on the particular properties of the substance of which the centre of attraction consists.

The time of revolution T (the time in which φ increases by 2π) can easily be calculated. It follows namely from (18^b) and (19) that

$$\dot{\psi} = Ac^2\gamma \,(a+\beta \cos \psi)^2 \left\{ 1 - \frac{2k}{c^2} \,(a+\beta \cos \psi) \right\},$$

and from this, accurate up to quantities of the second order of magnitude,

$$Ac^2\gamma dt = \frac{d\psi}{(a+\beta \cos \psi)^2} + \frac{2k}{c^2} \frac{d\psi}{a+\beta \cos \psi}.$$

From this it easily follows, that

$$Ac^2 T = \frac{2\pi}{\sqrt{a^2-\beta^2}} \left(\frac{a}{a^2-\beta^2} + \frac{k}{c^2} \right).$$

Let us call a half the major axis of the ellipse, then

$$a = \frac{a}{a^2-\beta^2}$$

and we get

$$a \left(a + \frac{k}{c^2} \right)^2 : T^2 = \frac{k}{4\pi^2}.$$

T depends therefore still exclusively on the major axis of the orbit; this is, however, not the case with the time of revolution in the ellipse. In the first member we may substitute $4\pi^2 a^3/c^2 T^2$ for k/c^2, and thus we get

$$a^3 \left[1 + \tfrac{2}{3} \left(\frac{2\pi a}{cT} \right)^2 \right]^3 : T^2 = \frac{k}{4\pi^2}$$

instead of the third law of KEPLER.

Chemistry. — "*On gas equilibria, and a test of* Prof. J. D. VAN DER WAALS Jr.'s *formula*". II. By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

7. *The equilibrium* $I_2 \rightleftarrows 2I$. (Continued).

In my preceding paper [1]) I have shown that from the determinations of the iodine equilibrium the value 0.41 10^{-8} cm. follows for the radius of inertia of the iodine molecule; the iodine dissociation can therefore be represented by equation 8, when $\lambda = 15\mu$ and $log\ M = -38.20$ are there substituted. That this equation sufficiently represents the experimentally found values, appears from

, [1]) These Proc. **17**, 695 (1914/15).

table V, in which the value 34690 cal. has been chosen for $\Sigma n E_{T=0}$ so that in my opinion the most probable expression for the dissociation constant is as follows:

$$log\ K = -\frac{7589}{T} + \frac{1}{2}\ log\ T + log\left(1 - e^{-\frac{972}{T}}\right) + 1.887 \quad . \quad (13)$$

T A B L E V.

t (Cels)	T	$log\ K$(found)	$log\ K$ (calc.)	difference
800	1073	0.111—4	0.104—4	— 0.007
900	1173	0.692—4	0.703—4	+ 0.011
1000	1273	0.199—3	0.206—3	+ 0.007
1100	1373	0.639—3	0.634 - 3	— 0.005
1200	1473	0.009—2	0.003 -2	— 0.006

The discrepancies between the found and the calculated values are smaller than the errors of observation.

8. Before proceeding with the calculation of chemical equilibria by the aid of the expressions for the gas entropy mentioned in § 2 and Prof. VAN DER WAALS Jr.'s expression mentioned in § 4, I will discuss the results at which STERN has arrived in his paper, which I mentioned in the "Postscript" of my latest communication.

The expressions for the gas entropy used by STERN, deviate in a very essential point from those mentioned in § 2. The entropy of a gas is determined by STERN with respect to the solid state at $T = 0$ as zero condition. The expression for monatomic gases agrees with equation 1 of my first paper, when there the value

$$\frac{3}{2}\ R\ ln\ 2\pi + \frac{5}{2}\ R + S_{solid\ at\ T=0}$$

is substituted for C_1. In the same way the value of a di-atomic gas is indicated by equation 2, if $\frac{7}{2}\ R + S_{solid\ at\ T=0}$.[1]) is taken for C_2. It is clear that in contrast with the application of the entropy values of § 2, therefore according to STERN the algebraic sum of the entropies of the solid substances at $T = 0$ occurs in the expressions

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[1]) Besides STERN takes the vibration in the diatomic molecule into account, which in equation 2 necessitates the addition of an expression with ν. Also the variability of the specific heats is therefore taken into account with this expression.

