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Chemistry. — “*On velocities of reaction and equilibria.*” By Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN).

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1. In a previous paper in conjunction with Prof. KOHNSTAMM¹⁾. I discussed the relation between the velocity of reaction and the thermodynamic potentials of the substances participating in the reaction. It then appeared that the velocity of a reversible reaction may be given by the expression:

$$-\frac{dc}{dt} = C \left(e^{\frac{\mu_I - F}{RT}} - e^{\frac{\mu_{II} - F}{RT}} \right), \quad \dots \quad (1)$$

in which μ_I represents the sum of the molecular thermodynamic potentials of the substances of the first member, μ_{II} the sum of the potentials of the substances of the second member of the reaction equation. The constant C accounts for the choice of the unities of concentration and time, and has therefore the same value for all reactions when the same unities are used. We have shown that the function F possesses the same value for both partial velocities, that it is independent of time and volume, and that it is equally in relation with both systems before and after the reaction. As further, quantities of energy and entropy must occur in the quantity F , we have tried to make clear that in general in case of chemical reactions “intermediate states” must be assumed, and we have pronounced the possibility that the energy and entropy of these transitional states are the only quantities dependent on the nature of the substances, which occur in the function F . By entropy we mean here the entropy “free from concentration”; we have namely shown in our cited paper that F is independent of the concentrations in case of gas reactions and reactions in dilute solutions; hence it can contain no terms originating from GIBBS’s paradox. The value of the two partial velocities would therefore be determined according to this by the difference in energy and entropy (free from concentration) of the reacting substances and the transitional state. This in my opinion obvious assumption comes to this that both the difference of energy and the difference of entropy between the first and the second system must be split up into two parts; the first part then gives the differences of energy and entropy of the first system with

¹⁾ These Proc. Jan. 1911. p. 789.

the transitional state, the other the differences of the second system with this transitional state.

As far as the values of energy are concerned such a solution was already proposed by VAN 'T HOFF in the *Etudes de dynamique chimique* and recently also TRAUTZ has tried an analogous splitting up of the values of energy, as we already mentioned in our previous paper. Though in his earlier papers on reaction velocities TRAUTZ considered a universally holding resolution possible, against which we thought we had to protest in the cited paper, TRAUTZ has introduced as possible ways different from reaction to reaction in his later papers, and with them different ways of splitting up, so that as far as the values of energy are concerned the difference between our considerations and those of TRAUTZ has partly disappeared. Yet also in this respect a difference continues to exist in our views, for TRAUTZ executes the splitting up of the energy at the absolute zero, and it seems more plausible to me to attribute the course of the reaction to the difference of energy at the reaction temperature. For the present it will certainly not be possible to obtain a definite decision of this question, as for the greater part the quantities occurring in the expressions for the velocity of reaction, have not yet been measured with sufficient accuracy, or sometimes are not even liable to direct measurement.

With regard to the splitting up of the entropy the difference between the mentioned views is still greater. Whereas TRAUTZ does not execute a splitting up of the entropy and introduces the absolute value of the entropy of the reacting system into the equation of velocity making use of the integration constants of the vapour pressure, an analogous splitting up seems necessary to us also for the entropy, especially when we adopt the views which BOLTZMANN has expressed on chemical actions in his *Gastheory*.

In the cited paper we have illustrated by the example of the chlorine-hydrogen equilibrium, how we think we have to imagine the transition states occurring there. If we adopt the standpoint of BOLTZMANN's theory, we must assume that the two hydrogen atoms in the hydrogen molecule are bound, in consequence of the fact that the "kritische Räume" of the two hydrogen atoms cover each other entirely or partially, and also those of the two chlorine atoms in the chlorine molecule. If we now inquire into the reaction between a chlorine and a hydrogen molecule, we must imagine that the two molecules get so close together that the four "kritische Räume" of the four atoms will entirely or partially coincide, so that the four atoms are in each others' sphere of action. After this transitional

state a separation takes place of the "kritische Räume" of the hydrogen atoms and the chlorine atoms inter se, the dissimilar atoms remaining bound. Hence the energy quantity F must be the energy which prevails, when the four "kritische Räume" coincide, while the value of the entropy must take account of the volume of the coinciding Räume.

When we consider that the difference of energy between the reacting substances and the transitional state is no more to be calculated aprioristically than any other chemical change of energy, and that as yet we have no means at our disposal either, to predict the volumes of the "kritische Räume" by the aid of the properties of the substances, it is clear that we cannot test the above considerations except by examining whether we can assign plausible values of the energy and the entropy to the transitional states to get into harmony with the known material of facts. It is true that NERNST'S theorem of heat, in the form as it is conceived by PLANCK, fixes the values of the entropy of solid substances at the absolute zero, so that the entropy constants of the gases are brought in relation with the integration constants of the vapour pressure, but even if one is convinced of the validity of the theorem of heat, yet the imperfect knowledge of the specific heats presents too great a difficulty up to now to calculate entropies a priori. With regard to the transitional states such a calculation is a fortiori impossible, as the facts known to us indicate that these transitional states greatly vary for different reactions, and are e. g. greatly influenced by catalysers.

