A CONTRIBUTION TO CHEMICAL STATICS

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IT seems to me that the theory, which I shall develop in this paper, is able to provide an explanation for some chemical facts for which no suitable hypothesis has yet been found. Among these facts are the phenomena of dissociation, the so-called mass-action effect, reciprocal and predisposing affinity, the equilibrium state between opposing reactions, and several other related phenomena.

I. Theory of Dissociation Phenomena

The observation of certain exceptions to the law of vapor densities initially resulted in the hypothesis that those compounds, which showed these exceptions, decompose in the vapor phase. The numerous experiments of Sainte-Claire Deville, Pebal, Würtz, Wanklyn, and of Robinson and Than have confirmed the hypothesis proposed by Hermann Kopp, Cannizzaro and Kekulé. Furthermore, they also prove that this decomposition is often incomplete – in fact, that it is only partial over a wide range of temperatures, such that, within this range, each degree of the temperature [scale] correlates with a different degree of decomposition. The majority of chemists view this partial decomposition as an entirely adequate explanation of the [observed] irregularities in the vapor densities. *However, it does not explain the partial decomposition itself.*

   In my opinion, the following two essentially different ideas can be formed concerning the state of a compound, AB, whose vapor has begun to decompose. Either all of the AB molecules experience the same change (a loosening of their bonds [and] an increase in the distance separating their components), and therefore pass into a state which is intermediate between their original state and that of complete decomposition; or this change impacts the individual molecules unequally, such that, for example, only a portion of them are completely decomposed, whereas the remainder remain undecomposed.

   At first glance, the former, rather than the latter, assumption seems to have a higher probability, even though it is inconsistent with the results of the experiments of Deville, Pebal and Würtz. Even if it were possible to explain the increase in the volume of the vapor as a consequence of the resulting relaxation of the connection between components A and B, it would still not be possible to understand how something other than a complete regeneration of the original compound could occur after cooling. Nor would cleavage by diffusion be un-

derstandable in this case. Eventually, even with this process, the final temperature-induced transition from the state of highest relaxation to the state of complete separation would have to occur in a single bound, whereas experience shows that the change in the vapor densities is continuous.

The second assumption explains the observed facts completely, but involves something which is difficult to imagine. One cannot quite conceive why, at the same temperature, a certain number of evidently identical molecules will decompose, while the remainder remain intact. If it is the temperature which determines their degree of decomposition, and this is the same for all, then all of them must suffer the same change, since identical causes must produce identical effects. I will now try to resolve this difficulty. It will be shown that it is not the correctness of the conclusions that is at fault, but rather that of the premises.

Deville has already emphasized the analogy[1] which exists between the partial decomposition of compounds below the actual decomposition temperature and the evaporation of liquids below the boiling temperature. This very same concept occurred to me while reading Clausius's paper, "On the Form of Motion Which We Call Heat,"[2] and led me to investigate whether, as a consequence of the similarity between these phenomena, an hypothesis, like that used by Clausius to explain evaporation, might also be useful in explaining dissociation. I found that his hypothesis was readily applicable to a certain class of dissociation processes. By way of contrast, it was not as directly applicable to the dissociation of vapors, though it is easy enough, using the same fundamental ideas, to construct an alternative hypothesis, which, in my opinion, completely explains this phenomenon as well.

Let us first look at the process of vaporization and its explanation, as given by Clausius. If one heats a liquid in a closed space, a portion of it evaporates – that is, a certain number of molecules on its surface are transferred to the space above until it contains a certain characteristic number. As long as the temperature remains constant, this number remains unchanged. At this point one might ask why all of the molecules at the surface of the liquid do not change into vapor, since their temperature is the same as those that are already in the vapor. This point is crucial for the analogy. Those who are content with the explanation that further evaporation is inhibited by the partial pressure of the vapor, might also be satisfied, when it comes to the dissociation of a compound, with the explanation that the partial pressures of the vapors of the separated components inhibit further decomposition of the compound as long as the temperature remains constant. If this is increased by a certain amount, a further number of molecules will decompose until the increase in the partial pressure of the released components is in equilibrium with the force of decomposition.

I think this explanation is still insufficient, since – apart from the fact that it still remains to be investigated whether one can talk of a partial pressure in this situation similar to that present in evaporation and whether this would have

a similar impact with respect to inhibiting the separation of chemically bonded molecules as it has with respect to those bound by cohesion – the difference in the behavior of the individual molecules is still unexplained. One has to look further into this matter and consider the nature *of partial pressure itself*. This has been done by Clausius. According to his theory, the equilibrium which ensues when the vapor pressure has reached its maximum is due to the fact that an equal number of molecules are now leaving the surface of the liquid for the space above it as are simultaneously returning from the vapor to the liquid surface.