for the equilibrium constant of the gas equilibrium. Hence whereas the expressions of § 2, which were exclusively derived from gas properties, leave the value for the entropy of solid out of account, and the calculations of the gas equilibria have nothing to do with the solid state either, so that the determination of the entropy of solid according to $S = k \log W$ remains a separate problem, the test of STERN's expressions can give a decision of the validity of NERNST's theorem of heat. If we assume STERN's derivations for the gas entropy to be correct, then on application to the iodine equilibrium it appears that the algebraic sum of the entropies of the solid sub- stances at $T = 0$ is not zero, which it ought to be according to the heat theorem, but about — 7. In this test it is assumed that the moment of inertia of the iodine molecules has the value that would follow from the mean molecule radius for iodine (from the index of refraction). We have here, however, two quantities at our disposal: the moment of inertia and ΣS_{solid}. It is clear that reversely the assumption that the sum of the entropies of the solid substances at $T = 0$ is zero (through which this algebraic sum disappears from the constant of equilibrium and the expression deviates from that of Prof. VAN DER WAALS Jr. only in this that it is assumed in the former that the specific heat of the vibration has already reached its amount of equipartition) changes the value of the moment of inertia. On this assumption it gets about the value which was indicated in my first paper.

9. The objection advanced by STERN against a small moment of inertia, is founded on the value of the chemical constant of I_2, which was calculated by SACKUR on the assumption of the mean molecule radius (from the index of refraction) for the moment of inertia, and with which the vapour pressure values of solid iodine can very well be represented as appears from SACKUR's test. [1] In virtue of this, however, I do not think myself justified in rejecting the moment of inertia calculated by me.

The said test of the vapour pressure line has been carried out by SACKUR on simultaneous assumption of the expression 2 of § 2 and of $S_{solid\ at\ T=0} = 0$. We are then led to the question whether these two assumptions are identical or in conflict with each other. Discussions with Prof. VAN DER WAALS Jr. concerning this question have led us to the following opinion. If the entropy of a gas is determined by means of $k \log W$, the expressions 1 and 2 of § 2 are found for

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[1] SACKUR, Ann. der Physik (4) **40** 87 (1913).

it ; these values are entirely independent of the entropy of the solid substance. The gas entropy is namely found then by examining the probability of the gas state; if this is done at temperatures where solid substance is impossible, so far above the melting-point, the chance to a solid configuration must be entirely excluded. When the iodine equilibrium is tested, where the temperatures amount to 1000° K. and more, the chance to solid substance (melting point 387° K.) may certainly be put zero. And therefore the expressions of SACKUR, TETRODE, and VAN DER WAALS will in my opinion yield the correct values for the moment of inertia, and the test remains entirely outside the theorem of heat, in whatever form it be.

If, however, for the entropy of gas $k \log W$ has been chosen — I will call these values the gas scale for the entropy — it is the question what will be the entropy of solid. This value might either be determined by means of $dS = \dfrac{dQ}{T}$, or by applying the expression $k \log W$ also to the solid state. The latter, however, is only feasible on the assumption of one or more hypotheses concerning the constitution of the solid substance; these derivations must, therefore, certainly remain arbitrary in a high degree. For a monatomic solid substance a comparatively simple mechanism may be devised corresponding to the properties of solid [1]), but for multi-atomic solid substances the model becomes necessarily more intricate, hence more arbitrary. [2])

If it is, however, assumed, as is often done, that the entropy of solid at $T = 0$ is zero, then starting from this the entropy of other states can be determined with the aid of $dS = \dfrac{dQ}{T}$. This scale of entropy, which I will call the scale for solid, need not coincide, however, with the gas scale in my opinion. And if it does so for one substance, this need not necessarily be the case for all. At any rate this coinciding of the two scales requires experimental verification.

The only data from the literature which can furnish such a test, are in my opinion :

1. the theoretical derivations of STERN's gas entropy.

2. the vapour pressure line of mercury.

3. the calculation of $\displaystyle\sum_{\substack{solid\ T=0}}^{gas} \dfrac{dQ}{T}$ for iodine.

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[1]) STERN, Physik. Zeitschr. **14** 629 (1913).

[2]) STERN, Ann. der Physik. (4) **44** 520 (1914).

1. STERN's derivations rest on the above mentioned assumptions concerning the mechanism of solid substance. STERN's expressions and those of § 2 agree in a high degree, but that in his expressions the constant part has been accurately represented holds only for the definite conception which STERN forms for the solid substance [1]). A rigorous proof for the coincidence of the two scales is in my opinion not furnished by this derivation.