When we now inquire into what the material of facts can teach us with regard to the transitional states, we will examine in the first place whether the energy in the transitional state is greater or smaller than in the initial or in the final state, or whether it perhaps lies between these two latter values. To answer this question I will (to keep the considerations as simple as possible), consider a reaction in a rarefied gas mixture that completely takes place in one direction. In this case the second partial velocity has a negligibly small value compared with the first. The velocity of the reaction is then represented by:

$$-\frac{dc}{dt} = C e^{\frac{\mu_f - F}{RT}} \dots \dots \dots (2)$$

If we now insert the value of μ_f for the dilute gas-mixture, which according to our preceding paper may be represented by:

$$\mu_f = \sum v_f \epsilon_{0_f} - T \sum v_f \eta_{0_f} + \sum v_f \int c_{1_f} dT - T \sum v_f \int \frac{c_{1_f}}{T} dT + \left. \begin{array}{l} \\ + RT \sum v_f \ln c_f + RT \sum v_f \end{array} \right\} \dots (3)$$

into equation 2, in which we write $\varepsilon_t - T\eta_t$ for F , where ε_t and η_t represent the above values of energy and entropy of the transitional states, and in which we separate the functions of concentration as separate factor, we get :

$$-\frac{dc}{dt} = \frac{\sum v_I \varepsilon_{o_I} - T \sum v_I \eta_{o_I} + \sum v_I \int c_I dT - T \sum v_I \int \frac{c_I}{T} dT + RT \sum v_I - \varepsilon_t + T \eta_t}{RT} \pi c_I \quad (4)$$

In this equation πc_I represents the recurring product of the concentrations of the reacting substances. The factor of πc_I is the so-called constant of velocity and is generally represented by the letter k . If we now determine the value of $\ln k$ and differentiate it with respect to T , we find :

$$\frac{d \ln k}{dT} = - \frac{\sum v_I \varepsilon_{o_I} + \sum v_I \int c_I dT}{RT^2} + \frac{\varepsilon_t}{RT^2} - \frac{1}{RT} \left(\frac{d\varepsilon_t}{dT} - T \frac{d\eta_t}{dT} \right) \quad (5)$$

If now ε_t and η_t have the signification of energy and entropy (free from concentration) of the transitional state, the last term of the second member of equation 5 is zero; this is clear when we consider that $F = \varepsilon_t - T\eta_t$ can contain no functions of volume. Hence equation 5 reduces to

$$\frac{d \ln k}{dT} = \frac{\varepsilon_t - \varepsilon_I}{RT^2} \dots \dots \dots (6)$$

in which ε_I represents the energy of the first system at the temperature of reaction.

If we now return to the reversible (gas)-reaction, the relations

$$\frac{d \ln k_1}{dT} = \frac{\varepsilon_t - \varepsilon_I}{RT^2} \quad \text{and} \quad \frac{d \ln k_2}{dT} = \frac{\varepsilon_t - \varepsilon_{II}}{RT^2} \dots \dots \dots (7)$$

will exist for the two partial velocities.

Hence the splitting up of the energy difference $\varepsilon_t - \varepsilon_{II}$ into two pieces $\varepsilon_t - \varepsilon_I$ and $\varepsilon_I - \varepsilon_{II}$ is very prominent. If we now consider that in general the velocity of chemical reactions increases with the temperature, it is clear that ε_t will be greater than ε_I and ε_{II} . The energy of the transitional states is therefore greater than the energies of the systems before and after the reaction. Accordingly this result necessarily leads us to the following conception: On coincidence of the "kritische Räume" of the reacting molecules gain of energy takes place, in other words there is work

done against *repulsive* forces; the transitional state possesses therefore a *maximum* of potential energy.

As is known when molecules draw near to each other attraction takes place; this led us to expect in our previous paper that the transitional state would possess a *minimum* potential energy. As appears from the above consideration at such a distance that the "kritische Rume" invade each other, the repulsive forces out-balance the attractive forces and oppose therefore the invasion of the sphere of action.

A similar conclusion concerning the energy of the transitional states occurs already in TRAUTZ's first papers. He imagined that the transitional state consists of free atoms. It is then clear that this state contains more energy than the initial and the final state, since heat will be required for dissociation into atoms. That TRAUTZ makes this resolution take place at the absolute zero does not involve an essential modification. For this question is in close relation to the question whether it is allowed with regard to these transitional states to speak of specific heats, or what is the same thing of a mean value of energy at a certain temperature. And so far as is known the difference of temperature between the reaction temperature and the absolute zero generally causes no reversal of the sign of chemical heat-effects.

