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THE EXCITATION AND IONIZATION PRODUCTS OF RADIATION

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INTRODUCTION

Although the discovery of x-rays and radioactivity, and the developments which followed, led to considerable work in the early years of this century in the fields of radiation biology and chemistry, the discovery of the chain reaction in uranium has initiated a new interest in these studies. The phenomenon of nuclear fission has become a practical instrument in the development of nuclear weapons, power sources, and important research tools. Many of these applications are limited by the biological and chemical implications.

A fairly satisfactory understanding of the nature of radiations has been attained. In fact, over-all pictures of the energy distributions of radiations in macroscopic portions of matter may be drawn. However, no detailed information exists regarding effects on large groups of atoms or complex biochemical substances. Even the simplest reactions, when induced by high energy radiation, become a very complex problem. The difficulty is that high energy radiation loses its energy in hundreds of steps, producing a wide range of excited and ionized molecules with different energies. Of course, monochromatic light (2-10 ev) produces a unique excited state which causes a photochemical reaction, and is relatively simple to analyze.

Another cause for complexity is the fact that many of the observed products are formed, not directly by the incident radiation but indirectly by secondary or succeeding radiations produced by the primary.

PRIMARY EFFECTS OF RADIATION

Excitation: An isolated atom can only exist in certain well-defined states, the so-called quantum states of its electronic system. Each of these states has its own characteristic set of properties, including total energy, total angular momentum of the electrons relative to the nucleus, and total (average) lifetime for spontaneous radiation, among others. Since the most important

property is the energy, the states are often called energy-levels. In principle, of course, there are an infinite number of energy levels.

The tightly bound electrons, i.e. those closest to the nuclei of heavy atoms are usually of little importance and have not been extensively investigated.

Transitions between states can take place by emission or absorption of electromagnetic radiation, or in impact with other systems. The excitation of these valence atoms involves energy differences of about 3-20 ev.

For a particular incident radiation, there are different probabilities for each transition. Some transitions are very rare and are termed "forbidden". If all the transitions from a given state are forbidden, it is termed a metastable state. Since transitions by emission or absorption of radiation are equal, excitation to a metastable state does not occur in this manner. Metastable states can, however, be very efficiently produced in some cases by collision with a slow electron. Very fast electrons though, show the same excitation probabilities as optical radiation. Slow moving heavy particles, either charged or uncharged, can also excite atoms on impact if their kinetic energy is higher than the particular excitation energy. This is termed a "collision of the first kind". An atom can also be excited by collision with another atom of the same or different species which is already excited. This process is termed a "collision of the second kind" for the atom which loses its excitation energy. It will be treated in more detail later.

There are other methods by which excited atoms are formed - namely, by dissociation ionized molecules, as products of the recombination of positive and negative ions, as products of the attachment of electrons to neutral molecules, and as products of elementary reactions involving nonexcited atoms and molecules (leading to chemiluminescence).

Ionization: An atom or molecule is said to be ionized when an electron is removed or added to the atom. Under intense radiation sources the effect of negative ions is negligible since their probability of formation and average lifetime are both low. We will therefore concentrate on the positive ion formation. This can result from absorption of a photon or from an impact with a charged particle if the energy transferred is sufficiently great. This minimum energy is defined as the ionization potential and varies from 3.9 ev to 24.6 ev. This, for a molecule is actually the "vertical ionization potential", the difference in energy between the original molecule and the positive ion when each have the identical configuration of atoms. The "adiabatic ionization potential" is the difference in energy between the lowest states of the molecule and the positive ion. The difference between these two definitions is a direct consequence of the Franck-Condon principle.

This principle is in turn a consequence of the application of the law of conservation of momentum with the additional recognition of the vastly smaller mass of a nucleus. It applies to atomic and molecular processes, both those involving emission and absorption of radiation, and those occurring in impacts. It states that ionization or excitation occurs without any change of internuclear separation during the very short time required for the motion of the electron. Applying this to the ionization of a molecule, we see from the potential curves, (Fig. 1) that a transition to the ionized state via a straight, vertical line produces a higher than ground state ionized molecule. In many cases, this excess energy leads to dissociation, as we will see later. There is a probability of a transition from the lowest vibrational state of one to the lowest vibrational state of the other. This has been measured. It has also been calculated approximately using quantum-mechanical methods. The diatomic molecule is treated as an anharmonic oscillator, and the vibrational wave functions for different vibrational levels have the form shown in Figure 2.

