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Harold C. Urey and D. Rittenberg

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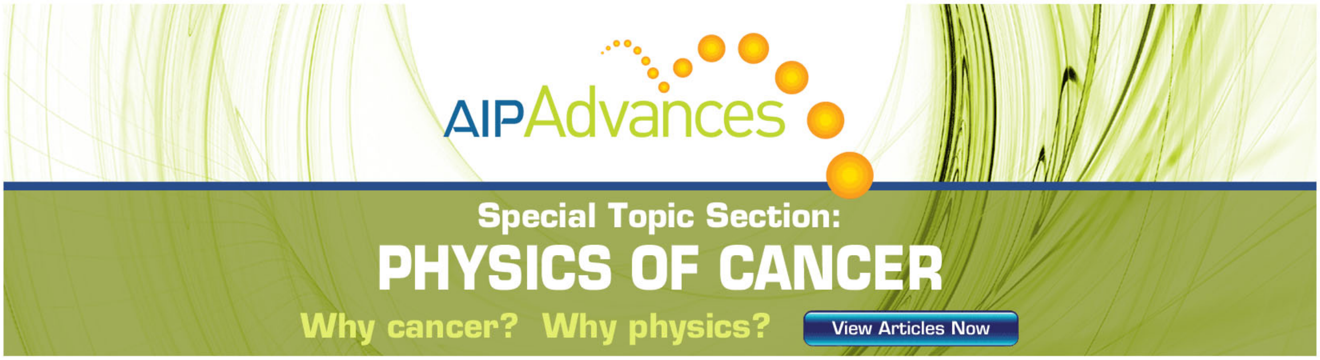

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Some Thermodynamic Properties of the H^1H^2, H^2H^2 Molecules and Compounds Containing the H^2 Atom

HAROLD C. UREY AND D. RITTENBERG, *Chemical Laboratory of Columbia University*

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The summations of state and free energies of the molecules $H_2{}^1$, $H_2{}^2$ and H^1H^2 have been calculated at temperatures from 20.4 to 700°K and their dependence on the spin and statistics of H^2 discussed and illustrated. The equilibrium constants of the reaction $H_2{}^1+H_2{}^2=2\,H^1H^2$ are found to deviate markedly from the value 4 expected from simple probability considerations. The equilibrium constants of the reactions $H_2{}^1+2\,H^2Cl\rightleftharpoons H_2{}^2+2\,H^1Cl$ and $H_2{}^1+2\,H^2I\rightarrow H_2{}^2+2\,H^1I$ have been calculated and found to be appreciably different from unity, showing that appreciable differences in equilibrium constants of chemical reactions may be expected depending on which isotope of hydrogen enters into the reaction. Small differences in the electrode potentials of the two hydrogen isotopes may be expected but no exact estimates have been made.

THE application of statistical methods to the calculation of thermodynamic properties of gases has been understood for many years, though the assignment of the proper statistical weights to the degenerate energy levels was only possible after the discovery of the electron spin, nuclear spin and the quantum mechanics. With this correct assignment and the detailed data of molecular spectra available, the calculation of the heat capacity, entropy, energy, and free energy of diatomic molecules was immediately possible. The careful researches of Giauque and his co-workers[1] especially have shown that entire confidence can be placed in the results of such calculations. As a result, it is possible to predict many properties of H^2,[2] and its compounds by the application of statistical mechanics and the known molecular spectrum of $H_2{}^1$ and its compounds though this isotope has not as yet been secured in sufficiently high concentrations to make measurements possible. It is the purpose of this paper to report the results of our calculations at this time, limiting our calculations for the most part to those quantities that are independent of the nuclear spin of H^2 and whether the symmetric or antisymmetric states occur. Thus no heat capacities at low temperatures on entropies have been calculated at this time. Experiments are in progress in this laboratory looking to the experimental verification of the theoretical calculations.

