

to iodic acid, formed before the end-point was reached, but may well have been due to the unavoidable errors in measuring such small volumes or to his method of stirring, which would certainly cause fluctuating voltage, dropping when stirring ceased and likely to cause reading the voltages too low.

In applying the method discussed, it is practicable to use back titration if the end-point is passed, as thus shown. In the same titration the end-point was noted, several cc. of permanganate in excess was run in. Now an excess of iodide was added and the end-point again found. This was repeated 5 times, giving the ratios of volumes of iodide to permanganate 1 to 1.032, 1.031, 1.031, 1.031, 1.0305. Separate titrations using larger volumes gave 1 to 1.0306.

Summary.¹

1. Iodide in dil. sulfuric acid has been accurately titrated electrometrically with permanganate. Chloride and bromide decrease and delay the sudden rise in voltage in proportion to concentration, but chloride at least equivalent to the iodide, or 25% of an equivalent of bromide is permissible.

2. Dichromate and iodate as oxidants in 0.02 *N* and 0.05 *N* solutions may be accurately titrated by adding the solutions of either to an excess of iodide in sulfuric acid and titrating the excess with permanganate. Silver has been determined in the same way. The details for iodate and silver will be presented in a later paper.

3. The high results obtained by Crotofino in titrating iodide with permanganate were not due to the formation of iodic acid before the end-point was reached.

4. Dichromate by this method shows its theoretical oxidizing capacity.

5. A simple potentiometer permitting speed, having high resistance and accurate enough for the work is described.

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THE MOLECULAR HEAT OF HYDROGEN.

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On the general basis of the quantum theory and making use of the Bohr model of the hydrogen molecule, Krüger² has attempted to calculate

¹ The author was made aware of the work of Kolthoff (*Rec. trav. chim.*, 39, 208 (1920), through *C. A.*, 14, 320 (1920)) after this paper had been sent to press. More than a year ago he tried to titrate iodide directly with iodate and dichromate. The results at that time and obtained since reading the paper of Kolthoff have not been satisfactory, though with solutions of at least 0.05 *N* concentration and sulfuric acid as the medium, results very near the true values have been obtained with the iodate.

² Krüger, *Ann. Physik.*, 50, 346; 51, 450 (1916).

that part of the specific heat of hydrogen which is due to the energy of rotation. Let a be the radius of the circle in which the electrons revolve, b , half the distance between the 2 positive nuclei, m , the mass of an electron, and M , the mass of a nucleus. Then the moments of inertia about the 3 principal axes of the hydrogen molecule will be

$$A = 2ma^2, B = 2Mb^2, C = 2Mb^2 + 2ma^2. \quad (1)$$

Evidently for most purposes we can take B as equal to C .

If the electrons are revolving with a frequency ω and if the molecule is acted on by an impulsive force, the ensuing motion of the molecule is a type of Poincot motion and may be briefly described by saying that the axis joining the 2 nuclei will describe the surface of a cone, the middle point of the axis being the apex. Each nucleus will, therefore, describe a curve in space which is very approximately circular and in a plane. If we call ν the frequency of revolution of each nucleus, the value of ν is given by the equation

$$\nu = \frac{A\omega}{B \cos \varphi}. \quad (2)$$

where φ is the semi-vertical angle of the cone described by the figure-axis. The kinetic energy of both nuclei will equal $4\pi^2 Mb^2 \nu^2 \sin^2 \varphi$. Krüger supposes that, at the absolute zero, there is no Poincot motion or "precessional vibration" so that $\varphi = 0$. If ν_0 is the value of ν at the absolute zero, $\nu_0 = A\omega/B$. Evidently at other temperatures, $\nu_0/\nu = \cos \varphi$ and $\nu^2 \sin^2 \varphi = \nu^2 - \nu_0^2$, so that the kinetic energy of "precessional vibration" is $4\pi^2 Mb^2 (\nu^2 - \nu_0^2) = 2\pi^2 B (\nu^2 - \nu_0^2) = p(\nu^2 - \nu_0^2)$, where $p = 2\pi^2 B$. For one mole of hydrogen, the energy, E_{pr} , due to rotation or precessional vibration will be, if N is Avogadro's number,

