Citation:

F.E.C. Scheffer, On gas equilibria, in:
KNAW, Proceedings, 14 II, 1911-1912, Amsterdam, 1912, pp. 743-758

and the difficulty to determine thermically such a very small sphere with certainty) which could be determined very sharply by the electric process. And this seems to us all the more of importance because a connection seems to exist between the appearance of solid solutions on the one side, photoelectric or photochemical effects and photoelectro- or triboluminosity on the other side.

We further got the impression that certain very small impurities may be of influence on the sensitiveness to light, and think we have observed at any rate an influence exerted by the kind of glass of which the melting tubes were constructed. In a whole series of experiments which took place, accidentally, with tubes constructed of a different kind of glass, we obtained not a single sensitive preparation, but when again using tubes of the old kind of glass the phenomenon reappeared as expected.

In this may be probably found, in our opinion, a partial explanation of the fact that, contrary to JAEGER's experience, we succeeded in remelting the native (Japanese) antimonite *without* this losing its sensitiveness to light. It is, however, necessary to operate, as we did, in sealed evacuated tubes. The compound at the melting point is already somewhat dissociated so that the operation in an open tube could not take place without loss of sulphur and change in the composition of the melt. According to our observations this loss of sulphur need amount to only 0.5 at °/₀ to obtain a totally inert preparation.

The conductivity power in darkness remained, on remelting, also quite of the same order. On the other hand it appeared that on powdering the mineral, which was then again compressed to a very solid pastille, the conductivity power very strongly decreased. The light effect, however, remained unaffected.

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Chemistry. — *"On gas equilibria"*. By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of December 30, 1911).

1. It may be accepted as known that the total energy, the free energy, the entropy and the thermodynamic potential are quantities which can only be determined with the exception of an additive constant. In the purely physical processes, i.e. changes of state, in which the molecules of the substances do not change, these constants need not be taken into account, and on the other hand a physical

change can teach us nothing about the values of these constants. In chemical changes, however, this *is* the case, at least partially. If in a mixture of substances a chemical reaction can take place, a determination of the energy of transformation under definite circumstances will make known to us the algebraic sum of the constants of energy of the reacting substances, at least if we know the energy in its dependence on the quantities that determine the state. Each of the constants in itself remains quite indefinite just as for physical changes; experiment only gives us the algebraic sum of the constants of energy, in which the constants of the substances of one member of the equation of reaction are taken positive, those of the other member negative.

We find something similar for the entropy. The constants of entropy for the purely physical processes are without any importance, but a chemical transformation which is conducted isothermic and reversible may make the algebraic sum of the constants of entropy known to us, provided we know how the entropy of each of the substances depends on the independent variables.

Of late the sum of the constants of energy, resp. entropy, and especially the latter have been the subject of many a treatise. As the sum of the constants of entropy occurs in the expression for the chemical equilibrium as a constant, its knowledge is of the greatest importance for the calculation of these equilibria. Hence Prof. HABER in his work on the "Thermodynamik technischer Gasreaktionen" repeatedly calls attention to the so-called "thermodynamisch unbestimmte Konstante", which is the aforementioned algebraic sum of the constants of entropy. And also Prof. NERNST's theorem of heat deals with the determination of these constants, for the so-called "constant of integration" of the chemical equilibrium contains these constants of entropy.

For a calculation of the constants of entropy from the theory a priori an idea of the chemical action i.e. the knowledge of the so-called forces of affinity, will be indispensable — BOLTZMANN carried out a first attempt to do so in his "Gastheorie" — for the present we shall have to content ourselves with a calculation of these constants from the observations.

In the first place, however, the knowledge of the energy and the entropy as function of the quantities which determine the state is required for such calculations. When, to take the simplest case, we confine ourselves to rarefied gases, we know that the molecular energy and the entropy of a simple gas can be represented by:

$$E = E_{T=0} + \int_0^T c_v dT \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$H = H_{\substack{T=1\\v=1}} + \int_1^T \frac{c_v}{T} dT - R \ln c, \quad . \; . \; . \; . \; . \quad (2)$$

in which $E_{T=0}$ and $H_{\substack{T=1\\v=1}}$ represent the aforesaid constants of energy and entropy, c_v the real molecular specific heat, T the absolute temperature, c the concentration (number of gramme molecules per Liter), and R the molecular gas constant (1,985 cal.).

If at a definite temperature we now measure the algebraic sum of the energies (ΣnE), i.e. the heat of transformation at constant volume, and the sum of the entropies (ΣnH), i.e. the latent heat for a reversible isothermic transformation divided by the absolute temperature, we can find the values of $\Sigma nE_{T=0}$ and $\Sigma nH_{\substack{T=1\\v=1}}$ by calculation, if we know c_v as function of T.

The value of $\Sigma nE_{T=0}$ is generally calculated, indeed, according to equation (1) from the calorimetric data. The sum of the constants of entropy, on the other hand, is generally not determined directly from the latent heat, but indirectly from the value of the constant of equilibrium.