The probability of transition from a state having a wave function ψ'' to a state having a wave function ψ' is given by

$$P = \left| \int \psi'' F \psi'^* d\tau \right|^2$$

where F (a function of E, r, θ , and ϕ in spherical coordinates) represents a perturbing function associated with the bombarding electron. F also depends on the nature of the two nuclei. By a series of approximations, the wave function ψ for a molecule is separated into the product of an electronic wave function, a vibrational wave function, and a rotational wave function. Further simplifying assumptions enable one to arrive at the equation

$$P = G \left[\int \psi_v'' \psi_v' dr \right]^2$$

For polyatomic molecules the general picture is the same. All the different internuclear separations must be taken into account, and a potential diagram such as in Fig. 1 must be plotted in multi-dimensional space. A more detailed discussion of ionization can be found in Mass Spectrometry by Robertson.

Nuclear Collisions: Although excitation and ionization are ordinarily the dominant processes for media composed of simple molecules, complex molecules of high molecular weight sometimes impose important differences. For instance, they may be resistant to the effects of small energy transfers. In such cases, noticeable reaction can be produced by the cumulative effect of small energy transfers, which is related to the specific ionization at the point, or by a large energy transfer due to some other process.

When any high-energy radiation penetrates a medium, there is an interaction between the Coulomb fields of the particle and the nucleus of the atom. This is customarily called a nuclear collision. In light media, the collision is very apt to remove the atom from its molecule. This process usually does not amount

to very much when comparing energy losses by various processes. But it is effective, for instance, in the disordering of the structure of a solid substance by heavy, charged particles.

Multiple Ionization: A complete analysis of multiple ionization has not been done to date. Although multiple processes produced by consecutive impacts of two different particles of radiation are neglected, the effect due to a single event has been observed. However, the simplifying approximations that one usually is obliged to use for the possible stationary states of the affected atom is such that the probabilities of multiple excitation and ionization is automatically zero. Multiple effects are rarely seen in a spectrograph since a doubly ionized molecule generally has a strong probability of forming two ionized radicals. This is observed to occur after double ionization following the Auger process.

Capture and Loss of Electrons by Positive Ions: A mode of energy loss peculiar to positively charged particles is the capture of an electron from a molecule into a discrete orbit about the particle and its subsequent loss in a later collision. This is the principle mode of energy loss for an alpha particle between 1 and 500 kev. Since the overall effect is one of a formation of an ion pair, and the total energy loss is small, the process is unimportant in chemical and biological reactions.

Auger Disruptions: The Auger process is a very remarkable one, and may play a significant role in radiation chemistry and biology. The tendency is for high-energy radiation to lose its energy to the valence electrons. A measurable portion, though, is transferred to inner electrons. In heavy atoms the result will be the emission of x-ray photons with the outer electrons dropping into the succeeding vacancies. In light atoms such in C, N, or O, the creation of a K-shell vacancy is followed by a radiationless transition in which an L electron drops into the vacancy and a second L electron is ejected from the atom. This process takes place in about 10^{-15} sec. A radiative transition ordinarily takes

10^{-8} sec. Therefore it is no surprise that the probability of the radiative transition is so low that a radiation yield of less than 1% in C, N, and O atoms is observed.

In large molecules, the total energy transferred to the molecule (284 ev for C, 400 ev for N, 531 ev for O) is retained. The Auger electron, or electrons, as the case may be, since enough energy might be present to eject two or more electrons, is often absorbed in the same molecule (within about 10^9 A°). Since the speed of these electrons is about 10^9 cm/sec (for 100 ev electrons), they are reabsorbed in about 10^{-15} sec. Therefore, the whole process is over before molecular rearrangement can occur.

The importance of the Auger process lies in the fact that a large amount of energy is communicated to a small region of space --- a single molecule or a portion of a large molecule. This might produce an effect usually ascribed to Delta rays, which transfer relatively much energy to a small volume.

REACTION PRODUCTS

Reactions between molecules proceed when the activation energy is available. The rate of a reaction can be increased by raising the temperature of the system. This increases the number of molecules having energies greatly in excess of the average (by the Maxwell - Boltzman distribution). The molecules can absorb energy by electronic excitation. Some of the molecules are electronically excited while others are ionized. The excited molecules can either dissociate or transfer their energy into kinetic energy of the constituents of the molecules. They would then behave chemically like molecules at high temperatures. Ions similarly produce radicals or molecular products, either directly or as a result of recombination.

