmetry and spin relations to each other. Thus, to see whether and under what conditions the molecule ion M_2^+ (or equivalently the system $M + M^+$) can capture an electron, one merely has to examine the potential energy curves for that molecule ion and for the possible products of its combination with an electron.

Mention has been made of a certain quantum mechanical probability of localization of the electron near M_2^+ during the instant of a crossing. When a system passes only once through a configuration corresponding to a crossing (where the transition is permitted), the probability of capture, which depends on localization of the electron, is extremely low. For example, in the case of H_3^+, if the electron concentration is as high as 10^9/cm.^{3} the probability for capture on such a crossing would be at most 10^{-10}. In other words, at the electron concentration indicated, an ion in a stable state could survive about 10^{10} crossings or about 10^{-3} sec.[6]

Thus far, we have mentioned explicitly capture of an electron by a system with a positive charge, but precisely similar statements could be made for capture by systems without charge or even for capture by systems with negative charge. In each case the potential energy curves under consideration would be the conventional potential energy curves with a thermal electron at infinite distance; *e.g.*, $M + M + \epsilon$ or $M + M^+ + \epsilon$. However, one special feature should be emphasized. Not all regions of the "box" are equally accessible to the electron. Coulombic repulsion between a negative system and an electron prevents their simultaneous occupancy of a small region of space or even of closely adjacent regions. The crossing of the potential energy curve of the system $M^- + M + \epsilon$ with that of the system $M^- + M^-$ can, in general, represent neither capture nor emission of a thermal electron.

In the light of these considerations, we shall not be surprised to find that electron capture processes are most probable when a positive ion is involved.

Potential Energy Curves.—Potential energy curves of the type required in this study have been used frequently and have been discussed at length in the literature. Consequently, minimum additional discussion is necessary here. The actual curves we have used in the figures of this paper were obtained in part from the literature and in part from our own calculations. The sources are given in the Appendix.

It might be well to emphasize that no claims can be made for absolute accuracy of the curves, because of the various uncertainties in calculations of this sort. It would certainly be unwise to extend their use without careful reference to the Appendix.

Relative Unimportance of Radiative Processes.—The non-radiative processes discussed in this paper are much more important than radiative capture of electrons. This topic is discussed in Part 5.

2. Electron Capture in Hydrogen and Its Ionization Products

In consideration of the significance of processes for radiation chemistry, two questions must be answered. One relates to the actual possibility of an isolated process. The other relates to the actual extent to which such a process need be considered as contributing in an important way to the over-all effect. Thus, for example, we can consider in a detailed way the interaction of H^+ ion and H^- ion even though under actual conditions of a reaction their concentrations are both so low that their mutual interaction can make no significant contribution to the total result. Repeated reference is made here to systems of just such type because they are nevertheless illustrative of processes which may occur in other systems, more complicated than those of hydrogen.

The principal purpose of this analysis of the hydrogen system is to elucidate more complex

---

(6) See Part 5.

problems of radiation chemistry. It is possible that, because of the magnitude of the approximations, conclusions we derive in certain cases regarding the hydrogen system *per se* may be in error. Nevertheless, we hope that the illustrative value of such conclusions and the applicability to more complex systems are not affected by possible inaccuracy of some of the details in the only system we can pretend at this time to examine in an adequately detailed manner.

The various possible processes are taken up in increasing order of complexity.[7]

$H^+ + H^+ + \epsilon$.—In Fig. 1 are given the curves for the H_2^+ system. An approach of the H^+ ions to each other (along the upper curve) which could correspond to electron capture occurs only at extremely high kinetic energies of the H^+ ions (*i.e.*, since there is a crossing at high values not shown). This is a result to be expected from very general considerations. Otherwise expressed, this statement is that the repulsion between two positive hydrogen ions is so great that they never come close enough to each other in a collision to coöperate in the capture of an electron in a radiationless process.

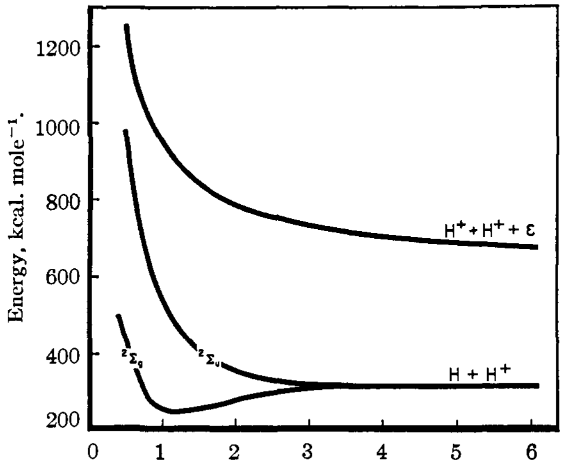

Fig. 1.—States of H_2^+.

$H + H^+ + \epsilon$; $H_2^+ + \epsilon$.— Figure 2 shows some of the curves for the system H_2. This figure includes two curves for $H^- + H^+$. Coulombic attraction for $H^- + H^+$ is important even at great distances. Consequently, the asymptotic dissociation limit is not approached on the diagram but is actually 16 kcal. mole^{-1} below the dissociation limit for H_2^+.

In this and in the following sections, the discussions are based only on the states chosen as representative. The choice is adequate to illustrate the various points we wish to make, but we should also emphasize that there are many other excited states. Some others are almost certainly important for a complete knowledge of the radiation chemistry of hydrogen. We do not deny the possibility of any process not specifically discussed.

