[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Heat Capacity Curves of the Simpler Gases. V. The Heat Capacity of Hydrogen at High Temperatures. The Entropy and Total Energy. A Corrected Table of the Free Energy above 2000°

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The specific heat of molecular hydrogen, in its various modifications, was accurately calculated from the spectroscopic data by Giauque[1] for the temperature interval 15 to 298.1°K. In this paper we extend these calculations to 5000°K. We also include tables of entropy and of "total energy" and a table showing the distribution of molecules among the vibrational levels, as a function of the temperature. A corrected table of "Free Energies" above 2000° is also included.

Our calculations were made by the tedious,[2] but accurate, Summation Method.[3] They were originally made with the spectroscopic constants of Birge, Hyman and Jeppesen, as quoted by Giauque,[1] but were later corrected, to the improved data of Jeppesen.[4,5]

The Results

The results are shown, in tabular form, in Tables I and II. These calculations were carried out, consistently, for the *non-equilibrium* mixture, which is the modification which is ordinarily of practical importance, but above room temperature identical results are obtained for the equilibrium mixture. The values of entropy are given with nuclear spin *excluded*, which is consistent with the treatment employed in the earlier papers in this series and with the specific recommendations of Giauque and Johnston[6] and of Giauque,[1] for hydrogen.

TABLE I

MOLAL HEAT CAPACITY (INCLUDING TRANSLATION), ENTROPY (AT 1 ATMOSPHERE AND EXCLUDING NUCLEAR SPIN) AND "TOTAL ENERGY" OF HYDROGEN IN THE IDEAL GASEOUS STATE

T, °K.	C_p° (cal./mole/degree)	S° (cal./mole/degree)	$(E^\circ - E_0^\circ)$ (cal./mole)
250	6.772	30.124	452.30
300	6.896	31.269	546.13
350	6.950	32.237	644.12
400	6.974	33.267	743.95
500	6.992	34.826	945.67
600	7.008	36.101	1148.0
700	7.035	37.184	1354.2
800	7.079	38.115	1563.4
900	7.141	38.964	1777.4
1000	7.220	39.721	1998.7
1200	7.408	41.053	2467.5
1500	7.718	42.739	3245.5
1750	7.963	43.948	3964.6
2000	8.181	45.026	4742.1
2500	8.531	46.891	6440.2
3000	8.796	48.471	8293.7
3500	8.997	49.841	10224
4000	9.155	51.054	12314
4500	9.286	52.140	14443
5000	9.392	53.125	16630

TABLE II

DISTRIBUTION OF HYDROGEN AMONG THE VIBRATIONAL LEVELS AS A FUNCTION OF THE TEMPERATURE

	v					
T, °K.	0	1	2	3	4	Higher than 4
500	100.00	0.00	0.00	0.00	0.00	0.00
1000	99.97	.03	.00	.00	.00	.00
1200	99.27	.73	.00	.00	.00	.00
1500	98.00	1.95	.05	.00	.00	.00
1750	96.47	3.38	.14	.01	.00	.00
2000	94.58	5.07	.32	.03	.00	.00
2500	90.12	8.76	.98	.12	.02	.00
3000	85.20	12.33	2.01	.36	.07	.03
3500	80.22	15.38	3.33	.78	.18	.11
4000	75.45	17.95	4.65	1.31	.40	.24
4500	71.12	19.82	6.01	1.92	.68	.46
5000	66.66	21.38	7.34	2.70	1.06	.86

The heat capacity curve, constructed from the values recorded in Table I, is shown in Fig. 1, together with experimental values obtained by

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(1) Giauque, THIS JOURNAL, **52**, 4816 (1930). Unfortunate arithmetical errors in Giauque's calculations at 3000 and 4000°K., which likewise influence the interpolations, necessitate corrections to all values in his free energy table above 2000°. Our Table IV is a corrected table covering this range. The largest correction, which amounts to a little less than 0.03 calorie/mole/degree, comes at about 3500°. At the request of Professor Giauque who finds arithmetical errors in his calculation of C_R for ortho hydrogen at two temperatures, we also call attention to the following corrections in the heat capacities: at 125°K. C_R should read 0.2501 and 0.7871 for the ortho variety and the non-equilibrium mixture ($^1/_4$ para, $^3/_4$ ortho), respectively, while at 225°K. the correct figures to go in these same columns are 1.4076 and 1.7001.

(2) Preliminary calculations by means of reliable approximation formulas (Johnston and Davis, THIS JOURNAL, **56**, 271 (1934)) showed that the numbers of terms required in the expansions of the approximation formulas were, in this case, so large that the method of direct summation was actually less laborious than the approximation procedure.

(3) For details of the calculations *cf.* Johnston and Chapman, *ibid.*, **55**, 153 (1933).

