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

(Communicated in the meeting of Sept. 26, 1914).

1. *Introduction.*

It may be supposed as known that the situation of the equilibrium of a gas reaction at a definite temperature can be calculated, when at that temperature we know the energy of reaction and the variation in entropy free from concentration for molecular conversion according to the chemical equation of reaction. Both quantities are algebraic sums of the energies and entropies of the reacting gases separately, in which the terms referring to substances of different members of the equation of reaction have opposite signs. Energy and entropy of a gas free from concentration are pure functions of the temperature; in the expression for the "equilibrium constant" as function of the temperature the transformation energy and the change in entropy free from concentration at one definite temperature and the temperature coefficients of both occur as constants. The transformation energy of a great number of reactions may be directly derived from BERTHELOT and THOMSEN's tables; the temperature coefficients are in simple relation with the specific heats, and for this a great number of data are found in the literature; the transformation entropy, however, is generally not determined directly, but from the chemical equilibria by the aid of the above expression.

If one purposes to calculate the chemical equilibria from caloric data, one will have to apply instead of the said mode of calculation of the transformation entropy either direct determinations, or another mode of calculation, in which exclusively quantities of the gases separately are used. The determination of electromotive forces of gas cells might be counted among the direct measurements; for the temperature coefficient of the electromotive force is a measure for the transformation entropy. But this method cannot be applied for a great number of reactions e.g. for dissociations in molecules or atoms of the same kind.

Hence the calculation of chemical equilibria will succeed only when we have a method at our disposal to calculate the entropies of the gases separately or the algebraic sum of the entropies of a gas equilibrium from the constants of the substances.

The thermodynamic entropy of a gas is a quantity, which through its definition is determined except for a constant, and it is therefore

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clear that the above mentioned calculations of the entropy of the gases separately have only sense for another definition of entropy. If the entropy is defined as a function of the probability of the condition, it is possible to find a definite value for this entropy ; but this value will vary with different meaning of the "probability". Thus the expressions derived by KEESOM [1]), TETRODE [2]), and SACKUR [3]) for the entropy of gases present differences which are the consequence of different definitions of probability. These differences only occur in the constant part ; if these differences cancelled each other in the algebraic sum, a test by the equilibrium determinations could not give a decision about the correctness of the entropy values. When, however, the algebraic sum of the entropies according to SACKUR and TETRODE are drawn up, it appears that these differences continue to exist also in the algebraic sums, and it must therefore be possible from experimental determinations at least if the accuracy is great enough to get a decision which expression is correct.

While these calculations yield a value for the entropy of the gases separately, Prof. VAN DER WAALS Jr. has derived an expression for the "equilibrium constant" of gas reactions, from which the algebraic sum of the entropies can be easily derived; the entropy of the gases separately is again determined here with the exception of a constant. Besides this expression tries to take the variability of the specific heat with the temperature into account [4]). I intend to test this formula and the above mentioned expressions of SACKUR and TETRODE by a number of data from the chemical literature.

2. *The expressions for the entropy of gases.*

For monatomic gases KEESOM, SACKUR, and TETRODE give the value for the entropy free from concentration (eventually after recalculation) successively by the following expressions:

$$H_{v=1} = \frac{3}{2} R \ln T + \frac{3}{2} R \ln R - \frac{5}{2} R \ln N + \frac{3}{2} R \ln m - 3 R \ln h + C_1 \quad . \quad (1)$$

in which C_1 represents according to KEESOM $R \ln \pi + R \left(4 + \ln \frac{4}{9} \left(\frac{3}{5} \right)^{3/2} \right)$,

according to SACKUR $\frac{3}{2} R \ln 2\pi + \frac{3}{2} R$, and according to TETRODE

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[1]) KEESOM. These Proc. XVI, p. 227, 669, XVII, p. 20.
[2]) TETRODE. Ann. de Phys. (4) **38**. 434. **39**. 255, (1912).
[3]) SACKUR. Ann. d. Phys. (4) **36**. 958, (1911); **40**. 67, 87, (1913).
[4]) These Proc. XVI p. 1082.