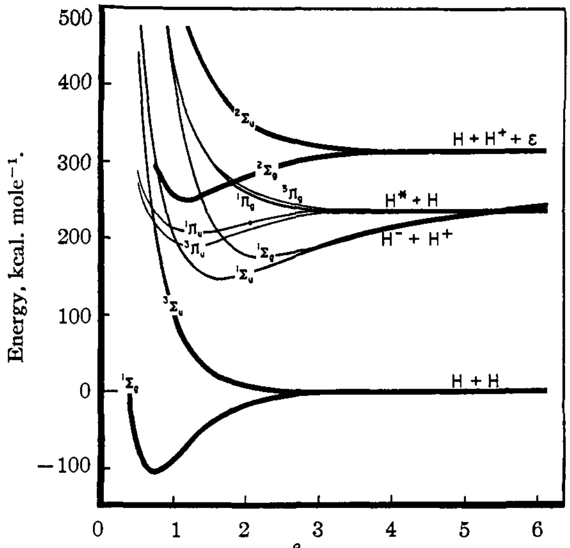

Fig. 2.—States of H_2.

Four points may be made: (a) Examination of the crossings of the H_2^+ attractive curve shows that capture of an electron in a collision of H^+ ion with H atom yields either H^+ and the negative H^- ion or a pair of H atoms, one of which is electronically excited.[8]

(b) Capture of an electron by the molecule ion H_2^+ may take place under a variety of conditions. H_2^+ in its lowest state can capture an electron (with very little activation energy) in a crossing to the polar $^1\Sigma_g$ state of H_2 below the asymptotic dissociation limit $H + H^+$. With E_a (activation energy) $\simeq$ 20 kcal. mole^{-1} capture can occur to either the $2p^1\Sigma_g$ state or the $2p^3\Sigma_g$ state, again below the asymptotic dissociation limit $H + H^+$. The products are actually H and H*. Capture to the $2p^1\Sigma_u$ state would require very roughly 40 kcal. mole^{-1} E_a; although this capture is energetically adequate to yield $H^+ + H^-$, this process yields only H and H*.[8] Obviously, production of H^+ and H^- by discharge of H_2^+ is energetically improbable. All processes by which H_2^+ is discharged are, on the other hand, at levels greater than the dissociation limit to yield $H(1^2S)$ and $H(2^2S)$, or $H(2^2P)$. Consequently, the corresponding reaction can only be

$$H_2^+ + \epsilon \longrightarrow H + H^*;\ E_a \simeq 0 \qquad (1)$$

---

(7) In the ensuant examination, the electron will not be counted as a particle in the reactions discussed. This treatment is analogous to that of the photon in photochemistry.

(8) Figure 2 is not complete. The Σ states of H* + H are not shown. Actually, they will be in the vicinity of the Π states, which are shown. The "crossing" of the Σ states of $H^- + H^+$ and the Π states of H* + H is real but the situation involving the Σ states of H* + H is more complicated. Interaction is such as to prevent "crossings" and thus a Σ state of H* + H which results from electron capture by the $H + H^+$ system *may* result in dissociation into H^- and H^+. Conversely, electron capture to yield, for example, the $^1\Sigma_u$ state of $H^- + H^+$ will give dissociation into H* + H.

The product atoms will each have about 10 kcal. mole^{-1} kinetic energy.

(c) The attractive state of H_2^+ crosses neither the $^3\Sigma_u$ (repulsive) state nor the $^1\Sigma_g$ (attractive) state of normal H_2. Consequently, H_2^+ cannot capture a thermal electron in an isolated process to yield either unexcited H_2 or two normal H atoms.

(d) Of the myriad of curves corresponding to various excited levels of H_2^* below H_2^+, only four are shown. Almost certainly, there are others which cross the attractive H_2^+ curve near its minimum and which in turn might interact with a suitable state (*e. g.*, $2p^1\Pi$) to yield unexcited H and H in its lowest excited state. Such crossings merely provide alternative paths for reaction (1). It will be seen in Section 4 that consideration of similar crossings is important for more complicated molecules.

These curves also throw light on the processes which can occur when the H^+ ion passes the H atom with some velocity or when the H_2^+ ion possesses rotational energy. The significant equation for the energy of the quantum state involved is

$$V_J(r) = V_0(r) + \frac{J(J+1)h^2}{8\pi^2\mu r^2} \tag{1}$$

where J is the rotational quantum, r is the distance between the H atoms and μ is the reduced mass. An intersection of two curves has meaning only when the J values of the two states are identical; the intersection itself represents the fact that the r values are identical. Thus, when two states cross in a way which permits a transition between them, the third term in equation (1) is identical for the two states. Consequently, the conclusion is that if two states intersect at a particular value of r when they have only zero-point rotational energy (*i. e.*, V_0 (r) identical), they intersect at the same value of r for any value of J (*i. e.*, $V_J(r)$ identical); thus, the crossing of two states is not affected as to position by angular momentum considerations.

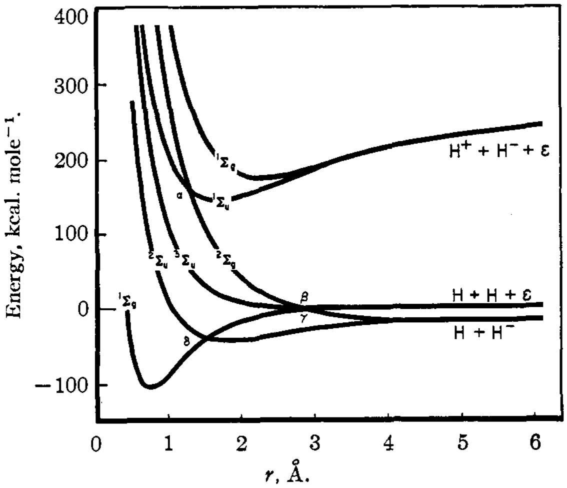

Fig. 3.—States of H_2^-.