Although it is presently the theory that radiochemical reactions proceed as a consequence of the steps just mentioned, this was not always the case. In 1907, Bragg noticed that the number of molecules of liquid water decomposed by radon was equal to the number of ions which the same amount of radon would have formed in air. He did not subscribe any importance to this "curious parallelism in numbers". Lind, in 1918, systematized the idea of the cluster hypothesis. This

stated that ionized molecules diffused until they attached themselves to polarized molecules or to molecules which could be inductively polarized. This process proceeds until a cluster is formed which reacts within itself to form the products. He tabulated values of the ratio of the number of molecules reacting to the number of ion-pairs ratio of the number of molecules reacting to the number of ion-pairs produced. Experimental results were very close to the theoretical ratios in many cases, notably the oxidation of H_2 , CO_2 , CH_4 . The very high yields of reactants to ion-pairs for reactions such as the polymerization of acetylene demanded the assumption of very large clusters. However, the completely divergent results for the formation of HCl and HBr from their elements led Hirschfelder and Taylor in 1936 to interpret the observed rates of radiochemical reactions in terms of ordinary reaction kinetics. The overall process is separated into primary and secondary parts. The primary reactions are those which the molecule undergoes immediately after capture. The secondary reactions are thermal steps involving the radicals or other products of the primary reaction steps.

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An isolated excited molecule will have a mean life of not less than 10 sec. and it will lose its energy by emitting a photon, unless delayed dissociation or rearrangement takes place. Probabilities of transition are determined by the selection rule that holds generally for large or complex molecules is that which forbids transitions between states of different multiplicities. For example, a transition from the singlet state where the total angular momentum J has only one possible value, to the triplet state where it has three possible values of J is about 10^{-6} times less probable than otherwise similar transitions which do not involve a change in multiplicity.

The excited molecule can lose its energy by emission (fluorescence), direct dissociation, simple predissociation, and collisions of the second kind. Complex excited molecules may also undergo internal conversion.

Direct dissociation: Since excitation usually weakens the binding energy of a molecule, the equilibrium position of the nuclei is at a greater separation than in the ground state. If this difference is sufficiently great, the excitation results in the formation of an electronically excited molecule with oscillational energy greater than its energy of dissociation (Fig. 3). It will then dissociate after a single vibration (10^{-13} sec.) An example of this is the photochemical excitation of hydrogen iodide.

Predissociation: If the molecule does not have enough oscillational energy to dissociate, it may cross over into a second excited state having the same nuclear configuration and total energy, providing there is such a state. This second state might be less stable, and dissociate. The time for this energy transfer can be anywhere from 10^{-13} sec. (one vibration) to 10^{-8} sec. (normal life of the excited state).

In Fig. 4, if the state B is formed by transition I, dissociation will be forbidden by the Franck-Condon principle. If the same state is formed by transition II, there is a definite probability for crossing over and hence a definite lifetime.

The corresponding process for the states shown in Fig. 5 is called internal conversion. This is ordinarily a "forbidden" transition for diatomic molecules, since the energy levels must coincide for transition to take place.

However, in a polyatomic molecule, where the electronic bands are usually diffuse, and often continuous, this process can and does occur. It is, in fact, a method of direct transformation of electronic energy into heat (vibration) since the final molecule usually has a lower electronic energy than the intermediate state.

A collision of the second kind involves the transfer of energy from the excited molecule to the unexcited molecule by direct collision. Many variations of collisions of the second kind are possible:

1. $A^* + e \longrightarrow A + e$ (with greater kinetic energy)
2. $A^* + B \longrightarrow A + B$ (with greater K.E. in both)
3. $A^* + B \longrightarrow A + B^*$
4. $A^* + B \longrightarrow A^{*'} + B^*$
5. $A^* + B \longrightarrow A + B^{\dagger} + e$
5. $A^* + B \longrightarrow AB^{\dagger} + e$
6. $A^* + BC \longrightarrow A + B + C$
7. $A^* + BC \longrightarrow AB + C$
8. $A^* + B + \text{Third body} \longrightarrow AB + \text{Third body}$

(The third body is necessary to receive the excess energy that otherwise would break the molecule apart, unless one or both of the participants are large molecules which could absorb the energy by oscillations of its many components).