2. The testing of the mercury line seems to plead for the coincidence of the two scales. In a recent paper in these Proceedings Prof. LORENTZ carries out a similar test [2]). In connection with the above I think I can state the result as follows: If coincidence of the above mentioned scales is assumed, the dimension of the "elementary regions" appears to be about h^3, but as the coincidence of the scales is not proved, little weight is to be attached to the conclusion concerning the extent of the "elementary regions". This is probably a too rigorous statement of the conclusion of the mentioned paper; for the other difficulties which attend this testing, I must refer to the cited paper. Let us now consider that the entropies of § 2 (of my preceding paper) rest on the assumption that the area of the regions is really h^3; then at least if the expressions are correct and may therefore be applied to the evaporation, the coincidence of the two scales would become probable for this case.

3. From the caloric data on iodine STERN has calculated the difference of entropy between solid iodine (I_2) at $T = 0$ and gaseous iodine (in atomic state) at $T = 323$ [3]). STERN now uses for the entropy of the gaseous atomic iodine the expression which was derived by him for monatomic gases, and in which (see § 8) the entropy of solid · atomic iodine at $T' = 0$ is taken as zero. It is clear that in this way the algebraic sum of the entropies of the solid substances at $T = 0$ can be calculated.

If, however, the values of § 2 are introduced for the entropy of atomic gaseous iodine, we do not find in this way the algebraic sum of the entropies of the solid substances, but only the entropy of solid iodine (I_2) at $T = 0$. If, therefore, the entropies of § 2 are assumed as the correct ones, it follows from this calculation that the entropy of solid iodine (I_2) at $T = 0$ does not become zero, but $- 7.6$. Thus interpreted, this would plead against the coinciding of the two entropy scales for iodine.

10. With this interpretation I think I can also get agreement with

[1]) STERN, l. c.
[2]) Verslagen Kon. Ak. Amsterdam, 23. 515. (1914/15), (still to be translated).
[3]) STERN, Ann. der Physik. (4) 44 513 et seq. (1914).

the determinations of the vapour tension of solid iodine. The "chemical constant" of iodine, which is given by $C = \dfrac{S'_{gas} - c_p + Rln R - S_{solid\,T=0}}{2.3\,R}$,

in which S'_{gas} represents the entropy constant according to the gas scale, and in which $S_{solid\,T=0}$ is generally also put zero (which in my opinion need not therefore be the case in the gas scale), is 3,27 according to SACKUR[1]). The entropy constant of the gas is calculated by SACKUR on the assumption that the moment of inertia calculated from the mean molecule radius (index of refraction) is the correct one. As the radius of inertia calculated by me in my first paper, is $\dfrac{2.26}{0\,41}$ or 5.5 times smaller, and the moment of inertia therefore about 30 times smaller, the value of S'_{gas}, in which the moment of inertia M occurs as $Rln M^2$), would become Rln 30 or 6,75 times smaller when the value found by me is used. Hence if we want to retain the value 3,27 for the "chemical constant", $S_{solid\,T=0}$ must not be taken zero, but — 6,75, which is in satisfactory agreement with the result at the end of § 9. I think therefore I am justified in taking this as a confirmation of the validity of my former calculation.

11. I would therefore summarize the above as follows:

1. from the vapour pressure line of mercury the entropy of solid mercury appears to be about zero at the absolute zero point in the gas scale.

2. it follows from the caloric data of iodine that the entropy of solid iodine (I_2) at $T = 0$ is about — 7.

3. it appears from the calculation of my preceding communication that the radius of inertia of I_2 is about five times smaller than the mean molecule radius determined from the index of refraction.

4. when this radius of inertia is used the test of the vapour pressure line of iodine yields for the entropy of solid iodine a value of about — 7 in agreement with the second conclusion.

5. the cited data do not allow of a test of the theorem of heat.

6. In agreement with the third conclusion MANDERSLOOT's calculations lead to moments of inertia which are smaller than would agree with the mean molecule radii (index of refraction, internal friction, and b-values of the equation of state)[3]).

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[1]) SACKUR, l. c.

[2]) These Proceedings, Vol. XVII p. 697, (equation 2).

[3]) MANDERSLOOT, Thesis for the Doctorate. Utrecht. 1914. See also: These Proc. Vol. XVII, p. 702. (1914/15).

12. *Other equilibria of the type $AB \rightleftarrows A + B$.*

None of the data which are to be found in the literature on other equilibria of the above type, allow of a sufficiently accurate calculation of the moments of inertia.