(4) Jeppesen, *Phys. Rev.*, **44**, 165 (1933).

(5) The influence of the small changes in the constants is nearly negligible. The maximum influence on the entropy was 0.001 cal./mole/degree; on the heat capacity, 0.002 cal./mole/degree and on the "total energy," 1 cal./mole/degree.

(6) Giauque and Johnston, THIS JOURNAL, **50**, 3221 (1928); *Phys. Rev.*, **36**, 1592 (1930).

calorimetric,[7] adiabatic expansion (or compression),[8] velocity of sound[9] and explosion[10] methods. The explosion data, and likewise the data of Crofts, are "mean heat capacities" plotted against the median temperatures of the intervals covered in the respective determinations.

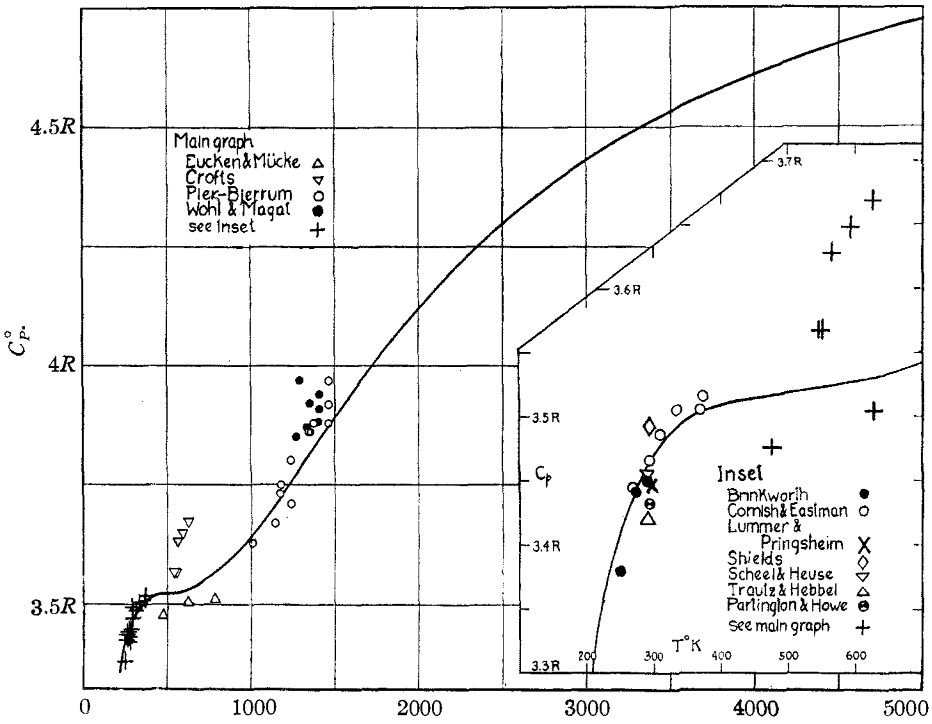

Fig. 1.—The heat capacity of hydrogen (the curve drawn from the spectroscopic data).

The influence of the non-ideal behavior, both in the matter of vibration and of rotation, is unusually large in hydrogen. This is best shown by Table III, which gives the values of these effects at several temperatures. The stretching effect was evaluated by a special set of calculations in which we arbitrarily excluded from our final sums the contributions of all levels except those associated with the (v = 0) vibrational state. The contribution arising from the anharmonic nature of the vibration was evaluated by comparing the increment resulting from the inclusion of all of the vibration states with that of a two dimensional Planck–Einstein oscillator with $h\nu$ = 4162 cm.$^{-1}$. Both of these treatments are arbitrary since the moment of inertia changes with the vibrational as well as with the rotational quantum number and, in a strict sense, the vibrational and the rotational effects cannot be treated independently. The large influence of the rotational stretching in hydrogen was first called to attention by Kemble and Van Vleck,[11] who commented on the relatively large influence of this effect compared with that of vibration at 1350°K. It is interesting to observe that the stretching contribution goes through a maximum at about 3500°.

TABLE III

CONTRIBUTIONS OF MOLECULAR STRETCHING AND OF ANHARMONIC VIBRATION TO THE MOLAR HEAT CAPACITY OF HYDROGEN

T, °K.	Stretching, cal.	Departure from Hooke's law, cal.
1000	0.072	0.010
2000	.135	.097
3000	.174	.223
4000	.181	.362
5000	.152	.519

In Table IV we list the values of the free energy function between 2100 and 5000°. This table

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[7] (a) Scheel and Heuse, *Ann. Physik*, **40**, 473 (1913); (b) Trautz and Hebbel, *ibid.*, **74**, 285 (1924). These authors used the "differential" method, which bears little resemblance to usual calorimetric methods.