$\frac{3}{2} R \ln 2\pi + \frac{5}{2} R.$[1]) This value of C_1 amounts successively to $3,567 R$, $4,257 R$ and $5,257 R$.

The values given by SACKUR and TETRODE for di-atomic gases, are:

$$H_{v=1} = \frac{5}{2} R \ln T + \frac{5}{2} R \ln R - \frac{7}{2} R \ln N + \frac{3}{2} R \ln m -$$

$$- 5 R \ln h + R \ln M + \frac{9}{2} R \ln 2 + \frac{7}{2} R \ln \pi + C_2 , \quad . \quad . \quad (2)$$

in which C_2 according to SACKUR amounts to $\frac{5}{2} R$, according to

TETRODE to $\frac{7}{2} R$.

We get for a tri-atomic gas:

$$H_{v=1} = 3 R \ln T + 3 R \ln R - 4 R \ln N + \frac{3}{2} R \ln m -$$

$$- 6 R \ln h + \frac{1}{2} R \ln M_1 M_2 M_3 + 6 R \ln 2 + 5 R \ln \pi + C_3 , \quad . \quad . \quad (3)$$

in which C_3 amounts to $3 R$ according to SACKUR, to $4 R$ according to TETRODE.

Besides the known values N and h, the moments of inertia of the molecules occur therefore in these expressions. For the di-atomic molecules M is the moment of inertia of the dumbbell shaped molecule with respect to an axis through the centre of gravity, normal to the bar of the dumbbell; for the tri-atomic molecules M_1, M_2 and M_3 are the three chief moments of inertia, which accordingly depend on the relative position of the three atoms in the molecule.

For equilibria in which only mon- or di-atomic molecules participate, the moments of inertia of the di-atomic particles therefore occur, which can be approximately calculated from the different determinations of the mean molecule radius. For a test of the formulae by equilibria of tri-atomic molecules, however, a hypothesis concerning the relative situation of the atoms is indispensable, which is more or less arbitrary, and can make the test less convincing.

3. The equilibrium $AB \rightleftarrows A + B$.

For the simplest gas equilibrium $AB \rightleftarrows A + B$, in which the atoms A and B can be of the same or of different kinds, we

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[1]) In the expressions of TETRODE l. c. the terms with z are omitted, which seems justified.

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find for the algebraic sum of the entropies free from concentration making use of the expressions of § 2:

$$\Sigma nH_{r=1} = 2(H_{c=1})_{\text{monat.}} - (H_{c=1})_{\text{diat.}} =$$

$$= \frac{1}{2} Rln T + \frac{1}{2} RlnR - \frac{3}{2} RlnN + \frac{3}{2} Rln \frac{m_A m_B}{m_A + m_B} - Rlnh -$$

$$- \frac{3}{2} Rln2 - \frac{1}{2} Rln\pi - RlnM + C_4,$$

in which C_4 amounts to $1/_2 R$ when SACKUR's values are used, to $3/_2 R$ when TETRODE's values are used.

SACKUR and TETRODE's calculations are based on the following assumptions for the specific heats:

$$C_{v\,\text{monat.}} = \frac{3}{2} R \quad ; \quad C_{v\,\text{diat.}} = \frac{5}{2} R.$$

The value of the transformation energy in its dependence on the temperature is therefore given by:

$$\Sigma nE = \Sigma nE_{T=0} + \frac{1}{2} RT.$$

In this expression and the following the molecular values n of the substances of the second member of the chemical reaction equation are always taken positive, those of the first member negative.

Inserting these values into the expression for K_c, we find:

$$RT \ln K_c = - \Sigma nE_{T=0} - \frac{1}{2} RT + T\Sigma nH_{v=1} - RT,$$

in which $\Sigma nH_{v=1}$ is represented by the above derived expressions. We can transform this expression as follows:

$$ln K_c = - \frac{\Sigma nE_{T=0}}{RT} + \frac{1}{2} ln T - ln M + ln C_5, \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

in which

$$ln C_5 = \frac{3}{2} ln \frac{m_A m_B}{m_A + m_B} - ln 2Nh + \frac{1}{2} ln k - \frac{1}{2} ln 2\pi + C_6; \quad (4a)$$

C_6 amounting to -1 according to SACKUR's expressions, to 0 according o TETRODE.

