PRIMARY DOCUMENTS

"The Theory of Dissociation"

A. Horstmann

Annalen der Chemie und Pharmacie, **1873**, *170*, 192-210.
(Received 11 October 1873)

It is characteristic of dissociation phenomena that a reaction, in which heat overcomes the force of chemical attraction, occurs for only a portion of a substance, even though all of its parts have been equally exposed to the same influences. In the remaining portion, the forces of chemical attraction, which are the only reason for the reaction to proceed in the opposite direction, maintain the upper hand. Hence, for such reactions there is a limiting state which the molecular system in question approaches irrespective of the initial state and, once it is reached, neither heat nor chemical forces can produce further change so long as the external conditions remain constant.

The degree of dissociation, i.e., the size of the portion encompassed by the reaction in the limiting state, depends upon the following external conditions: the temperature, the pressure and volume, the relative quantities of the reacting substances, etc., and indeed the influence of these various factors varies with the state of aggregation and the nature of the substances in question.

A complete theory of dissociation has to explain in general why an equilibrium state, rather than a complete reaction, is possible and, for each individual case, which circumstances are able to influence the degree of dissociation. I believe I can demonstrate the basis for such a theory in the following.

W. Thomson was the first to take note of one of the consequences of the mechanical theory of heat (1) - namely that the entire world is continuously approaching, via the totality of all natural processes, a limiting state in which further change is impossible. Repose and death will then reign over all and the end of the world will have arrived.

Clausius (2) knew how to give this conclusion a mathematical form by constructing a quantity—*the entropy*—which increases during all natural changes but which cannot be decreased by any known force of nature. The limiting state is, therefore, reached when the entropy of the world is as large as possible. Then the only possible processes that can occur are those for which the entropy remains constant, e.g. stationary movements such as those which we attribute to the smallest particles of a body at constant temperature. The cause of the limiting state for dissociation phenomena is, in my opinion, identical; it occurs when the entropy has become as large as possible for the change in question. Hence our problem is solved if we know by what circumstances and in what manner the entropy of the process in question may be altered.

If we follow the approach of Clausius, we find, first of all, that the more the energy of the world takes the form of heat and the lower the temperature of that heat, the greater the entropy.

If a quantity of heat Q is produced at absolute temperature T, e.g. from mechanical work or chemical potential, then the entropy is increased by Q/T. The reverse process corresponds to an equal decrease in the entropy and, since the total entropy cannot decrease, this will never happen without an increase of equal or greater magnitude occurring at the same time.

From what has been said, it is apparent that the entropy will also increase if a quantity of heat Q is withdrawn from a body at temperature T and is transferred to another at a lower temperature T', since then $Q/T < Q/T'$ if $T > T'$. From this follows the well-known theorem of Carnot that heat cannot be transformed into work without heat being simultaneously transferred from a hotter to a colder body.

However, this theorem is only valid for the production of mechanical work via so-called cyclic processes (i.e., via processes in which all of the participating materials return to their initial states) since, in the transformation of heat into mechanical work or chemical potential, the heat always causes an accompanying (3) alteration in the arrangement of the particles of a body and thereby overcomes the internal and external forces which oppose the change without this being associated with a transport of heat in the sense of Carnot's theorem.

The decrease in the entropy which corresponds to the transformation of heat into potential energy is accompanied in such cases only by a change in the arrangement of the particles of the respective body, and thus it can be seen that the entropy must also be dependent on this arrangement. It is increased by any change in arrangement in which the heat must do work and by at least as much as is required to compensate for the simultaneous decrease. Clausius (4) has described the arrangement of the particles in a body by introducing a new quantity—*the disgregation*—which is dependent on this arrangement and which specifies how large the entropy is for a given arrangement. For the details of how to determine this magnitude, the reader is referred to his original memoir.

Those changes in arrangement which correspond to an increase in disgregation are easily identified because, like those in which the entropy increases, they can occur by themselves without any other accompanying change. In contrast, a decrease in disgregation is only possible if the entropy is also simultaneously increased, e.g. via the conversion of mechanical work or chemical potential into heat.

The disgregation is increased by melting and vaporization, and by the decomposition of chemical compounds. It decreases in all chemical processes which occur with the release of heat.

