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NOTE ON THE HEAT OF DISSOCIATION OF IODINE

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ABSTRACT

New measurements of the visible absorption bands of iodine in the immediate neighborhood of their convergence have lead to a revised value for the heat of dissociation, 1.535 ±0.001 volts, which is in satisfactory agreement with chemical data.

PROFESSOR BIRGE,[1] in the preliminary report of his new analytical methods for obtaining heats of dissociation from known vibrational energy levels of diatomic molecules, has pointed out that in the case of the visible absorption bands of iodine there exists some uncertainty as to the way in which the extrapolation to the point of convergence should be made. The value now generally accepted,[2] 1.544 ± 0.003 volts, requires that the $dG/d\omega$ curve, which is linear in the region covered by the measurements of Mecke,[3] should continue linear to $\omega = 0$. Birge has shown that this implies an infinite value of the vibrational quantum number at dissociation and he has expressed the opinion that at very small values of ω the $dG/d\omega$ curve departs from linearity in such a way that $dG/d\omega$ becomes zero at $\omega = 0$.

Mecke's measurements of the $v'' = 0$ progression extend from λ5029.5A ($v' = 59$) toward longer wave-lengths. He states that the bands to be observed at shorter wave-lengths are too diffuse and faint for measurement. However, while it is true that these bands are faint, the heads remain sharp and with high dispersion bands up to $v' = 73$ have been measured. The photographs were taken with the first and second order of a 21 ft. concave grating (property of the Department of Physics, University of California) giving a dispersion in the second order of 1.3 A/mm. The wave-lengths given in Table I are the means from measurements of three plates, the agreement with one exception being better than 0.1A. A Pyrex absorption tube, 1 m in length, contained the iodine vapor at a temperature of about 25°C.

In Fig. 1 (curve *a*) the observed frequencies of band heads have been plotted against the corresponding values of the classical frequency of vibration (ω_v, as used here, is the mean of $\Delta G_{v+1/2}$ and $\Delta G_{v-1/2}$). The derivative, which can be identified with $dG/d\omega$ since $\nu = G + \text{const.}$, is plotted against ω as curve *b* and was calculated from a least squares solution, using the rapid method of Birge and Shea, of ω as a second degree polynomial in v. This curve is approximately linear down to $=12$ cm^{-1}. At smaller values of ω it shows the decided curvature toward the origin predicted by Birge and in making

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[1] R. T. Birge, Trans. Faraday Soc. **25,** 707 (1929).

[2] G. E. Gibson and W. Heitler, Zeits. f. Physik **49,** 465 (1928); Also H. Sponer, Landolt-Börnstein Tabellen, 6th Ed. in press.

[3] R. Mecke, Ann. d. Physik **71,** 103 (1923).

TABLE I. *Band heads of the $v''=0$ progression of iodine in the neighborhood of the convergence.*

V'	λ air I.A.	$\nu_{\text{vac.}}$ cm^{-1}	$\Delta G_{v+\frac{1}{2}}$
49	5093.66	19626.8	33.9
50	5084.88	19660.7	30.1
51	5077.09	19690.8	29.5
52	5069.52	19720.3	28.7
53	5062.13	19749.0	25.3
54	5055.67	19774.3	25.0
55	5049.27	19799.3	22.1
56	5043.65	19821.4	21.6
57	5038.15	19843.0	21.0
58	5032.82	19864.0	18.3
59	5028.20	19882.3	17.6
60	5023.76	19899.9	15.9
61	5019.75	19915.8	14.9
62	5016.00	19930.7	13.3
63	5012.65	19944.0	12.4
64	5009.54	19956.4	11.8
65	5006.58	19968.2	9.5
66	5004.18	19977.7	9.2
67	5001.88	19986.9	8.6
68	4999.74	19995.5	7.2
69	4997.94	20002.7	6.9
70	4996.22	20009.6	5.9
71	4994.74	20015.5	4.7
72	4993.56	20020.2	4.2
73	4992.51	20024.4	

the small remaining extrapolation we have assumed that the curve proceeds to the origin.

