

*Citation:*

Kohnstamm, Ph. & F.E.C. Scheffer, Thermodynamic potential and velocities of reaction, in: KNAW, Proceedings, 13 II, 1910-1911, Amsterdam, 1911, pp. 789-804

**Physics.** — “*Thermodynamic potential and velocities of reaction.*”

By Prof. PH. KOHNSTAMM and Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of December 24, 1910).

§ 1. In the preceding communication one of us has shown that the number of molecules of a substance in a homogeneous phase which is able to escape from the attraction of this phase in the unity of time is indicated by the expression:

$$N = C \sqrt{T} e^{\frac{\mu'}{RT}}, \dots \dots \dots (1)$$

in which  $\mu'$  represents the thermodynamic potential of this substance in that phase deprived of its mere temperature functions, and  $R$  the molecular gas constant. This formula was applied there to find the condition of the stationary state, in which an equal number of particles enter a solution as leave it through a semi-permeable membrane, but another use of this formula is conceivable. We may, namely, put the question: When there is no equilibrium of exchange between solution and solvent through the membrane, how many more particles per unit of time will then leave the solution than enter it, or in other words how great will be the velocity in a certain state with which the whole system tends to reach equilibrium? It will be expected that in the case mentioned the velocity may be represented by the difference between two expressions of the form (1), the former of which represents the number of particles which leaves the solution, and the second the number of molecules that leaves the solvent, and so enters the solution. We then get for this velocity the expression:

$$N = C \left\{ \sqrt{T_1} e^{\frac{\mu'_1}{RT_1}} - \sqrt{T_2} e^{\frac{\mu'_2}{RT_2}} \right\}.$$

Such a formula would, of course, have to hold for all analogous cases; e.g. for that of the osmotic pressure and for the evaporation of liquids. These velocities, however, do not act a very prominent rôle in physics, and application of the formula to these cases does not seem to open new vistas, the less so as there would hardly be any experimental material to test them by. The problem of the velocities of reaction, on the contrary, plays a most important part in

chemistry, and in this department there is a rich experimental material at our disposal. When we now consider that with these chemical velocities also a great number of particles leaves the reacting mixture with formation of new substances, the question naturally suggests itself whether the expression found will not be able to throw some new light on this region.

So we shall have to investigate whether the velocity of reaction can be expressed in the following form:

$$-\frac{dc}{dt} = C \left( e^{\frac{\mu_I + F_1}{RT}} - e^{\frac{\mu_{II} + F_2}{RT}} \right) \dots \dots \dots (2)$$

in which  $\mu_I$  and  $\mu_{II}$  are the sum of the molecular thermodynamic potentials resp. for the disappearing and forming systems, and  $F_1$  and  $F_2$  functions of the temperature, and further of constants which refer to the reacting substances or perhaps to the intermediate states occurring in the reaction <sup>1)</sup>. The two functions  $F_1$  and  $F_2$  have the dimension of an energy, and the value of the constant  $C$  accounts for the choice of our unity of concentration and time. For its dimension is  $c/t$ , and accordingly may be taken equal for the two partial reactions.

§ 2. Now in the first phase we shall show that both for rarefied gases and for dilute solutions equation (2) leads to the well-known expression for the law of mass-action. If in (2) we substitute the value of  $\mu$  for a mixture of rarefied gases:

$$\begin{aligned} \mu_I = \sum v_I \epsilon_{oI} - T \sum v_I \eta_{oI} + \sum v_I \int c_{vI} dT - T \sum v_I \int \frac{c_{vI}}{T} dT + \\ + RT \sum v_I \ln c_I + RT \sum v_I \end{aligned}$$

and

$$\begin{aligned} \mu_{II} = \sum v_{II} \epsilon_{oII} - T \sum v_{II} \eta_{oII} + \sum v_{II} \int c_{vII} dT - T \sum v_{II} \int \frac{c_{vII}}{T} dT + \\ + RT \sum v_{II} \ln c_{II} + RT \sum v_{II} \end{aligned}$$

we get:

<sup>1)</sup> According to equation (2) not the thermodynamic potential itself, but an exponential function of it would be the function characteristic of the reaction. Cf. also Chem. Weekblad 7, p. 920 (1910).