THE METHODS OF CALCULATING THE FREE ENERGY

The standard free energy of a diatomic molecule is given by the equation,[3]

$$F^0=Mc^2-(3/2)RT\ln M-(5/2)RT\ln T + RT\ln P + 7.2646T-RT\ln Q' \quad (1)$$

where Mc^2 is all the energy of the molecule at absolute zero except the zero point energy due to molecular vibration, and $Q'=\Sigma p\exp(-E/kT)$, and all the other symbols have their usual meaning. Since the term Mc^2 does not concern us it may be ignored. The statistical weight, p, is equal to $2J+1$ multiplied by a factor which depends on the nuclear spin. If the nuclei are not identical, and the electronic state is E^+_g as in the case of H_2, HCl and HI, this factor is $(2i_1+1)\times(2i_2+1)$ the i_1 and i_2 being the nuclear spins. If the nuclei are identical, then this factor is $(2i+1)(i+1)$ for the even values of J and $(2i+1)i$ for the odd levels, if the nuclei follow the Bose-Einstein statistics, and if the Fermi-Dirac statistics, the factors are $(2i+1)i$ and $(2i+1)\times(i+1)$ for the even and odd levels, respectively.

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[1] W. F. Giauque and Roy Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932). J. O. Clayton and W. F. Giauque, ibid. **54**, 2610 (1932); W. F. Giauque, ibid. **52**, 4816 (1930); W. F. Giauque and H. L. Johnston, ibid. **50**, 3221 (1928).

[2] H. C. Urey, F. G. Brickwedde and G. M. Murphy, Phys. Rev. [2], **40**, 1; **39**, 164 (1932); see also Walker Bleakney, Phys. Rev. [2], **41**, 32 (1932).

[3] An excellent summary of the relation between heat capacities, free energies, and energies and the summation of state has been given by Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

The energy, E, follows a formula of the form,[4]

$$E/hc=\tilde{\omega}_e(v+1/2)-x\tilde{\omega}_e(v+1/2)^2+[B_e-\alpha(v+1/2)+\gamma(v+1/2)^2-\delta(v+1/2)^3]J(J+1)$$
$$+[D_e+\beta(v+1/2)]J^2(J+1)^2+F_eJ^3(J+1)^3. \quad (2)$$

The zero point energy is then,

$$E_0{}^0/hc=(\tfrac{1}{2}\tilde{\omega}_e-\tfrac{1}{4}x\tilde{\omega}_e)N, \quad (3)$$

(N=Avogadro number) and it is convenient to remove this energy from the expression for Q', so that $\ln Q'=E_0{}^0/kT+\ln\Sigma pe^{-E/kT}$ where E now contains all the terms of (2) except those of $E_0{}^0$ as here given by the Eq. (3).[5] This separation has the advantage that the zero point energy is an additive term in the free energy and need not be considered again in the summations. The new summation of state now becomes,

$$Q=\sum p\exp-E/kT. \quad (4)$$

This gives results equivalent to those secured by previous authors.

Mulholland[6] has given a rapidly converging series for this summation insofar as it depends on the exponential term containing $J(J+1)$ and Giauque and Overstreet[7] have extended the work to include higher terms in $J^2(J+1)^2$. The resulting formula is

$$Q=\sum Q_v=\sum_v\left[\frac{kT}{B_vhc}+\frac{1}{12}+\frac{7}{480}\frac{B_vhc}{kT}-\frac{2D_v}{B_v}\left(\frac{kT}{B_vhc}\right)^2\right]\exp\frac{hc}{kT}\left[\frac{B_v}{4}+\frac{D_v}{16}-\tilde{\omega}_ev+x\tilde{\omega}_ev(v+1)\right]. \quad (5)$$

This formula can be used for calculating the free energy if $T/B_v\geqq 4$ (approximately), but if used to calculate the heat capacity will give incorrect results unless the heat capacity has reached nearly classical values. It does not include the contribution of the nuclear spins to the *a priori* probabilities; to include the contribution of these spins, it is necessary to add a term to the free energy, $-RT\ln(2i_1+1)(2i_2+1)$, i_1 and i_2 being the spins of the two nuclei, if the nuclei are unlike and $-RT\ln[(2i+1)^2/2]$ if the nuclei are identical. The formula cannot be used in the cases of H^1H^2, H^1H^1, and H^2H^2 at temperatures below about 298.1°K, since it holds only in the region where $\Sigma(2J+1)\exp(-E/kT)$ over the even values of J is equal to this summation over odd values of J.