There exists a very interesting investigation on hydrogen dissociation by LANGMUIR, who concludes to dissociation of the hydrogen molecules from the abnormally high energy required to keep the tungsten wires in a hydrogen atmosphere at high temperature, and who tries to calculate the degree of dissociation from these energy measurements. [1]) On account of the insufficient accuracy of the required quantities these calculations cannot yield any but rough values. From the values of the degree of dissociation, which LANGMUIR considers the most probable, I have calculated the moment of inertia by the aid of equation 4 and 4a, resp. 6 and 6a of my preceding communication ; the limits for the values for $log\ M$ found thus amount to -44.3 (TETRODE and VAN DER WAALS at $\lambda = 0$), and -45.3 (VAN DER WAALS at $\lambda = 20\,\mu$). From this moment of inertia the value 8.10^{-11} resp. $2.5.10^{-11}$ cm. would follow for the atom distance. The moment of inertia of hydrogen, however, is in my opinion sufficiently accurately known to justify us in rejecting these values, and in concluding that the values given by LANGMUIR, are not accurate.

Reversely it would certainly be of importance to seek an interpretation of the phenomena found by LANGMUIR, by the aid of equations 4 and 6 and of the value of the moment of inertia of hydrogen, as it is found according to other methods. [2]).

The chlorine dissociation has been examined at temperatures between 1700 and 2000 K. by PIER ; owing to the great experimental difficulties accompanying this investigation, these values are not accurate either. [3]) If we calculate for this case the value of the moment of inertia, we find values for $log\ M$ varying between about -54 and -37. Now we can certainly disregard the smallest values, because they are found from the determinations at the lowest temperatures, where the degree of dissociation is very small, and a small absolute error manifests itself greatly enlarged in the equilibrium constant. But also at the higher temperatures the value of $log\ M$ varies too much to allow us to draw satisfactory conclusions.

The case of the bromine dissociation is somewhat more favourable. If we apply the equations 4 and 6 to the values found by PERMAN

[1]) LANGMUIR, Journ. Amer. Chem. Soc. 34. 860. (1912).

[2]) Cf. for the moment of inertia of hydrogen among others EINSTEIN and STERN, Ann. der. Physik. (4) 40. 551. (1913).

[3]) PIER, Zeitschr. f. physik. Chemie. 62. 417. (1908).

and Atkinson [1]) we find further that the determinations at the lowest temperatures, where the degree of dissociation is very small, are useless for the calculation. If the term with v is omitted from equation 6, it can be brought into the following form for the bromine dissociation :

$$\frac{\Sigma nE_{T=0}}{4.571\,T} + log\,M = -log\,\frac{x^2}{1-x^2} + \frac{3}{2}\,log\,T - 38\,302, \quad . \quad (14)$$

in which x represents the degree of dissociation at atmospheric pressure. Application of this expression to the experimental determinations yields the following table :

TABLE VI.

t	x	2nd member of (14)	$(TC_9)_{\lambda=0}$	$\left(\frac{\Delta TC_9}{\Delta T}\right)_{\lambda=0}$
900	0.0148	—30.039	35236	
				—40.75
950	0.0253	—30.477	37273	
				—39.85
1000	0.0398	—30.845	39266	
				—40.75
1050	0.0630	—31.220	41304	

mean —40.45

The thus found value of — 40.45 yields 4.10^{-10} cm. for the radius of inertia. If the experimental determinations do not contain great errors, a very small radius of inertia follows from this calculation. And this radius would be found still smaller, if the term with v was taken into account. I think, however, that no great importance is to be attached to this value, because the values of the fifth column differ too much from each other, and the determinations are less numerous and less accurate than for the iodine dissociation. The accuracy is here again smaller, because the equilibrium lies strongly on one side in these determinations.

13. *The equilibrium* $2AB \rightleftarrows A_2 + B_2$.

When Prof. van der Waals Jr.'s considerations are applied in a perfectly analogous way to the equilibrium $2\,AB \rightleftarrows A_2 + B_2$, we find for the dissociation constant:

$$\frac{n_{A_2}\,n_{B_2}}{n_{AB}^2} = e^{-\frac{\Sigma nE_{T=0}}{RT}}\,\frac{m_{A_2}^{3/2}\,m_{B_2}^{3/2}}{m_{AB}^3}\,\frac{M_2 M_4}{M_1^2}\,\frac{\left(1-e^{-\frac{v_1 h}{kT}}\right)^2}{\left(1-e^{-\frac{v_2 h}{kT}}\right)\left(1-e^{-\frac{v_3 h}{kT}}\right)}, \quad (15)$$

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[1]) Perman and Atkinson, Z. phys. Chem. **33**. 215. 577 (1900) Cf. also: Abegg. Handbuch 4. 2. 233 (1913).

in which M_1, M_2, and M_3 represent the moments of inertia, r_1, r_2, and r_3 the vibrations of the molecules AB, A_2, and B_2.