$$E_{pr} = N.2\pi^2 B (\nu^2 - \nu_0^2) = Np(\nu^2 - \nu_0^2). \quad (3)$$

Krüger applies the quantum theory by supposing that as regards the energy of vibration, ν is the characteristic frequency. He also assumes that this energy corresponds to 2 degrees of freedom, thus obtaining the equation

$$E_{pr} = Np(\nu^2 - \nu_0^2) = \frac{R\beta\nu}{e^{\beta\nu/T} - 1}, \quad (4)$$

where $\beta = h/k = 4.779 \times 10^{-11}$. The constant k is the gas constant per molecule and h is the Planck constant. Equation 2 may be written

$$\nu = \frac{A.2\pi\omega}{2\pi B \cos \varphi}.$$

Now, $A.2\pi\omega$ is the angular momentum of the 2 electrons and hence, according to Bohr, equal to $2 \times h/2\pi$. Thus Krüger obtains

$$\nu = \frac{h}{2\pi^2 B \cos \varphi} = \frac{h}{p \cos \varphi}; \quad \nu_0 = \frac{h}{p}.$$

Equation 4 may be written

$$E_{pr} = \frac{R\beta}{\nu_0} (\nu^2 - \nu_0^2) = \frac{R\beta\nu}{e^{\beta\nu/T} - 1} \quad (5)$$

From (5) it is not difficult to derive the following:

$$T = \frac{\beta\nu}{\log_e \left(1 + \frac{\nu\nu_0}{\nu^2 - \nu_0^2} \right)}; \quad C_{pr} = \frac{dE_{pr}}{dT} = \frac{2R\beta\nu^2}{\nu_0 T} \left(\frac{1}{1 + \frac{T\nu_0(\nu^2 + 2\nu\nu_0 - \nu_0^2)}{\beta(\nu^2 - \nu_0^2)(\nu^2 + \nu\nu_0 - \nu_0^2)}} \right). \quad (6)$$

Taking $m = 8.99 \times 10^{-28}$, $e = 4.775 \times 10^{-10}$, $h = 6.547 \times 10^{-27}$, $N = 6.062 \times 10^{23}$, we obtain from Bohr's model, $a = 0.505 \times 10^{-8}$ cm., $b = 0.292 \times 10^{-8}$ cm., and finally $\nu_0 = 1.173 \times 10^{13}$. Krüger used the value $\nu_0 = 1.006 \times 10^{13}$.

The molecular heat of hydrogen at constant volume has been determined by Eucken¹ from 36° A to 273° A. If from his values we subtract 2.98, we shall obtain what we may call C_{pr} (observed).

In Table I are given the values of C_{pr} so obtained and also those calculated by Krüger.

TABLE I.

T .	C_{pr} (observed).	C_{pr} calc. by Krüger.
0	0	0
67.5	0.09	0.036
79.5	0.16	0.159
103.1	0.51	0.385
157.8	1.0 (interpolated)	0.871
299.6	1.90	1.38

We see from Table I that the values of C_{pr} calculated by Krüger are much too low, and this disparity between observed and calculated values would be increased if Krüger had used the more nearly correct value of ν_0 , viz., 1.173×10^{13} instead of 1.006×10^{13} . This conclusion is evident from an examination of Equation 6. It might be objected that we have not taken into account the contribution to the molecular heat due to the vibration of the nuclei with reference to each other. Now it is not difficult to calculate the frequency of this vibration. According to Bohr, the frequency μ of this atomic vibration is given by the equation

$$\mu = 1.323 \omega_0 \sqrt{m/M} = 2.028 \times 10^{14}, \quad (7)$$

where ω_0 is the frequency of revolution of the electron in the hydrogen atom. From Equation 7 we obtain

$$\beta\mu = 9696. \quad (8)$$

From the value $\beta\mu$ in Equation 8, it is evident that at 273° A the con-

¹ *Sitzb. kgl. preuss. Akad.*, 1912, p. 142.

tribution to the molecular heat due to the atomic vibration will be negligible.