As representative of the general dissociation phenomena to which this hypothesis may be immediately applied, I choose the decomposition of [solid] calcium carbonate. When heated in a closed space, this undergoes a dissociation, beginning at a certain fixed temperature, which means that a number of its molecules, whose internal motions have exceeded [the allowed] maximum, decompose. The molecules of liberated carbon dioxide gas are moving in the space [above the solid] in a rectilinear fashion and will increase until the number reabsorbed per unit time is as great as the number expelled per unit time. If the temperature is slightly decreased, then the number of molecules that recombine will exceed the number being expelled and the material will *absorb* carbon dioxide. If the carbon dioxide molecules in the space [above the solid] are now displaced by air (or some other indifferent gas), the expulsion of the molecules of carbon dioxide does not stop, because its cause has not been eliminated, but the absorption of the molecules does, since they are being removed [by the air flow]. Therefore the calcium carbonate *evolves* carbon dioxide in the air stream at the *same* temperature as it absorbs carbon dioxide in its absence. The calcium carbonate and carbon dioxide behave in the air stream in a manner similar to that of a hydrated substance that is being dried.[3]

I will now pass to an explanation of the *dissociation of vapors* and, for that purpose, will hypothesize that, in the vapor of a partially decomposed [gaseous] compound at constant temperature, *as many molecules are being cleaved as are being recombined by the [molecular] motions*. This manner of explanation necessarily implies that *not all of the* molecules *simultaneously experience the same state of motion*, just as the explanation of evaporation by Clausius postulates that the states of motion of the molecules on the surface of the liquid are unequal. According to the mechanical theory of heat, such an inequality is highly probable.

The process of decomposition for a compound AB may therefore be thought of in the following fashion: As long as the compound has not yet decomposed, all of the molecules will have the composition AB. They will move in a rectilinear fashion. Furthermore, the components of these molecules will also move relative to each other. However, this movement of the components (as well as the rectilinear motion) is not of equal magnitude for every molecule because, even if they were momentarily equal, they would not remain so as a result of their [mutual] collisions and their collisions with the wall [of the con-

tainer]. Only the average *vis viva* [i.e. kinetic energy] of these motions remains unchanged at constant temperature and in a certain ratio to the *vis viva* of the rectilinear motion of the molecules. But in the individual molecules it will sometimes be larger and sometimes smaller.

If the temperature is now increased, the *vis viva* of both [kinds of] motion increases. As a result, it may happen that the increase in the internal motion of those molecules, for which, at this instant, the [internal] motion already happens to be quite large, will then become so large that it will result in a complete separation of the components A and B. It is impossible for this separation to happen to all of the molecules at the same time. Rather it must occur first for those whose internal motion happens to be larger than the rest. These separated components, which are now free molecules themselves, now possess rectilinear motion as well. Meanwhile a new selection of previously undecomposed molecules will attain the upper limit for their internal motions, and will, in turn, also decompose. This will happen to equal numbers per unit time and continuously increase the number of dissociated molecules. However, these will, in part, collide with one another. Not all of these collisions will result in the dissociated molecules recombining, but rather only those whose states of motion are such that, when the dissociated compound is reformed, the resulting combined motions of its components are no greater than that required for the original separation. Hence, it necessarily follows that, at a given constant temperature, the free molecular fragments will continue to increase until the number of reuniting molecules per unit time becomes as great as those produced per unit time by cleavage. From this point on an *equilibrium* between decomposition and recombination will dominate, provided that the temperature remains constant. But if this increases, the number of dissociating molecules must also increase, while the number of reuniting molecules will initially decrease. The equilibrium can only be restored when the number of molecules, A and B, in the unbound state is large enough that as many recombine as decompose. If the temperature continues to increase, one will finally reach the point where all of the molecules decompose without being able to recombine. At this juncture the dissociation phase will finally terminate in one of complete decomposition.

If during the dissociation phase, an opening is made in the wall of the container, or the walls are porous, both the undecomposed and decomposed molecules will pass through in a rectilinear fashion, but since their speeds are inversely related to the square root of their masses,[4] the dissociation fragments will diffuse faster than the undissociated molecules and, among the former, the lighter faster than the heavier. Based on this, the experiments of Pebal and Deville may be explained and it also leads to the conclusion that it should be possible to use diffusion to gradually increase the [degree of] dissociation of the remaining material in the container without increasing the temperature.[5] The same result could be obtained using a chemical medium to absorb both of the components, *or only one* of them (Therefore an analysis of the gas mixture is

not feasible without a chemical interaction between the absorbing material and the compound). The fact that decomposition can only occur gradually seems to me to provide the correct explanation for why many reactions require a certain period of time for their completion.

If one cools down a partially or completely decomposed vaporous compound, the process [of decomposition] will generally be reversed. However, it is conceivable, especially with rapid cooling, that the separated components will pass over into a state in which they can no longer recombine before they have had time to reunite. This explanation has already been employed by Deville.

II. Theory of States of Equilibrium Between Reciprocal Reactions, Explanation of Mass Action, etc.

It has been frequently observed that a compound AB is decomposed by material C at the same temperature as compound BC is decomposed by A. Likewise, it is a known fact that reactions of the form AB + CD = AD + BC may become reciprocal at the same temperature, whether one decreases the amounts of the compounds to the left of the equal sign or increases those to the right. As a matter of fact, the affinity of a material is a function of its mass.

At that period when the principle of definite proportions was not as certain as it is today, this and similar facts provided a great deal of support for the theory of Berthollet. They still form a dark chapter in the theory of affinity. The arguments which one can deduce from them in opposition to presently accepted theories are, it seems to me, perhaps silenced by the overwhelming number of supporting arguments, but not altogether eliminated.