If by the aid of the entropy values of § 2 the value of K is determined we get, disregarding the term with the r-values, an identical expression. Hence the expressions of Sackur, Tetrode, van der Waals Jr., and also those of Stern, when at least with regard to the latter it is assumed that Nernst's heat theorem is valid, yield the same result here.

With regard to the test of this expression we must remark that there occur three moments of inertia in equation 15, and that the ratio of the moments of inertia can only be determined from the equilibrium values.

The value of $\Sigma n E_{T=0}$, which naturally cannot be directly determined with the equilibrium $I_2 \gtrless 2I$, can generally be calculated here from the caloric data of Berthelot, Thomsen, and others.

From equation 15 follows for the transformation energy:

$$\Sigma n E = \Sigma n E_{T=0} + \frac{N h \nu_2}{e^{\frac{\nu_2 h}{kT}}-1} + \frac{N h \nu_3}{e^{\frac{\nu_3 h}{kT}}-1} - 2\frac{N h \nu_1}{e^{\frac{\nu_1 h}{kT}}-1} \quad . \quad . \quad (16)$$

If we, therefore, know the ν-values from the specific heats, the value of $\Sigma n\, E_{T=0}$ can be determined from the thermo-chemical determination of $\Sigma n E$. The ν-terms are generally so small that they do not cause appreciable deviations between these quantities.

At low temperatures in equation 15 the term with the frequencies has about the value 1. The material that admits of testing, now consists for a great part of determinations of electromotive forces of gas cells, in which the term of vibration may therefore be left out. Then, however, the agreement with Sackur's expressions becomes perfect, and 1 can therefore refer to his paper for the testing of these determinations.[1] Sackur finds good agreement between the experimental determinations and his expressions, which are founded on the moment of inertia, which follows from the mean molecule radii (b of the equation of state, index of refraction and internal friction). At higher temperatures, however, the term with ν asserts its influence, and we shall, therefore, have to examine it; for the sake of completeness 1 have inserted the values of the gas cells also in the subjoined tables.

14. *The equilibrium* $2HCl \gtrless H_2 + Cl_2$.

The heat of formation of $2HCl$ from H_2 and Cl_2 is given by

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[1] Sackur, Ann. der Physik. (4) 40 101 (1913).

THOMSEN and BERTHELOT in good agreement at 44000 cal. The specific heats of H_2 and HCl differ little from 5 at room temperature; the energy of vibration is, therefore, still imperceptible here. Hence the corresponding terms with ν can be omitted in 16. The specific heat of chlorine amounts to $8.130 - 1.985 = 6.145$ at $T = 616.4$ according to STRECKER (for constant volume) [1]. This value corresponds to $\lambda = 9.5\,\mu$ (see equation 12). If this is substituted in equation 16, the term with ν_3 appears to have no appreciable value at room temperature either; we may, therefore, take $\Sigma n E$ and $\Sigma n E_{T=0}$ equal, and for the hydrochloric acid equation 15 may be transformed into:

$$ \log K = - \frac{44000}{4.571\,T} + \log \frac{\left(1 - e^{-\frac{\lambda_1 h}{kT}}\right)^2}{\left(1 - e^{-\frac{\lambda_2 h}{kT}}\right)\left(1 - e^{-\frac{\lambda_3 h}{kT}}\right)} + \log \frac{M_2 M_3}{M_1{}^2} - 1,458 \quad (17) $$

or

$$ \log \frac{M_2 M_3}{M_1{}^2} + \log \frac{\left(1 - e^{-\frac{\lambda_1 h}{kT}}\right)^2}{\left(1 - e^{-\frac{\lambda_2 h}{kT}}\right)\left(1 - e^{-\frac{\lambda_3 h}{kT}}\right)} = \log K + \frac{9626}{T} + 1,458 \quad (18) $$

The experimental determinations which admit of a test of 18, are the determinations of the gas cells of DOLEZALEK[2] and MÜLLER[3] and the direct determination of the dissociation of LÖWENSTEIN[4].