It seemed to the author that the cause of the disagreement between Krüger's theory and the results of experiment might be due to his assuming that the motion of rotation or of "precessional vibration" (to use his nomenclature) corresponds to but 2 degrees of freedom. It would seem more natural to assume 3 degrees of freedom. If we make this assumption, we obtain, instead of Equations 5 and 6,

$$E_{pr} = \frac{R\beta\nu}{\nu_0} (\nu^2 - \nu_0^2) = \frac{3/2 R\beta\nu}{e^{\beta\nu/T} - 1} \quad (9)$$

$$T = \frac{\beta\nu}{\log_e \frac{(2\nu - \nu_0)(\nu + 2\nu_0)}{2(\nu + \nu_0)(\nu - \nu_0)}} \quad (10)$$

$$C_{pr} = \frac{2R\beta\nu^2}{\nu_0 T} \left(\frac{1}{1 + \frac{3T\nu_0(\nu^2 + \nu_0^2)}{\beta(2\nu - \nu_0)(\nu + 2\nu_0)(\nu + \nu_0)(\nu - \nu_0)}} \right) \quad (11)$$

Values of C_{pr} obtained on the basis of Equations 9, 10 and 11 are compared with the experimental results of Eucken in Table II.

TABLE II.

$\nu \times 10^{-13}$.	T .	C_{pr} (calc.).	$C_{pr} + 1.981$.	C_v (Eucken).
1.173	0	0
1.1732	66.82	0.048	3.029	3.07
1.1733	70.23	0.065	3.046	3.10
1.1735	75.04	0.094	3.075	3.12
1.174	82.73	0.155	3.136	3.17
1.175	92.20	0.250	3.231	3.29
1.176	98.85	0.325	3.306	3.40
1.179	112.7	0.500	3.481	3.67
1.193	149.4	0.954	3.935	..
1.218	191.4	1.374	4.355	4.36
1.273	262.4	1.735	4.716	..
1.280	270.7	1.765	4.746	..
1.282	273.0	1.773	4.754	4.84
1.303	297.3	1.850	4.831	..
1.342	342.2	1.958	4.939	..

Molecular Heat at High Temperatures.

At high temperatures we must take into account the atomic vibrations. If E_a and C_a are the energy and heat capacity, respectively, of a mole of hydrogen due to these atomic vibrations, and if μ is the constant frequency, we have

$$E_a = \frac{R\beta\mu}{e^{\beta\mu/T} - 1}; \quad C_a = \frac{Re^{\beta\mu/T} (\beta\mu/T)^2}{(e^{\beta\mu/T} - 1)^2}; \quad \beta\mu = 9696. \quad (12)$$

In Table III are given the values of C_{pr} (Equation 11), C_a (Equation 12), and $C_v = .2.981 + C_{pr} + C_a$, for temperatures from 273° A to

2675° A. It will be observed that the atomic vibration is without appreciable effect on the molecular heat until 1000° A is reached. In the last column are given what Nernst¹ considers to be the most probable values of C_v .

TABLE III.

$\nu \times 10^{-14}$.	T .	C_{pr} .	C_a .	$C_v = 2.981 + C_{pr} + C_a$.	C_v (Nernst).
1.282	273.0	1.773	...	4.754	4.75
1.303	297.3	1.850	...	4.831	..
1.343	342.2	1.958	...	4.939	..
1.373	375.3	2.019	...	5.00	4.78
1.573	597.3	2.239	...	5.22	5.02 (200° C.)
1.773	833.1	2.346	0.002	5.33	5.2
1.973	1088	2.413	0.021	5.42	..
2.173	1363	2.465	0.082	5.53	5.6
2.413	1721	2.512	0.227	5.72	..
2.573	1976	2.541	0.385	5.91	..
2.643	2091	2.552	0.422	5.96	..
2.773	2313	2.571	0.544	6.02	6.0
2.893	2437	2.580	0.611	6.17	..
2.973	2675	2.594	0.735	6.31	..