But bodies can also undergo changes in disgregation without a change in their chemical composition or state of aggregation. This is recognizable by means of specific criteria, e.g. the disgregation of a gas increases when it occupies a larger volume. But at constant volume it will be constant and will remain so even if a second gas is introduced into the same space.

Like the density, the disgregation of a liquid is constant at constant temperature. It can only be changed by mixing it with other liquids. The disgregation of each of the two components depends on their ratio in the mixture.

Lastly, the disgregation of a solid body does not change upon mixing with other solids. At constant temperature it can differ only for allotropic modifications of the same solid. Thus one can conclude that the state of aggregation leads to intrinsic differences which also influence the phenomena of dissociation.

In general, save for a few exceptions (5), the disgregation of a body will increase whenever its atoms or molecules are further separated from one another. Hence one is now able to form a picture of the nature of the equilibrium state for dissociation. That is to say, one sees that the process of dissociation may be divided into a series of processes by means of which the entropy is partially increased or partially decreased. If we consider a particular case, e.g., the decomposition of a gaseous compound into gaseous products at constant volume, then the entropy:

1) decreases during the conversion of heat into chemical work;

2) increases as the separation between the atoms of the decomposed molecules increases;

3) increases because the remainder of the undecomposed molecules must expand to fill the same volume;

4) and 5) decreases because the number of molecules for the two decomposition products increases and they are thus forced closer together.

The entropy will therefore will be greatest when as many molecules as possible are decomposed but the least possible amount of heat is consumed, and when the molecules of each of the three gases are separated from one another as much as possible. This is generally not the case for complete decomposition and hence only a portion is decomposed.

A reaction, whatever its type, can only begin and proceed so long as the collective sum of the various entropy changes contributed by the individual processes increases, since, as we know, the total entropy cannot decrease. The reaction must therefore stop at the very instant when the decreases become larger than the increases, i. e. at that point when the total increase becomes zero. Thus one arrives at a mathematical expression for the condition for an equilibrium state for dissociation. This requires that $dS = 0$, where S denotes the entropy of the system. This equation contains the entire theory of dissociation. It says that, in general, the degree of dissociation will depend upon all those circumstances which determine the entropy of the system. In order to deduce yet further conclusions we must give this equation another form.

For this purpose let x denote the relative amount, in units of molecular weight [i. e. moles], of a substance that either decomposes or reacts with other substances. Then x can serve as a measure of the degree of dissociation and all other quantities that change during the reaction, such as the entropy, will become functions of x. Thus one can write the condition for the equilibrium state as follows:

$$dS = (dS/dx)dx = 0$$

or

$$(dS/dx) = 0$$

Furthermore, if Q denotes the quantity of heat required to decompose totally one mole of a compound, then for completion of the reaction the quantity of heat Qx is required which must be considered when calculating the entropy of the system. If T is the absolute temperature and Z is the disgregation of the system, then:

$$S = (Qx)/T + Z$$

and, if equlibrium occurs, then:

$$(dS/dx) = [Q + x(dQ/dT)]/T + dZ/dx = 0$$

This equation will be further elaborated only for individual cases, and especially for that case in which a single substance is decomposed into two others. If one mole of this substance is initially present and, at a given moment, x moles remain undecomposed, and if every molecule splits into r and s molecules, respectively, of the decomposition products, and if m moles of one of the products was present initially, then it follows that the relative amounts of the three reacting substances are x, $r(1 - x) + m$, and $s(1 - x)$, respectively, and that:

$$Z = xZ_1 + [r(1 - x) + m]Z_2 + s(1 - x)Z_3$$

where Z_1, Z_2 and Z_3 represent the disgregation per mole of each substance.