If we suppose a reaction

$$n_1 A_1 + n_2 A_2 + \ldots\ldots \rightleftarrows n'_1 A'_1 + n'_2 A'_2 + \ldots\ldots$$

to be possible, the total change of energy, resp. change of entropy on transformation of n_1 gramme molecules A_1 with n_2 gramme molecules A_2 etc. with formation of n'_1 gramme molecules A'_1 etc. is represented by:

$$\Sigma nE = \Sigma nE_{T=0} + \Sigma n \int_0^T c_v dT \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1a)$$

and

$$\Sigma nH = \Sigma nH_{\substack{T=1\\v=1}} + \Sigma n \int_1^T \frac{c_v}{T} dT - R \Sigma n \ln c \quad . \; . \quad (2a)$$

The algebraic sum of the molecular thermodynamic potentials, which must be equal to zero in case of equilibrium, becomes therefore:

$$\Sigma n\mu = \Sigma nE - T\Sigma nH + \Sigma npV\,{}^{1)} =$$

$$\Sigma nE_{T=0} + \Sigma n \int_0^T c_v dT - T\Sigma n \int_1^T \frac{c_v}{T} dT + RT\Sigma n \ln c - T\Sigma nH_{\substack{T=1\\v=1}} + RT\Sigma n.$$

If now in the state of equilibrium we represent $\Sigma n \ln c$ by $\ln K$, in which K denotes the "constant of equilibrium", then:

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[1] In this V is the molecular volume, p the partial pressure.

$$lnK = -\frac{\Sigma nE_{T=0}}{RT} - \frac{1}{RT}\Sigma n\int_0^T c_v dT + \frac{1}{R}\Sigma n\int_1^T \frac{c_v}{T} dT + \frac{1}{R}\Sigma nH_{\substack{T=1\\ v=1}} - \Sigma n \quad (3)$$

So if we have now calculated $\Sigma nE_{T=0}$ from the calorimetric data (according to equation 1^a), we can calculate the value of $\Sigma nH_{\substack{T=1\\ v=1}}$ from an observation of K at a definite temperature.

2. For these calculations c_v is generally represented in a series of terms with ascending powers of T, which is then continued as far as is necessary for agreement with the generally insufficiently known values of the specific heats. For bi-atomic gases the series can already be broken off after the term with T, for tri-atomic gases after that with T^2.

Hence if we put in general:

$$\Sigma nc_v = a + bT + cT^2$$

and thus determine the integrals in equation (3), we get:

$$lnK = -\frac{\Sigma nE_{T=0}}{RT} + \frac{a}{R} lnT + \frac{b}{2R} T + \frac{c}{6R} T^2 + C, \quad . \quad . \quad (4)$$

in which

$$C = \frac{1}{R}\Sigma nH_{\substack{T=1\\ v=1}} - \Sigma n - \frac{2a + 2b + c}{2R} \quad . \quad . \quad . \quad . \quad (5)$$

In the above equation (4) the constant of equilibrium is expressed in concentrations; to find the value of the constant in partial pressures from this, which is generally used for gas equilibria, we must bear in mind that

$$p = RTc, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which p is the partial pressure of the gas concerned, and that therefore:

$$lnK = \Sigma\, n\, ln\, c = \Sigma\, n\, ln\, p - \Sigma\, n\, ln\, R - \Sigma\, n\, ln\, T.$$

If we now put $\Sigma\, n\, ln\, p = lnK_p$, in which K_p represents the constant of equilibrium in partial pressures, then after some transformations and transition from Neperian to common logarithms:

$$logK_p = -\frac{\Sigma nE_{T=0}}{2.303RT} + \frac{a + \Sigma nR}{R} logT + \frac{b}{2.2.303R} T + \frac{c}{6.2.303R} T^2 + C', \quad (7)$$

in which $C' = 0.4343\, C + \Sigma n\, log\, R$. . . . . (8)

In this we must bear in mind that the value of R should be expressed in calories in equation (7), because the energy and the specific heats are measured in calories, whereas in equation (8) the unity in which R is expressed, depends on the unity of pressure and volume in equation (6). If we express the concentrations in gramme molecules per liter, and so if we choose the liter as volume unity, and the atmosphere as pressure unity, R must be expressed in liter-atmospheres in equation (8). So in this case we must substitute $R = 1.985$ in equation (7), on the other hand $R = 0.0821$ in equation (8).

From the equations (7), (8), and (5) we see accordingly that C', the so-called constant of integration of the chemical equilibrium does not contain only the sum of the constants of entropy, but also Σn and the constants yielded by the integrals occurring in equation (3).

C' owes its name of constant of integration of the chemical equilibrium to this that equation (7) can also be found by integration of the well-known law of VAN 'T HOFF:

$$\frac{dlnK}{dT} = \frac{Q}{RT^2},$$

in which K represents the constant of equilibrium either in concentrations or in partial pressures, and Q the heat of transformation, in the first case for constant volume, in the second case for constant pressure. If, however, we derive equation (7) in this way, we do not get equations (5) and (8), because in this way the constant of integration does not become known in its dependence on the constants of the reacting substances.