$$\begin{aligned}
-\frac{dc}{dt} = C \left\{ e \frac{\sum v_I \varepsilon_{oI} - T \sum v_I \eta_{oI} + \sum v_I \int c_{vI} dT - T \sum v_I \int \frac{c_{vI}}{T} dT + F_1 + RT \sum v_I}{RT} \Pi c_I^{\nu_I} - \right. \\
\left. - e \frac{\sum v_{II} \varepsilon_{oII} - T \sum v_{II} \eta_{oII} + \sum v_{II} \int c_{vII} dT - T \sum v_{II} \int \frac{c_{vII}}{T} dT + F_2 + RT \sum v_{II}}{RT} \Pi c_{II}^{\nu_{II}} \right\} (3)
\end{aligned}$$

in which  $\Pi c_I^{\nu_I}$  and  $\Pi c_{II}^{\nu_{II}}$  represent the product of the concentrations of the first, resp. the second member of the equation of reaction, taking the number of molecules into account. If we call:

$$\frac{\sum v_I \varepsilon_{oI} - T \sum v_I \eta_{oI} + \sum v_I \int c_{vI} dT - T \sum v_I \int \frac{c_{vI}}{T} dT + F_1 + RT \sum v_I}{RT} = k_1,$$

and

$$\frac{\sum v_{II} \varepsilon_{oII} - T \sum v_{II} \eta_{oII} + \sum v_{II} \int c_{vII} dT - T \sum v_{II} \int \frac{c_{vII}}{T} dT + F_2 + RT \sum v_{II}}{RT} = k_2,$$

(3) reduces to:

$$-\frac{dc}{dt} = k_1 \Pi c_I^{\nu_I} - k_2 \Pi c_{II}^{\nu_{II}} \dots \dots \dots (4)$$

In the second place we must prove the validity of this formula for reactions in dilute solution. For this purpose we introduce a new quantity,  $\mu'_1$ , determined by the relation:

$$\mu_1 = \mu'_1 + RT \log n_1 \dots \dots \dots (5)$$

So  $RT \log n_1$  is that part of the thermodynamic potential that is in connection with GIBBS's paradox, and  $\mu'_1$  the remaining part. Now as is known, the differential quotient of  $\mu'_1$  with respect to the concentrations<sup>1)</sup> remains finite, whereas that of the second part

<sup>1)</sup> In contradiction to what is usual in the treatment of velocities of reaction, we define the concentrations here as molecular percentages of a certain substance in a definite mixture, and not as this quantity divided by the total volume. But it is clear that this does not affect the conclusions about the constancy of  $k_1$  and  $k_2$ , as in every reaction in a dilute solution the change of volume during this reaction is disregarded.

becomes infinite for exceedingly dilute solutions. For the (of course also very slight) changes to which the concentrations in an exceedingly dilute solution can be subjected we may, therefore, consider  $\mu'_1, \mu'_2$  etc. as invariable, independent of the concentrations, when we take the variations of  $RT \log n_1$  etc. with the concentration into account. If we now substitute the value (5) for  $\mu_1$ , and bring down the term  $RT \log n_1$  from the exponent, we get again:

$$-\frac{dc}{dt} = k_1 \Pi n_1 - k_2 \Pi \mu'_1 \dots \dots \dots (4a)$$

where:

$$k_1 = e^{\frac{\Sigma \mu'_1 + F_1}{RT}} \quad \text{en} \quad k_2 = e^{\frac{\Sigma \mu'_2 + F_2}{RT}} \dots \dots \dots (6)$$

may be considered as constants according to the above, as is required by the law of the mass-action.

We conclude from this equation (4 and 4a) that really equation (2) can properly account for a highly important property of the course of the reaction. This result was by no means to be considered as certain beforehand. For we have drawn up this equation by analogy, and drawn attention to the close agreement with the use of equation (1) in this and the preceding communication, but not to the existing differences. It is here the place to set forth these differences. It is true that in the case of the "osmotic temperatures" the final state is no state of equilibrium, but each of the two homogeneous phases may yet be considered as in equilibrium, if we leave the immediate neighbourhood of the membrane out of consideration. So we are undoubtedly justified in speaking of quantities as temperature, entropy, thermodynamic potential in each of the phases, and there the formula was applied only to that final state "of equilibrium of mass exchange". But not without justification it might be doubted whether the same thing is allowed for states in which the equilibrium of mass exchange has not yet set in, and a fortiori this holds for the case under consideration. For the homogeneous phase in which the reaction takes place, is not in equilibrium in itself; it is not certain that MAXWELL'S distribution of velocities holds there, and even if with BOLZMANN we want to introduce a definition for the entropy of a state of non-equilibrium, it will, of course, in general have another value than the  $\eta$  from equation (2).