Assume that both the substance being decomposed and one of the decomposition products are solids but that the second decomposition product is a gas which obeys the law of Gay-Lussac and Mariotte [G-M]. Then Z_1 and Z_2 are independent of x, and Z_3 depends only on the volume that is available to the gas, i.e., on the density of the gas. If u is the volume per mole, then, according to Clausius, it follows that:

$$Z_3 = Z_3' + ARln(u/u_0)$$

where Z_3' is the disgregation for the same quantity of gas referred to a normal [i.e. standard] volume u_0, R is the constant per mole for the G-M law, and A is the caloric equivalent for work. Thus, if p is the pressure of the gas, one has

$$up = RT$$

In most cases, including that under consideration, Q consists of two parts, one being the actual heat of decomposition, q, which is transformed into chemical potential, and the other being the amount of heat required to generate the mechanical work used in overcoming the pressure p, which is equal to Apu or to ART. Both parts are independent of x. If one uses these data, then for the case under consideration, our basic equation assumes the following form:

$$q/T - ARln(u/u_0) + C = 0$$

where $C = Z_1 - rZ_2 - sZ_3'$ is the change in the disgregation when the newly formed gas occupies the volume u_0—a quantity which, like q, no longer depends on x but only on the temperature. Hence the equation contains only one variable, u, that can be altered by the reaction and requires that either u or (since $up = RT$) the pressure of the gas must assume a unique value at equilibrium.

This conclusion is confirmed by the well-known dissociation of calcium carbonate, ammonium chloride, and compounds containing water of crystallization. According to the observations of Debray, Lamy and Isambert, the pressure of a gas over solid compounds, like that in the vaporization of a liquid, depends only on the temperature, but not on the ratio of the compound being decomposed and its solid decomposition product (6), as is required in general by our theory

The maximum pressure at constant temperature can only change if, for some reason, q and C assume different values. This is the case, for example, with the above mentioned compounds if only a portion of the water or ammonia is set free because the remaining portion is perhaps bound in a different manner.

C and q may have different values in the decomposition of *aragonite* versus *calcite* [i .e., two polymorphs of $CaCO_3$], assuming that this difference persists at the high temperature of the experiment, and hence the pressure of the carbon dioxide may be different. (A difference in the vapor pressures for the two modifications of phosphorus, for which precisely the same considerations apply, was demonstrated by Troost and Hautefeuille).

In accord with the experiments of Joulin (7), yet another factor may disturb the process of dissociation for some metal carbonates. Because of the high temperatures, the oxides undergo a modification which makes it impossible for them to rebind the carbon dioxide upon cooling and consequently, bit by bit, a complete decomposition ensues. In keeping with our definition, these cases no longer qualify as dissociation phenomena.

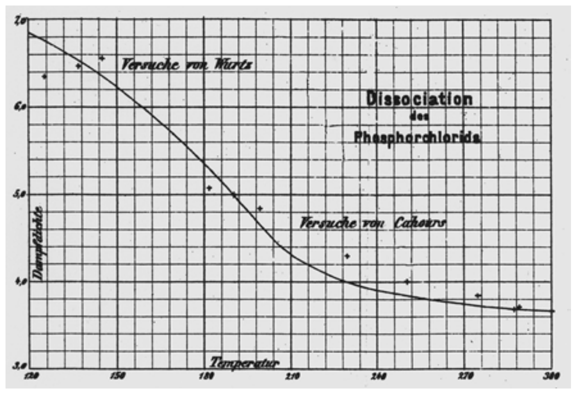
If q and C (which are actually temperature dependent) are treated, to a first approximation, as constant, one obtains the same relation between p and T as was observed earlier for the vaporization of a liquid under similar conditions using a different approach (8).

Looking at a second case—the decomposition of a gaseous compound into two gaseous components—Z_1 and Z_2 have the same form as Z_3 had earlier. Like the partial pressures of the three gases, the disgregations in the gas mixture are additive.

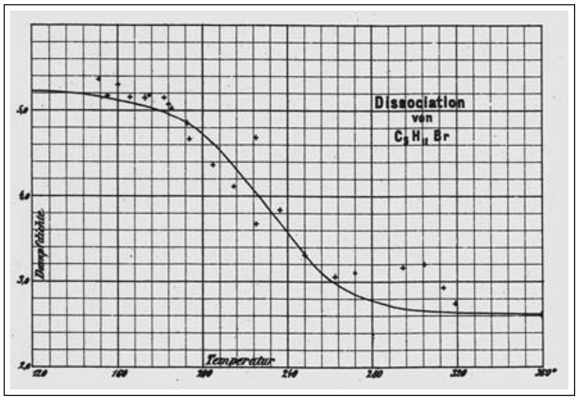
In experiments relating to this case, one mole of the initial compound decomposes by forming one mole of each of the decomposition products and during the decomposition the total pressure remains constant. Under these conditions our basic equation assumes the following rather complicated form:

$$q/T + AR\{1 + [2x/(2 - x + m] - \ln(1/u_0)[x/(1 - x + m)(1-x)]\} + C = 0$$

Here C is the change in disgregation when one mole is decomposed, provided that the gases have the molar volume u_0 before and after the reaction, C is independent of temperature, and the G-M law applies. All other symbols have the same meaning as before. If $m = 0$, then the equation is valid for the well-known experiments of Cahours with PCl_5 and Wurtz with $C_5H_{11}Br$. The degree of dissociation, which is known to depend on the vapor density, must be a function of T alone, as shown by experiment. Again, if one considers, as a first approximation, that C and q are constant, then, by examining the following graphs, it is possible to convince oneself that the form of the function also agrees with experiment (see Graphs 1 and 2).



Graph 1



Graph 2

I stress that the absolute pressure at which decomposition takes place does appear in our equation. Hence the curve for phosphorus pentachloride, whose constants are taken from Cahour's experiments at atmospheric pressure, must also be valid for Wurtz's observations at lower pressures (9). For purposes of comparison, the mean values are shown in the graph.

If m is not equal to zero, then a surplus of one of the decomposition products has been added and, at a given temperature, the value for x will be larger. The degree of dissociation has been decreased by "mass action," an influence which decreases as the decomposition increases, as shown in the following table. Since it is impossible to solve the above equation for x, this lists the temperatures at which x (and the vapor density d) have the same value with and without admixture.

m	*x*	*d*	*t*°
9	0.99	7.13	67
0.5	0.99	7.13	213
0	0.027	3.65	300
0.5	0.027	3.65	322

In the experiments cited above, Wurtz always added more than 0.5 mole of excess PCl_3, the temperature was always lower than 213°, and the average density was 7.2. It must be emphasized that, according to our theory, the addition of chlorine would have the same effect. Each of the gaseous decomposition products can alter the degree of dissociation via "mass action," but solid decomposition products cannot, as we saw in the previous case.

Dissociation phenomena are observed not only during decompositions but also in double displacements. Elsewhere (10) I have pointed out how one can imagine the mechanism by which heat counteracts chemical force in these cases. In my opinion, the effect of heat is always involved whenever an equilibrium is observed whose direction can be arbitrarily changed by external circumstances. In any case, our basic equation is valid for all systems which display an equilibrium since the cause of this equilibrium cannot be anything other than the maximization of entropy.

At this juncture the reactions of steam with iron, of sulfuric acid with sodium chloride in solution, and of potassium carbonate in solution with barium sulfate will be further examined, as all three reactions attain equilibrium before the reaction is complete and have been studied in detail.

Let Z_1, Z_2, Z_3, and Z_4 represent the disgregations for one mole of each reacting substance. In the first example, Z_1 and Z_3 have the form required for gases, whereas Z_2 and Z_4 refer to solids and are hence independent of the degree of dissociation. The external work cancels because for each volume of H_2O an equal volume of H_2 is formed. Hence $Q = q$ and the condition for an equilibrium in a closed space becomes:

$$q/T + ARln(p_1/p_3) + C = 0$$

where C once more stands for the change in the disgregation when the gases are in their normal states [i.e. standard states], and p_1 and p_3 are the partial pressures of the individual gases [*in the original Horstmann inconsistently used* p_2 *instead of* p_3]. The ratio of the two is constant at a constant temperature. The amount of one gas cannot be increased without increasing the density of the other in the same ratio. However, the equilibrium state does not depend on the relative amounts of the two solids. If q and C are considered constant, then this equation gives the approximate relationship between p_1/p_3 and T. These conclusions were all tested earlier (10) and were found to correspond to experiment. At that time the equation was deduced using another method, but the present approach provides a stronger justification for its application.

The other two examples cannot be as rigorously subjected to calculation since the relationship between the disgregation of a salt in solution and its concentration is not known. However, it is known, as mentioned earlier, that the disgregation changes with the concentration and this is sufficient to deduce an important conclusion.