§ 3, We shall now apply the calculation of the constants of entropy to the equilibrium:

$$2\,CO + O_2 \rightleftarrows 2\,CO_2$$

The value of ΣnE can be found from the calorimetric determinations of THOMSEN and BERTHELOT, which yielded resp. 67960 and 68200 cal. for the heat of combustion of one gramme molecule CO under constant pressure and at 18° C. From the mean value $Q_p = 68080$ we calculate $Q_v = 67790$, and so:

$$\Sigma nE = 135580 \quad \text{at} \quad T = 291 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now we derive from equation 1^a:

$$\Sigma nE_{T=0} = \Sigma nE - aT - {}^1/_2\, bT^2 - {}^1/_3\, cT^3.$$

So for the further calculation we must first know c_v as function of T.

4. For the dependence of c_v on the temperature all kinds of different expressions have been proposed in course of time. From this large number of expressions I will only choose some of the most reliable ones. In the first place I will use the expressions which follow from the experiments of HOLBORN and AUSTIN, which

were carried out in 1905. The real specific heats can be represented pretty accurately up to 800° C by

$$c_v = 4.68 + 0.000536\ T \text{ (bi-atomic gas)}^{1)} \text{ and}$$
$$c_v = 5.112 + 0.00729\ T—22.05\ 10^{-7}\ T^2 \text{ (carbonic acid)}^{2)}$$

From these values follows:

$$\Sigma nc_v = 3.82—0.01297\ T + 44{,}1\ 10^{-7}\ T^2.$$

So in the above equations 7, 8, and 9 must be substituted:

$$a = 3{,}82 \quad ; \quad b = -0{,}01297 \quad \text{and} \quad c = 44{,}1\ 10^{-7}. \quad . \quad . \quad (10)$$

If we substitute these values in equation 9, we get:

$$\Sigma nE_{T=0} = 134980$$

and the expressions 7 and 8:

$$log\ K_p = -\frac{29530}{T} + 2{,}92\ log\ T—0{,}001419\ T + 1{,}61\ 10^{-7}\ T^2 + C'. \quad (11)$$

in which:

$$C' = \frac{\Sigma nH_{\substack{T=1\\v=1}}}{4{,}571} - 2{,}35. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The values of $log\ K_p$ in the third column of the following table have been calculated from the most accurate determinations of the carbonic acid equilibrium, which have been inserted in the first two columns[3]; in the fourth, fifth, sixth and seventh columns the values of the other terms of the second member of equation 11 have been given, and the last column gives the value of C'.

TABLE I.

T	x	$log K_p$	$-\frac{29530}{T}$	2.92 $log\ T$	0.001419 T	1.61 $10^{-7}\ T^2$	C'
1300	$4.14.10^{-5}$	—13.45	—22.72	9.09	1.84	0.27	+1.75
1395	$1.42.10^{-4}$	—11.84	—21.17	9.18	1.98	0.31	+1.82
1400	$1.5\ 10^{-4}$	—11.77	—21.09	9.19	1.99	0.32	+1.80
1443	$2.5\ 10^{-4}$	—11.11	—20.46	9.23	2.05	0.34	+1.83
1478	$3.2\ 10^{-4}$	—10.79	—19.98	9.26	2.10	0.35	+1.68
1498	$4.71.10^{-4}$	—10.28	—19.71	9.27	2.13	0.36	+1.93
1500	$4\ 10^{-4}$	—10.50	—19.69	9.27	2.13	0.36	+1.69
1565	$6.4\ 10^{-4}$	— 9.88	—18.87	9.33	2.22	0.39	+1.49

So the value of C' appears to oscillate round a mean **+ 1,75.** If this value is substituted in equation 12, we get:

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[1] See ABEGG, Handb. III, 2, 181.

[2] Recalculated from the expression of HOLBORN and AUSTIN. Sitz. Ber. preuss Akad. 1905. 175.

[3] ABEGG, Handb. III, 2, 183.

$$\Sigma n H_{\substack{T=1\\ v=1}} = +\mathbf{18.7}.$$

5. The equation derived above deviates only little from the equation given by Prof. NERNST in his "Theoretische Chemie" for the equilibrium of carbonic acid [1]), which may be written after recalculation:

$$log\, K_p = -\frac{29600}{T} + 2{,}93\, log\, T - 0.001286\, T + 1{,}61\ 10^{-7} T^2 + C',. \quad (11^a)$$

in which $C' = 1.51$ according to Prof. NERNST.

The oscillations of C' appear from the following table:

TABLE II.

T	$log\, K_p$	$-\frac{29600}{T}$	$2.93\ log\, T$	$0.001286\ T$	$1.61\ 10^{-7}\ T^2$	C'
1300	−13.45	−22.77	9.12	1.67	0.27	+1.60
1395	−11.84	−21.22	9.21	1.79	0.31	+1.65
1400	−11.77	−21.14	9.22	1.80	0.32	+1.63
1443	−11.11	−20.51	9.26	1.86	0.34	+1.66
1478	−10.79	−20.03	9.29	1.90	0.35	+1.50
1498	−10.28	−19.76	9.30	1.93	0.36	+1.75
1500	−10.50	−19.73	9.31	1.93	0.36	+1.49
1565	− 9.88	−18.91	9.36	2.01	0.39	+1.29

So C' oscillates round the middle value $+\mathbf{1{,}57}$, which differs but very little from the above mentioned value of 1,51.