4. In the fifth communication on the law of partition of energy Prof. VAN DER WAALS Jr. derives the following equation for the dissociation equilibrium of a di-atomic molecule:

$$\frac{n_1^2}{n_v} = e^{\frac{\varepsilon_1 - \varepsilon_0}{\Theta}} \left(\frac{m_A m_B}{m_A + m_B} \right)^{3/2} \frac{1}{M} \frac{1 - e^{-\frac{vh}{\Theta}}}{h} \frac{1}{2} \sqrt{\frac{\Theta}{2\pi}} \quad \cdot \quad \cdot \quad (5)$$

$\varepsilon_1 - \varepsilon_0$ here represents the transformation energy at the absolute zero for one particle; n_1 and n_2 represent the number of split and unsplit molecules per volume unity; hence we get:

$$\frac{\varepsilon_1 - \varepsilon_0}{\Theta} = -\frac{\Sigma n E_{T=0}}{NkT} = -\frac{\Sigma n E_{T=0}}{RT} \; ; \; K_c = \frac{n_1{}^2}{n_v}\frac{1}{N} .$$

Equation (5) can, therefore be written in the following form:

$$ln K_c = -\frac{\Sigma n E_{T=0}}{RT} + \frac{1}{2} \ln T - \ln M + \ln\left(1 - e^{-\frac{vh}{kT}}\right) + \ln C_7, \quad . \;(6)$$

in which

$$ln C_7 = \frac{3}{2} \ln \frac{m_A m_B}{m_A + m_B} - \ln 2Nh + \frac{1}{2} \ln k - \frac{1}{2} \ln 2\pi \quad . \quad . \;(6a)$$

Equation (6) differs from equation (4) in this that in (6) the term with v occurs, which takes a vibration of the two atoms in the molecule into account; equation (6a) quite agrees with (4a), if in the latter Tetrode's value is substituted; Sackur's value yields a unity difference.

5. *The equilibrium* $J_2 \rightleftarrows 2J$.

In the chemical literature a series of accurate observations occur of Starck and Bodenstein [1]); the dissociation constant of iodium is given by them in concentrations, i.e. gram molecules per litre. The equations (4) and (4a), resp. (6) and (6a) yield for their dissociation constant:

$$ln K_{SB} = -\frac{\Sigma n E_{T=0}}{RT} + \frac{1}{2} \ln T - \ln M + \left[\ln\left(1 - e^{-\frac{vh}{kT}}\right)\right] + \ln C_8, \;(7)$$

in which $log\, C_8 = log\, C_7 + 3$ (according to Tetrode and v. d. Waals Jr.);
$log\, C_8 = log\, C_7 + 2{,}566$ (according to Sackur).

Making use of the values: $N = 6.85\ 10^{23}$. (Perrin), $k = 1.21\ 10^{-16}$, $h = 5.88\ 10^{-27}$, $m_A = m_B = \dfrac{127}{6.85\ 10^{23}}$, we find:

$$log\, C_8 = -36.313 \text{ (according to Tetrode and van der Waals Jr)}$$
$$-36.747 \text{ (according to Sackur)} \quad . \; . \; . \; . \; . \; . \;(7a)$$

In equation (7) there occur two (resp. three) quantities, which can be calculated from the observations: $\Sigma n\, E_{T=0}$, M (and v).

As the term with v can only have slight influence on the result, we write equation (7) as follows:

$$\frac{\Sigma n\, E_{T=0}}{2.303\, RT} + log\, M = -log\, K_{SB} + \frac{1}{2} log\, T + \left[log\left(1 - e^{-\frac{vh}{kT}}\right)\right] -$$
$$-36.313\ (resp. -36.747) \quad . \; . \;(8)$$

Let us now assume that λ remains below 20μ, which seems justified

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[1]) Zeitschr. f. Elektrochem. **16**, 961 (1910).

in virtue of the observations of the absorption lines and their influence on the specific heats of other gases (see among others BJERRUM); we then find as extremes for the term with ν:

$$\text{zero and } log\left(1-e^{-\frac{3\,.\,10^{14}\,.\,4.86\,.\,10^{-11}}{20\,T}}\right).$$

STARCK and BODENSTEIN's observations now yield the following table for the terms of 8:

TABLE I.