Now it appears from equation (4) that all the same these undoubtedly weighty objections need not lead to a rejection of equation (2). For the very extensive material of facts concerning the reaction

velocities proves conclusively that equation (4) applies to a great number of reactions that proceed with measurable velocities. Particularly it has been ascertained by numerous measurements that  $k_1$  and  $k_2$  are really constants in reactions that proceed normally<sup>1)</sup>, so they are not quantities that depend on the time. If the influences which we mentioned, made themselves so strongly felt that equation (2) had to be rejected, this result would be impossible. For as the mixture more and more approaches the state of equilibrium during the reaction, and at last reaches it, the difference between the entropy which really exists at any moment (BOLTZMANN'S  $H$ -function) and the entropy of the state of equilibrium will continually decrease, and at last become zero; and this remark applies to all the other mean values occurring in equation (2). But then also the  $k_1$  and  $k_2$  would necessarily become dependent on the time, and not only the  $\Pi c_1^{\nu_1}$  and  $\Pi c_{II}^{\nu_{II}}$ , as experiment teaches. So we must conclude that the systems with measurable velocities of reaction may be considered as quasi-stationary systems, for which not only an entropy, a thermodynamic potential etc. exist, but for which these quantities (leaving the influence of the concentration unconsidered, of course) even differ immeasurably little from the corresponding quantities in the state of equilibrium. Now an experimentally firm basis has been given as a support for us in our further examination and development of equation (2). More particularly it has now been proved, that  $F_1$  and  $F_2$  can really only depend on quantities which are constant during the reaction as we supposed in § 1. However more ensues from this supposition than has been proved yet. We come back to this in § 5.

§ 3. Our second step is now to show that equation (2) differs from the equation (11) of the preceding paper holding for "osmotic temperatures" in this that here  $F_1$  does not comprise the pure temperature functions of the thermodynamic potential with negative sign, as it did there. For the equation of the equilibrium requires the equality of the sums of the thermodynamic potentials of the two systems, and so for rarefied gases:

---

<sup>1)</sup> We mean here by "abnormal" reactions of course reactions for which further investigation makes it plausible that the inconstancy of  $k$  is to be ascribed to after reactions, by-reactions, catalysis or too great concentrations.

$$\begin{aligned} & \sum v_I \varepsilon_{0I} - T \sum v_I \eta_{0I} + \sum v_I \int_{v_I}^{v_{vI}} dT - T \sum v_I \int \frac{c_{vI}}{T} dT + RT \sum v_I \ln v_I + RT \sum v_I = \\ & = \sum v_{II} \varepsilon_{0II} - T \sum v_{II} \eta_{0II} + \sum v_{II} \int_{v_{II}}^{v_{vII}} dT - T \sum v_{II} \int \frac{c_{vII}}{T} dT + RT \sum v_{II} \ln v_{II} + \\ & \quad + RT \sum v_{II} \dots \dots \dots (7) \end{aligned}$$

on the other hand equation (2) requires that:

$$\mu_I + F_1 = \mu_{II} + F_2 \dots \dots \dots (8)$$

for the equilibrium, where the velocity = 0.

If  $F_1$  were the same function as in equation (11) of the preceding paper, this would lead to:

$$\sum v_I \varepsilon_{0I} + RT \sum v_I + RT \sum v_I \ln v_I = \sum v_{II} \varepsilon_{0II} + RT \sum v_{II} + RT \sum v_{II} \ln v_{II} \quad (9)$$

and this equation is in conflict with the undoubtedly valid equation (7) as in general the specific heats of the reaction products and of the reacting substances are not equal and the constants of entropy do not occur in the latter equation. This observation is not new. It is namely at bottom identical with the argumentation on p. 45—51 in Mr. DE LANGEN'S Thesis for the doctorate<sup>1)</sup>, that the omission of the pure functions of the temperature from the formula for the thermodynamic potential for chemical reactions brings us in collision with VAN 'T HOFF'S equation. For the latter is immediately obtained by differentiation from (7), whereas differentiation from (9) yields the equation of p. 46 of Mr. DE LANGEN'S Thesis for the doctorate, which is in opposition to it. Mr. DE LANGEN concludes from this that the kinetic gas theory and thermodynamics are here in conflict.

But this conclusion cannot be maintained. For it has been overlooked that for the kinetic derivation of the thermodynamic potential of a mixture of chemically interacting substances, we shall have to take BOLZMANN'S<sup>2)</sup> "kritische Räume" into consideration, and that when the heat of reaction varies with the temperature, terms must appear which are dependent on the difference of the specific heats<sup>3)</sup>. What the relation must be between these terms and the temperature and the specific heats, could only be revealed by a perfectly developed kinetic theory, which could at the same time give an account of the value of the specific heat of the different substances. So at present thermodynamics leads us further in this respect, though it naturally

<sup>1)</sup> Groningen 1907.

