Examination of the Raman and infrared data[7-11] for 2,2,3-trimethylbutane showed that in the region below 1350 cm.$^{-1}$ there were 22 observed frequencies that could reasonably be assigned as fundamentals. The 8 skeletal bending, 6 C–C stretching, 10 CH_3 rocking and 2 C–H wagging modes, 26 in all, are expected to have frequencies in this region. Four frequencies are therefore unobserved. Regularities in the frequencies of related molecules suggest that one of these four is a skeletal bending frequency, probably the very lowest, and that the other three are in the upper half of the range, *i.e.*, between 675 and 1350 cm.$^{-1}$. The parameters that had to be evaluated from the calorimetric data included these four unobserved frequencies in addition to the heights of the potential barriers hindering internal rotation. It was practical to evaluate at most three empirical parameters from the available calorimetric data. These parameters were selected to be: (a) the average value of the heights of the barriers hindering internal rotation, (b) the value of the unobserved skeletal bending frequency and (c) the average value of the three unobserved higher frequencies. The validity of assuming the same barrier heights for all internal rotations, as has previously been done in the cases of 2,2-dimethylbutane and 2,2,3,3-tetramethylbutane, is discussed in refs. 2 and 3. A satisfactory fit to the calorimetric data was obtained with the following values of the parameters: (a) 4200 cal. mole^{-1} for the average barrier height, (b) 232 cm.$^{-1}$ for the skeletal bending frequency and (c) 1330 cm.$^{-1}$ for the average value of the three higher frequencies. Average or conventional values were used for the CH_3 bending and C–H stretching frequencies, which are not all resolved in the observed spectra. The complete set of vibrational frequencies that was used for the thermodynamic calculations is as follows (the empirical values are italicized): *232*, 261, 298, 362, 392, 442, 462, 524, 686, 832, 923,[12] 957, 1000, 1011, 1027, 1084, 1107, 1160, 1209, 1224, 1252, 1320, *1330* (*3*), 1334, 1375 (5), 1460 (10) and 2950 (16) cm.$^{-1}$.

The satisfactory fit obtained with the calorimetric data may be judged by the following comparison of observed and calculated values. The units of $S°$ and $C_p°$ are cal. deg.$^{-1}$ mole^{-1}.

T, °K.	298.16	313.84	353.96
$S°$, obsd.	91.64	93.69	98.82
$S°$, calcd.	91.60	93.68	98.91

T, °K.	328.80	348.85	369.20	400.40	434.30	461.80
$C°_p$, obsd.	42.74	45.09	47.39	50.92	54.54	57.36
$C°_p$, calcd.	42.81	45.09	47.40	50.87	54.53	57.36

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF 2,2,3-TRIMETHYLBUTANE

T, °K.	$-(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$C°_p$, cal. deg.$^{-1}$
273.16	67.21	21.05	5.751	88.26	36.52
298.16	69.12	22.48	6.703	91.60	39.33
300	69.26	22.58	6.776	91.85	39.54
400	76.56	28.25	11.30	104.8	50.83
500	83.45	33.81	16.91	117.3	61.04
600	90.07	39.10	23.46	129.2	69.61
700	96.47	43.97	30.78	140.4	76.74
800	102.7	48.44	38.76	151.1	82.73
900	108.6	52.54	47.28	161.1	87.88
1000	114.3	56.30	56.30	170.6	92.32
1100	119.9	59.75	65.72	179.6	96.16
1200	125.2	62.92	75.50	188.1	99.48
1300	130.4	65.83	85.58	196.2	102.4
1400	135.4	68.52	95.94	203.9	104.8
1500	140.2	71.03	106.5	211.2	107.0

The calculated values of the functions $(F° - H_0°)/T$, $(H° - H_0°)/T$, $H° - H_0°$, $S°$ and $C_p°$ for selected temperatures up to 1500°K. are listed in Table II. For reasons of internal consistency, all values are given to four digits, although in some places in the table the retention of the last digit is not justified by the accuracy of the molecular-structure parameters used in the calculations or by the reliability of the approximations employed.

CONTRIBUTION NO. 32, THERMODYNAMICS LABORATORY
PETROLEUM EXPERIMENT STATION, BUREAU OF MINES
BARTLESVILLE, OKLAHOMA

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(12) Fermi resonance of this frequency with the overtone, 2 × 462 = 924, accounts for the doublet, 919–927 cm.$^{-1}$, in the observed spectra.

The Free Energies and Entropies of Hydrogen, Chlorine and Hydrogen Chloride from Spectroscopic Data[1]

BY R. H. SHERMAN AND W. F. GIAUQUE

RECEIVED NOVEMBER 14, 1952

Recent work in this Laboratory has required the use of the free energy function for hydrogen chloride and it became apparent that no correct table of this function, in terms of recent values of the "natural" constants concerned, was available in the literature.

We have used the natural constants given by Du Mond and Cohen[2] and recently recommended by Rossini, Gucker, Johnston, Pauling and Vinal[3] to correct the $(F° - H_0°)/T$ functions for hydrogen, chlorine and hydrogen chloride.

Hydrogen Chloride.—The free energy function for hydrogen cyloride was tabulated by Giauque and Overstreet.[4] It has recently been retabulated in Tables of the National Bureau of Standards[5] in terms of natural constants not much different than those of the Du Mond and Cohen (1951). We had expected to be able to use these values but it be-

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[1] This work was supported in part by the Office of Naval Research, United States Navy.