For the value of $\Sigma n H_{\substack{T=1\\ v=1}}$ we find for this case $+\mathbf{17{,}9}$.

The discrepancies between these values and those of § 4 must be partly ascribed to another assumption about ΣnE, for the greater part, however, to the changed value of b in the expression of the specific heats.

6. In the second place we can use the more recent determinations of HOLBORN and HENNING [2]). After recalculation these yield for the real specific heats:

$$c_v = 4{,}32 + 0{,}00107\ T \text{ (bi-atomic gas)}$$

$$c_v = 4{,}90 + 0{,}00783\ T - 2{,}38\ 10^{-6}\ T^2 \text{ (carbonic acid)},$$

from which follows:

$$\Sigma n\, c_v = 3{,}16 - 0.01245\ T + 4{,}76\ 10^{-6}\ T^2.$$

So in this case we must substitute in equations 7, 8, and 9:

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[1]) Theor. Chemie (1909) 681. See also ABEGG Handb. III, 2, 181.

[2]) Ann. der Physik. (4) 23 809 (1907).

$$a=3{,}16 \;;\; b=-0{,}01245 \text{ and } c=4{,}76\ 10^{-6} \quad . \quad . \quad (13)$$

This substitution yields:

$$\Sigma n E_{T=0} = 135150$$

$$log\ K_p = -\frac{29570}{T} + 2{,}59\ log\ T - 0.001362T + 1{,}74\ 10^{-7}T^2 + C', . (14)$$

in which:

$$C' = \frac{\Sigma n\ H_{\substack{T=1\\ \upsilon=1}}}{4{,}571} - 2{,}21 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The calculation from the observations will be clear from the subjoined table without further elucidation:

TABLE III.

T	$log\ K_p$	$-\frac{29570}{T}$	$2.59\ log\ T$	$0.001362\ T$	$1.74\ 10^{-7}\ T^2$	C'
1300	—13.45	—22.75	8.07	1.77	0.29	+2.71
1395	—11.84	—21.20	8.14	1.90	0.34	+2.78
1400	- 11.77	—21.12	8.15	1.91	0.34	+2.77
1443	—11.11	—20.49	8.18	1.97	0.36	+2.81
1478	—10.79	—20.01	8.21	2.01	0.38	+2.64
1498	--10.28	—19.74	8.22	2.04	0.39	+2.89
1500	-10.50	—19.71	8.23	2.04	0.39	+2.63
1565	— 9.88	—18.89	8.27	2.13	0.43	+2.44

So C' oscillates round the mean value $+$ **2.71**.

Now it follows from equation (15) that:

$$\Sigma n H_{\substack{T=1\\ \upsilon=1}} = +\ 22.5.$$

7. In the first paper on the theorem of heat[1]) Prof. NERNST proposed the expression:

$$log\ K_p = -\frac{29600}{T} + 1{,}75\ log\ T - 0{,}00066\ T + C' \quad . \quad . \quad (16)$$

If we use this expression for the calculation of C' from the observations, we have:

TABLE IV.

T	$log\ K_p$	$-\frac{29600}{T}$	$1.75\ log\ T$	$0.00066\ T$	C'
1300	—13.45	—22.77	5.45	0.86	+4.73
1395	—11.84	—21.22	5.50	0.92	+4.80
1400	—11.77	—21.14	5.51	0.92	+4.78
1443	—11.11	—20.51	5.53	0.95	+4.82
1478	—10.79	—20.03	5.55	0.98	+4.67
1498	—10.28	—19.76	5.56	0.99	+4.91
1500	—10.50	—19.73	5.56	0.99	+4.66
1565	— 9.88	—18.91	5.59	1.03	+4.47

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[1]) Gött. Nachr. 1906. 1.

C' oscillates round the mean value $+\mathbf{4.73}$ in table IV.

If we calculate the sum of the constants of entropy from this value of C' we find:

$$\Sigma n H_{\substack{T=1\\ v=1}} = +\mathbf{30.1}$$

8. It will be sufficiently clear from what precedes that the results of the calculations of the constants of entropy depend entirely on the expressions which are assumed for the specific heats as function of the temperature. Up to quite recently we had to content ourselves with the above discussed expansions into series; not long ago, however, appeared a paper by Dr. NIELS BJERRUM, in which two expressions derived from the theory of indivisible units of energy are proposed and tested by the latest observations.[1] It has appeared there that with a suitable choice of the oscillation frequencies of the atoms in the gas-molecules it is possible to account for the observed influence of the temperature on the specific heat. The most remarkable thing is now that with regard to the order of magnitude these frequencies really agree with the vibrations which occur in the absorption spectra of the gases concerned, as was predicted by theory. According to NERNST the specific heat of the gases can be divided into three parts. The translatory energy, which is exclusively determined by the motion of the gas molecules as such, is represented by $^3/_2\, RT$ independent of the number of atoms in the molecule.