<sup>2)</sup> Gastheorie II Abschnitt VI.

<sup>3)</sup> loc. cit. p. 192.

must leave the question undecided why and how the specific heat varies with the temperature and with the character of the substances.

§ 4. If we now compare equation (7) and (8), it appears that:

$$F_1 = F_2 \dots \dots \dots (10)$$

and as according to § 2 neither  $F_1$  nor  $F_2$  can be dependent on the time during the reaction, equation (8) is satisfied throughout the reaction. The same reasoning holds of course with very little change for dilute solutions too, and then also leads to equation (10). So it appears that in § 1 we have defined these functions not closely enough, when we introduced them as functions of the temperature and of constants characteristic of the reacting substances, and eventually of the occurring intermediate states. For the supposition:

$$F_1 = F_1(T, a_1, b_1, c_1 \dots)$$

$$F_2 = F_2(T, a_2, b_2, c_2 \dots)$$

would be in accordance with this definition, in which  $a_1, b_1, c_1$  are characteristic of the system before the reaction,  $a_2, b_2, c_2$  for the system after the reaction, and mutually independent. Nay, this supposition would even be the most obvious one. Equation (10), however, shows that it must be rejected. The constants in  $F_1$  cannot be independent of those in  $F_2$ ; they must be quantities which in some way or other are equally in relation with the two systems, that before and that after the reaction<sup>1)</sup>.

The simplest supposition then would be that all these constants were = 0, and so that  $F$  would be a pure general function of the temperature, like the  $\frac{1}{2} RT \ln T^2$  from equation (11) of the preceding paper, or that possibly this too would be wanting, and  $F = 0$  might be put. However, on this supposition we come to just such an absurdity as made us reject equation (4) in the preceding paper. For from experimental determinations of:

$$k_1 = Ce \frac{\sum v_I \epsilon_{0I} - T \sum v_I \eta_{0I} + \sum v_I \int c_{vI} dT - T \sum v_I \int \frac{c_{vI}}{T} dT + RT \sum v_I}{RT}$$

and

$$k_2 = Ce \frac{\sum v_{II} \epsilon_{0II} - T \sum v_{II} \eta_{0II} + \sum v_{II} \int c_{vII} dT - T \sum v_{II} \int \frac{c_{vII}}{T} dT + RT \sum v_{II}}{RT}$$

<sup>1)</sup> So the above considerations lead to the assumption of two opposed reactions, which are, however, not 'independent' of each other. For the functions  $F$  occurs in both velocities, i.e. both partial velocities depend on the same "intermediate states".

<sup>2)</sup> If the  $\sqrt{T}$  is brought into the exponent.



at two temperatures (or the corresponding expressions for dilute solutions) we could determine  $\epsilon_{01}$ ,  $\epsilon_{011}$ ,  $\eta_{01}$ , and  $\eta_{011}$ , in other words we could find the absolute values of the energy and of the entropy experimentally, though both contain indefinite additive constants according to our definition, so that only differences of energy and entropy are liable to be measured.

So we are certain that  $L'$  must contain values of energy and entropy which reduce the values of the energy and the entropy in the exponent to differences of energy and entropy. And, to confine ourselves for the present to the difference of energy, one difference of energy must determine one velocity of reaction, the other the other, their algebraic sum being the total difference of energy in the conversion, so the heat of reaction. Accordingly it is not possible that the *total* heat of reaction appears in *both* the velocities of reaction, as we might be inclined to suppose. Or in other words the total heat of reaction must be split up into two parts, of which the first determines one velocity, the second the other velocity. What is now the "intermediate state", which determines this splitting up of the heat of reaction? First of all we might think of the state in which the reacting compounds are entirely split up into their atoms, so that one velocity is determined by the energy of dissociation of the reacting substances, the other by that of the reaction products. But this supposition has sense only when we assume that the reaction really takes place over the free atoms. How in the opposite case the really occurring process would be entirely determined by the then altogether fictitious heat of dissociation in the atoms, is difficult to see <sup>1)</sup>. And though for the kinetic theory the supposition of dissociation may have some attraction, because it is an analogue to the thesis that every substance has a vapour-pressure however slight, and admits of continuous transitions, it is easy to see that the assumption of such a course "over the atoms" does not decide the question, but on the contrary only displaces and complicates the difficulty.