$t\,(Cels)$	T	$K_{S.B.}.10^3$	$log\,K_{S.B.}$	$(\nu term)_{\lambda=20\mu}$	$^1/_2\,log\,T$	Second member of 8	
						$\lambda = 0$	$\lambda = 20\,\mu$
800	1073	0.129	0.111– 4	0.693—1	1.515	— 30.909	— 31.216
900	1173	0.492	0.692—4	0.665—1	1.535	— 31.470	— 31.805
1000	1273	1.58	0.199 - 3	0.639—1	1.552	— 31.960	— 32.321
1100	1373	4.36	0.639—3	0.615 –1	1.569	— 32.383	— 32.768
1200	1473	10.2	0.009—2	0.591—1	1.584	32.738	— 33.147

VAN DER WAALS's equation for $\lambda = 0$ and TETRODE's entropy expressions yield, therefore, the values of the seventh column of the above table; SACKUR's values always yield 0,4343 less; VAN DER WAALS's equation with $\lambda = 20\,\mu$ yields the values of the eighth column.

If we now write equation 8 in the form:

$$\frac{\Sigma n\,E_{T=0}}{2.303\,R} + T\,log\,M = T\,C_9 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

we find:

TABLE II.

T	$(T C_9)_{\lambda=0}$	$\left(\frac{\Delta T C_9}{\Delta T}\right)_{\lambda=0}$	$(T C_9)_S$	$\left(\frac{\Delta T C_9}{\Delta T}\right)_S$	$(T C_9)_{\lambda=20\mu}$	$\left(\frac{\Delta T C_9}{\Delta T}\right)_{\lambda=20\mu}$
1073	— 33166		— 33631		— 33494	
		— 37.5		— 37.9		— 38.1
1173	— 36915		— 37423		— 37308	
		— 37.7		— 38.15		— 38.4
1273	— 40685		— 41238		— 41145	
		— 37.8		— 38.2		— 38.5
1373	— 44462		— 45058		— 44990	
		— 37.6		— 38.0		— 38.3
1473	— 48222		— 48862		— 48824	
		mean — 37.6		mean-38.05		mean — 38.3

It will be clear that the values of $\dfrac{\Delta T C_9}{\Delta T}$ represent the values for *log M* calculated from equation (9). Therefore the value of M becomes $10^{-37.6}$ according to Tetrode, $10^{-38.05}$ according to Sackur, $10^{-37.6}$ according to Van der Waals for $\lambda = 0$, $10^{-33.3}$ for $\lambda = 20 \mu$.

It is clear from the calculation that the variation of λ from zero to 20μ does not cause a change in the order of magnitude of M, that therefore the fact that the frequency is unknown yet renders the rough calculation of M possible, and that reversely the frequency cannot be calculated but from exceedingly accurate observations. With the measurements available at present this is not yet possible, as appears from table 2.

If the iodine molecule is represented by two spheres, the masses of which are thought concentrated in the centres, and if the distance from the centres is d, the moment of inertia with respect to an axis through the centre of gravity and normal to the molecule axis is $2 m \left(\dfrac{d}{2}\right)^2$. From this follows for the limits of d:

$$10^{-37.6}, \text{ resp. } 10^{-38.3} = 2 \frac{127}{6.85 \; 10^{23}} \frac{d^2}{4} \text{ or } d = 1.6 . 10^{-8}, \text{ resp. } 7 \; 10^{-9} \quad (10)$$

a value which as far as the order of magnitude is concerned is in satisfactory concordance with the diameter calculations according to other methods.

6. Sackur and Tetrode's entropy expressions which were used in the preceding paragraph are founded on the assumption that the specific heats of the gases are independent of the temperature; the test of these formulae can therefore only be a rough one.[1] In the expression proposed by Van der Waals, the variability of the specific heats is, however, taken into account.