The rotatory energy is found by multiplying the number of degrees of freedom by $^1/_2\, RT$, and amounts to RT for bi-atomic gases, to $^3/_2\, RT$ for tri-atomic and multi-atomic gases. So for the specific heats these two parts of the energy yield two expressions independent of the temperature (bi-atomic $^3/_2\, R + R$; tri-or multi-atomic $^3/_2\, R + {}^3/_2\, R$). The third part, the energy of vibration of the atoms in the molecule will, however, depend on the constitution of the molecule in a much more intricate way. This energy of vibration, which in its dependence on T furnishes a part of the specific heats which depends on T, is now found by means of the expressions drawn up by EINSTEIN, resp. NERNST and LINDEMANN according to the theory of indivisible units of energy.

The real specific heat of a bi-atomic gas is now found by differentiation of the said three parts of the energy with respect to T:

$$c_v = {}^3/_2\, R + R + \frac{d}{dT}(RT\varphi), \quad . \quad . \quad . \quad . \quad . \quad (17)$$

in which according to EINSTEIN φ is represented by:

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[1] Zeitschr. für Elektrochemie. 1911. 731.

$$\frac{\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}}-1},$$

according to NERNST and LINDEMANN by:

$$\frac{1}{2}\,\frac{\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}}-1}+\frac{1}{2}\,\frac{\frac{\beta\nu}{2T}}{e^{\frac{\beta\nu}{2T}}-1}.$$

The universal contant β has here the value $4.86\ 10^{-11}$, ν being the frequency of oscillation of the two atoms with respect to each other.

Quite analogously the specific heat of a tri-atomic gas is represented by:

$$c_v = {}^3/_2\,R + {}^3/_2\,R + \frac{d}{dT}\{RT\,(\varphi_1+\varphi_2+\varphi_3)\}, \quad . \quad . \quad . \quad (18)$$

in which φ_1, φ_2 and φ_3 refer to the three vibrations possible in the tri-atomic molecule.

9. If we now also apply these equations for the specific heats to the carbonic acid equilibrium, we find:

$$\Sigma n \int_0^T c_v dT = \{1{,}5 + 2\varphi_A + \varphi_B - 2(\varphi_1+\varphi_2+\varphi_3)\}\,RT \quad . \quad . \quad (19)$$

and

$$\Sigma n \int_1^T \frac{c_v}{T}\,dT = \frac{3}{2}\,R\ln T + R\int_1^T \frac{2\varphi_A + \varphi_B - 2(\varphi_1+\varphi_2+\varphi_3)}{T}\,dT +$$

$$+ R \Big|_1^T \{2\varphi_A + \varphi_B - 2(\varphi_1+\varphi_2+\varphi_3)\}, \quad . \quad . \quad . \quad (20)$$

in which the indices A, B, 1, 2, and 3 resp. refer to carbonic oxide, oxygen, and carbonic acid.

If now the expressions (19) and (20) are substituted in equation (3), we find:

$$\ln K = -\frac{\Sigma n E_{T=0}}{RT} + 1{,}5\ln T + \int_1^T \frac{2\varphi_A + \varphi_B - 2(\varphi_1+\varphi_2+\varphi_3)}{T}\,dT + C, (21)$$

in which

$$C = -2\,5 - \{2\varphi_A + \varphi_B - 2(\varphi_1+\varphi_2+\varphi_3)\}_{T=1} + \frac{1}{R}\,\Sigma n\, \Pi_{\substack{T=1,\\ v=1}}$$

$$\text{as}\quad \Sigma n = +1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The integral occurring in equation (21) can, if we use the φ-value according to EINSTEIN (see § 8), be found, if we bear in mind that:

$$\int \frac{\varphi}{T}\, dT = \int \frac{\beta\nu}{T^2\left(e^{\frac{\beta\nu}{T}}-1\right)}\, dT = \int \frac{\beta\nu e^{-\frac{\beta\nu}{T}}}{T^2\left(1-e^{-\frac{\beta\nu}{T}}\right)}\, dT = -\, ln\left(1-e^{-\frac{\beta\nu}{T}}\right); \quad (23)$$

if we use the value of φ of NERNST and LINDEMANN, we get:

$$\int \frac{\varphi}{T}\, dT = \tfrac{1}{2}\int \frac{\beta\nu}{T^2\left(e^{\frac{\beta\nu}{T}}-1\right)}\, dT +$$

$$+ \tfrac{1}{2}\int \frac{\frac{\beta\nu}{2}}{T^2\left(e^{\frac{\beta\nu}{2T}}-1\right)}\, dT = -\,{}^1/_2\, ln\left(1-e^{-\frac{\beta\nu}{T}}\right)\left(1-e^{-\frac{\beta\nu}{2T}}\right) \quad . \quad . \quad . \quad . \quad (24)$$

Finally it appears from equation (1^a) that:

$$\Sigma nE = \Sigma nE_{T=0} + \{1{,}5 + 2\varphi_A + \varphi_B - 2(\varphi_1+\varphi_2+\varphi_3)\}\, RT \quad . \quad (25)$$

When using the φ-expression of EINSTEIN we must, according to BJERRUM, substitute resp. 3.6 μ, 3.6 μ, 14.7 μ, 6.2 μ and 6.2 μ for λ, or 4050, 4050, 992, 2350, and 2350 for $\beta\nu$ in φ_A, φ_B, φ_1, φ_2 and φ_3.