For when the reaction takes place over intermediate bodies present in an appreciable quantity, whatever they be, the total reaction will no longer consist of two, but of four partial reactions, because also these intermediately formed bodies will be converted to the original and the forming substances with definite velocities. The process of the reaction then becomes more complicated, and can be expressed

<sup>1)</sup> In our opinion quite arbitrarily TRAUTZ introduces as determinative for reactions without intermediate products the heat of splitting up of the reacting substances into atoms deprived of their kinetic energy, and a part of their potential energy absolute zero, solid state). See TRAUTZ, Zeitschr. phys. Chem. 64 et seq.

by the following equations:

$$\frac{-dc_1}{dt} = k_1 \Pi c_1 - k_{a_1} \Pi c_a$$

and

$$\frac{dc_{11}}{dt} = k_{a_2} \Pi c_a - k_2 \Pi c_{11}$$

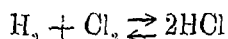
in which the change in concentration of the intermediate product is indicated by:

$$\frac{dc_a}{dt} = -\frac{dc_I}{dt} - \frac{dc_{11}}{dt} = k_1 \Pi c_1 - k_{a_1} \Pi c_a - k_{a_2} \Pi c_a + k_2 \Pi c_{11}.$$

So in general the velocity will not be represented by the simple expression of the law of mass-action<sup>1)</sup>; this is the case only when  $k_{a_1}$  and  $k_{a_2}$  are both very great with respect to  $k_1$  and  $k_2$ , in other words when no appreciable quantities of the intermediate products occur in the reaction mixture<sup>2)</sup>.

An example of this furnishes the reaction  $\text{Ni} + 4\text{CO} \rightleftharpoons \text{Ni}(\text{CO})_4$ , in which the measurements of the velocity show that the reaction takes place from the left to the right over  $\text{Ni}(\text{CO})_2$ , which, however is so quickly decomposed, and combines so rapidly with an excess of CO ( $k_{a_1}$  and  $k_{a_2}$  great), that it cannot be demonstrated in the reaction mixture.

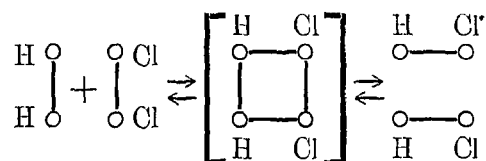
But there is little reason to assume that every reaction should be thought to be such that the reacting substances break up into pieces (either atoms or groups of atoms), which unite again as free components in another way; on the contrary room should be left for the possibility that throughout the reaction no other independently moving particles occur than the molecules of the initial and the final products. This supposition is undoubtedly greatly supported by the fact that substances which are in themselves exceedingly stable, and do not present the slightest trace of dissociation in pure condition at a definite temperature, are yet liable to be analysed by means of an added substance. If to take a concrete example, we consider the reaction:



1) That in this case the reaction heat must be split up into two parts one of which is the heat of reaction of the decomposing substances in the intermediate product, the other that of the forming substances into the intermediate body, seems to us not doubtful; this refers, however, to the splitting up of a constant of equilibrium into two other constants of equilibrium, each of which must then again be split up into two constants of velocity.

2) Zie SCHEUREINEMAKERS Chem. Weekblad 1. 625 (1904).

at least the possibility will not be denied that the reaction does not take place so, that  $H_2$  and  $Cl_2$  are dissociated to atoms H and Cl, and these atoms meet again with formation of HCl, but so that a molecule  $H_2$  meets a molecule  $Cl_2$ , and that with a suitable position of these molecules the bond between the H atoms and the Cl atoms inter se is only broken in consequence of the mutual attraction of the H and the Cl atoms and immediately passes into a new bond. If we imagine the course of the reaction in this way, a value of the energy may be indicated which undoubtedly with greater justice may be expected to determine the velocity of reaction than the heat of dissociation in the atoms which is here devoid of any chemical significance. In consequence of the approach of the molecules  $H_2$  and  $Cl_2$  there is, namely, a certain loss of potential energy through the action of the attracting forces; when the two molecules have approached each other to a certain distance, the potential energy will attain a minimum value, a condition which is indicated by what is contained between the brackets in the following symbolic representation:



If then the molecules of hydrochloric acid again separate, the potential energy will rise again in consequence of the work done against the attractive forces.

Now in our opinion it may certainly not be considered as impossible that this state of minimum potential energy is to be considered as the above-mentioned "intermediate state". In the value of  $I^7$  of equation (10) the corresponding potential energy and entropy, at least the corresponding constants, will have to occur.