The correlation of these facts with those of dissociation and the generality of this phenomenon were first specifically remarked on by Adolf Lieben in his paper: "On the Vapor Densities Known as Abnormal."[6] There he cites the same example of calcium carbonate, which I used earlier; then the facts concerning the decomposition of water, which we owe to Deville; and, finally, the results of the beautiful experiments of Berthelot and Péan de Saint-Gilles concerning the formation and decomposition of compound ethers [i.e., esters], which are, without doubt, of greatest importance for the subject under discussion. Related to this are the recently published and equally interesting discoveries of Berthelot concerning the equilibrium between the opposing reactions for the synthesis and decomposition of hydrocarbons, which Berthelot also compares to dissociation.

All of these facts allow for a single explanation formulated with the help of an hypothesis based upon Clausius' theory of the [three] states of matter and which consequently replicates his theory of evaporation. Let us assume there are equal numbers of the molecules of three gases, A, B and C, in a closed space. Furthermore, at room temperature, the gases A and B are combined in the form of the gaseous compound AB. Initially two kinds of molecules are

moving in this space: AB and C. Now, if the temperature is progressively increased, a number of AB molecules can, as shown earlier, decompose, which means that the compound AB will enter into a state of dissociation. Then the separated molecules, A and B, will, like the others, move in a straight line within the [available] space and will occasionally encounter the molecules of C. Let us assume that substance B has an affinity for C – thus the molecules of B and C can combine on colliding provided that the sum of their motions does not result in a state of motion which makes their attachment impossible.

However, in this case the following process is likely: Even before the temperature has reached a level sufficient to induce the dissociation of AB, the same result can be initiated by the influence of molecule C. Let us examine a molecule of the substance AB, which, because of the high temperature, has already acquired sufficient motion of its components that it is close to decomposition, and which now encounters a molecule C. The external motion of both molecules is now completely or partially converted into internal motion by the impact. The result now depends on whether the affinity is or is not strong enough, given this enhanced internal motion, to keep all three bodies together. If not, then the components are repelled again, which means a part of the internal motion is once again converted to external motion. Apparently the mode of separation now depends on how the internal motion is distributed among the individual parts. If the internal motion of the original AB molecule was already very large prior to impact, and was further increased by the impact, then the cleavage of the transient ABC molecule to form A and BC is more likely than to form AB and C. Therefore, a certain definite portion of the AB molecules which collide with the C molecules will react according to the equation AB + C = A + BC. Here we have a dissociation process which is different from pure dissociation; but also equally different from a complete chemical decomposition in which all of the molecules are decomposed at once. The peculiarity of our process consists in the necessity of only *partial* decomposition.

Besides AB and C molecules, we now have those of A and BC. Provided that even the most favorable combination of motions fails to create a net motion capable of decomposing BC, the reaction will now, in the course of time, proceed to completion without a further increase in temperature (i.e., until all of the molecules of AB have encountered molecules of C under conditions favorable for decomposition) and will terminate in the completion of the equation AB + C = A + BC. If this is not the case, but rather at some other temperature the motion of the components within even a few BC molecules increases to the point that (with the simultaneous assistance of the affinity of A for B) it causes their decomposition, then the process must stop at a certain composition of the mixture, provided that the temperature is held constant. Indeed, decompositions still constantly occur, but they will now be compensated by an equal number of recombinations. Within a certain temperature range, changes in temperature will only affect the reciprocal proportion of the different molecules and a cer-

tain [composition of the] mixture will correspond to a certain degree of temperature. It matters which of the combined molecules is most affected by the increase in temperature and approaches the upper limit for its internal motions faster.

Now we want to investigate how the process has to proceed if one adds, without an increase in temperature, more of gas AB to a gaseous mixture of AB, BC, A and C. Thereby the equilibrium between recombination and decomposition must be disturbed, since the number of decomposing AB molecules increases in a manner proportional to the amount present. As a result of this, the number of free molecules of C likewise decreases. More molecules of BC are formed, but more than before are decomposed as well. Equilibrium is only possible at a different composition which contains fewer molecules of C. The larger the amount of gas AB becomes, the smaller that of gas C will be become. This reaction would also be promoted by the removal of the molecules of A, as that would have the result that the accumulated molecules of BC are no longer decomposed by the molecules of A and hence the molecules of C will no longer regenerate. Therefore, if we implement both methods at once – supply of gas AB and removal of gas A – gas C will completely disappear without the need of a higher temperature, as required previously when an equilibrium between decomposition and recombination dominated.

The reverse result will occur when, in the mixture of AB, BC, A and C, we decrease the number of AB molecules, or increase the molecules of A, or both simultaneously. The decrease in AB will result in a decrease in the decompositions of AB and the formation of BC; hence more free molecules of C will remain. An increase in the molecules A will cause an increase in the decompositions of molecule BC, whereby molecules of C are released. Therefore, this reaction can only end with the complete isolation of gas C.

If the three substances, A, B and C, and their compounds are gases, as assumed so far, it is perhaps easy to add arbitrary amounts of each individually, but not to remove each individually, if one cannot use chemical methods. Therefore, one will rarely, if ever, succeed in bringing a reaction to completion solely by changing the proportions. However, one can approach completion to an arbitrary degree through addition of the appropriate gas.