The E_a for a capture process represented by a crossing corresponds to the vertical distance from the zero-point energy (approximately) of the initial state to the crossing. In general, this vertical distance is *not* invariant with changes in the J value. Practically, however, this conclusion is of little effect. We have seen that even in the case of H_2^+ there is a sufficient number of crossings near the minimum of the curve that some crossings can be found with $E_a \simeq 0$ which leads to H and H*. The crossing corresponding to $E_a \simeq 0$ may be to some different state for higher values of J; the products will be the same and only the path of reaction (1) could be changed by conferring angular momentum on the molecule ion.

$H^+ + H^- + \epsilon$; $H_2 + \epsilon$.—Figure 3 shows curves for the system H_2^-. Of the four crossings (α, β, γ, δ) shown, α and δ are of particular interest. Crossing α indicates that H^+ and H^- can capture an electron in a collision process to yield H and H^-.

$$H^+ + H^- + \epsilon \longrightarrow H + H^- \tag{2}$$

The ions H^+ and H^- can combine to give an excited state of H_2, which dissociates immediately into the parent ions, unless an electron is available for capture. The absence of crossing with either of the states of normal H_2 means simply that H^+ and H^- do not directly interact in a two-body process to give either two H atoms or H_2 molecule.

H atoms formed by either of the processes described have considerable kinetic energy and might react in the first collision with other molecules present provided the conditions of that collision are correct. In particular, the reaction

$$H' + H_2 \longrightarrow 3H \tag{3}$$

can occur; *i. e.*, discharge of the H^+ ion in the way described could lead to production (from two ions and a molecule) of three H atoms—although not very frequently.

Another conclusion is apparent from crossing δ. This crossing has been previously discussed by EHT[9] and by Hirschfelder.[10] The H_2 molecule can capture an electron to give H_2^- but the activation energy for the process would be about 65 kcal. mole^{-1}; this activation energy would have to reside in vibrations of the H_2 molecule—a rather unlikely event at ordinary temperatures. If H_2^- were formed in this way, it would be metastable and would have to be deactivated in collision to survive. However, even this possibility is remote for, as EHT indicate, the zero-point energy of H_2^- is ~1 kcal. mole^{-1}; *i. e.*, almost at the crossing point for loss of an electron to give the parent H_2. EHT also indicate that H_2 may capture a high-velocity electron (shown

---

[9] EHT, ref. 3a, say "The probability for $[H_2^-]$ to be formed is so low that it is not surprising that it has never been experimentally observed."

[10] J. O. Hirschfelder, *J. Phys. Colloid Chem.*, **52**, 447 (1948).

in Fig. 3 to be of energy >7 ev.) because of the Franck–Condon principle but the H_2^- so formed would be unstable and would dissociate immediately into H and H^- particles possessing very high kinetic energy. Thus, they in turn could furnish the requisite activation energy for a number of other reactions with other molecular species present. The reaction

$$H_2 + \epsilon(>7 \text{ ev.}) \longrightarrow H + H^- \qquad (4)$$

is significant because it does show a path by which H^- ion may be formed.

$H + H^- + \epsilon$.—Figure 4 gives the curves for the system $H_2^{=}$. This figure is included only for completeness. The wave function of a free thermal electron is vanishingly small at a distance of only 18 Å. from a negative ion and consequently the reaction

$$H^- + H^- \rightleftarrows H + H^- + \epsilon$$

cannot go either way. One can understand this observation from a classical consideration. The coulombic repulsion of H^- for an electron at this distance is 16 kcal. mole^{-1}, while the energy of the thermal electron is only 0.6 kcal. mole^{-1}. Thus it is clear that the electron cannot be involved in such a reaction.

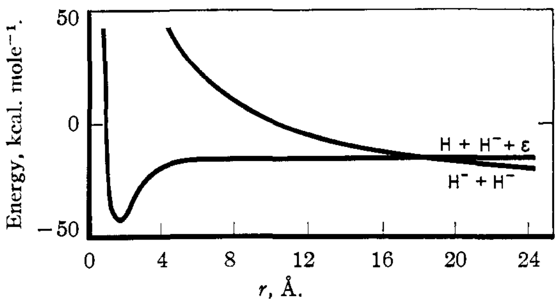

Fig. 4.—States of $H_2^{=}$.

It is generally true that slow electrons cannot react with any kind of negative ion.

$H_2 + H^+ + \epsilon$; $H_3^+ + \epsilon$.—Figure 5 shows the pertinent curves. The stable state of H_3^+ is triangular.[11] All the curves shown are for the approach of a hydrogen atom (or ion) perpendicular to the line of centers of the two other particles.

On the basis of these curves the discharge of H_2^+ in collision with H is utterly improbable—quite apart from the rarity of the collision itself. The reason is that the state of the system $H_2^+ + H + \epsilon$ is repulsive and does not cross any low-lying states of H_3.