We may state once more that we by no means mean to say that in the mentioned reaction, or any other reaction, the process must be exactly as we sketched it. We only wanted to make clear first of all that it necessarily follows from the value for  $k$  that "intermediate states" play a part; further that these intermediate states may be of various kinds, and can be entirely different in one reaction from that in another. So a *universally* holding splitting up of the heat of reaction into two parts, for reactions in which no intermediate products occur, as of late was tried by TRAUTZ, will probably be impossible. There is still less chance that it is to be

decided now, whether besides the quantities determined by the "intermediate state" there is still a general function of the temperature, as  $1/2 RT \ln T$  which occurs in  $F$ .<sup>1)</sup> Only a further development of the kinetic theory and an accurate analysis of the experimental material in the light of such a theory, can lead us further.

§ 5. We must now return to the conclusion of § 2. We said there that there is more involved in our suppositions about  $F_1$  and  $F_2$  than could be proved by the facts mentioned there. For these prove that  $F$  can only depend on quantities constant in the reaction. If we now imagine a reaction in rarefied gas state, in which the total number of molecules changes, then the concentrations, the pressure, and the specific volume change during the reaction. So in this case these quantities cannot occur in  $F$ . But by far the most important part of the material concerning the law of the mass-action refers to reactions in dilute solutions, and during these reactions the pressure does not change. If we want to compare our supposition that  $F$  does not depend on the pressure with the experiment for these reactions, we must examine the influence of the pressure on the velocity of reaction. In this we must, however, take note of a circumstance, which it was unnecessary to mention expressly in the foregoing discussion: the influence of catalytic agents<sup>2)</sup>, and that because in general the possibility exists that the solvent itself works as a catalytic agent, i.e., that the solvent participates in the "favourable" collisions, and thus occasions the exchange of the absorbed resp. generated heat. So we shall have to keep the possibility in view that the presence of the solvent, or of other dissolved substances, whose quantity remains invariable (catalytic agents) is yet of great influence on the velocity of reaction. According as this influence in this sense exists or does not exist, the thermodynamic potential of these substances must be added to the other thermodynamic potentials in equation (6).

Let us now first consider the case that neither the solvent nor the catalytic agent takes part in the collisions favourable for the reaction, we shall have to sum the  $\mu'_1$  of the different reacting substances

---

1) See TRAUTZ papers *Zschr. f. phys. Ch.* 64, et seq. and SACKUR's criticism of them *Zeitsch. f. Elektroch.* 15 (1909).

2) We refer to homogeneous catalysis, as appears from the text. Also elsewhere in this paper we have disregarded heterogeneous catalysis, particularly in the gas-reactions discussed in § 2, which we assumed to take place in the homogeneous phase, leaving undecided whether such reactions really occur, or whether every gas-reaction represents a case of heterogenous catalysis.

under the  $\Sigma$  sign in equation (6), whereas  $l'$  is only dependent on the temperature and on the quantities characteristic of the different substances according to our suppositions. Hence

$$\frac{dlk}{dp} = \frac{1}{RT} \frac{\Sigma d\mu'_i}{dp}$$

or as according to equation (5)

$$\begin{aligned} \frac{\partial \mu'_1}{\partial p} &= \frac{\partial \mu}{\partial p} \\ \frac{\partial lk}{\partial p} &= \frac{1}{RT} \left( \frac{\partial \Sigma \mu'_i}{\partial p} \right) \dots \dots \dots (11) \end{aligned}$$

Now for a mixture of  $n$  components, of which resp.  $n_1, n_2, \dots, n_n$  gram-molecules are present

$$d\varepsilon = Td\eta - pdv + \mu_1 dn_1 + \mu_2 dn_2 \dots \mu_n dn_n$$

where  $\mu$  is the molecular thermodynamic potential.

Or:

$$d\zeta = -\eta dT + v dp + \mu_1 dn_1 + \mu_2 dn_2 \dots \mu_n dn_n$$

and so:

$$\left( \frac{\partial \mu_1}{\partial p} \right)_{T, n_1, n_2, \dots, n_n} = \left( \frac{\partial v}{\partial n_1} \right)_{p, T, n_2, \dots, n_n}$$

in consequence of which (11) passes into:

$$RT \frac{dlk}{dp} = \Sigma \left( \frac{\partial v}{\partial n_i} \right)_{p, T, n_1, n_2, \dots, n_m, \dots, n_n} = \left( \frac{\partial v}{\partial n_1} \right)_{p, T, n_2, \dots, n_n} + \left( \frac{\partial v}{\partial n_2} \right)_{p, T, n_1, n_3, \dots, n_n} + \text{etc.} (12)$$

So in order to examine the change of the velocity of reaction with the pressure, we have to determine for every substance of the disappearing system (resp. the forming system) the change of volume, which takes place when we add one gram molecule to the whole system (reacting substances, reaction products, solvent), the quantity of this last being thought so great that it does not change the concentrations. The sum of these variations gives  $\frac{dlk}{dp}$ .