THE H^1H^2 AND $H_2{}^2$ MOLECULES

The atomic weights of H^1 and H^2 relative to O^{16} as 16.0000 are 1.00778[8] and 2.01353.[9] With Mecke and Childs'[10] values for the relative abundancies of the oxygen isotopes, the values corrected to the chemical scale are 1.00756 and 2.01309. The reduced masses of the molecules $H_2{}^1$, H^1H^2 and $H_2{}^2$ in atomic weight units are: 0.50378, 0.67148, and 1.00654 and the ratios of these needed to calculate the energy level formulae are:

$$\rho_{12}=(\mu_{11}/\mu_{12})^{1/2}=0.86617$$
$$\rho_{22}=(\mu_{11}/\mu_{22})^{1/2}=0.70746. \quad (6)$$

Birge, Jeppesen and Hyman[11] discussed the energy levels of hydrogen. The $\Delta G(1/2)$ value is larger than is to be expected by using a smooth formula derived from the remaining ΔG's. Also

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[4] We use $J(J+1)$ instead of the usual $(J+\tfrac{1}{2})^2$ because the former has the better theoretical support. (Private communication from J. L. Dunham.) In most cases no appreciable difference is encountered due to the use of one or the other. In our problem an important difference arises for the latter form gives a zero point rotational energy of $\tfrac{1}{4}Bhc$ which in the case of $H_2{}^1$ amounts to about 42 calories per mole, which is not negligible at all.

[5] $E_0{}^0$, as here defined differs from that used by Giauque and his co-workers. These authors use $E_0{}^0$ to include the zero point vibrational energy, the Mc^2 term mentioned above and also rotational zero point energy. We assume the rotational zero point energy to be zero and ignore the Mc^2 term since it does not concern us. M is the rest mass in the hypothetical vibrationless state.

[6] Mulholland, Proc. Camb. Phil. Soc. **24**, 280 (1928).

[7] W. F. Giauque and Roy Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

[8] F. W. Aston, Proc. Roy. Soc. **A115**, 487 (1927).

[9] K. T. Bainbridge, Phys. Rev. [2], **41**, 115 (1932).

[10] R. Mecke and W. H. Childs, Physik **68**, 362 (1931).

[11] R. T. Birge, H. H. Hyman and C. R. Jeppesen, Nature **123**, 277 and 462 (1930); H. H. Hyman, Phys. Rev. **36**, 187 (1930).

the $B_0(=59.331)$ is somewhat irregular since it cannot be calculated from a formula derived from the higher B_v values. These authors regard these irregularities as a perturbation, though it is difficult to understand what can possibly perturb the normal state of the hydrogen molecule. They give a formula for the higher energy levels and advise its use for most purposes. Unfortunately it is the lowest levels that are of interest to us here. The question arises as to whether these irregularities would be present in the H^1H^2 and H_2^2 molecules as well, a question which probably cannot be answered experimentally for some time. Therefore, we have made these calculations assuming two energy level formulae for the hydrogen molecule, (1) the smooth formula of Birge, Jeppesen and Hyman, and (2) a formula derived from the data on the first three vibration levels of the molecule, but which will not fit the higher levels. We believe the latter formula to be better for our purposes. A comparison of the results from the two formulae enables us to estimate our possible error due to this uncertainty.

The molecular constants of the H_2^1 and H^1H^2 and H_2^2 molecules with the Birge-Jeppesen-Hyman formula for H_2^1 referred to as I and with our formula covering the lower vibrational levels only referred to as II are given in Table I.

TABLE I.

I

	H_2^1	H^1H^2	H_2^2
$\tilde{\omega}_e$	4371	3786.0	3092.3
$x\tilde{\omega}_e$	113.5	85.2	56.8
B_e	60.564	45.439	30.312
α	2.7931	1.8151	0.98898
γ	0.0105	0.00591	0.00263
δ	0.002406	0.001173	0.000426
$-D_e$	0.0465	0.0262	0.0116
β	1.35×10^{-3}	6.58×10^{-4}	2.39×10^{-4}
F_e	5.18×10^{-5}	2.19×10^{-5}	0.649×10^{-5}