It is different when one of the substances is a liquid or a solid. One example of this case would be the reaction of copper, water vapor and hydrogen.[7] If one directs water vapor (AB) over glowing copper (C), hydrogen (A) and copper oxide (BC) are formed. If one directs hydrogen (A) over copper oxide at the same temperature, water vapor (AB) and copper (C) are formed. Here water vapor, in the first case, and hydrogen, in the second case, were added in excess to a limited amount of copper or copper oxide, and the emerging (by)products were simultaneously removed as gases. But if a limited amount of water vapor is heated in a closed tube with a limited amount of copper, only a part of the water is going to be decomposed and a part of the copper is going to be oxi-

dized and, for each degree of temperature, there has to be a certain ratio between the amount of water vapor, hydrogen, copper and copper oxide, at which there is an equilibrium between the oxidations and the reductions. The same occurs if one directs hydrogen over iron oxide and, conversely, water vapor over iron. Zinc, tin, cobalt, nickel, uranium and cadmium behave similarly.[8]

If one directs hydrogen chloride gas over glowing silver, silver chloride and hydrogen form – conversely silver chloride is reduced by hydrogen. Zinc, tin and iron behave similarly towards carbon dioxide and carbon monoxide gas. These reciprocal reactions occur at the *same* temperature, as shown by specially designed experiments, (Gay-Lussac, Regnault).

Also related is the observation that many substances, formed by reaction with a gas, can only be distilled or stored in an atmosphere of the same gas (e.g., sulfur chloride in chlorine gas). Conversely, the escape of hydrogen bromide facilitates the action of bromine on organic substances in sealed tubes. Cases of predisposing affinity also belong here and are satisfactorily explained in a similar way. I would be able to multiply my examples indefinitely, but I believe that those given so far are sufficient to illustrate the proposed hypothesis and facilitate its application. It is applicable whenever a partial decomposition occurs. Moreover, the presence of the latter is revealed by a number of characteristics, among which are: the influence of time on the progress of a reaction; the incompleteness of a reaction when occurring in a closed space; reversibility; the necessity of excess reactants; the acceleration of a reaction by removal of products, etc.

III.   The Relation of Williamson's Theory of Exchanges to the Proposed Hypothesis and Its Application to the Case of Double Elective Affinity

Already some sixteen years ago Alexander Williamson proposed an hypothesis concerning the nature of decomposition in his paper on the "Theory of Etherification," which is to some extent related to the one just presented. There he developed the view that "in an aggregate of molecules of every compound, there is an exchange constantly going on between the elements which are contained in it." Williamson's hypothesis has little to do with the theory of dissociation phenomena which I have developed in Section I, but is related to my method of explaining mass action and reciprocal affinity. This explanation is based on the assumption of the simultaneous occurrence of opposing reactions in keeping with [the operation of] simple and double elective affinities. These reactions may also be interpreted as *exchanges*, whence the similarity of both hypotheses. However, they also differ substantially on several points:

Firstly I do not assume that *every* compound undergoes a partial decomposition (exchange), but rather only some compounds – though perhaps a great many – and these only above a certain temperature limit (which, of course, in many

cases may be so low that we are only aware of the compound when in a state of partial decomposition).

Secondly my hypothesis includes the essential assumption that, within certain temperature limits, *not all* molecules are subject to decomposition (exchange) *at the same time*.

Thirdly I do not base my opinions entirely on the "motion of atoms," but rather on differences in the *momentary states of* motion *of individual molecules* and view this as the basis for the possibility of simultaneously opposing reactions.

Fourthly I would like to assign the merit of greater universality to my hypothesis since all partial decompositions – even those which occur by heat alone without the intervention of another body (dissociation) – may be explained from the very same point of view, whereas I will now demonstrate that Williamson's hypothesis cannot explain this latter mode of decomposition and was never intended to do so.

I will review these points in reverse order and will begin with the fourth one, which, it seems to me, most easily illustrates the relation between both view points.
    The following schemes give an overview of three groups of reaction, along with their counter reactions, on whose simultaneous occurrence the phenomena to be explained are based:[9]

I. Partial decomposition by means of heat alone (dissociation):
AB = A + B and A + B = AB.

II. Partial decomposition by means of so-called simple elective affinity:
AB + C = CB + A and CB + A = AB + C.

III. Partial decomposition by means of so-called double elective affinity:[10]
AB + CD = AD + CB and AD + CB = AB + CD.

Williamson's hypothesis is restricted to the explanation of reactions II and III and does so by the simple assumption that atoms (or groups of atoms) A and C constantly change places. The ensuing state of equilibrium is a simple result of the number exchanges of A with B [*sic.* C] being equal to the number of exchanges of B [*sic.* C] with A. If we now try to apply this same manner of explanation to case I, it seems to work there as well. One simply needs to assume that the A within the compound is constantly interchanged with the A found in the free state. The state of equilibrium is thereby explained.

If the hypothesis is supposed to be correct for all three cases, it must not only explain the phenomenon of equilibrium, but also those phenomena which occur when the equilibrium is disturbed. These disturbances occur when:

1) One or more products of the reaction are removed.

2) The temperature is changed.