2. Before entering into a discussion of the energy and entropy values of the transitional states, I shall insert here some considerations on the energy and entropy differences between the systems before and after the reaction, referring to a paper on gas-equilibria that has appeared earlier in these Proceedings¹⁾. The algebraic sum of the entropies of the substances participating in a gas-reaction was represented in the cited paper by :

$$\sum nH = \sum nH_{T=1} + \sum n \int_1^T \frac{c_p}{T} dT - R \sum n \ln c. \quad \dots \quad (8)$$

If we join the first two terms of the second member of equation 8, and represent it by $\sum nH_{c=}$: (the entropy free from concentration) this equation passes into :

$$\sum nH = \sum nH_{c=} - R \sum n \ln c. \quad \dots \quad (9)$$

According to the cited paper the equilibrium condition for the gas mixture is :

¹⁾ These Proc. Dec. 1911. p. 743.

$$\Sigma n\mu = \Sigma nE - T\Sigma nH + \Sigma nRT = 0.$$

If in this we introduce the entropy free from concentration, this equation may be written as follows:

$$\Sigma nE - T\Sigma nH_{c=1} + RT\Sigma nlc + \Sigma nRT = 0.$$

If we now express Σnlc by $\ln K_c$, in which therefore K_c represents the so-called equilibrium constant (in concentrations), then:

$$RT\ln K_c = -\Sigma nE + T\Sigma nH_{c=1} - \Sigma nRT \quad \dots \quad (10)$$

Differentiating this equation with respect to T after division by RT , we easily find the well-known equation of VAN 'T HOFF:

$$\frac{d\ln K_c}{dT} = \frac{\Sigma nE}{RT^2} \quad \dots \quad (11)$$

If we now imagine ΣnE to be a very weak temperature function, which may be put practically constant over a limited temperature-range, equation 11 yields on integration:

$$\ln K_c = -\frac{\Sigma nE}{RT} + C \quad \dots \quad (12)$$

On comparison of equation 12 with 10, it appears that on this supposition also the entropy free from concentration may be put independent of the temperature. This conclusion is moreover also clear when we consider that both the change of ΣnE and that of $\Sigma nH_{c=1}$ with the temperature is exclusively determined by the value of Σnc_i . If therefore really the value of Σnc_i in a certain range of temperature is negligibly small, the observations in this range may be represented by equation 12, in which two constants occur: $\frac{\Sigma nE}{R}$, the change of energy divided by the gas constant, and C , which contains the change of entropy and the gas constant.

And inversely when it appears that the constant of equilibrium as function of the temperature may be represented in an equation with two constants like 12, a measure will be found in the value of these constants for the change of energy and entropy during the reaction. If therefore in one graphical representation $R\ln K_c$ is represented as function of $\frac{1}{T}$, and in another $T\ln K_c$ as function of T , and

if the observations in the first graphical representation give a straight line, this is also the case in the second. The inclination of the line in the first representation yields the energy value, that in the second the value of C in equation 12, so the entropy value, at least if the fact is taken into account that according to equation 10 C also contains the gas constant and Σn . If we now assume that the observations have been made with great accuracy, in gene-

ral the curve in the first graphical representation will deviate from a straight line. If we now connect two points from this graphical representation, the slope of this straight line will indicate the value of energy which belongs to a temperature which lies between those of the two connected points. It will then be clear that if we wish to determine the energy value in a similar way, the found value will differ the less from that which corresponds to the two observation temperatures as Σnc_v is smaller. Hence the energy value will also be found with the greater relative accuracy as the energy value itself is greater, i.e. the energy found graphically will then proportionally differ only little from the energy values at the observation temperatures. If we now fill in the graphically found value in equation 12 and if we apply equation 12 to the two observation temperatures, a too great value for the energy difference will have been chosen for the one temperature, a too small value for the other. For a temperature between the two temperatures of observation the energy value is then chosen exactly right; hence the correct entropy value has therefore been yielded by equation 12 for this temperature. Therefore when equation 12 is used the found values of entropy will deviate somewhat from the real ones at the two temperatures of observation.