9. $A^* + \text{surface} \longrightarrow A + e$ (The electron is ejected from the surface)

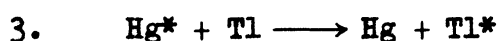
Two factors influence the probability of these collisions. The first is that the probability is greater, the smaller the electronic energy that has to be transformed into or from translational energy of atoms. This follows from the Franck-Condon principle and has been verified experimentally. The second is that the probability is greater for that process in which the total resultant spin of the two collision partners is unchanged. This is an approximate result of a quantum-mechanical calculation which cannot be carried through with accuracy. It has been verified in only a few cases and is much less important than the first factor.

The "exchange reaction", the type indicated as number 7, is very common. It is required that the sum of the excitation energy of A and the dissociation energy of AB is greater than the dissociation energy of BC. If this energy is much greater, there is a possibility that AB will dissociate, giving as a final product, reaction 6. It is not known what proportion of reaction 6 occurrences actually proceed from reaction 7.

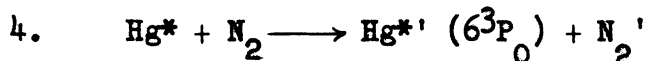
Examples of these reactions have been observed in Hg which has a first excitation energy at 4.86 ev - the 6^3P_1 line (The 6^3P_0 and 6^3P_2 states are metastable).



(A look at the potential diagram for this case (Fig. 6) shows that the probability is very low until high temperatures are reached).

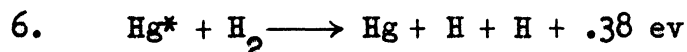


(This is observed as the sensitized fluorescence of Tl^*).

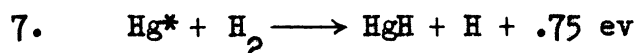


N_2' is an excited vibrational state. The metastable state is observed by absorption lines originating from it, or by noting a delay in the fluorescence of Hg. This latter observation occurs when the 6^3P_0 returns to 6^3P_1 in a collision with an N_2 molecule.

5. No example is observed for Hg^* of this reaction since no atom or molecule has such a low ionization potential.



(Dissociation energy of H_2 is 4.48 ev)



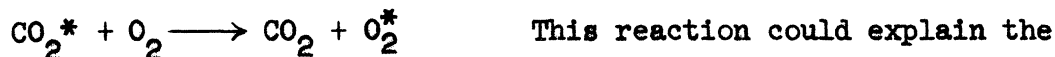
(Dissociation energy of HgH is .37 ev)



9. This reaction is observed with the metastable (6^3P_0) atoms.

Collisions of the second kind following excitation of polyatomic molecules have not often been observed, although several reactions have been postulated.

For example, type 3:

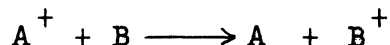


observed radiation by excited oxygen in CO flames.

Another example is type 6: $\text{CO}_2^* + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} + \text{O}$

Reactions following ionizations are analagous to the excited reactions.

The charge exchange type of collision of the second kind is the most important in its category.



The probability of this reaction is higher the closer the ionization potentials of the two elements.

This explains why the observed mobility of He_2^+ ions is greater in Helium than the mobility of He^+ ions.

In a very large polyatomic molecule, charge exchange may occur internally, the electron vacancy migrating until a more stable configuration is reached.

Exchange reactions of the type $\text{H}_2 + \text{Br}_2^+ \longrightarrow \text{HBr} + \text{HBr}^+$ can also occur.

Just as in the excited molecule, the ionized molecule receives more energy than the actual difference in energy levels. This extra energy goes to molecular vibration which may cause it to dissociate. This effect is easily seen on a mass spectrograph.

The neutralization of the charge on a primary positive ion or an ion which is one of its dissociation products may take place by recombination with an electron, or with a negative ion.

To recombine with a positive ion, a free electron has to lose energy by radiation; it does so because it is accelerated in the positive field of the ion. A small energy loss connected with relatively small accelerations is enough for transition of the free electron into an orbit of the highly excited states. Unless a head-on collision occurs, which is highly improbable, the capture of electrons to the highly excited states is most probable. This electron capture by an ionized molecular ion often leads to dissociation.

— Electrons can attach themselves to neutral molecules:

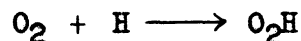


(If the B element has a high electron affinity such as O, O₂, or the halogen atoms).