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came evident that they were not correct. We do not know if the table of Giauque and Overstreet[4] was used as a basis for the recalculation but in any case it appears that the values are approximately those which would result if the presence of hydrogen chloride resulting from chlorine mass 37 had been overlooked. The corrections which should be applied to the table of Giauque and Overstreet are given in Table I. The correction can be applied to any of the isotopic species or their mixture. The effect of deuterium is not appreciable.

Chlorine.—Correction of the tables of Giauque and Overstreet for chlorine to the new natural constants gave results which differed from the retabulation in the Bureau of Standards Tables[5] by appreciable amounts which increased with temperature. No reason for this is evident since no revision of the molecular data has appeared. The corrections found are given in Table I.

TABLE I

CORRECTIONS TO BE ADDED TO TABLES OF $(F^0 - H_0^0)/T$ REFERRED TO ABOVE

Note: Values in tables are for $-(F^0 - H_0^0)/T$; thus the additive correction reduces the numerical values

Correction cal. deg.$^{-1}$ mole^{-1}	H_2	Cl_2	HCl
0.018	298-450°K.	250-400°K.	250-700°K.
.019	500-1300	450-750	750-1600
.020	1400-2200	800-1400	1700-2700
.021	2300-2700	1500-2400	2800-3000
.022	2800-3700	2500-2900	
.023	3800-4300	3000	
.024	4400-5000		

Hydrogen.—The $(F^0 - H_0^0)/T$ function was tabulated to 5000°K. by Giauque.[6] Davis and Johnston[7] called attention to errors at 3000 and 4000°K. in the calculations of Giauque and showed that values used for interpolation above 2000°K. were affected. They published a corrected table above 2000°K. The above calculations on hydrogen were made in terms of natural constants given in the "I.C.T."[8] Davis and Johnston had sent details from their calculation sheets to Giauque and comparison with his calculation sheets disclosed the two basic arithmetical errors involved in Giauque's table. Thus the two pieces of work are now in agreement with respect to the details which determine the free energy function.

Wagman, Kilpatrick, Taylor, Pitzer and Rossini[9] have corrected the data of Giauque and of Davis and Johnston to constants available in 1945. They do not differ much from the present constants but as there is a small effect we have included corrections in Table I which should be applied to the table of Giauque up to 2000°K. and to the table of Davis and Johnston in the range 2000-5000°K. In addition the amount $R \ln 4 = 2.754$ cal. deg.$^{-1}$ mole^{-1} should be added to the absolute values of $(F^0 - H_0^0)/T$ given by Giauque and by Davis and Johnston to eliminate the contribution of nuclear spin as is customary. The value 2.754 is in terms of "I.C.T." constants to correspond to the original table. Wagman, *et al.*,[9] have also corrected the values of $(H^0 - H_0^0)/T$ given by Davis and Johnston. The correction to the new natural constants is trivial amounting to a maximum of -0.0002 at 5000°K. Thus corrected values of the entropy of hydrogen can be obtained by combining the values of $(F^0 - H_0^0)/T$ resulting from Table I with the $(H^0 - H_0^0)/T$ values of Wagman, *et al.* The corrected values of C_p for hydrogen given by Wagman, *et al.*, are also not changed by the newer constants.

The values of the entropies at a fugacity of one atmosphere and 298.16°K. for H_2, Cl_2 and HCl are 31.208, 53.290 and 44.645 cal. deg.$^{-1}$ mole^{-1}, respectively.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

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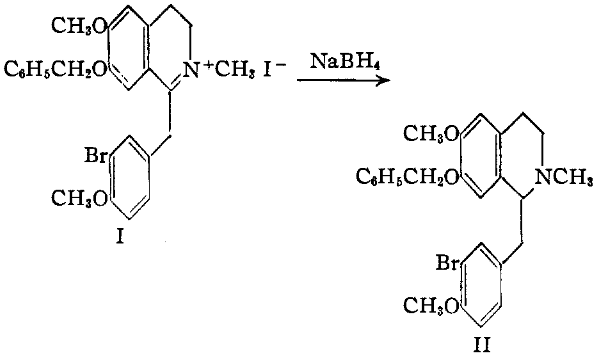
Sodium Borohydride Reduction of N-Alkyl-3,4-dihydroisoquinolinium Iodides[1]

BY WILSON M. WHALEY AND CHARLES N. ROBINSON

RECEIVED DECEMBER 22, 1952

The reduction of isoquinolinium salts with lithium aluminum hydride to the corresponding N-alkyl-1,2-dihydro- compounds[2] and of pyridinium salts with potassium borohydride to the N-alkyl-1,2-dihydro- and 1,2,3,4-tetrahydro- compounds[3,4] has been reported in the literature. Since the reduction of N-alkyl-3,4-dihydroisoquinolinium iodides containing other functional groups which are also reduced by lithium aluminum hydride is often of considerable importance in the synthesis of isoquinoline alkaloids, it seemed desirable to find a more specific reagent. Sodium borohydride is such a reagent. The present paper shows that N-alkyl-3,4-dihydroisoquinolinium iodides can also be reduced in very good yields to the corresponding N-alkyl-1,2,3,4-tetrahydroisoquinolines. Chaikin and Brown[5] have reported that, although this reagent reduces aldehydes, ketones and acid chlorides



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[1] The authors wish to express their appreciation to the Tennessee Eastman Corporation for a Grant-in aid to the University of Tennessee which made this work possible.

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