If the φ-expression of NERNST and LINDEMANN is used, we must substitute for λ: 2.59 μ, 2.59 μ, 8.1 μ, 5.0 μ and 5.0 μ and for $\beta\nu$: 5630, 5630, 1800, 2920 and 2920.

If now in equation (25) we substitute these values with the values of ΣnE from equation 9, we get:

$$\Sigma nE_{T=0} = 134850 \text{ (EINSTEIN) resp.}$$
$$= 134800 \text{ (NERNST and LINDEMANN).}$$

Hence the expressions for the carbonic acid equilibrium become:

$$log\, K_p = -\frac{29500}{T} + 2{,}5\, log\, T - 3\, log\left(1-e^{-\frac{4050}{T}}\right) + 2\, log\left(1-e^{-\frac{992}{T}}\right) +$$

$$+ 4\, log\left(1-e^{-\frac{2350}{T}}\right) + C'_E \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$log\, K_p = -\frac{29490}{T} + 2.5\, log\, T - {}^3/_2\, log\left(1-e^{-\frac{5630}{T}}\right)\left(1-e^{-\frac{5630}{2T}}\right)$$

$$+ log\left(1-e^{-\frac{1800}{T}}\right)\left(1-e^{-\frac{1800}{2T}}\right) + 2\, log\left(1-e^{-\frac{2920}{T}}\right)\left(1-e^{-\frac{2920}{2T}}\right) + C'_{NL} (27)$$

In both expressions the constants C'_E and C'_{NL} have the values:

$$C'_E = 0{,}4343\, C_E + log\, 0{,}0821 \text{ and}$$
$$C'_{NL} = 0{,}4343\, C_{NL} + log\, 0{,}0821,$$

in which the constants without accents are represented by equation (22), because the lower limit of the integral occurring in equation 21 may be neglected.

If we consider that also the values for φ in equation (22) for $T = 1$ may be put zero, we get finally:

$$C'_E = C'_{NL} = 0.4343 \left(-2\,5 + \frac{1}{R} \Sigma n H_{\substack{T=1\\ v=1}} \right) + \log 0.0821$$

or

$$C'_E = C'_{NL} = \frac{\Sigma n H_{\substack{T=1\\ v=1}}}{4.571} - 2{,}17 \quad . \quad . \quad . \quad . \quad . \quad (28)$$

TABLE V.

T	$-\frac{29500}{T}$	$-\frac{29490}{T}$	$2.5 \log T$	$\Sigma \log_E$	$\Sigma \log_{NL}$	C'_E	C'_{NL}
1300	−22.69	−22.68	7.78	−0.80	−0.78	+2.26	+2.23
1395	−21.15	−21.14	7.86	−0.87	−0.85	+2.32	+2.29
1400	−21.07	−21.06	7.87	−0.87	−0.85	+2.30	+2.27
1443	−20.44	−20.44	7.90	−0.91	−0.88	+2.34	+2.31
1478	−19.96	−19.95	7.92	−0.93	−0.91	+2.18	+2.15
1498	−19.69	−19.69	7.94	−0.95	−0.92	+2.42	+2.39
1500	−19.67	−19.66	7.94	−0.95	−0.93	+2.18	+2.15
1565	−18.85	−18.84	7.99	−0.99	−0.97	+1.97	+1.94

So the mean values of C'_E and C'_{NL} amount to:

$+$ **2.25** and $+$ **2.22.**

From equation 28 follows:

$\Sigma n H_{\substack{T=1\\ v=1}} = +$ **20.2** and $+$ **20.1.**

10. If we now consider the results of the five tables, it appears that all five have been calculated with the aid of the same data concerning the chemical equilibrium, that the same value $\Sigma n E$ was used for tables I, III, and V, that the values on which tables II and IV are based, differ at the most some tenths of percentages from them, which accordingly can only bring about a deviation of some hundredths in the value of C', and that therefore the greatly varying values of C' resp. $\Sigma n H_{\substack{T=1\\ v=1}}$ must be attributed to the different expressions which are introduced for the specific heats.

The term, produced by the constants of energy, differs at the most 0,1 in the five tables; the great influence, to which the difference of the obtained C' values is to be ascribed, lies chiefly in the different factor of $\log T$, which varies between 2.93 (table II) and 1,75 (table IV).

This can bring about a difference of more than 3 in the terms concerned, because *log T* is of the order 3.