II

	H_2^1	H^1H^2	H_2^2
$\tilde{\omega}_e$	4403	3813.75	3114.95
$x\tilde{\omega}_e$	120.5	90.4	60.3
B_e	60.871	45.670	30.466
α	3.124	2.0302	1.106
γ	0.0875	0.0493	0.0219
δ	—	—	—
$-D_e$	0.0465	0.0262	0.0116
β	1.35×10^{-3}	6.58×10^{-4}	2.39×10^{-4}
F_e	5.18×10^{-5}	2.18×10^{-5}	0.649×10^{-5}

The zero point energies of the three molecules in calories per mole are:

	H_2^1	H^1H^2	H_2^2
I	6133.8	5323.1	4356.9
II	6175.5	5358.9	4386.6

Since the known spins of nuclei are observed to be integral if the atomic weight is even, and half integral if it is odd, we may expect that the H^2 will have a spin of 0 or 1. Also since nuclei of even atomic weight will follow the Bose-Einstein statistics and those of odd atomic weight the Fermi-Dirac statistics, we expect that H^2 will follow the former. Thus N^{14}, which may be regarded as a C^{12} nucleus plus the fundamental particles present in the H^2 nucleus, has an integral spin and the wave functions symmetric in the nuclei are observed. We may expect that the rotational states with even J will be present, if $i_2=0$, and have a higher *a priori* probability than those with odd J, if $i_2=1$. We have considered these two values of the spin and also the difference due to the two possible statistics, Bose-Einstein and Fermi-Dirac. At the higher temperatures considered, the equilibrium constants are independent of the statistics and spin, but at lower temperatures this is not the case.

The results of the calculations are listed in Table II. The temperatures for which calculations have been made have been selected because of the possibility of checking the results experimentally in various ways in the neighborhood of these temperatures.

The equilibrium constant for the reaction

$$H^1H^1+H^2H^2\rightarrow 2\,H^1H^2 \qquad (7)$$

can be calculated with the results of the previous tables, though it is given more directly by the equation

$$-RT\ln K=\Delta F^0=\Delta E_0^0-\frac{3}{2}RT\ln\frac{M_{12}^2}{M_{11}M_{22}}-RT\ln\frac{Q_{12}^2}{Q_{11}Q_{22}}. \qquad (8)$$

The equation also permits one to see how the uncertainty of energy levels affects K. Since the Q's are approximately inversely proportional to the B_0's, and the B_0's of the three molecules are nearly proportional to each other, the errors cancel largely and K is independent of the un-

TABLE II. *Thermodynamic constants of* H_2^1, H^1H^2, H_2^2. *Formula II was used in these calculations.*[4]

	H_2^1, $i=1/2$, F.-D.			H^1H^2, $i=1/2$, $i_2=0$[2]			H_2^2, $i_2=0$, B.-E.[3]			H_2^2, $i_2=0$, F.-D.[3]		
T	Q	$-\frac{F^0-E_0^0}{T}$	F^0	Q	$-\frac{F^0-E_0^0}{T}$	F^0	Q_e	$-\frac{F^0-E_0^0}{T}$	F^0	Q_0	$-\frac{F^0-E_0^0}{T}$	F^0
50	1.303	14.776	+ 5436.7	2.471	17.253	+ 4496.2	1.029	16.370	3568.1	0.540	15.089	3632.1
100	2.682	19.652	+ 4210.3	3.897	21.601	+ 3198.9	1.385	20.402	2346.4	1.314	20.298	2356.8
200	5.390	24.481	+ 1279.3	6.986	26.202	+ 118.5	2.514	25.028	− 619.0	2.513	25.028	618.9
298.1	7.764	27.187[1]	− 1929.1	10.072	28.911	− 3259.4	3.665	27.759	− 3888.3	3.665	27.759	− 3888.3
400	10.185	29.187[1]	− 5499.3	13.291	30.922	− 7009.9	4.866	29.782	− 7526.3	4.866	29.782	− 7526.3
575	14.371	31.673	−12036.6	18.857	33.419	−13857.0	6.940	32.290	−14179.9	6.940	32.290	−14179.9
700	17.387	33.028[1]	−16944.4	22.854	34.778	− 1895.6	8.431	33.653	−19170.5	8.431	33.653	−19170.5

[1] These agree with Giauque's values when account is taken of the different value of R used. Throughout we have used the values of the natural constants given by R. T. Birge, Rev. Mod. Phys. 1, 1 (1929).