Discharge of H_2 in collision with H^+ can occur without activation energy.

$$H_2 + H^+ + \epsilon \longrightarrow H_2 + H \qquad (5)$$

The extreme possibilities are transitions to $H_2(^3\Sigma) + H$ and $H_2(^1\Sigma) + H$. $H_2(^3\Sigma)$ dissociates immediately to yield two H atoms

$$H_2(^3\Sigma) \longrightarrow 2H \qquad (6)$$

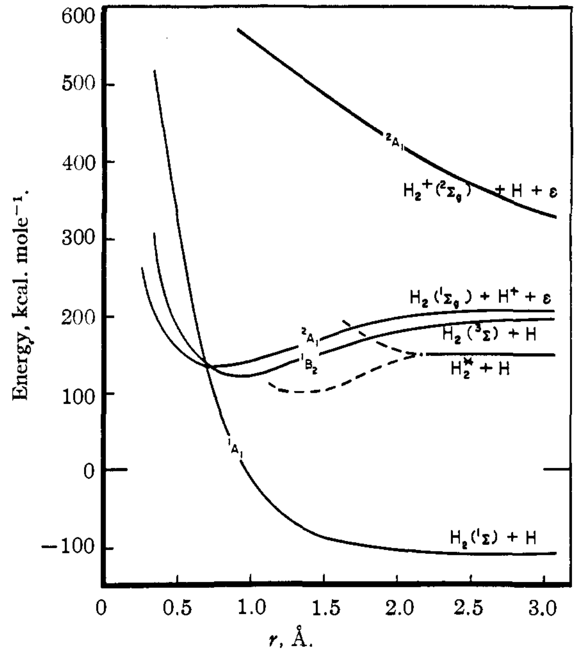

Fig. 5.—States of H_3.

When $H_2(^1\Sigma)$ is formed, the product partners in this case divide 312 kcal. mole^{-1} of excess energy. Much of this energy goes to the H atom. Subsequent collisions of the latter with other H_2 molecules (bond strength = 103 kcal. mole^{-1}) can result in production of two other H atoms. On the other hand (as we shall see in the discussion of $H_3^+ + \epsilon$), a substantial fraction of the $H_2(^1\Sigma)$ is primarily produced with energy exceeding 103 kcal. mole^{-1} and thus will also dissociate immediately into two H atoms.

One incomplete dotted line represents that one of the attractive states of $H_2^* + H$ which dissociates at the indicated energy. One of such attractive curves intersects $H_2 + H^+ + \epsilon$ somewhere near its minimum. Thus, there is a possibility that H_2^* is a product of reaction (5). The H_2^* so formed can be stabilized by radiation, but in gas at reasonably high pressure there is considerable probability that it may disrupt another H_2 molecule in a process akin to photosensitization. We might add that, since H_2^* is formed also in primary excitation processes by high-velocity particles, its fate is a matter of some considerable interest even though we do not discuss it here.

The H_3^+ ion corresponds to a low vibrational level on the $H_2 + H^+$ curve. In order to understand the phenomena which may occur in this case more detailed information is required than can be shown in Fig. 5. Figure 6 (see Appendix for discussion) gives the energy contour for the portion of the H_3 hypersurface which corresponds to the lower energy part of the system $H_2 + H^+ + \epsilon$ where the H_2 and H^+ approach in isosceles triangle configuration; *i. e.*, the approach

---

[11] J. O. Hirschfelder, *J. Chem. Phys.*, **6**, 795 (1938).

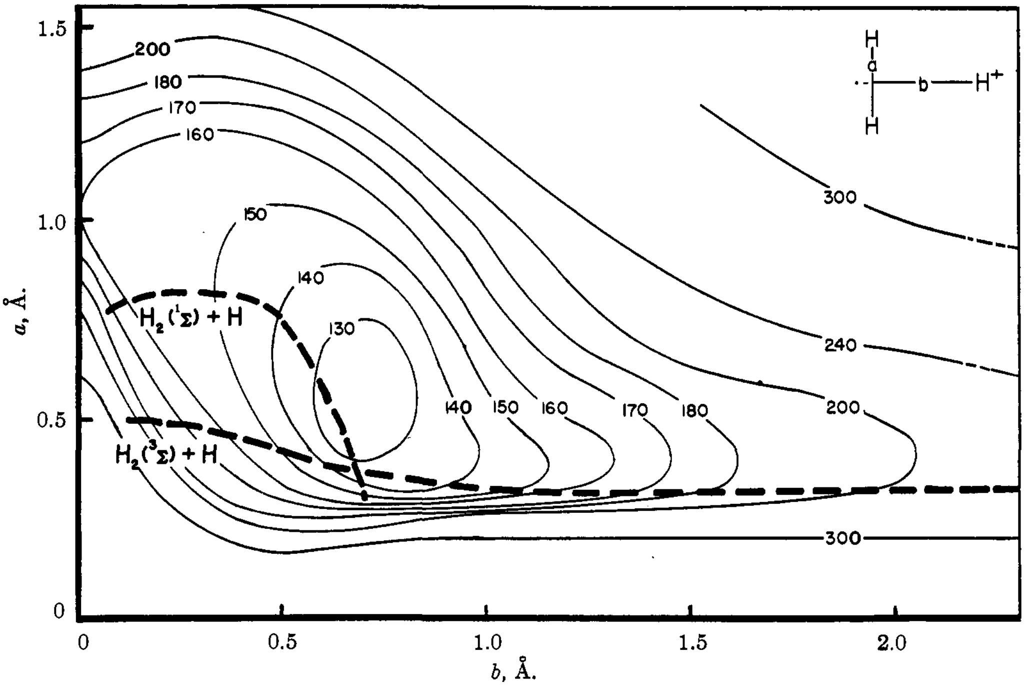

Fig. 6.—Isosceles $H_2 + H^+ + \epsilon$ energy surface intersections with $H_2(^1\Sigma)$ + H and $H_2(^3\Sigma)$ + H; contours in kcal. mole^{-1}.

which gives an energetic minimum corresponding to stable H_3^+. In addition, Fig. 6 includes the intersections with those portions of the same hypersurface which are described as $H_2(^3\Sigma)$ + H and $H_2(^1\Sigma)$ + H in Fig. 5.