Though accordingly the different assumptions concerning the specific heats give a maximum deviation in the constants of energy of at the most some tenths of percentages, they give rise to variations from 17,9 to 30,1 for the constants of entropy. So the accuracy of the constants of entropy is far inferior to that of the constants of entropy.

It will be clear from the above that the extrapolation of the specific heat from the region of observation to the lower temperatures is the cause of the deviations. For where e.g. for bi-atomic gases the expression $Cv = a + bT$ implies that the specific heat retains its linear dependence with descending temperature, it becomes constant at low temperatures on assumption of the expression of BJERRUM. The line that represents the specific heat as function of the temperature, exhibits the same shape (with a point of inflection) in the latter case as the specific heats for solid substances, which of late have become known specially by the investigations in the laboratory of Prof. NERNST.

We may call here special attention to this that all the five expressions which have been mentioned for the carbonic acid dissociation equilibrium, account equally well for the observations, for the oscillations of C' have the same value in all the tables. And we have here only to take the absolute, not the relative deviations of C' into consideration.

That a change in the expression of the specific heats can have a great influence on the value of C', is moreover a conclusion which is not new. Everybody who knows the work of Prof. HABER already mentioned in § 1, which appeared already in 1905, and which treats the gas-equilibria with the facts known at the time in a very clear way. will find back this conclusion there. As it appeared to me, however, that this conclusion is not generally known, and the newer data have hardly modified it, I have thought it necessary to elucidate it in what precedes by one of the most fully studied reactions.

If we ask which value of the constants of the entropy must be taken as the most probable, we come to the conclusion that this is certainly the value of Table V. In the first place the expression proposed by BJERRUM has a theoretical foundation in the theory of indivisible units of energy, and besides this formula renders the newest investigations of HOLBORN and HENNING and those of PIER very well, as appears with the greatest clearness from the cited paper by BJERRUM.

A drawback mentioned by Bjerrum, exists, however also when we use this expression. It is namely pretty certain that this formula will not rigorously retain its validity at low temperatures, because the rotatory energy at low temperatures will deviate from the value given in the expression. This, however, does not detract from the fact that in my opinion this theoretical formula is to be preferred to the empirical expansions into series.

11 If we apply Bjerrum's data to the equilibrium of the water-dissociation we find at $T = 273$ for ΣnE the value 115660, resp. 115260 according to Berthelot and Matignon, resp. to Thomsen.

If we take a mean from this, we get according to equation 25:

$$\Sigma n\, E_{T=0} = 114650.$$

If the φ-values according to Einstein, resp. Nernst and Lindemann are used, the expressions for the equilibrium become:

$$log\, K_p = -\frac{25080}{T} + 2.5 log T - 2\, log\left(1-e^{-\frac{4860}{T}}\right) - log\left(1-e^{-\frac{4050}{T}}\right) +$$

$$+ 2\, log\left(1-e^{-\frac{2650}{T}}\right) + 4\, log\left(1-e^{-\frac{5610}{T}}\right) + C'_E \quad . \quad . \quad . \quad (29)$$

and

$$log\, K_p = -\frac{25080}{T} + 2.5\, log\, T - log\left(1-e^{-\frac{7290}{T}}\right)\left(1-e^{-\frac{7290}{2T}}\right)$$

$$-{}^1/_2 log\left(1-e^{-\frac{5630}{T}}\right)\left(1-e^{-\frac{5630}{2T}}\right) + 3 log\left(1-e^{-\frac{6075}{T}}\right)\left(1-e^{-\frac{6075}{2T}}\right) + C'_{NL} \quad (30)$$

The most accurate observations, which were carried out in Prof. Nernst's [1]) laboratory, now yield:

TABLE VI.

T	$log\, K_p$	$-\frac{25080}{T}$	$2.5\ log\, T$	$\Sigma\, log_E$	$\Sigma\, log_{NL}$	C'_E	C'_{NL}
1300	—14.01	—19.29	7.78	—0.10	—0.09	—2.40	—2.41
1397	- 12.63	—17.95	7.86	—0.12	- 0.10	- 2.42	—2.44
1480	—11.47	—16.95	7.93	—0.14	—0.12	—2.31	—2.33
·1500	—11.42	—16.72	7.94	—0.14	—0.12	- 2.50	—2.52
1561	—10.71	—16.07	7.98	—0.15	—0.13	—2.47	—2.49
1705	— 9.28	—14.71	8.08	—0.18	—0.16	—2.47	—2.49
2155	— 6.08	—11.64	8.33	—0.27	—0.26	—2.50	—2.51
2257	— 5.55	—11.11	8.38	—0.29	—0.28	—2.53	—2.54
2300	— 5.04	—10.90	8.40	—0.30	—0.29	—2.24	—2.25

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[1]) Theor. Chem. 1909. 680.