Experience shows that, when the equilibrium is disturbed by the removal of the products, the partial reaction changes into a complete [reaction] and the reciprocal reaction ceases to function. In the case of schemes II and III, this agrees with Williamson's hypothesis; as may be seen if we consider scheme II:

$$AB + C = CB + A$$
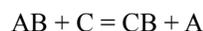
If we remove all of the free A or CB that is formed or both, then the reverse exchange of A in place of C is no longer possible, though the exchange of C in place of A in AB can still occur and must lead to completion of the reaction. Conversely, the removal of AB or C or both results in completion of the reciprocal reaction. As with the above, so Williamson's hypothesis also completely works for the reactions in scheme III. *But it no longer works* as an explanation for the disturbance of the equilibrium in scheme I, for, if this equilibrium also depended only on exchange, it would not be clear how just the removal of A or B or both would give the results that are, in fact, observed. We have the scheme:

$$AB = A + B, \ A + B = AB$$

If, for example, we now remove all of the free A, the exchange with the bound A will stop. The same is true for B. Its removal could only result in a cessation of the reaction and not in its completion, which is, however, what actually occurs, as shown by experience.

This situation clearly occurs in the specific example that I used earlier to illustrate the phenomenon of dissociation. We heat calcium carbonate in a closed tube. Carbon dioxide is formed. If we keep the temperature fixed at a constant value, the amount of carbon dioxide will also stay constant. This state of equilibrium can now be explained by both hypotheses. According to the hypothesis of exchange, free carbon dioxide molecules constantly switch position with bound molecules, which are, in turn, set free. According to the other hypothesis, it is assumed that the number of released carbon dioxide molecules is equal to the number taken up by the quicklime per unit time, *although the absorbed [molecules] do not necessarily substitute for the released [molecules]*. Therefore, according to the first hypothesis, every single release is necessarily

coupled to an uptake, whereas, according to the second hypothesis, each release is independent of any given uptake, though the total number of both is constrained by the requirement of equality. This distinction seems to be negligible, but it immediately becomes crucial when we look at the following process. We direct air (or some other inert gas) through the tube and displace the carbon dioxide. Instantly fresh carbon dioxide is released. Now the first hypothesis is no longer sufficient because, in that case, one would need to assume that the air switches positions with the bound carbon dioxide, which is not the case. In contrast, the second hypothesis corresponds completely [to the facts], since, according to it, the combinations and decompositions are independent of one another [and] the first are easily reduced or eliminated by removal of the carbon dioxide, while the latter continue.

If one had caused the generation of carbon dioxide using [another] gas, capable of chemically combining with the chalk, then the difference between the two hypotheses would have remained undetected. Only the circumstance that the generation [of carbon dioxide] is also possible using an inert gas proves that only the second hypothesis can be correct.

One would reach the same conclusion on trying to explain the disturbance of the equilibrium caused by a change in temperature. According to the exchange hypothesis,[11] the exchanges in cases II and III would become more frequent in one direction than in the opposite, until, as a result, the relative numbers of the different molecules had changed to such an extent that, once again, equal numbers of opposing exchanges are produced. From this point on, equilibrium would be established once more. [For these cases] the exchange hypothesis is sufficient. For case I it is not sufficient, as one may be convinced after brief consideration. This may again be demonstrated using the previous example. The fact that calcium carbonate releases more carbon dioxide upon increasing the temperature of a closed space can only be explained by the assumption that the number of detached molecules becomes greater than the number which are simultaneously absorbed. This is not possible using a simple exchange. If one wished to maintain this [mechanism], one would have to consider two processes side by side – the exchange and the decomposition. However, it is simpler to assume that the individual combinations and decompositions are, in general, independent of each other. Thus the concept of an exchange requiring a pairwise coupling of both processes may be abandoned.

One could restrict the exchange hypothesis to cases II and III, for which they were devised by Williamson, and use the second hypothesis to explain case I. However, it seems to me more expedient to extend these hypotheses until they apply equally to all three cases, and this is most easily accomplished if one replaces the narrow conception of exchange with the broader conception of simultaneous individual and independent decompositions and combinations.

More important than the difference discussed above is the one found in *point three*. Williamson assumes an alternating transfer of the molecules [*sic*.

atoms] in opposite directions, and hence an opposite movement of the same, without stating a cause for how these opposite effects are brought about. I find this cause, as already stated many times, in the momentary differences in the states of motion of individual molecules, as assumed in the hypothesis of Clausius. I have already explained the reactions found in schemes I and II, now I will attempt to explain the transfer found in scheme III.

We have molecules of AB and CD in a given volume. Depending on whether they are gaseous or liquid, they move throughout this volume in a linear or an irregular, but progressive, direction (external motion). Furthermore, their components move relative to each other, but are bound to a common center of gravity (internal motion). If one does not change the temperature, the sum of the *vis viva* of both motions will remain constant. Even the sum of the *vis viva* of the external motion alone, like that for the internal motion, will remain constant, since Clausius has proven that they must be in a constant ratio to one another. However, the external motion, as well as the internal, must be very unevenly distributed among the individual molecules. Therefore we have the following limiting cases:

1) Molecules possessing the maximum external and internal motion.

2) Molecules possessing the minimum external and internal motion.

3) Molecules possessing the minimum external and maximum internal motion.

4) Molecules possessing the maximum external and minimum internal motion.

Between these limiting cases, there exists, of course, all possible intermediate cases. The maximum for the internal motion is determined by the magnitude of the affinity. We do not know how the magnitude for the external motions is limited – indeed, it seems to me that the existence of such a maximum is not yet proven. However, this does not affect our method of explanation.