Figure 6 is sufficiently precise to indicate that the transition from $H_3^+ + \epsilon$ to $H_2(^1\Sigma)$ + H is preferable. The intersection is practically at the minimum and several kcal. mole^{-1} lower than the minimum of the intersection with the $H_2(^3\Sigma)$ + H portion of the hypersurface. The conclusion is that the discharge of H_3^+ in its lowest energy state goes almost exclusively to yield $H_2(^1\Sigma)$ + H. Although $H_2(^1\Sigma_g)$ is attractive, the path of decomposition in that portion of the hypersurface which yields H_2 + H is so tortuous that the chances are probably high that it is formed with vibrational energy exceeding 103 kcal. mole^{-1}. Thus, we see that in this case, since the vibrational energy may be sufficiently great, the over-all reaction is frequently

$$H_3^+ + \epsilon \longrightarrow 3H \qquad (7)$$

although the path is actually via the attractive $^1\Sigma_g$ state.

Discharge of H_2^+ **by** M^-.—Reference to Fig. 3 shows that sufficiently energetic bombardment of H_2 by an electron may yield H_2^- with immediate dissociation to H and H^-. On the other hand, H_2^- cannot be formed in a stable state by any readily evident process. Since the only negative ion available is thus H^-, we have only to consider the nature of the reaction $H_2^+ + H^-$. Regarding the specific details of this reaction we make only the following statement: The most probable reaction yields at least one of the products in an excited state.

Some idea of the nature of such a reaction could be obtained by calculation of a curve for $H_2^+ + H^-$ and adding it to Fig. 5. However, in this case such detailed calculation is not necessary for our immediate purpose. The $H_2^+ + H^-$ system is attractive with a minimum at large distances (2–3 Å.) and repulsive near 1 Å. with an energy of the order of 350 kcal. mole^{-1}. If the reader would sketch such a curve on to Fig. 5, he would see that there are simply no low-lying intersections with unexcited states. Detailed contours (such as are shown in Fig. 6) would indicate possible transition from the $H_2^+ + H^-$ portion of the hypersurface only to portions for excited systems (*e. g.*, $H_2(^3\Sigma_g)$, attractive, + H) which are not shown in Fig. 5. Although H_2^+ could conceivably be discharged by H^- in a radiative process, the probability of such a process is relatively extremely low. On the other hand, curves such as suggested show that the reaction $H_2^+ + H^- \rightarrow H_2$ (normal) + H is not possible. The same curves would show that the only possible mechanism of discharge of H_2^+ by H^- involves the production of an excited molecule $H_2^+ + H \rightarrow H_2^* + H$ in a continuous transition within the same hypersurface.[12]

---

(12) As a practical matter, some such reaction is conveniently assumed to account for the continuous emission spectrum in a hydrogen discharge tube. H_2^* is the source of the radiation attributed to the transition $^3\Sigma_g \longrightarrow {}^3\Sigma_u + h\nu$. The $H_2(^3\Sigma_u)$ ultimately formed is in the lowest repulsive state; *cf.* W. Finkelnburg, *Physik. Z.*, **34**, 529 (1933).

The conclusion for radiation chemistry is that a discharge process involving a negative ion will almost always result in the production of an excited molecule. However, we cannot on the basis of our present approach to the problem state categorically that reaction (IIb) can occur only in that form. Either

$$A^+ + M^- \longrightarrow A^* + M$$

or

$$A^+ + M^- \longrightarrow A + M^*$$

might occur.

3. The Contribution of Negative Ions

In the previous section we have examined the mechanism of discharge of H_2^+ by negative ions. However, we have also seen that there is little tendency to form either H_2^- or H^- ions from the interaction of electrons with H_2. Consequently one expects that the discharge of positive ions by negative ions in this system is relatively unimportant, and that the principal discharge mechanism will be the capture of electrons by positive ions. This same situation holds for many other systems, for example saturated hydrocarbons. In other words, there are certain systems in which the effects of negative ions are expected to be small.

It is true that in many cases negative ions are very important and reaction IIb will furnish the principal discharge mechanism. Oxygen gas is undoubtedly such a system, for example. This situation will prevail when the capture of electrons in neutral molecules of the system is a very probable process. Bradbury[13] and Massey[14] have investigated and discussed the capture of electrons in molecules. We shall not consider the problem in this paper.

In a given system the important discharge process will be either reaction (IIa) or reaction (IIb), and probably never a significant contribution from both simultaneously. Here we have been discussing the mechanism of (IIa) exclusively. In a later work we shall consider effects of negative ions.

4. Complicated Molecules

The illustrations afforded by consideration of hydrogen atoms, ions, and molecules have the advantage of simplicity. In some cases, they are so simple as to appear almost trivial. Their principal value is as a guide in considerations of more complicated cases. It must be emphasized that for polyatomic molecules we deal with hypersurfaces, that the intersections are complicated, and that any particular curve which can be drawn on a plane represents a condition where all the bonds except those under particular examination are frozen. Nevertheless, some conclusions can be drawn by analogy to the very simple case of hydrogen.

We consider the H_2^+ ion and the H_3^+ ion and draw inferences about the more complicated reaction $M^+ + \epsilon$, where M is a large molecule. In the last case, unlike the first, ultimate molecules and molecule ions may also be among the products and, in principle, we may expect a larger variety of possible radical and radical ion products. If we consider the factors which affect the probability of the various reactions, we see that, apart from unnecessarily involved speculations, there are some simple statements that can be made.

1. Usually, one ultimate-molecule pair A + B is energetically so much lower than all other such possible pairs that we need consider that possibility alone (*cf.* the decomposition of a fatty acid into carbon dioxide and a paraffin hydrocarbon).
2. There are very many ways in which M^+ can capture an electron to yield A + B where either one of them is excited to a variety of possible levels, whereas there are very few ways, if more than one, in which it can capture an electron to yield the unexcited molecule partners.
3. Above a certain energy determined by the bond strengths involved, the variety of radical partners near a given energy level can, in general, be large.
4. Any or all of the attractive and repulsive hypersurfaces for the arbitrary pairs $R_i + X_i$, one of which may be excited, can intersect the hypersurface for M^+ and many of them do so near the zero-point level of M^+.