If the values found by them are filled in in 18, we find:

TABLE VII.

t	T	$\log K$	Second member of 18	$\log \frac{M_2 M_3}{M_1{}^2}$	Observer
25	298	— 33.18	0.58	0.58	MÜLLER
30	303	— 32.37	0.86	0.86	DOLEZALEK
1556	1829	— 5.772	0.95	0.70	LÖWENSTEIN

mean 0.71

[1] STRECKER Wied. Ann. 17. 102 (1882). Cf. also PIER. Zeitschr. f. physik. chem. 62 416 (1908).

[2] DOLEZALEK. Zeitschr. f. physik. Chem. 26 321 (1898). BODENSTEIN and GEIGER. ibid. 49 72 (1904).

[3] MÜLLER. Zeitschr. f. physik. Chem. 40 158 (1902). NERNST. Sitz. Ber. Preuss. Akad. 1909. 263.

[4] LÖWENSTEIN. Zeitschr. f. physik. Chem. 54, 715 (1906). The value given in the table VII has been corrected for the dissociation of chlorine into atoms. See NERNST. Zeitschr. f. Elektroch. 15 689 (1909).

In the first two determinations the v-term has no perceptible influence; in the last it has. The value of the term for chlorine will certainly predominate here. If this is taken into account ($\lambda = 9.5\,\mu$), we find the value of column 5. When the value of $log\,\dfrac{M_2 M_3}{M_1{}^2}$ is calculated from the mean molecule radii, as they are given by Sackur, we find 0.82, which is therefore in satisfactory agreement with the mean value 0,71. We must therefore conclude, that if the centres in Cl_2 and H_2 are closer together than corresponds with the mean molecule radius, the same thing is the case in about the same degree with HCl.

15. The equilibrium $2\,HBr \gtrless H_2 + Br_2$.

When for ΣnE we substitute in 15 the value 24200 cal., which was calculated by Ostwald from Thomsen's measurements[1], this equation may be transformed into:

$$log\,\frac{M_2 M_3}{M_1{}^2} + log\,\frac{\left(1 - e^{-\frac{v_1 h}{kT}}\right)^2}{\left(1 - e^{-\frac{v_2 h}{kT}}\right)\left(1 - e^{-\frac{v_3 h}{kT}}\right)} = log\,K + \frac{5294}{T} + 1.968 \quad . \quad (19)$$

Application to the determinations of Bodenstein and Geiger[2] and Vogel von Falckenstein[3] here yields:

TABLE VIII.

t	T	$log\,K$	Second member of 19	Observer
30	303	—18.43	1.01	Bodenstein and Geiger
1024	1297	— 5.20	0.85	Vogel von Falckenstein
1108	1381	— 4.87	0.93	"
1222	1495	— 4.53	0.98	"

At $T = 303$ the influence of the v-term is still imperceptible; $log\,\dfrac{M_2 M_3}{M_1{}^2}$, therefore, amounts to 1,01 according to this determination.

From the mean molecule radii we find $log\,\dfrac{M_2 M_3}{M_1{}^2} = 1,11$ in good harmony with it.

[1] Ostwald. Allgem. Chem. II. 1, 110.

[2] Bodenstein and Geiger. Zeitschr. f physik. Chem. 49, 70 (1904).

[3] Vogel von Falckenstein. Zeitschr. f. physik. Chem. 68, 279 (1909) and 72, 115 (1910).

With regard to the observations at high temperatures it should be borne in mind that the term with v is positive, because the influence of the bromine vibration will be the greatest. Hence the value of $log \frac{M_2 M_3}{M_1^2}$ becomes smaller than the values of the fourth column of the above table. But moreover the value for $log K$ has been calculated on the assumption that at the test temperatures bromine is not dissociated into atoms. From the expression of the bromine dissociation of § 12 (equation 14) it would, however, follow, that under the circumstances of these experiments the bromine is split up for a great part, and that thence a large correction is to be applied for $log K$. This correction, however, makes $log K$ smaller, hence the value in the fourth column also becomes smaller, which would render the agreement with the first value of $log \frac{M_2 M_3}{M_1^2}$ still worse. I have not succeeded in bringing these determinations in satisfactory concordance with the electromotive ones. If the correction which is to be applied in VOGEL VON FALCKENSTEIN's observations for the dissociation of bromine into atoms, was sufficiently accurately known, an attempt would be justified to get agreement between the values of $log \frac{M_2 M_3}{M_1^2}$ by a change in $\Sigma n E$. We should then have to choose a smaller value for the heat of reaction; the energy term in 19 then yields a greater decrease of the value of $log \frac{M_2 M_3}{M_1^2}$ at the lowest temperature than at the higher temperatures. The consequence of this would then be that the value of $\frac{M_2 M_3}{M_1^2}$ became smaller than corresponds to the mean molecule radii. But then the value which can be derived from BERTHELOT's observations, and which is not smaller, but greater than that of THOMSEN, would plead against this attempt.