Upon the collision of two different molecules, the external motions can be increased at expense of the internal, or the internal at expense of the external, or, as a limiting case, both may remain unchanged. Among the diverse results of such a collision, the following cases should be stressed:

1) Two molecules, whose external and internal motions are very large, meet in such a fashion that, in the next moment, the external motions are completely, or for the most part, converted into internal motions which exceed the upper limits in both molecules. As a consequence, a separation into four parts, A, B, C and D, occurs.

2) Two molecules, whose external and internal motions are very small, collide.

Here it is possible that the resulting internal motions are not only too small to split both of the original molecules, but also to prevent their permanent combination. An aggregated ABCD molecule results.

3) Two molecules collide under such conditions that the resulting internal motion is too small to split the molecules, but large enough to prevent a permanent connection. Hence they fly apart like elastic spheres and AB and CD remain as AB and CD.

4) The molecules collide under such conditions that the interplay of the internal motions of the components of the transient double-molecule induce its splitting in a different direction. AB and CD collide and momentarily form ABCD. If the impact was – as we wish to assume in the simplest case, – linear and central, the whole system will continue to initially move in accordance with the redistribution of various quantities of motion, the lost external motion having been transformed into internal motion. Now it depends on the magnitude of the affinity of A, B, C and D for one another and, at the same time, on the previously existing internal motions of the components of AB and CD, as to whether the split due to the increased internal motions occurs in the direction of AB/CD or in direction of AC/BD. The larger the internal motions of the molecules prior to collision, the greater the preparation for the separation of A, B, C and D and the easier it is for a split in the direction AB/CD to occur. One can see that, in general, the best conditions [for a double decomposition] are in those given earlier under limiting case 4.

In this manner it becomes obvious that, in addition to the affinities, the mode of decomposition further depends on the state of motion, and that, consequently, even those reactions that are apparently opposed by affinity may occur (reciprocal reactions).

The first two of the four cases listed earlier require a larger difference in the states of motion of the individual molecules than do cases three and four. Hence it is highly likely that these are not fully achieved in many processes for which the difference is not large enough. This assumption may be made for all those reactions for which there is no basis for assuming the presence of the [product] molecules ABCD, A, B, C or D in addition to the molecules AB, AD, BC and CD. But it is also possible that one will find examples whose explanation makes this assumption necessary.[12]

Now I come to the difference between the two hypotheses indicated in point 2. It is self-evident from the above. Although the collision of the molecules is random, they must, according to the principles of probability, result in regularity when the number of impacts becomes extremely large, such that the number of impacts resulting in decomposition always corresponds to the same

fraction of the [total] number of impacts under the same circumstances. There-fore, in addition to those molecules that are decomposed (whose parts are ex-changed), there will always be those that rebound without decomposition, which means, as I stated in point 3, that *not all of the molecules are being de-composed at the same time*.

Finally, in point 1, I have described as essential to my hypothesis the as-sumption that a partial decomposition (exchange) does not occur at every tem-perature. When one considers that, according to the theory of heat, absolutely no motion of the molecules exists at -273° C, it is also apparent that for a con-siderable number of degrees [above zero] the motion may be so small that it does not exceed the upper limit for internal motion and so induces no decom-position. For this reason there must be an upper temperature limit at which the reactions under consideration first begin. If, for a compound, this is situated higher than the temperature at which we are able to examine it, we will not be able to observe any hint of a decomposition (exchange), and in *this sense* I wish it to be known that Williamson's assumption that "in an aggregate of molecules of every compound, there is an exchange constantly going on be-tween the elements which are contained in it," is restricted in the manner just described.

This also agrees with experience. As evidence, I will cite the same example which led Williamson to the discovery of his hypothesis, namely the formation of ether. This process divides into two reactions, each of which may be re-versed. The first is given by the equation:

$$C_2H_5OH + H_2SO_4 = (C_2H_5)HSO_4 + H_2O$$
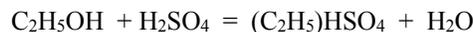
Alcohol + sulfuric acid = ethyl sulfuric acid + water

and the second by:

$$C_2H_5OH + (C_2H_5)HSO_4 = H_2SO_4 + (C_2H_5)_2O$$

Alcohol + ethyl sulfuric acid = sulfuric acid + ether

Both reactions show features that correspond to partial decomposition. In par-ticular, both remain incomplete if one does not remove the products and they may also be reversed. A mixture of sulfuric acid and alcohol never forms so much ethyl sulfuric acid that some portion, not only of the alcohol but also of the sulfuric acid, does not remain unreacted. This is because the products formed – ethyl sulfuric acid and water – continuously give rise to the opposite reaction. These reciprocal reactions can become dominant if the proportions are favorable. It is known that ethyl sulfuric acid changes back to sulfuric acid and alcohol when boiled with water. This last reaction is reduced by removal of

water (or ethyl sulfuric acid)[13] – hence, the less water added, the more ethyl sulfuric acid is formed initially.

By continuous removal of water and addition of alcohol the [first] reaction must go to completion in one direction. By addition of water and removal of alcohol it will go [to completion] in the other direction. At a certain ratio of the initial reagents, [the question of] whether the equilibrium between the opposing reactions will correspond to a greater or lesser degree of decomposition will depend on the temperature. Hence there must be a temperature value at which the reaction of the sulfuric acid with the alcohol has not yet begun, at which the internal motions of the molecules – even those in which it is at a maximum – is insufficient, even with support from affinity, to cause a reaction. It is still unknown just how low this temperature value is, but the circumstance that dilute sulfuric acid only forms ethyl sulfuric acid upon heating, suggests that it cannot be very low.