These considerations lead us to propose the following apparently reasonable conclusions: (a) The unexcited molecule pair A + B is almost never formed, since it can be produced by only one path (*i. e.*, from only one intersection). (b) The pairs $A^* + B$ and $A + B^*$ are formed relatively infrequently, although there are many more possibilities for these processes. (c) A radical pair $R_i^* + X_i$ or $R_i + X_i^*$ is formed almost invariably since there are the most possibilities for this reaction.

It is interesting to examine the liquid state in a detailed manner. This effect has already been discussed by one of us.[15] Essentially, the ideas of Franck and Rabinowitch apply. An excited molecule M^* may be formed by electron capture and with insufficient energy to dissociate. The state may lose energy of the order of kT to its surrounding molecules while near the extremities of its vibration. Transition occurs to an attractive lower lying level (which may be only weakly attractive) and ultimately, by a process of collisional deactivation, transition to a stable excited level occurs. From this level, fluorescence may occur if the selection rules permit. Alternatively, in one phase of the vibration, crossing of a re-

---

[13] N. E. Bradbury, *J. Chem. Phys.*, **2**, 827 (1934); N. E. Bradbury and H. E. Tatel, *ibid.*, **2**, 835 (1934).

[14] H. S. W. Massey, "Negative Ions," Cambridge University Press, 1938.

[15] M. Burton, *J. Phys. Colloid Chem.*, **52**, 564 (1948).

pulsive state of two stable molecules may occur. While such a process is relatively improbable, compared to free radical decomposition its relative probability may be enhanced in the liquid state. Obviously, only the most favored transition will occur to any great extent and we would consequently expect that in liquids a preferred path of decomposition into ultimate molecules should be detectable just as has been found for the fatty acids.

5. Electron Capture Probabilities

In Part 1 a non-radiative electron capture was treated as an ordinary non-adiabatic chemical reaction. From this point of view, the electron is captured from a standing wave eigenfunction (which fills all the container) as the nuclei pass through a crossing point. In appropriate cases the Zener–Landau formula for the probability of non-adiabatic processes will apply.[16] The probability for capture on each passage of the nuclei through the crossing point is given by

$$P = 1 - \exp\left\{ - \frac{4\pi^2|\epsilon|^2}{hV|S|} \right\} \qquad (2)$$

Here $|\epsilon|$ is the absolute value of the quantum mechanical matrix element connecting the free and bound states of the electron; h is Planck's constant; V is the nuclear velocity; and $|S|$ is the absolute value of the difference in slope of the two potential curves at the crossing point.

For this formula to be valid, there must be approximately "classical" motion of the nuclei; *i. e.*, the vibrational quantum numbers of both initial and final states must both be large. The transition from a high vibrational state to a dissociated state would usually meet the conditions.

The principal advantage in using this point of view is that of the unification of electron capture reactions with the more ordinary chemical processes and the determination of reaction mechanisms and products. It is difficult to make actual calculations of capture probabilities and little progress has been made in this direction. For the purpose of comparison with available experimental data, it is easier to follow the more customary procedure and describe phenomena in terms of "cross sections" and "probability per collision" of the electron with the molecule or ion. The number of captures of a certain type per unit volume per second is given either by

$$\omega_i = \nu_i P_i N_i \qquad (3a)$$

or

$$\omega_i = \sigma_i v N_e N_i \qquad (3b)$$

N_i is the number of molecules or ions per unit volume which undergo the ith type reaction; ν_i is the number of times per second the nuclei pass through the crossing point; P_i is the transition probability. In terms of a cross section σ_i for the same process we have expression (3b); N_e is the number of electrons per unit volume and v is their velocity. In general σ_i will depend on v, but for our purpose we can assume that all electrons have the average thermal velocity 10^7 cm./sec. Of course, ν_i will be approximately 10^{13} sec.$^{-1}$ for most processes, since this is the order of molecular vibration frequencies.

Unfortunately there are no experimental data for the cross sections of most interest in the present discussion. Measurements of electron cross sections at thermal energies have not been made at all. There are reasons to believe that the cross section for an electron capture such as

$$H_3^+ + \epsilon \longrightarrow 3H \qquad (7)$$

is considerably larger than most examples one finds in the literature for electron capture such as

$$O_2 + \epsilon \longrightarrow O_2^- \qquad (8a)$$

or

$$O_2 + \epsilon \longrightarrow O + O^- \qquad (8b)$$

Reaction (8a) forms a stable O_2^- molecule in some particular vibrational state. Consequently the initial electron energy must be carefully adjusted or the capture is not possible at all, and the average cross section for a group of electrons with a distribution of velocities must be very small. Bradbury[17] finds the cross section to be approximately 10^{-20} cm.^{2} for a certain distribution of electrons having average energy of the order of one volt, or a probability of capture per electron collision of about 10^{-4}.