[2] To secure values for other values of i_2, multiply the Q's as given by $(2i_2+1)$, add $-R\ln(2i_2+1)$ to $(F^0-E_0^0)/T$ and $-RT\ln(2i_2+1)$ to F^0.

[3] The values of the Q, $(F^0-E_0^0)/T$, and F^0 for H_2^2 for any other value of i_2 can be secured from the values of Q_e and Q_0 which are the summations over the even and odd levels respectively. Thus the Q by using the Bose-Einstein statistics is $Q=(2i_2+1)(i_2+1)Q_e+(2i_2+1)i_2Q_0$, and by using the Fermi-Dirac is $Q=(2i_2+1)i_2Q_e+(2i_2+1)(i_2+1)Q_0$, and the corresponding values of $(F^0-E_0^0)/T$ can be calculated from the tabulated values by adding $R\ln Q_e$ to and subtracting $R\ln Q$ from the values $F^0-E_0^0/T$ given under (H_2^2, $i_2=0$, B.-E.) and those of F_0 by adding $RT\ln Q_e$ to and subtracting $RT\ln Q$ from the F^0 values given under the same heading.

[4] If formula (I) is used instead of formula (II) the Q's are increased by about one part in 600 decreasing F^0 by about 2.7 calories at 700°K. A more important change is made in F^0 by the change in zero point energy. The F^0 values of H_2^1 must be decreased by 41.7 calories, those of H^1H^2 by 35.8 calories and those of H_2^2 by 29.7 calories, if formula (I) is used.

certainty in the B_0's of the three molecules, unless only part of them are irregular. The effect of the uncertainty in the zero point energy is greater, but amounts to only 1.4 percent of K at the lowest temperature and the uncertainty at higher temperatures is less. The total error in these values of K can hardly be greater than this.

The values of the equilibrium constants are given in Table IIIA. A marked deviation from the classical value of 4 is evident over the entire range and becomes very great at low temperatures. The equilibrium constants are independent of i_2 and the statistics of the H^2 nucleus at temperatures above 200°K.

It is of interest to consider the equilibrium constants at some temperature at which they are appreciably affected by the spin and statistics of the H^2 nuclei. Such a temperature is that of liquid hydrogen, 20.4°K. The values of the Q's of the H^1H^1, H^1H^2 and H^2H^2 molecules at this temperature if $i_1=1/2$ and $i_2=0$ are: $Q(H^1H^1)=1.022$; $Q(H^1H^2)=2.0114$; $Q_e(H^2H^2$, Bose-Einstein$)=1.0000$; $Q_0(H^2H^2$, Fermi-Dirac$)=0.04485$.[12] The equilibrium constants calculated, assuming that i_2 may be 0, 1/2, 1, or 3/2 and that the nuclei may follow either the Bose-Einstein or Fermi-Dirac statistics, are given in Table IIIB.

With these constants it is possible to calculate the ratios of the number of molecules of one variety to that of another variety. Such ratios

TABLE IIIA.

	Bose-Einstein statistics		*Fermi-Dirac statistics*	
T	$-\Delta F^0$	K	$-\Delta F^0$	K
		$i_2=0$		
50	12.3	1.132	76.4	2.157
100	159.0	2.227	169.4	2.346
200	423.4	2.903	423.5	2.904
298.1	701.4	3.269	701.4	3.269
400	994.1	3.494	994.1	3.494
575	1497.5	3.710	1497.5	3.710
700	1856.2	3.800	1856.2	3.800
		$i_2=1$ The constants are independent of spin above 200°K.		
50	29.4	1.345	50.3	1.659
100	162.4	2.265	165.9	2.311
200	423.5	2.903	423.5	2.903

TABLE IIIB.

i_2	K(B.-E.)	K(F.-D.)
0	0.1032	2.302
1/2	0.1356	0.3640
1	0.1515	0.2842
3/2	0.1609	0.2562

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[12] See footnotes to Table II for the method to be used in securing the Q's for other values of i_2.