The point of convergence can be conveniently calculated by adding to the frequency of any particular band head the area under the $dG/d\omega$ curve up to the corresponding value of ω. We take ν20,020 cm^{-1} and add the area under the dotted portion of curve b, 17 cm^{-1}, giving 20,037 cm^{-1} as the frequency of the convergence limit. From this is to be subtracted the separation of the ^2P normal terms of the iodine atom, 7598 ± 2 cm^{-1}. This value is the mean of the twelve combination differences listed by Turner[4] in addition to four others not noted by him, viz:

$$67289-59690=7599 \qquad 76735-69131=7604$$
$$68606-61005=7601 \qquad 77541-69947=7594$$

The stated error is the probable error. For the heat of dissociation of iodine we have $20{,}037-7598=12{,}439$ cm^{-1}, or 1.535 volt-electrons, which is believed to be trustworthy within 0.001 v.e.

While the chemical data, of which the equilibrium measurements of Starck and Bodenstein[5] alone need be considered, cannot be pressed to the same degree of accuracy it is of interest to note that the value deduced above agrees with the experimental data as well as the value, 1.544 volts, used by Gibson and Heitler.[6]

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[4] L. A. Turner, Phys. Rev. **27**, 397 (1926).

[5] G. Starck and M. Bodenstein, Zeit. f. Elektrochem. **16**, 965 (1910).

[6] G. E. Gibson and W. Heitler, reference 2.

The values of log K at various temperatures, calculated by means of the Gibson and Heitler equation for $D=1.535$ and $D=1.544$, are compared with the experimental values in Table II.

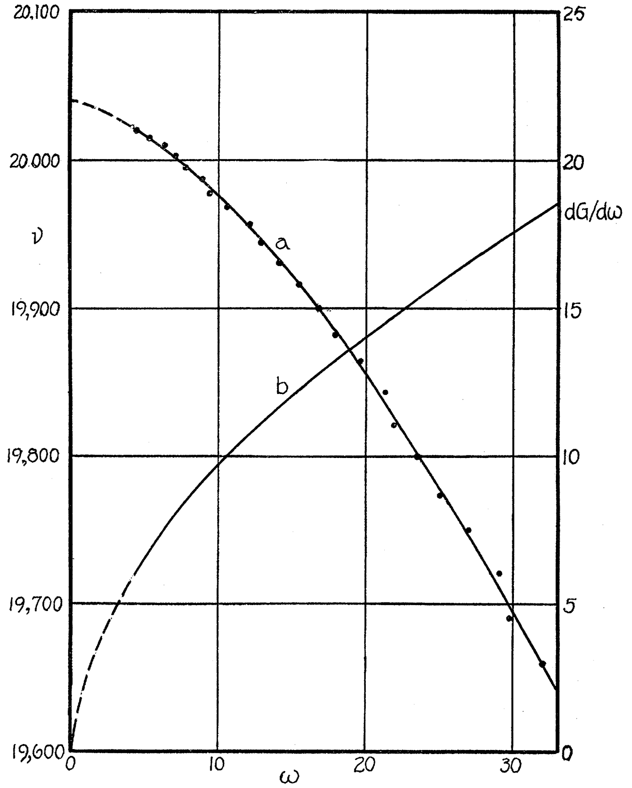

Fig. 1

TABLE II. *Experimental and calculated equilibrium constants for the dissociation of iodine.*

T °K	log $K_{\text{exp.}}$	log K calc. $D=1.544$ v.e.	calc.-obs.	log K calc. $D=1.535$ v.e.	calc.-obs.
1073	−1.943	−1.977	−0.034	−1.935	+0.008
1173	−1.324	−1.335	−0.011	−1.297	+0.027
1273	−0.782	−0.792	−0.010	−0.757	+0.025
1373	−0.308	−0.327	−0.019	−0.295	+0.013
1473	+0.090	+0.075	−0.015	+0.106	+0.016
		Mean	−0.018	Mean	+0.018