It is clear that it will be a great exception if one of the quantities  $\left( \frac{\partial v}{\partial n} \right)$  becomes negative. For this would mean that there was a contraction so considerable that the mixture occupies a smaller volume after the mixing than the solvent alone. Yet it must not be considered as impossible a priori; and a negative value of  $\left( \frac{\partial v}{\partial n} \right)$  seems

even to occur for some aqueous solutions. It is, however, required for a negative value of  $\frac{dlk}{dp}$ , that the sum of  $\left(\frac{\partial v}{\partial n}\right)$  becomes negative for all the substances of the system, and this is of course, still less probable. Hence it may be safely assumed that a negative value of  $\frac{dlk}{dp}$  will not occur in the case considered up to now. When the solvent takes part in the reaction (in the above-mentioned sense, that only those collisions are favourable in which also the solvent participates, so without change of its quantity during the reaction), also the thermodynamic potential of the solvent will have to be inserted under the  $\Sigma$  sign in our equation. So in equation (12) one more term  $\left(\frac{\partial v}{\partial n}\right)$  will occur on the right side, which refers to the solvent. This will, however, not easily affect our conclusions about the sign of  $\frac{dlk}{dp}$ . It is, however, a different matter, when also a catalytic agent plays a part. If e.g. we think the H-ions of an added acid active as a catalyser, the change of the thermodynamic potential of these H-ions with change of the pressure will not be represented by a term as  $\left(\frac{\partial v}{\partial n}\right)$ , because there neither the possible modification of the degree of dissociation by the increase of pressure, nor the appearance of hydrations has been taken into account. So the fact that ROTHMUND found a negative value of  $\frac{dlk}{dp}$  in the conversion of cane-sugar under influence of HCl, need not be in contradiction with equation (2), and equation (12) derived from it. In the few other cases known to us, where the influence of the pressure on the velocity of a reaction has been examined, a positive value is found, but this experimental material is certainly still too scanty to justify a conclusion concerning equation (2). A more complete knowledge of the facts, preferably concerning reactions where the last mentioned complications do not occur, might possibly enable us to decide about the suppositions which lead to equation (2).

Other conclusions from equation (2), which may be tested by experiment, will be found for concentrated solutions. For it is clear, that then the values  $\mu'$ , etc. must no longer be considered independent of the concentrations, in other words that the  $k_1$  and  $k_2$  can no longer be constant, so that deviations from the law of mass-action present themselves, as has actually been found in the inversion of cane-sugar. We hope to return to this point later on.

§ 6. Here we intend only to add some general remarks in connection with the above-given considerations. For even though we emphatically point out that we are entirely in the region of suppositions about the nature of the "intermediate states" holding for every reaction, we consider it proved by the considerations of § 4 that for every reaction<sup>1)</sup> such "intermediate states" must possess a real signification as far as their velocity is concerned. And in consequence of this we think we are able, also in connection with the other considerations which we have given in this communication, to make an attempt to give a more general and lucid classification of the conception catalysis and allied phenomena, than had been possible up to now. In doing this we shall have to distinguish strictly — as VAN 'T HOFF already does in his Vorlesungen Heft I p. 210 et. seq. — between influences which only affect the velocity, the real catalytic agents and "shifters of the equilibrium". Hence we distinguish the following cases:

1. A reaction which does not take place between the pure substances, or which only proceeds slowly, is started or accelerated by a substance which is present in small quantity and does not take part in the reaction. The equilibrium that establishes itself is, however, independent of the nature of the catalytic agent. We think e.g. of the equilibrium acetaldehyde, paraldehyde, metaldehyde or of the conversion of oxyhydrogen gas. For each of these cases we have undoubtedly to do with phenomena of retardation, false equilibria; the condition without a catalytic agent is, indeed, a local maximum of entropy at given energy, but not an absolute maximum. The catalytic agent does not change the specific energy or entropy of the substances in any respect, but only enables them to reach the absolute maximum of entropy by change of concentration. So it may be compared to a crystal brought into a supercooled liquid. But what was said in § 4 can make this action somewhat clearer to us. This action consists in the creation of an intermediate state, or if this existed already in changing its potential energy in consequence of which the difference of energy which determines the velocity, is increased. Different catalytic agents act differently in this respect, and so they give rise to another velocity.

2. A substance which is added in an exceedingly slight quantity not only changes the velocity of reaction, but also the equilibrium.