For the second reaction between the alcohol and the ethyl sulfuric acid the same relationship occurs. On reversal, ether and sulfuric acid result in ethyl sulfuric acid and alcohol. Hence even here, if the ether cannot be removed, the degree of conversion must remain fixed at equilibrium, where both opposing reactions occur side by side with the same frequency.

Now, if the water as well as the ether are continuously removed by distillation during production of the latter, both processes will go to completion in one direction, as in both the reaction favoring ether formation outweighs the reverse reaction. If both processes occurred at all temperatures, ether would form at all temperatures sufficient to remove the ether and water by distillation. But this does not happen because only the alcohol distills off below 126° C [at which temperature] the second reaction, at least, cannot have yet begun. This single example will serve for many additional examples that could be quoted in support of the statement that (partial) decomposition (exchange) is correlated with a certain temperature value. I believe that I have now sufficiently discussed the relationship between my proposed hypothesis and the exchange hypothesis of Williamson.

IV. Summary and Conclusions

The assumption that atoms are in a state of rest was first challenged by physicists. However, for quite some time their work attracted little attention and was nearly forgotten. As far as I know, Williamson was the first chemist who – independent of physical arguments and based on chemical facts alone – rejected the assumption of static atoms. His inspired theory of ether formation was accepted, but his simultaneous, and more important, presentation of his theory of the continuous exchange of elements remained almost unnoticed.

The epoch-making papers by Krönig, and especially those of Clausius, abolished the assumption of static atoms forever. Sooner or later the triumphant

progress of the mechanical theory of heat had to attract the attention of chemists and invite attempts to apply the highly fruitful assumptions of this new theory to the explication of as yet unexplained chemical phenomena. The present work is such an attempt. Starting with the theory of evaporation proposed by Clausius, I first attempted an explanation of dissociation. Generalization of this approach allowed a transition to reciprocal reactions and the mass action effect. The results of my approach clearly show that the theory of gases as given by Krönig is insufficient and that the more elaborate theory of Clausius is quite indispensable.

It was of great interest to me that volume 101 of this journal contained a paper by Clausius [entitled]: "On the Electrical Conductivity of Electrolytes," in which the fact that very small currents can cause decomposition is explained by postulating that the parts have previously been in partial conversion. Here Clausius refers to Williamson's paper. It now seems to me that my method of explanation agrees even better with the theory of electrolysis. The increase in the conductivity of liquids with temperature may be related to their increasing dissociation. Those that do not conduct are unaffected by dissociation at the temperature in question. However, these are mere assumptions. In the near future, I will amplify this communication with some ideas concerning the constitution of mixtures and solutions, which are related to the above topic.

V. Addendum[14]

Only after completion of this contribution did I discover the critique of Deville's theory of dissociation by Dr. H. W. Schröder van der Kolk[15]. Although I now believe that the most important objections which it raised have been refuted by the above arguments, in order to ensure a complete resolution of this interesting and important matter, I will allow myself, even at the risk of repetition, to add the following [remarks].

I completely agree with Schröder van der Kolk that the extensive measurements of flame temperatures by Deville are open to several objections. Likewise, I think his opinion that the temperature of the flame – even without the assumption of dissociation – should be lower than the calculated values is reasonable. Thus one argument in favor of the theory of dissociation is no longer applicable.

However, in spite of this objection, I have to retain the assumption of dissociation and the belief that there is a profound analogy between this and evaporation. I was led to this opinion independently and without knowing that Deville had already mentioned it earlier, for the reasons discussed above.

It appears to me that the disagreements between Schröder van der Kolk, on the one hand, and Deville and myself, on the other, are focused on the following point: According to the former, it is solely the absorption of heat from the decomposition of the initial molecules which serves to "cool"[16] the neighboring

molecules and thus accounts for the *delay in* the decomposition of *all of the* molecules (and which, for lack of time, also prevents it).

According to the opposing view, this retarding influence is certainly present and is sufficient as an explanation for many partial decompositions; but in addition to this retarding influence there is, for compounds undergoing dissociation, yet another cause, which, within certain temperature limits, not only delays the *complete* decomposition but altogether prevents it, however long the temperature is maintained. In opposition to this Schröder van der Kolk then raises a most important argument, which I will directly quote, while retaining only the most important parts:

It seems to me that this theory appears to contain an inner contradiction. Water vapor is decomposed at [temperature] T through simple heating. This decomposition gradually progresses and will be complete at constant temperature T provided that a sufficient amount of heat is supplied. This temperature T may change with the pressure, but, in any case, is always the same at the same pressure. At a lower temperature decomposition apparently cannot happen, otherwise it would not be T, but a lower decomposition temperature [that would correspond to the dissociation temperature]. Indeed, the author (Deville) says that in this case the decomposition is only partial; but if it occurs partially, then it must also be possible for it to become total as soon as the decomposition is viewed as a function of only the temperature, as is the case with Deville.

This is the very same difficulty which I pointed out at the beginning of my contribution and which I think I have eliminated by the necessary assumption of unequal states of motion for the individual molecules.