TABLE IIIC.

	i_2	$(H_2^1)/(H^1H^2)$	$(H_2^1)/(H_2^2)$	$(H^1H^2)/(H_2^2)$
B.-E.	0	63.99	422.7	6.606
	1/2	60.97	504.2	8.269
	1	59.91	543.6	9.074
	3/2	59.37	567.0	9.550
F.-D.	3/2	55.91	800.8	14.32
	1	55.30	869.1	15.72
	1/2	54.03	1063.	19.67
	0	49.86	5719.	114.7

are given in Table IIIC for a sample of hydrogen containing 1 atomic percent of H^2. These ratios are sufficiently different to make possible the determination of the spin and statistics of H^2 by any method which can determine the relative numbers of the three types of molecules in a sample of hydrogen which has been brought to equilibrium at 20.4°K. It seems that this equilibrium would be established under the same conditions as those necessary for the ortho-para equilibrium of the H_2^1 molecule. Also it does not seem likely that this equilibrium will be established more rapidly than the ortho-para equilibrium. If these assumptions prove to be true, it should be possible to prepare a sample of hydrogen having the relative numbers of the three molecules characteristic of the equilibrium at 20.4°K and to hold it at ordinary temperatures for a time sufficient to determine the relative numbers of the molecules by a magnetic deflection of ions such as that used by Bleakney.[13] This appears to us as a most promising method for securing the spin and statistics of H^2 with concentrations of H^2 now available.

THE FREE ENERGY OF H²Cl

Giauque and Overstreet have given tables of $F^0-E_0^0/T$ for H^1Cl and for Cl_2^{35}, Cl_2^{37}, and $Cl^{35}Cl^{37}$. They have used the atomic weight of natural hydrogen as the atomic weight of H^1, but this makes only a slight difference in the results. The energy levels of the H^1Cl^{35} molecule are given by the formula,[14]

$$E/hc=2989.68(v+1/2)-51.90(v+1/2)^2 +(10.585-0.3062(v+1/2) +0.0016(v+1/2)^2)J(J+1) -5.0\times 10^{-4}J^2(J+1)^2. \quad (9)$$

The energy levels of the H^2Cl^{35} molecule become

$$E/hc=2144.44(v+1/2)-26.70(v+1/2) +(5.4459-0.1130(v+1/2)+0.00042 (v+1/2)^2)J(J+1)-1.3 \times 10^{-4}J^2(J+1)^2. \quad (10)$$

The zero point energies of H^1Cl^{35} and H^2Cl^{35} are 4214.4 and 3030.4 calories per mole respectively.

We are particularly interested in the ratio of the equilibrium constants of the two reactions:

$$H_2^1+Cl_2^{35}\rightarrow 2\ H^1Cl^{35}, \quad (11)$$

$$H_2^2+Cl_2^{35}\rightarrow 2\ H^2Cl^{35}. \quad (12)$$

Subtracting these pairs of reactions, we secure

$$H_2^1+2\ H^2Cl^{35}=H_2^2+2\ H^1Cl^{35}, \quad (13)$$

and the equilibrium constant of this reaction is the ratio of the equilibrium constants of the reactions (11) and (12). The ratio of equilibrium constants is given by the equation:

$$-RT\ln\frac{K_1}{K_2}=\Delta E_0^0-\frac{3}{2}RT\ln\frac{M^2_{H^1Cl}M_{H_2^2}}{M^2_{H^2Cl}M_{H_2^1}}-RT\ln\frac{Q^2_{H^1Cl}Q_{H_2^2}}{Q^2_{H^2Cl}Q_{H_2^1}}. \quad (14)$$

At the temperatures considered here, the nuclear spins have no influence on the numerical values.

The quantities, Q, $-(F^0-E_0^0)/T$, and F^0 at temperatures from 200° to 700° are listed in Table IV. The spin of Cl^{35} is taken as zero since it does not affect the observable quantities.

The ratio of the equilibrium constants, K_1 and K_2, of the reactions (11) and (12) respectively, and the free energy change in reaction (13) are given in Table V.

THE FREE ENERGY OF H²I

The energy levels of hydrogen iodide are not well known. Czerny has observed the rotation bands from which the B_0 and D_0 can be secured. The values of the vibrational constants $\tilde{\omega}_e$ and

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[13] W. Bleakney, Phys. Rev. [2], **41**, 32 (1932).