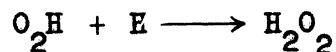
REACTIONS IN MATTER

Although the effects so far described refer to gases, we can use the same theory in solutions. In solutions, the solvent is in close contact with the solute at various times. At these moments, it can be described as a polyatomic pseudo-molecule. Thus the excitation energy can be lost by internal conversion. In fact, that is the usual case. Even if enough energy is transferred so that dissociation occurs, the solvent acts as a "cage", making the recombination probability high.

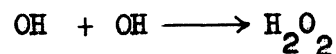
The events following the ionization of water are very complex. Apparently, most of the energy transferred to the medium is dissipated almost at once as heat. This is evidenced by the observation that the recombination of H⁺ and OH⁻ evolves only .6 ev as compared to about 15 ev for the gaseous state. Ultimately, if there is dissolved oxygen in the water, the hydrogen atoms combine



and



also



Biologists, studying the effect of ionizing radiations on cell multiplication or mutation explain the effects on the basis of the production of ionization in or in the immediate vicinity of the vital molecule, the so-called "target". Sizes and shapes of the targets have been calculated. In biological systems, the thermal effect is often the important one. For these large complex molecules, luminescence is rarely observed. Dissociation is often followed by recombination due to the "caging" effect. There is a possibility that the

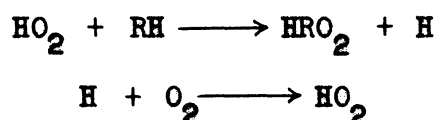
molecule will reorganize slightly and thereby cause the activation energy for recombination to be great enough to hinder the back reaction. Most often, excitation brings on internal conversion, bringing the molecule to a state of high oscillational energy which it may lose to the environment as heat. Thus the excitation usually has no permanent effect unless the molecule is structurally sensitive to its high "internal temperature".

A single ionization is often reversed by recapture. It then behaves as an excited molecule. Another possibility is that the primary ion dissociates into two or more fragments.

Chemists, studying the effects of ionizing radiations on substances in aqueous solutions, attributed the effects to the action of the radiation products of water. This is the "Indirect action" theory.

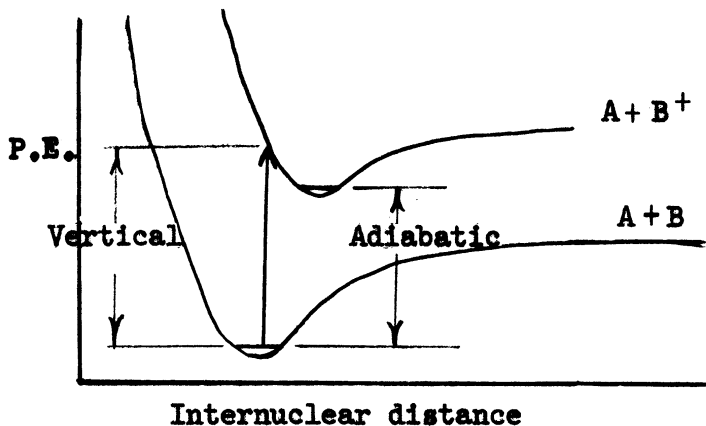
Usually, this means the effect of the products of water irradiation on the solute. The "poison" as it might be called can be H_2O_2 which is formed in pure water by alpha particles. The high density of OH radicals makes the formation of H_2O_2 probable. Beta and gamma radiation do not permanently effect pure water (due to the sparseness of ionization, recombination of the radicals is predominant). However, when O_2 is present, the reactions to H_2O_2 occur as previously noted.

There is also a chain reaction possibility with free radicals like HO_2



This chain would cause both heating and a partial "burning" of the original material.

It appears that both of these effects occur. With high doses, the hit or target theory will predominate. At low doses, indirect action, which in biological systems predicts mainly oxidations is the primary process.