According to the mechanical theory of heat, the temperature is proportional to the average *vis viva* of the molecules. If one transfers this concept of temperature to individual molecules, one could argue that the temperature of the individual molecules is unequal, although the parts of the body to which they belong have attained a mutual equilibrium of temperature. The temperature of the body is the average temperature of all its molecules.

The decomposition is now a result (function) of temperature, and hence it is now possible that, within certain limits of the average temperature of the body, it extends only to that portion of the molecules which have exceeded a certain temperature limit. The circumstance that the initial decomposition of a molecule depends only on its *internal* motions requires, in turn, that one distinguish between the internal and external temperature of the individual molecules. This has led me to not employ this extension of the term "temperature," not least because the phrase "internal and external motions" expresses the meaning much better than the phrase "internal and external temperature."

In resolving this *internal* contradiction of the theory of dissociation, it seems to us of greater importance to prove by experiment that partial dissocia-

tion, even at temperatures produced by sufficient heat input over long periods, does not proceed to complete dissociation (except in the cases presented by me e.g. by diffusion). Likewise, I consider this evidence as already provided by the often mentioned experiment with calcium carbonate, and hence it seems unnecessary for me to explore additional reasons for partial dissociation. Another proof are the so-called abnormal vapor densities[17] measured using the method of Gay-Lussac, which, as I have convinced myself by experiment, result in constant numbers with prolonged heating so long as the temperature of the vapor remains constant.

In the end Schröder van der Kolk expresses the view (page 507) that, based on the molecular theory of chemical compounds, it should be possible to develop a [theory of] partial decomposition related to mass action. I would be delighted if I have succeeded in this paper in making a contribution to the foundations of such a theory.

VI.   References and Notes

1.   I take this from the abstract of his paper "On Dissociation in Homogeneous Flames" in *Chem. Centralblatt,* **1865**, p. 662, since the original paper is not available to me.

2.   This journal, Vol. 100, p. 353.

3.   In time I will show that sulfuric acid may be dried with air just as one is accustomed to drying air with sulfuric acid.

4.   Krönig already derived the principle of diffusion from his theory of gases (this journal, Vol. 99, p. 320). I briefly mention this because in the widely known monograph of Paul Beis on *The Nature of Heat*, page 150, it is erroneously stated that Krönig did not state this correlation.

5.   Two things follow from this: Firstly, that the two methods of vapor density determination by Gay-Lussac and by Dumas should show different results under the same circumstances, since diffusion is impossible with the first, but possible with the second. Secondly, that with the second method, the resulting values would not only be dependent on the temperature, but also on the duration of the experiment. (See note 14).

6.   *Bull. soc. chim.*, **1865** p. 90. The remark in question reads: "In fact one frequently finds that it appears to be the general state of affairs that, when a body is decomposed, the presence of the products of the decomposition exercises an influence on the progress of the reaction. There is a tendency to establish a chemical equilibrium between certain proportions of the original products [i.e. reactants] and the products of their decomposition. When in the course of time equilibrium is attained, the decomposition is arrested, etc ... A result which one may express in general terms using the specific case of ammonium chloride, etc..."

7.   However, I will later show that, technically speaking, this example belongs to the case of double decomposition discussed later.

8.   Gmelin, Vol. I, p. 118.

9.   But it should not be said that this scheme includes all reactions requiring a

similar explanation. If anything, more complicated ones can exist. The three cases listed are sufficient, since the more complicated ones may be referred back to them.

10. The following reactions could be considered as special instances of case III:

IIIa AB + CC = AC + CB and AC + CB = AB + CC

IIIb AA + BB = AB + AB and AB + AB = AA + BB

Scheme IIIa will be assumed to be the correct one for many reactions, for which scheme II appears to occur. The same goes for scheme IIIb, which can be assumed in place of the often occurring scheme I. For example, the instances cited by me in Part I [of this paper] as special examples of case II would come under IIIa, since, free hydrogen is considered to be HH rather than H.

11. Williamson did not mention the influence of temperature on the rate of exchange. However, it should behave as indicated.

12. For example, the development of so-called condensed compounds at high temperatures. This journal, Vol. 131.

13. Lieben assumed that, in order to remove the disturbing influence of the products of a reaction on its progress, one had to remove *all* of the resulting products. According to the proposed hypothesis, the removal of only one is necessary, as this is sufficient to make the reverse reaction impossible. This is in keeping with experience.

14. Supplement to the addendum. Since the molecules of gaseous bodies under increased pressure are closer together, they will collide more often. As a result of this, reactions based on partial decomposition reach an equilibrium or end faster than under otherwise identical conditions. It seems to me that the dissociation of *vapors* can progress further, before equilibrium is reached, at lower pressures than at higher [pressures], because the number of decompositions, which decreases for compounds in the first case and increases in the second, remain equally great. Hence, when determining the vapor density according to [the method of] Gay-Lussac, one will increase (although less severely) the [degree of] dissociation (and hence the error in the molecular [weight] determination) by a decrease in pressure, as well as by an increase in temperature, if the vapor is already in a state of dissociation, Only by decreasing the pressure at a temperature low enough that dissociation has *not yet occurred*, can one can avoid error when determining the density.

15. This journal, Vol. 129 p. 481.

16. I would substitute "hinders greater heating."

17. In particular, those leading to values that do not exhibit a simple relation to those that are calculated.