16. *The equilibrium* $2 HI \rightleftarrows H_2 + I_2$.

The value for the reaction energy having a very great influence on the value of the moments of inertia also at this equilibrium, I will try to derive this value directly from the observations themselves in an analogous way as in the iodine dissociation. This is possible here because the number of observations of the iodine hydrogen dissociation equilibrium is much greater than the bromine hydrogen equilibrium.

When in 15 we fill in the values for the masses of the reacting·

molecules, and bear in mind that in HI and H_2 the vibration of the atoms at ordinary temperature does not yet manifest itself in the amount of the specific heats, but that this *is* the case for iodine, (see § 6), so that the term of vibration of the iodine molecule will be the predominating one, then with neglect of the v-terms for HI and H_2, equation 15 may be transformed into:

$$ log \frac{M_2 M_2}{M_1^2} - \frac{\Sigma n E_{T=0}}{4.571\ T} = log\ K + log \left(1 - e^{-\frac{\nu h}{kT}} \right) + 2.263 \quad . \quad (20) $$

If we now fill in the value $15\,\mu$ for λ_3 (see § 6), the observations of STEGMÜLLER (gas cells)[1] and of BODENSTEIN (direct dissociation determinations)[2] yield the following table: (p. 1024)

If equation 20 is written in the form:

$$ C = T\ log \frac{M_2 M_3}{M_1^2} - \frac{\Sigma n E_{T=0}}{4.571}, \quad . \quad . \quad . \quad . \quad (21) $$

in which C represents the value of the second member of 20, every time multiplied by the corresponding absolute temperature, then in a graphical representation, in which C is laid out as function of T, the observations must form a straight line. Then it appears graphically that a straight line can be drawn through the observations with the parameters $log \dfrac{M_2 M_3}{M_1^2} = 1{,}184$ and $\dfrac{\Sigma n E_{T=0}}{4.571} = 529$; the observed points are then spread on both sides of this line. Then follows for the expression of the iodine hydrogen equilibrium:

$$ log\ K = - \frac{529}{T} - log \left(1 - e^{-\frac{972}{T}} \right) - 1{,}079 \quad . \quad . \quad . \quad (22) $$

It will certainly be possible to make a slight modification in the parameters without appreciably impairing the agreement between calculated and found values; it appears from the subjoined table that the errors in the observations at the lowest temperatures are pretty large, but that the expression 22 satisfactorily represents the other observations.

Dissociation determinations at high temperatures have been made by VOGEL VON FALCKENSTEIN[3]. They have been carried out by measurement of the partial pressure of the hydrogen, use being made of the permeability of platinum to this gas, and of its impermeability to the other gases. The equilibrium constants, which have

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[1] STEGMÜLLER. Zeitschr. f. Elektrochem. **16**. 85 (1910).

[2] BODENSTEIN. Zeitschr. f. physik. Chem. **29**, 295 (1899).

[3] loc. cit.

TABLE IX.

t	T	$\log K$	J term	Second member of 20	Observer
31.6	304.6	— 2 925	— 0.018	— 0.680	STEGMÜLLER
55.2	328.2	— 2.692	— 0.023	— 0.452	"
81.6	354.6	— 2.416	— 0.029	— 0.182	"
280	553	— 1.931	— 0.082	+ 0.250	BODENSTEIN
300	573	— 1.905	— 0.088	0.270	"
320	593	— 1.878	— 0.094	0.291	"
340	613	— 1.851	— 0.100	0.312	"
360	633	— 1.823	— 0.105	0.335	"
380	653	— 1.794	— 0.111	0.358	"
400	673	— 1.765	— 0.117	0.381	"
420	693	— 1.735	— 0.123	0.405	"
440	713	— 1.705	— 0.128	0.430	"
460	733	— 1.675	— 0.134	0.454	"
480	753	— 1.644	— 0.140	0.479	"
500	773 -	— 1.612	— 0.145	0.506	"
520	793	— 1.580	— 0.151	0.532	"

TABLE X.