When all four substances are in solution, as in the case of the interactions between Na_2SO_4, HNO_3, $NaNO_3$, and H_2SO_4, then the relative amounts of each must influence the degree of dissociation because the disgregation of each changes as the reaction progresses.

The investigations of J. Thomsen (11) confirm this. Each of the four substances can exert a mass action effect, and there is an equilibrium only at a certain ratio of the relative amounts of the reacting substances. The relation which must exist at equilibrium may be approximated, according to Thomsen, by the equation:

$$apq = p'q'$$

where p, q, p' and q' are the relative amounts and a represents a constant.

I want to mention that our theory would lead us to a relationship of this kind if one assumes that in dilute solutions the disgregation of a salt depends on the separation of its particles in a manner similar to that of a permanent gas, an assumption which is highly probable.

In the third example, only two of the reacting substances (K_2SO_4 and K_2CO_3) are in solution, the other two ($BaSO_4$ and $BaCO_3$) being solids, which, according to our theory, should have no influence on the degree of dissociation. This is confirmed by the experiments of Guldberg and Waage (12), who noted themselves that "the action varies only slightly upon increasing the amounts of these solids." I take the following numbers from their work, which show that the relationship between K_2SO_4 and K_2CO_3 in solution is independent of the relative amounts of the solids. Compared with the variation in the ratio $BaSO_4/BaCO_3$, the value of the ratio K_2SO_4/K_2CO_3 at the same temperature may be considered constant, which is what would be expected from our theory if the previously mentioned hypothesis concerning the disgregation of dilute salt solutions is correct.

Interactions Between $BaSO_4$, K_2CO_3, $BaCO_3$ and K_2SO_4 in Solutions Containing 1 Mol. of Salt per 500 Mol. of Water

Initial Conditions			*Final Conditions*	
$BaSO_4$	K_2CO_3	Temp.	K_2SO_4/K_2CO_3	$BaSO_4/BaCO_3$
1.0	0.25	100°	0.17	26.8
1.0	0.5	100°	0.19	11.5
1.0	1.0	100°	0.25	4.0
1.0	1.0	100°	0.21	4.7
1.0	2.0	100°	0.22	1.4
1.0	3.0	100°	0.23	0.75
1.0	4.0	100°	0.24	0.17
1.0	5.0	100°	0.24	0.08
1.0	5.0	15°	0.04	4.3

According to the table, the ratio K_2SO_4/K_2CO_3 also depends on temperature, as is generally required by our theory.

It must be noted here that it is possible that the influence of temperature on the degree of dissociation may become negligible if, for example, *Q/T* is very small in comparison with the other terms in the basic equation and if the disgregation of the reacting substances varies only slightly with temperature. According the work of Péan de St. Gilles and Berthelot (13), this may be the case for the reaction of organic acids with alcohols.

The theory of dissociation developed here may require yet further testing and verification, though it is in keeping with the examples that have been cited. It correctly predicts which circumstances determine the degree of dissociation in general and how in individual cases the degree of dissociation may be altered by changing these circumstance to the extent that we are able to control them. Summarizing the results of the theory, we find that, in addition to the chemical natures of the reacting substances, the most important influences are the temperature (though at times only to a small degree), as well as the volume which is occupied by the reacting substances, and the pressure to which they are subjected, especially when changes in these quantities affect the disgregations of the individual substances in different ways—for example, when some are liquids or solids and some are gaseous. Lastly, there is also the matter of the relative amounts of the reacting substances, but only when their disgregation depends on these relative amounts. It is primarily the state of aggregation of the reacting substances which determines whether they can or cannot alter the degree of dissociation by means of "mass action." Such "mass action" effects are always to be exerted by gaseous and dissolved reactants but never by solids and liquids that are immiscible, since they may be removed from the reaction without affecting the disgregation of the whole system. It seems to me that these conclusions concerning mass effects are the most important results of the theory and are worthy of further examination.

Until now one has attempted to explain the phenomenon of dissociation (14) on the assumption that the temperature of individual molecules is different from the average temperature which we measure and that, due to random fluctuations, the molecules of a substance capable of undergoing dissociation will, at a given instance, favor reaction in one sense or the other, and thus not all of the molecules will be able to react simultaneously in the same way.