The mean value of C_v from 0° to high temperatures has been determined by Pier,² who represents his results by the equation (valid only for values of t greater than 1000)

$$(\text{mean}) C_v (0^\circ \text{ to } t^\circ \text{C.}) = 4.700 + 0.00045 t. \quad (13)$$

In Table IV we have compared our results with those obtained by using Pier's equation.

TABLE IV.

T° .	$t^\circ \text{C.}$	E_{pr} .	E_a .	Mean C_v 0° — $t^\circ \text{C.}$	Mean C_v (Pier).
273	0	216.6	..	4.75	..
242.2	69.2	346.2	..	4.85	..
375.3	102.3	412.2	..	4.89	..
833.1	560.1	1431	0.17	5.15	..
1028	815	2038	2.6	5.22	..
1363	1090	2709	15.7	5.28	..
1721	1448	3600	69.0	5.37	5.35
1976	1703	4245	143.5	5.43	5.47
2091	1818	4540	188.5	5.47	5.52
2313	2040	5111	296	5.53	5.62
2437	2164	5430	367	5.56	5.67
2675	2402	6041	528	5.63	5.78

The Molecular Heat of Hydrogen.

The author is well aware of the fact that in recent years many objections have been raised to Bohr's model of the hydrogen molecule. Granting that these objections are valid, the actual hydrogen molecule may still have gyroscopic properties similar to those assumed in this paper.

¹ Nernst, *Physik. Z.*, **13**, 1064 (1912).

² Pier, *Z. Elektrochem.*, **15**, 536 (1909); **16**, 897 (1910).

The number of degrees of freedom to be assigned to the rotational energy of diatomic molecules has for a long time been a debatable question. For many years, during which the impression prevailed that the molecular heat at constant volume was approximately constant and equal to $5/2 R$ in the case of hydrogen, nitrogen, oxygen and carbon monoxide, it was felt that a diatomic molecule could have only 5 degrees of freedom, 3 corresponding to translation and 2 to rotation. The missing degree of freedom of rotation was accounted for by supposing that a diatomic molecule was incapable of rotation about the axis joining the 2 atoms. It could also be accounted for by the assumption that the molecule rotates about the axis with a constant angular velocity, unchangeable by collisions. My assumption of 3 degrees of freedom of rotation means that I assume that the angular velocity of rotation of the hydrogen molecule about the axis joining the 2 nuclei is not an absolute constant but can be changed by collisions or otherwise. I assume, therefore, that the rotational energy corresponds to 3 degrees of freedom. To this rotational energy I have applied the theory of quanta, supposing that the characteristic frequency is given by the frequency of the "precessional vibration."

The view that diatomic molecules have 3 degrees of freedom as regards rotation is strengthened by a consideration of the molecular heat at constant volume of chlorine. Reduced to the ideal state, Nernst¹ gives 5.85 as the value of C_v for chlorine at 0°C . I do not know of any satisfactory way of accounting for this high value other than by assuming 3 degrees of freedom for the rotational energy. I do not think that the energy of vibration of the atoms with reference to each other can possibly be sufficiently great at 0°C . to allow us to suppose that the chlorine molecule has but 2 degrees of freedom of rotation.

Summary.

We may summarize the results of this paper in the statement that the molecular heat of hydrogen can be calculated for temperatures ranging from the very lowest up to 2600°A on the basis of Bohr's views as to the constitution of the hydrogen molecule, if we assume that the rotational energy corresponds to 3 degrees of freedom.

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¹ Nernst, *Physik. Z.*, 13, 1064 (1912).