[8] (a) Lummer and Pringsheim, *ibid.*, **64**, 536 (1898); (b) Crofts, *J. Phys. Soc.*, **107**, 290 (1915); (c) Shields, *Phys. Rev.*, **10**, 525 (1917); (d) Brinkworth, *Proc. Roy. Soc.* (London), **A107**, 510 (1925); (e) Partington and Howe, *ibid.*, **A109**, 286 (1925); (f) Eucken and Mücke, *Z. physik. Chem.*, **B18**, 179 (1932).

[9] Cornish and Eastman, THIS JOURNAL, **50**, 627 (1928).

[10] (a) Pier, *Z. Elektrochem.*, **16**, 87 (1910), recalculated by Bjerrum, *ibid.*, **18**, 101 (1912); (b) Wohl and Magat, *Z. physik. Chem.*, **B19**, 117 (1932).

[11] Kemble and Van Vleck, *Phys. Rev.*, **21**, 653 (1923).

TABLE IV

"FREE ENERGY" OF GASEOUS HYDROGEN (NUCLEAR SPIN ENTROPY INCLUDED)

T, °K.	$-\left(\frac{F^\circ - E_0}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$
2100	40.800	3100	43.746	4100	45.959
2200	41.144	3200	43.992	4200	46.154
2300	41.475	3300	44.234	4300	46.345
2400	41.793	3400	44.467	4400	46.532
2500	42.100	3500	44.696	4500	46.716
2600	42.396	3600	44.919	4600	46.897
2700	42.684	3700	45.136	4700	47.073
2800	42.962	3800	45.349	4800	47.246
2900	43.232	3900	45.557	4900	47.417
3000	43.493	4000	45.761	5000	47.584

should be used to supplement Giauque's[1] table, which is reliable up to 2000°. In order that this table may be consistent with that of Giauque we have *included* the effect of nuclear spin. We wish to point out that this is inconsistent with our own custom of publishing both free energy and entropy tables with nuclear spin *excluded*. The values in Table IV may be converted to values with the spin *excluded* by reducing (arithmetically) each number by $R \ln 4$ ($= 2.755$).

Probable Errors.—The reliability of the spectroscopic values of the molecular constants of hydrogen is so high that it is probable that the small uncertainty in the molar gas constant contributes more to the probable errors of the entries in the tables than do the spectroscopic uncertainties. One or two hundredths of a calorie should, therefore, cover the probable error in either free energy, entropy or heat capacity at any temperature while the error in $E^\circ - E_0^\circ$ might attain five to ten calories.

We wish to acknowledge the assistance of the National Research Council, through its committee on grants in aid, which provided the calculating machine used in making these calculations.

Summary

Accurate values of the heat capacity, of the entropy and of the "total energy" of hydrogen are calculated for the temperature interval 250 to 5000°K., and are tabulated. A corrected table of the free energy function between 2100 and 5000°K. is also included.

The influence of anharmonic vibration is particularly large in hydrogen and amounts, at 5000°K., to about 0.5 cal./mole/degree. The influence of molecular stretching is also relatively large and goes through a maximum at about 3500°K., at which temperature it makes a contribution, to the heat capacity, of about 0.18 calorie.

A table is included which shows the percentage distribution of H_2 molecules among the various vibrational levels, as a function of the temperature.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Indium Trimethyl[1]

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In the Third Group of the Periodic Table from boron to thallium, either the normal trimethyl or triethyl compounds, or both, of all the elements with the exception of indium have been prepared. The present article deals with the synthesis and study of indium trimethyl.

Experimental

Pure indium was prepared by dissolving the commercial metal in nitric acid, precipitating indium hydroxide with ammonium hydroxide, dissolving the hydroxide in sulfuric acid and depositing the indium by electrolysis.[2] The metal was then redissolved in sulfuric acid and redeposited electrolytically. Spectroscopic examination by Professor Papish of the final deposit showed that it contained about 0.001% cadmium but no other foreign metal.

Metallic indium, 34 g., mercury dimethyl, 54 g., and mercuric chloride, 0.1 g., were brought into bulb A, Fig. 1, and the air in the apparatus was displaced by dry carbon dioxide which was introduced through B. Around the neck of A was coiled a rubber tube through which cold water was passed to return the $Hg(CH_3)_2$ (b. p. about 95°) to A during the heating of the bulb. A was heated to about 100° for eight days, stopcocks B, D and E being closed. The heating was then discontinued, A was surrounded by an ice-bath, and the mercury dimethyl that had not reacted was distilled into the reservoir C by immersing that bulb in liquid air. The stopcock D was then closed.

There remained in A a mass of clear, colorless crystals. The U-tube G, which had been weighed, was attached

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[1] The investigations upon which this article is based were supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Mathers, THIS JOURNAL, **29**, 485 (1907).