The assumption of random fluctuations, which can cause the molecules to deviate more or less from the average condition, cannot be avoided given a variety of facts and our present views concerning the nature of heat. This is why I believed for a while that I could use it as a basis to develop a theory of dissociation (15). But one soon encounters contradictions with experiment. In particular, one cannot explain in a satisfactory manner the fact, mentioned earlier, that the mass of solids has no influence on the degree of dissociation. I do not wish to describe further the difficulties which discouraged me from pursuing this approach; rather I wish only to discuss how this fact agrees with the present theory. This employs to a certain degree a reversal of the approach used by statistics. The latter assumes a series of identical individual processes and must infer from their resultant in bulk the general laws for the whole, which also prevail for particular cases but which are masked by random fluctuations. In contrast, we know very little of what happens to the individual molecule, but we know the general laws which cannot be infringed upon by any particular process, and we must investigate how much scope remains for the operation of random fluctuations.

We know that there is no reaction between individual molecules which can lead to a lowering of the entropy. This is why, in general, only those changes can occur in which the entropy increases. If this happens, for example, during a decomposition, then in general the decomposition can only proceed if the individual molecules also continuously recombine under randomly favorable conditions.

It is possible to show that, at a certain stage of dissociation, every further change corresponds to a decrease in entropy. In this state as a whole further changes are no longer possible, however many fluctuations the individual molecules may undergo in one direction or the other. As mentioned previously, since the assumption of such random fluctuations cannot be avoided, one must imagine, like Pfaundler, that the state of equilibrium for dissociation phenomena is a stationary state in which the forward and reverse reactions are continuously and simultaneously occurring with the same frequency. However, the existence of these fluctuations and the equal number of reactions proceeding in both directions are no longer the reason for the stationary state, as assumed by Pfaundler.

The limits which a molecule can attain via random fluctuations are, in any case, of great importance for the reaction process and are mainly responsible for determining the velocity with which it proceeds. Probably many processes which are slow are only possible because some molecules deviate so far from the average. They would not occur if all of the molecules were in the average state. In contrast, many other reactions cannot occur, even though they would be accompanied by an entropy increase and the atoms would thereby attain a more stable state of equilibrium, because none of the possible molecular fluctuations are able to attain the necessary extremes.

Also with regard to the phenomenon of dissociation, there will be fluctuations which will, bit by bit, make the reaction possible for individual molecules, thereby driving the reaction, faster or slower, towards the stationary limiting state. However, when this limiting state is reached, it is not maintained by randomness, but rather by a general law which governs all individual processes, be they in limited molecular systems or in the world at large. The state remains stationary because the entropy can no longer increase.

Heidelberg, September 1873

REFERENCES AND NOTES

1. *Phil. Mag*. [4], 4, 304.
2. *Abhandlungensammhung II*, 34.
3. See Clausius, *Abhandlungensammlungen I*, 247.
4. *Ibid*., 248
5. See Clausius, *ibid*., 250.
6. This is contradicted by A. Weinhold, *Pogg. Ann*., 149, 217.
7. *Compt. rend*., 76, 1588.
8. *Annalen Suppl*., 8, 125 ff
9. *Berichte der deutschen chemischen Gesellschaft*, 6, 450.
10. *Berichte der deutschen chemischen Gesellschaft*, 4, 636.
11. *Pogg. Ann*., 238, 94 ff.
12. *Etudes sur les affinités chimiques*. Programm de l'université Christiana, 1867, 59.
13. *Jahresber. für Chemie*, 1861, 592.
14. Compare Naumann, *Thermochemie*, 55 ff.
15. *Berichte der deutschen chemischen Gesellschaft*, 1, 210.

SHAC AWARDS

The Society for the History of Alchemy and Chemistry (SHAC) would like to invite applications from Society members for its new award scheme. Two types of award are available: support for research into the history of chemistry or history of alchemy by New Scholars (up to £500) and support for Subject Development of either history of chemistry or history of alchemy (up to £1000). Closing date for applications: 31 May, 2010.

For more information, and an application form, please contact the Hon Secretary to the Society, Dr Georgette Taylor, at g.taylor@ucl.ac.uk. Membership enquiries to the Hon Treasurer of the Society, John Perkins at shacperkins@googlemail.com.