Adiabatic and Vertical Ionization Potentials

FIGURE 1

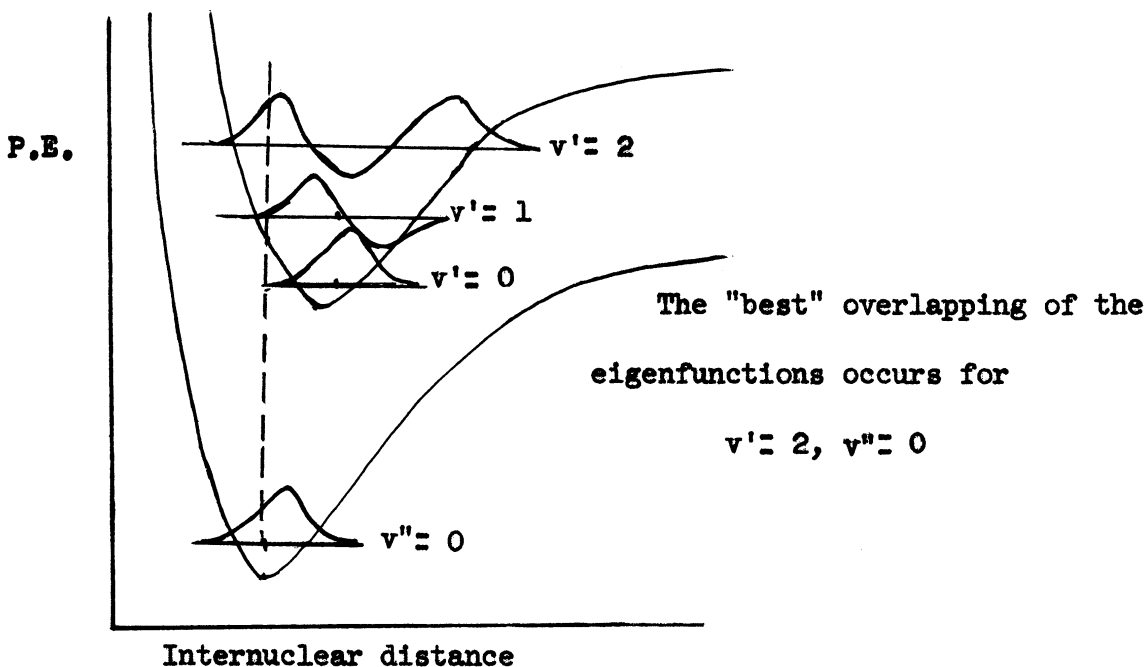
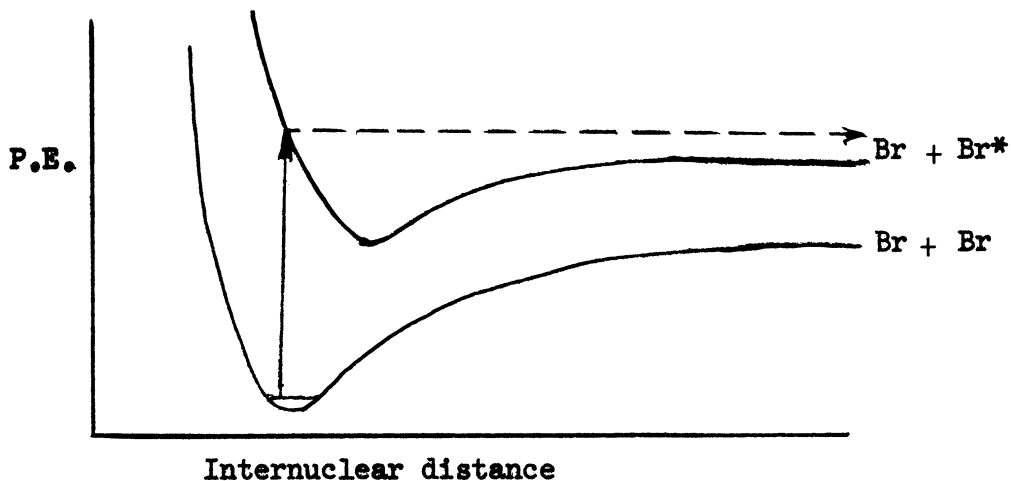
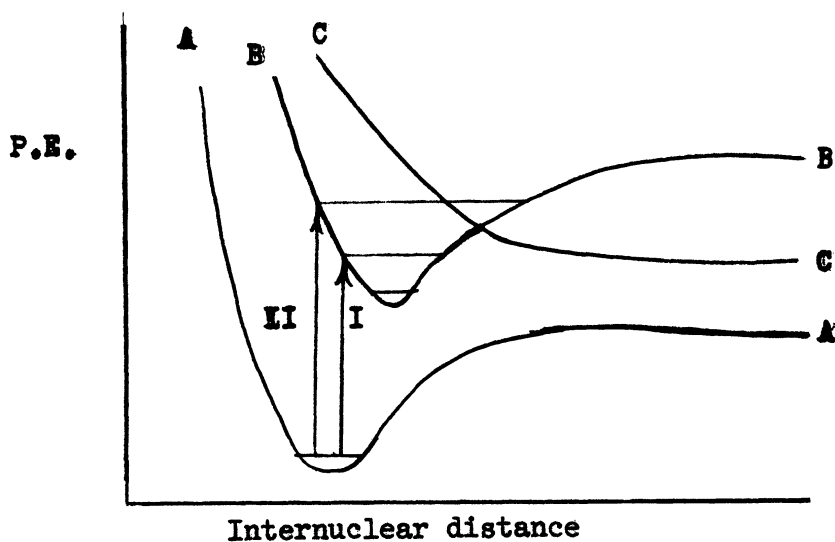