T	$\log K$ (found)	$\log K$ (calc.)	T	$\log K$ (found)	$\log K$ (calc.)
304.6	— 2.925	— 2.798	653	— 1.794	— 1.778
328.2	— 2.692	— 2.668	673	— 1.765	— 1.748
354.6	— 2.416	— 2.542	693	— 1.735	— 1.719
553	— 1.931	— 1.954	713	— 1.705	— 1.693
573	— 1.905	— 1.914	733	— 1.675	— 1.667
593	— 1.878	— 1.877	753	— 1.644	— 1.642
613	— 1.851	— 1.842	773	— 1.612	— 1.618
633	— 1.823	— 1.810	793	— 1.580	— 1.595

been inserted in the above table in the fourth column, were calculated from the values of this pressure.

TABLE XI.

t	T	x	log K	log K (corr.)	log K (from 22)
1022	1295	0.329	— 1.221	— 1.368	— 1.210
1217	1490	0.3755	— 1.044	— 1.384	— 1.115

The values of the fourth column have been calculated on the assumption that all the iodine is present as I_2^-; this now is certainly not the case according to the determinations of the iodine dissociation (see § 5). At these temperatures the iodine has already perceptibly been split up into ·atoms, and specially at the low iodine tension of these experiments the splitting up will be great. Through the correction which is to be applied for this, $log K$ of column 4 becomes smaller.

Let us suppose the iodine to be partially split up into atoms (degree of splitting y), then the total iodine pressure is not equal to the hydrogen pressure, but $1 + y$ times greater. Let us call the hydrogen pressure P_{H_2}, the total pressure P, then we have for the partial tensions of hydrogen, iodine atoms, iodine molecules and iodine hydrogen:

$$P_{H_2} \ , \quad 2y\, P_{H_2} \ , \quad (1-y)\, P_{H_2} \quad \text{and} \quad P-(2+y)\, P_{H_2}.$$

Hence the equilibrium constant for iodine hydrogen becomes:

$$K_{HI} = \frac{P_{H_2}^2(1-y)}{[P-P_{H_2}(2+y)]^2} \quad \cdots \cdots \quad (23)$$

and that for the iodine dissociation expressed in partial pressures:

$$K_{I_2} = \frac{4y^2}{1-y}\, P_{H_2}. \quad \cdots \cdots \cdots \quad (24)$$

Now from the equation for the iodine dissociation (equation 13) follows for the equilibrium constant (in partial pressures; pressure unity the atmosphere):

$$T = 1295 \qquad log\ K_{I_2} = -\ 0.668$$
$$T = 1490 \qquad log\ K_{I_2} = +\ 0.148 \qquad \Big\} \ \cdots \ (25)$$

If we now introduce the values of 25 and the found values of P_{H_2} into 24, y may be calculated from it. This value of y substituted in 23, yields the values $log\ K$ (corr.) of table XI. When

68

the value of $log\,K$ is calculated from 22, we get the values of the sixth column of table XI, which appreciably differ from those of the fifth column. This deviation can, however, be accounted for by this that the terms with v of HI, and possibly also those of H_2 play a part at these high temperatures; the term with HI will render the value of $log\,K$ according to 22 smaller. The iodine vibration which prevails at low temperatures, will also continue to do so at high temperatures. The value of the iodine term amounts to -0.277 at $T = 1295$, and to -0.319 at $T = 1490$; the term, therefore, which occurs in expression 22 through the vibration of the atoms in HI, remains below this value; and in this way an agreement may be probably arrived at, as the discrepancies between the values of the fifth and the sixth columns are smaller than the mentioned ones. Moreover some variation is still possible in the choice of the parameters of the straight line (equation 21).

The equation 22, which is accordingly in satisfactory agreement with all the determinations of the iodine hydrogen equilibrium, yields the value 1,184 for $log\,\dfrac{M_2 M_3}{M_1{}^2}$. If from the mean molecule radii, as they are given by SACKUR, the value of the expression mentioned is calculated, we find 1,21 which is therefore in good agreement with the preceding one.

From formula 22 the value 2530 cal. follows for $\Sigma n E_{T=300}$, this value differs but little from that used by NERNST in his calculations [1]; most of the data which can be derived from direct caloric determinations, are useless.

17. From the calculations of the dissociation equilibria of the three halogen hydrogens we come therefore to the conclusion that the quotient of the moments of inertia agrees with that calculated from the mean molecule radii

This conclusion, at which SACKUR by the aid of his expressions had arrived already before, but which was only meant to be roughly valid, appears also to be in good harmony with Prof. VAN DER WAALS Jr.'s expression, in which the vibrations of the atoms are taken into account.

Amsterdam. Dec. 1914.   *Anorg. Chem. Lab. of the University.*

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[1] Zeitschr. f. Elektrochem. **15**, 687 (1909).