The mean values of C'_E and C'_{NL} amount to **2,43** and **—2,44.** It appears from equation (28), which holds here unmodified that:

$$\Sigma n\, H_{\substack{T=1\\ v=1}} = -\mathbf{1{,}19} \text{ and } -\mathbf{1{,}23}.$$

12. The water gas equilibrium can be found by calculation from the water and carbonic acid equilibrium.

From $K_{H_2O} = \frac{c_{H_2}^{\,2}\, c_{O_2}}{c_{H_2O}^{\,2}}$, $K_{CO_2} = \frac{c_{CO}^{\,2}\, c_{O_2}}{c_{CO_2}^{\,2}}$ and $K_w = \frac{c_{H_2}\, c_{CO_2}}{c_{CO}\, c_{H_2O}}$ it appears, that

$$\log K_w = {}^1/_2\,(\log K_{H_2O} - \log K_{CO_2}).$$

Hence if we subtract equation 26 from 29 resp. 27 from 30, we find after division by 2:

$$\log K_w = \frac{2210}{T} - \log\left(1-e^{-\frac{4860}{T}}\right) - \log\left(1-e^{-\frac{992}{T}}\right) - 2\log\left(1-e^{-\frac{2350}{T}}\right)$$
$$+ \log\left(1-e^{-\frac{4050}{T}}\right) + \log\left(1-e^{-\frac{2650}{T}}\right) + 2\log\left(1-e^{-\frac{5610}{T}}\right) + C'_{w_E} \quad (31)$$

and

$$\log K_w = \frac{2205}{T} - {}^1/_2 \log\left(1-e^{-\frac{7290}{T}}\right)\left(1-e^{-\frac{7290}{2T}}\right) - {}^1/_2 \log\left(1-e^{-\frac{1800}{T}}\right)\left(1-e^{-\frac{1800}{2T}}\right)$$
$$- \log\left(1-e^{-\frac{2920}{T}}\right)\left(1-e^{-\frac{2920}{2T}}\right) + {}^1/_2 \log\left(1-e^{-\frac{5630}{T}}\right)\left(1-e^{-\frac{5630}{2T}}\right)$$
$$+ {}^3/_2 \log\left(1-e^{-\frac{6075}{T}}\right)\left(1-e^{-\frac{6075}{2T}}\right) + C'_{w_{NL}} \quad . \; . \; . \; . \; . \; . \; . \quad (32)$$

For the calculation of the constants we use the determinations of HAHN [1]).

TABLE VII.

T	K^{-1}	$\log K$	$\frac{2210}{T}$	$\frac{2205}{T}$	$\Sigma \log_E$	$\Sigma \log_{NL}$	C'_{w_E}	$C'_{w_{NL}}$
959	0.534	0.27	2.30	2.30	0.23	0.24	- 2.26	—2.27
1059	0.840	0.08	2.09	2.08	0.27	0.27	—2.28	—2.27
1159	1.197	- 0.08	1.91	1.90	0.30	0.30	—2.29	—2.28
1259	1.571	—0.20	1.76	1.75	0.33	0.33	—2.29	—2.28
1359	1.96	—0.29	1.63	1.62	0.36	0.36	—2.28	—2.27
1478	2.126	—0.33	1.50	1.49	0.40	0.39	—2.23	—2.21
1678	2.49	—0.40	1.32	1.31	0.45	0.44	—2.17	—2.15

So the mean values amount to **— 2.26** and **— 2.25.**

The constants of entropy can be found from:

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[1]) ABEGG. Handb. III. 2. 198.

$$\frac{\Sigma n H_{T=1 \atop v=1}}{4\,571} = C',$$

into which for this case equation (22), in which $\Sigma n = 0$, passes.

The calculation yields:

$$\Sigma n H_{T=1 \atop v=1} = -\ \mathbf{10.3} \text{ and } -\mathbf{10.3}.$$

If we now compare the values which the direct determinations of the watergas equilibrium have yielded, with the values which are calculated from the constants of the water and carbonic acid equilibrium, we find:

TABLE VIII.

Carbonic acid		Water		Watergas			
				Calculated		Direct	
C'	$\Sigma n H_{T=1 \atop v=1}$	C'	$\Sigma n H_{T=1 \atop v=1}$	C'	$\Sigma n H_{T=1 \atop v=1}$	C'	$\Sigma n H_{T=1 \atop v=1}$
+2.25	+20.2	−2.43	−1.19	−2.34	−10.7	−2.26	-10.3
+2.22	+20.1	−2.44	−1.23	−2.33	−10.7	−2.25	−10.3

This agreement proves that the observations on which table VII is founded, correspond sufficiently well with those of the tables V and VI. This, however, cannot be advanced as a proof of the accuracy of the used expressions for the specific heats, as such an agreement may also be obtained on other assumptions concerning the specific heats.

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Physiology. — "*The effusion of acoustic energy from the head, according to experiments of* Dr. P. Nikiforowsky". By Prof. Zwaardemaker.

(Communicated in the meeting of December 30, 1911).

In the months just past, Dr. P. Nikiforowsky from St. Petersburg has carried on in the Physiological Laboratory at Utrecht an investigation as to the effusion of acoustic energy from the head whilst the sound was introduced, either from the head or from the vocal organs or from the crown of the head along the stem of a vibrating tuning-fork which had been placed there. The intensity of the sound produced, was about uniform, which appeared from special measure-