Reactions of the type (8b) are expected to have larger cross sections in general since the final state is not quantized and any electron (provided it has at least threshold energy) can be captured. This particular reaction has a cross section of about 10^2 greater than (8a).[18]

Another factor which makes cross sections large is the presence of a net positive charge on the capturer. This is especially important for slow electrons. Since reaction (7) is of this type and is furthermore accompanied by dissociation, it is expected to have a very large cross section. According to the contour of Fig. 6 it would appear probable that there is no activation energy involved. This reaction may take place on almost every electron collision. The maximum possible cross section is

$$\sigma_{\max} = \pi(\lambda/2\pi)^2$$

Where λ is the de Broglie wave length of the electron. For thermal electrons

$$\sigma_{\max} \approx 10^{-13}\text{cm.}^2$$

If there are 10^9 electrons per cm.^{3}, the specific rate of capture as given by (3b) is

$$\omega/N(H_3^+) = 10^{-13} \times 10^7 \times 10^9 = 10^3$$

---

[16] C. Zener, *Proc. Roy. Soc. (London)*, **A137**, 696 (1932); **A140**, 666 (1933); L. Landau, *Phys. Z. Sovjetunion*, **1**, 88 (1932); **2**, 46 (1932).

[17] N. E. Bradbury, *Phys. Rev.*, **44**, 883 (1933); *J. Chem. Phys.*, **2**, 827 (1934). See also F. Bloch and N. E. Bradbury, *Phys. Rev.*, **48**, 689 (1935), and Massey's discussion in reference 14, pp. 60 ff.

[18] H. S. W. Massey, ref. 14, p. 53.

Now using (3a)

$$10^3 = 10^{13} P$$

or $P = 10^{-10}$ as mentioned in the discussion of Method of Attack on Problem in Part 1.

Radiative Capture.—This process has been neglected in the above considerations since it has a smaller probability than most of the non-radiative processes of interest. The actual magnitude of the cross section depends upon the type of transition involved (*i.e.*, whether the final state of the atom is S or P, since these are the only cases of usual interest) and whether the capturing system has a net positive charge or not.[19] However, for electron energies of approximately one volt or so, all radiative capture cross-sections are about 10^{-22} cm.^{2} This means that the *probability* of radiation on collision with electron capture is $\approx 10^{-6}$ or less, since the total collision cross section is approximately 10^{-16} cm.^{2}.

For thermal electrons with energies about 1/40 ev. the cross section is somewhat higher. As an example we can give below an equation for the cross section of the process

$$H^+ + \epsilon \longrightarrow H(^2S) + h\nu$$

$$\sigma = \pi a_0^2 \frac{32}{3\sqrt{3}} \left(\frac{1}{137}\right)^3 \frac{I^2}{h\nu \times E} \text{ cm.}^2 \tag{4}$$

Here a_0 is the Bohr radius, or 0.529×10^{-8} cm. Of course, the energy of the quantum $h\nu$ and the energy of the incident electron are related to the ionization potential of the H atom by the relation

$$h\nu = E + I$$

For an electron having an energy 5 ev., $\sigma = 4.5 \times 10^{-22}$; for 1/40 ev., $\sigma = 1.2 \times 10^{-19}$ cm.^{2}. It is unlikely that any other radiative capture process of interest has a value appreciably greater than this. Noting from the previous section that $\sigma_{\max}$ is 10^{-13} cm.^{2}, we see that the probability of radiative capture on collision even for thermal electrons remains at $\sim 10^{-6}$.

Equation 4 is obtained by using a semi-classical treatment of the absorption coefficient of hydrogen-like atoms. It should hold approximately for H_2^+ and H_3^+ if the proper values of I are used.

6. Appendix. Potential Energy Curves and Surfaces

The systems H_2^+, H_2, H_2^*, H_2^-, H_3^+, H_3, have all been considered previously, most of them by several different investigators. In this paper the emphasis has not been upon the quantitative features of the potential surfaces. We have, however, made a reasonable effort to have all essential features correct, since we are interested in the location of crossing points. Where possible, we have taken published results for our curves and surfaces. When these could not be found, we made the simplest calculation consistent with our aims.

The sources of the various curves are given below along with appropriate comments.

H_2^+.—This has been given by Teller.[20]

H_2.—($^1\Sigma_g$), normal state, is given by Herzberg.[21]

($^3\Sigma_u$), triplet repulsive state, is given by Sugiura.[22]

($^1\Sigma_u$), the "B state", is the end state for the most intense ultraviolet absorption of H_2. Although this state has been discussed many times,[23] we could find no complete potential curve. The curve used here was calculated with the polar wave function

$$\Psi = a(1)a(2) - b(1)b(2)$$

where $a(1)$, $b(1)$ are 1 S hydrogen-like wave functions. No parameter was varied. Since this simple treatment does not give the correct electron affinity of the H atom and consequently does not give the correct dissociation energy, the calculated energy was lowered everywhere by the amount necessary to give the correct asymptotic limit for dissociation into H^+ and H^-. The B state, of course, actually dissociates into one normal H atom and one excited H atom (2 quantum p states). The interaction with all 2 quantum states was ignored.

The subtraction of a constant energy so as to get the correct dissociation energy was done by Pauling[24] (for He_2^+) and Eyring, Hirschfelder and Taylor[3] (for H_2^-).

($^1\Sigma_g$) is an ionic state. Herzberg discusses this state and its interaction with the ground state (ref. 21, p. 399). Our curve was calculated as the upper energy of a quadratic secular equation, using the simple functions

$$\Psi_1 = a(1)b(2) + a(2)b(1)$$
$$\Psi_2 = a(1)a(2) + b(1)b(2)$$

A constant energy was subtracted, as for the B state, to give the correct asymptotic energy for dissociated $H^+ + H^-$.

H_2^*.—There are numerous excited states of H_2. We chose, as illustrative, four Π states which had been calculated by Kemble and Zener.[25] The ($^1\Pi_u$) state is the end state for strong ultraviolet absorption (the Werner bands).

H_2^-.—($^2\Sigma_u$) is taken from Eyring, Hirschfelder and Taylor.[3] ($^2\Sigma_g$) is calculated with the wave function

$$\Psi = \begin{pmatrix} a & a & b \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} a & b & b \\ \alpha & \beta & \alpha \end{pmatrix}$$

There was a subtraction of a constant from the energy to give the correct asymptotic limit.