If we denote the two temperatures of observation by T_1 and T_2 and the temperature for which the graphically found value of the energy holds, by T_3 , and if we imagine the value of energy found at T_3 and the corresponding entropy substituted in equation 10, we may question what deviation equation 10 gives us for the values of K_c at the temperatures T_1 and T_2 . The error made in the energy

when we apply equation 10 as T_1 , amounts to $\int_{T_1}^{T_3} \frac{d\Sigma nE}{dT} dT$, that in

the entropy-term amounts to $T_1 \int_{T_1}^{T_3} \frac{d\Sigma nH_{v=1}}{dT} dT$. If we now consider

that the energy and the entropy occur with opposite sign in the second member of equation 10 and that

$$\frac{d\Sigma nE}{dT} = T \frac{d\Sigma nH_{v=1}}{dT},$$

we see that these two errors cancel each other for the greater part in the second member of equation 10, and that therefore in spite of these approximations a pretty accurate value of K_c can be found. This fact explains why notwithstanding an appreciable value of the

specific heats many gas equilibria can be accounted for by means of two constants, not only over a small temperature range, but sometimes even over a very large one, at least if the observations are not particularly accurate. The dissociation constant of the nitrogen tetroxide can e. g. be expressed by an equation of the form 12 (SCHREBER's equation), and also the dissociation equilibrium of carbonic acid, the errors of observation being comparatively large here, can be accounted for by equation 12 over a temperature range of hundreds of degrees.

These considerations teach us accordingly that observations of equilibrium constants with comparatively large energy and entropy values enable us to calculate them pretty accurately, but that generally no conclusion can be drawn about the influence of the temperature on energy and entropy, the errors of observation being generally too great for this. Thus the above formula of SCHREBER enables us to find a mean value for the heat of dissociation of the nitrogen tetroxide and for the "kritische Raum" of the NO_2 -molecule¹⁾, but the influence of the temperature on either is not to be derived from the measurements of the equilibrium.

3. If we now return to the reaction velocities, we can also apply the considerations mentioned in the preceding paragraph here mutatis mutandis. Equation 6, which indicates the dependence of the velocity constant with the temperature, presents great analogy with VAN 'T HOFF's equation of equilibrium (equation 11). If $\epsilon_I - \epsilon_t$ is a very weak temperature function, equation 6 yields on integration:

$$\ln k = \frac{\epsilon_I - \epsilon_t}{RT} - B, \dots \dots \dots (13)$$

in which as appears from equation 4 B does not contain any constants depending on the nature of the substances, except the difference of entropy. So in this case too the difference of entropy between initial and transitional state is practically independent of the temperature. Here too we can therefore graphically represent $R \ln k$ as function of $\frac{1}{T}$, and determine the differences of energy between initial and transitional state. It seems therefore natural to examine whether the material of facts referring to the reaction velocities can be represented by equations of the form 13, where $\epsilon_I - \epsilon_t$ and B are considered as constants.

In his *Etudes de dynamique chimique* VAN 'T HOFF for the first time gave an expression for the dependence of the velocity con-

¹⁾ BOLTZMANN. Gastheorie II. § 66.

stant on the temperature. Led by his relation of equilibrium (equation 11) he pronounced the supposition that for the velocity constant an equation would hold of the shape :

$$\frac{d \ln k}{dT} = \frac{A}{T^2} + B \dots \dots \dots (14)$$

This equation has been repeatedly put to the test in later times, generally, however, for reactions in dilute solutions. First of all the question suggests itself whether the considerations which have led us to equation 6, may also be applied to dilute solutions. Though the velocity of 6 for dilute solutions cannot be rigorously proved, an application also for these reactions does not seem open to serious objections. We have, namely, tested our original equation, by reactions in dilute solutions in the cited paper; it proved to be able to account for the course of reaction, and the reasons which led us to the assumption of transitional states, hold unchanged also for reactions in solution. Accordingly the shape of equation 6 leads us to expect that this will be generally valid. VAN 'T HOFF's equation (equation 11), moreover, holds also for equilibria in dilute solution, and it is therefore certainly natural to assume, that the splitting up of the value of energy will be essentially the same for all reactions.

Van 't Hoff's equation is generally not applied in the form as it is given by 14, but in the form which arises when either A or B is put zero in 14. The expression which arises by the introduction of zero for B has been later defended by ARRHENIUS, and has appeared to be compatible with a great part of the material of facts. If, however, one puts B equal to zero in 14, really equation 13 is obtained by integration, and all the reaction-velocities which satisfy ARRHENIUS' expression, can therefore be represented with the aid of the two constants $\epsilon_1 - \epsilon_2$ and B of equation 13. Reversely equation 13 furnishes us also with the possibility of pretty accurately calculating the differences of energy, at least if they are not too small; the absolute value of the difference of entropy, however, remains unknown, because B among others contains the unknown constant, which accounts for the unity of concentration and time. The above considerations, however, suggest that besides the difference of entropy B will not contain any constants dependent on the nature of the substances. In perfect analogy with the conclusion of § 2 we conclude also here that measurement of reaction velocities, at least if they have not been very accurately executed cannot decide whether the difference of energy and of entropy depends on the temperature.

I will apply the above considerations in my next paper to a series of experimental data from organic chemistry.