FIGURE 2



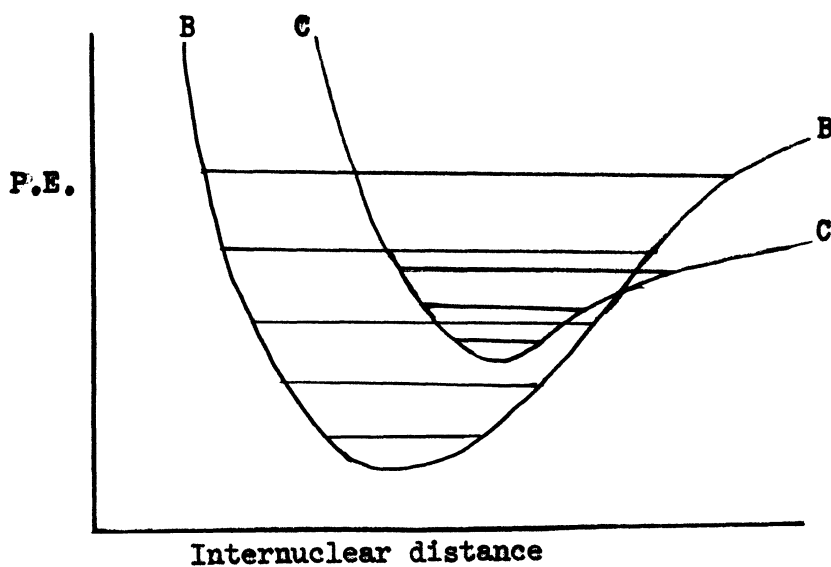
DIRECT DISSOCIATION

FIGURE 3



PREDISSOCIATION

FIGURE 4



INTERNAL CONVERSION

FIGURE 5

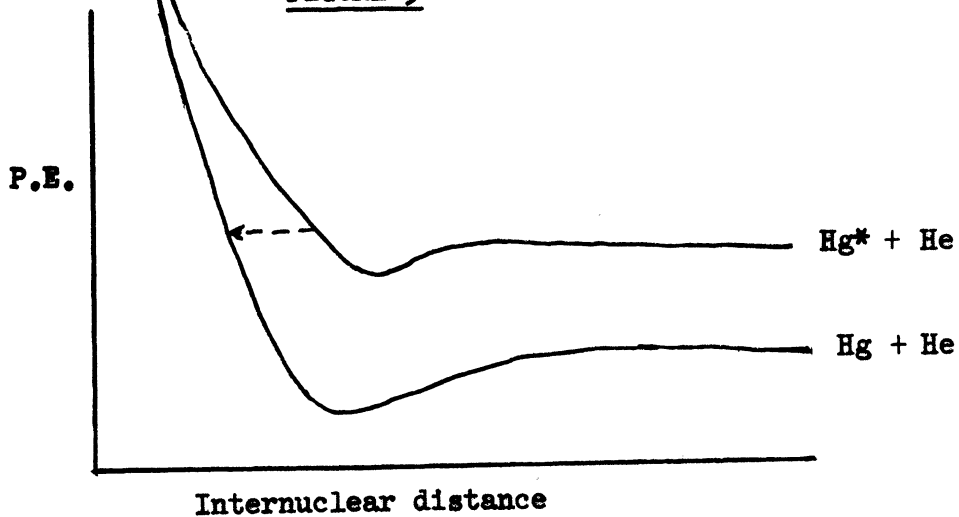


FIGURE 6

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