H_3^+.—All energies for H_3^+ were obtained from

---

[19] A discussion is given in reference 12, pp. 30–35. See also H. S. W. Massey and R. A. Smith, *Proc. Roy. Soc.* (*London*), **A155**, 472 (1936).

[20] E. Teller, *Z. Physik*, **61**, 458 (1930).

[21] G. Herzberg, "Molecular Structure and Molecular Spectra," Prentice-Hall, New York, N. Y., 1939, p. 106.

[22] Y. Sugiura, *Z. Physik*, **45**, 484 (1927). This repulsive curve lies somewhat too high, since it comes from a simple Heitler–London calculation. See H. M. James, A. S. Coolidge and R. D. Present, *J. Chem. Phys.*, **4**, 187 (1936).

[23] C. Zener and V. Guillemin, *Phys. Rev.*, **34**, 999 (1929).

[24] L. Pauling, *J. Chem. Phys.*, **1**, 56 (1933).

[25] E. C. Kemble and C. Zener, *Phys. Rev.*, **33**, 512 (1929).

the papers of Hirschfelder and collaborators on the subject.[26]

H_3.—The only use of H_3 energies was to determine the crossing points with the H_3^+ contour (Fig. 6). In view of the extreme difficulty in calculations involving three electrons and three centers, an empirical method was used. The London formula

$$E = q_1 + q_2 + q_3 \pm \frac{1}{\sqrt{2}}\sqrt{(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_2 - \alpha_3)^2}$$

was assumed to give the energies of the two H_3 surfaces of interest. This formula only takes into account interaction of pairs of atoms in the complex. The values of q (coulombic energy) and α (exchange energy) for a pair were obtained from the two lowest potential curves of H_2. It was assumed that

$$E(^1\Sigma_g) = q + \alpha$$
$$E(^3\Sigma_u) = q - \alpha$$

Energies obtained in this way agreed satisfactorily with those calculated by Hirschfelder, *et al.*,[26] by more complicated means.

Clearly much reliance cannot be placed on the quantitative features of Fig. 6. It can be pointed out, however, that due to the nature of the surfaces, the crossings must be approximately correct. The H_3^+ surface is near a minimum at the crossing point, while the H_3 surfaces are rising very steeply. Thus the interatomic distances indicated in Fig. 6 probably give the crossing points with rather good accuracy. The precise energy values, on the other hand, are much less well known.

Acknowledgment.—The authors are indebted to Priscilla Magee for her generous assistance in the computations.

Summary

1. For purposes of this study, capture of an electron by a molecule or ion is treated as a non-adiabatic chemical process.

2. Necessary potential energy curves are given for application of this method to hydrogen systems. A contour surface is calculated for the isosceles H_3^+ system (plus an electron) and the intersections of that surface with the isosceles $H_2(^3\Sigma) + H$ and $H_2(^1\Sigma) + H$ surfaces have been calculated to a required degree of approximation.

3. It is shown that probability of non-radiative capture of an electron by a positive ion exceeds that of radiative capture by a factor of 10^6.

4. Capture of an electron by normal H_2^+ leads with maximum probability to one normal and one excited H atom.

5. Capture of an electron by normal H_3^+ considerably favors transition to the $H_2(^1\Sigma) + H$ state rather than to the $H_2(^3\Sigma) + H$ state because of a sensible activation energy difference between the two processes. No comparison is made with the probability of transition to the system $H_2^* + H$, although it is shown that transitions of this class are important for complicated-molecule systems. The transition to $H_2(^1\Sigma) + H$ leads to immediate dissociation into three H atoms.

6. Capture of an electron by an isolated complicated-molecule ion appears to lead in most cases to immediate dissociation into two particles, one of which is excited. Dissociation into radicals is favored over dissociation into molecules. In the liquid state the ultimate molecule mechanism increases in relative importance.

NOTRE DAME, INDIANA RECEIVED AUGUST 4, 1949

---

(26) J. O. Hirschfelder, H. Eyring and N. Rosen, *J. Chem. Phys.* **4**, 130 (1936); J. O. Hirschfelder, H. Diamond and H. Eyring, *ibid.* **5**, 695 (1937); D. Stevenson and J. O. Hirschfelder, *ibid.*, **5**, 933 (1937); J. O. Hirschfelder, *ibid.*, **6**, 795 (1938).

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

An Experimental Technique for Micro-conductometric Analysis of Moving Boundary Systems

BY HARRY SVENSSON[1]

Introduction

In the electrophoretic analysis of a protein mixture by the Tiselius method[2,3] each peak in a pattern, except that due to the δ or ϵ effect, corresponds to a boundary in which the concentration of one of the proteins falls to zero with increasing height in the channel. Moreover, the area under this peak is taken as proportional to the concentration of the protein that thus "disappears" in the boundary. At each of the moving boundaries the theory[4,5] of ionic migration requires, however, the superposition, upon the concentration gradient of the disappearing ion, of gradients of all other ion species that are present. These superimposed gradients, which are comparatively small under the conditions of standard electrophoresis, not only introduce an error into the analysis but are also largely responsible for the conductivity changes at the

---

[1] Present address: Institutes of Physical Chemistry and Biochemistry, University of Uppsala, Uppsala, Sweden.

(2) Tiselius, *Nova Acta Reg. Soc. Sci. Upsal.*, IV, 7, No. 4 (1930).

(3) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(4) Svensson, *Arkiv. för Kemi, Mineralogi och Geologi*, **17A**, No. 14 (1943); **22A**, No. 10 (1946).

(5) Dole, THIS JOURNAL, **67**, 1119 (1945).