According to this expression the transformation energy for the iodine dissociation is represented by:

$$\Sigma n E = \Sigma n E_{T=0} + \tfrac{1}{2} RT - \frac{N \nu h}{e^{\frac{\nu h}{kT}} - 1} \quad . \quad . \quad . \quad (11)$$

Hence the algebraic sum of the specific heats becomes:

$$\frac{d \Sigma n E}{dT} = \frac{1}{2} R - R \left(\frac{h\nu}{kT}\right)^2 \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2} .$$

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[1] A number of calculations of chemical equilibria carried out by the aid of his formula are found in Sackur. Ann. d. Phys. (4) **40.** 87 (1913).

The specific heat of the two iodine atoms is $3R$, that of the iodine molecule therefore

$$\frac{5}{2}R + R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}}-1\right)^2} \quad \cdots \cdots \quad (12)$$

The real specific heat of iodine at 300° C. is according to STRECKER $8.53 - 1.985 = 6.545$. If this expression is substituted for (12), the equation is satisfied for $\lambda = \mathrm{cir.}\ 15\,\mu$. If we use this value for equation (8), we get in analogy with tables 1 and 2 :

TABLE III.

t (Cels)	$(\nu\text{-}term)_{\lambda=15\mu}$	Second member of 8 $\lambda = 15\,\mu$	$(TC_9)_{\lambda=15\mu}$	$\left(\frac{\Delta\,TC_9}{\angle\,T}\right)_{\lambda=15\mu}$
800	0.775—1	— 31.134	— 33406	
				— 38.01
900	0.751—1	— 31.719	— 37207	
				— 38.25
1000	0.728—1	— 32.232	— 41032	
				— 38.35
1100	0.705—1	— 32.678	— 44867	
				— 38.21
1200	0.684—1	— 33.054	— 48688	
				mean — 38.20

This value yields for the atomic distance :

$$d = 0.82\ 10^{-8}\ c.m.$$

If this value is compared with that for the mean molecule radius, which has been determined in three different ways, it appears that the value for the atomic distance as it is found above, is smaller than the mean molecule radius. We must derive from this that the atom centra in the iodine molecule lie closer together. Remarkable is the agreement of the found d-value with that of the atom distances, which were calculated by MANDERSLOOT from the width

TABLE IV.

Gas	Radius of Inertia 10^8
CO	0.566
HCl	0.22
HBr	0.165
J_2	0.41

of the infra-red bands for three gases [1]). This agreement appears from the foregoing table, in which the values of the three first mentioned gases are derived from MANDERSLOOT.

I hope soon to come back to the application of the used expressions to some other equilibria.

Postscript. During the correction of the proofs a treatise by O. STERN in the Annalen der Physik of June came under my notice, in which an expression is derived which shows close resemblance with that of Prof. VAN DER WAALS. Application on the iodine equilibrium can also here lead to a small moment of inertia, which is however considered improbable by STERN.

Amsterdam, Sept. 1914.   *Anorg. Chem. Laboratory*
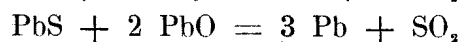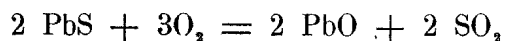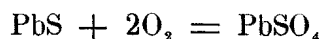*of the University.*

Chemistry. — *"Equilibria in the system Pb—S—O; the roasting reaction process"*. By Prof. W. REINDERS. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of Sept. 26, 1914).

Introduction.

1. The manufacture of galena into metallic lead is mostly carried out in this manner that the sulphide is first partially roasted and the mass then again strongly heated with unchanged or freshly added lead sulphide out of contact with air. Lead is then formed with evolution of SO_2.

The reactions that take place in this process known under the name of "Rostreactionsarbeit" are generally given in the text-books as follows:

$$PbS + 2O_2 = PbSO_4$$
$$2 PbS + 3O_2 = 2 PbO + 2 SO_2$$
and then: $PbS + PbSO_4 = 2Pb + 2 SO_2$
$$PbS + 2 PbO = 3 Pb + SO_2$$

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[1]) MANDERSLOOT. Thesis for the Doctorate. Utrecht. 1914.