---

<sup>1)</sup> Perhaps pure dissociations e.g.  $N_2O_4 \rightleftharpoons 2NO_2$  will only have to be excepted.

Such an influence<sup>1)</sup> would occur, if the specific entropy of the parts of the reacting mixture should be changed by the catalytic agent, but not the specific energy. The mutual entropy of the system catalytic agent + reacting mixture in the ideal gas state would have another value in this case, than is given by GIBBS's paradox, while as usually in the ideal gas state no mutual energy would occur. To explain this we should have to accept a change of the chemical volumes (BOLTZMANN's "kritische Räume") of the reacting mixture by the catalytic agent. A modified intermediate state would, of course, occur here too; hence the equilibrium will be reached with another velocity.

3. By the addition of a substance which does not take part in the reaction also the specific energy of the reacting substances is changed either because only the mutual attraction in the mixture becomes different — new  $\alpha$ 's appear in the equation of state — or because stronger causes are active (association of the solvent with one of the reacting substances). Of course also the velocity of reaction will change in both cases. To this category belong all "milieu" influences, of course, (e. g. changes of electrolytic dissociation with change of solvent). Also the displacements of the equilibrium under influence of light or electric discharges may belong to it, e. g. the light-equilibrium of sulphur in  $CS_2$ , which sets in with a certain intensity of illumination, and which returns to its former state when the old state of illumination is restored. Here too it must be assumed that in consequence of the illumination the energy of the reacting substances is modified<sup>2)</sup>.

4. The last mentioned cases, however, can also belong, either all of them or partly, to another category. For it is possible that they are no real equilibria, but are in the same relation to them as the case of the "osmotic temperatures" to that of real equilibrium, or in other words that the modified state must always be accompanied by a "current of energy", an absorption of heat or electric energy and emission of heat. Then the displacement would not be maintained

<sup>1)</sup> We will leave it an open question whether the cases cited as such in the literature should not really be ranged under 3, but think that we should at least mention this possibility for completeness' sake because the considerations of VAN 'T HOFF l.c. p. 21 which indeed only seem to be intended for heterogeneous catalysis, do not prove as far as we can see, that a case of homogeneous catalysis of this kind is excluded by the second law of thermodynamics.

<sup>2)</sup> Cf. SMITHS. These Proc. XII p. 356. Of course the false equilibria, which are reduced to the absolutely stable state by light or an electric spark do not belong to this category; they belong under 1.



if we could enclose the system between absolutely reflecting walls in the new state, and if we could thus maintain the same state of radiation, but without absorption of new energy. Such a system would no longer respond to the laws of thermodynamics, even if we included among them the thermodynamics of radiation, in the same way as we found that for the "osmotic temperature" the thermodynamic law of constancy of the thermodynamic potential is not fulfilled. Our experimental and theoretical knowledge is not sufficiently advanced to decide whether the photo- and electrochemical "equilibria" belong to this or the preceding category <sup>1)</sup>.

**Physics.** — "*Some remarks on the mechanical foundation of thermodynamics.*" I. By Dr. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENZ).

(Communicated in the meeting of December 24, 1910).

In order to deduce the second law of thermodynamics the theory of ensembles of systems is often used. This theory has been largely discussed by J. W. GIBBS in his well-known Elementary Principles of Statistical Mechanics. In his book two kinds of ensembles, the canonical and the microcanonical, come to the fore. The latter kind of ensembles has been used by Dr. PAUL HERTZ who held some views which give me occasion for a few remarks <sup>2)</sup>.

§ 1. In the beginning of his paper Dr. HERTZ explains that it is rational to use for the study of the phenomena shown in a given system the ensemble of states taken by that system when left to itself. Such an ensemble is usually termed a time-ensemble. As the observed phenomena must be considered as the result of many phases adopted by the system during the time of observation, we have every reason to presume, that our observation teaches us something of the mean value in the time-ensemble. By using the terminology of poly-dimensional geometry we can put the following

<sup>1)</sup> We will point out that it is sometimes still impossible to assign a place in this classification to a phenomenon in the department of catalysis. It is e. g. difficult to explain in what connection with the mentioned cases the fact is that the thermodynamic potential of perfectly dry solid  $\text{NH}_4\text{Cl}$  is so considerably modified by the addition of the slightest trace of moisture, as appears from the totally modified partial vapour pressure of the  $\text{NH}_4\text{Cl}$  molecules. Perhaps this case will appear to be an example of 2.

<sup>2)</sup> Ann. der Phys. Bd. 30, p. 236, 1910.