[14] This equation is taken from the recent paper of Meyer and Levin (Phys. Rev. **34**, 44 (1929) and Colby (ibid. 53 (1929)) and differs slightly from that used by Giauque and Overstreet. Only negligible errors are introduced by the change in rotational constants, though the zero point energies are changed by a few calories.

TABLE IV.

	H^1Cl^{35}, $i_1=1/2$			H^2Cl^{35}, $i_2=0$		
T	Q	$-(F^0-E_0^0)/T$	F^0	Q	$-(F^0-E_0^0)/T$	F^0
200	27.493	36.306	− 3046.8	26.287	36.299	− 4229.3
298.1	40.666	39.065*	− 7431.0	39.001	39.064	− 8614.7
400	54.375	41.103*	−12226.6	52.331	41.109	−13413.0
575	78.013	43.622	−20868.1	75.532	43.640	−22062.4
700	95.083	44.992*	−27279.9	92.722	45.024	−28486.3

* These values agree with those of Giauque and Overstreet when account is taken of the spin of H^1 the slightly different energy formula used and the different value of R used.

TABLE V.

	$H_2^1+2\ H^2Cl^{35}\rightleftarrows H_2^2+2\ H^1Cl^{35}$					
T	0	200	298.1	400	575	700
ΔF	579.1	466.8	408.2	345.8	245.1	186.7
K_1/K_2	0.000	0.309	0.502	0.647	0.807	0.874

$x\tilde{\omega}_e$ are less certainly known. Czerny[15] reports a value of 2270 cm^{-1} for the $\Delta G(1/2)$ of this molecule which is also the value secured from the relation $\tilde{\omega}_e=2B^{3/2}/D^{1/2}$. Salant and Sandow[16] have secured 2233 cm^{-1} for the $\Delta G(1/2)$ of gaseous HI. Further work by Kirkpatrick[17] on the $v'=2\rightarrow v''=0$ infrared band gives approximately the following values for $\tilde{\omega}_0$ and $x\tilde{\omega}_0$; $\tilde{\omega}_0=2299$, $x\tilde{\omega}_0=33$. These latter values have been used in these calculations. The α-constant is unknown, but its neglect introduces but small errors. We take as the formula for the energy levels of H^1I

$$E=2299(v+1/2)-33(v+1/2)^2+6.420J(J+1)-0.000205J^2(J+1)^2, \quad (15)$$

and for the energy levels of H^2I,

$$E=1632.8(v+1/2)-16.6(v+1/2)^2+3.2385J(J+1)-0.0000522J^2(J+1)^2. \quad (16)$$

The zero point energies of H^1I and H^2I are 3245.7 and 2310.0 calories per mole, respectively.

The quantities for H^1I and H^2I are calculated for temperatures from 298.1° to 700°K since experimental tests of the theory are possible for this region. The results are given in Table VI.

The ratio of the equilibrium constants of the reactions,

$$H_2^1+I_2\rightleftarrows 2\ H^1I \quad (17)$$

and

$$H_2^2+I_2\rightleftarrows 2\ H^2I \quad (18)$$

TABLE VI.

	H^1I, $i_1=1/2$			H^2I, $i_2=0$		
T	Q	$-(F^0-E_0^0)/T$	$+F^0$	Q	$-(F^0-E_0^0)/T$	F^0
298.1	65.670	43.797	− 9810.2	64.786	43.793	−10744.7
400	87.973	45.838	−15089.5	87.097	45.841	−16026.4
575	126.722	48.365	−24564.3	127.034	48.393	−25516.0
700	155.218	49.745	−31575.8	157.674	49.799	−32549.4

is again equal to the equilibrium constant of the reaction,

$$H_2^1+2\ H^2I\rightleftarrows H_2^2+2\ H^1I \quad (19)$$

and can be calculated as in the case of the analogous reactions involving hydrogen chloride. The calculated values of K_1/K_2 for the hydrogen and iodine, hydrogen iodide reactions are given in Table VII.

The use of formula (1) for the hydrogen levels changes K_1/K_2 by $10^{-2.43/T}$, which amounts to a decrease of 1.9 percent at 298.1° and 0.8 percent at 700°K. A change of 10 cm^{-1} in the $x\tilde{\omega}_e$ of HI changes these constants by the factor $10^{2.17/T}$ which is 1.7 percent at 298.1° and 0.7 percent at

TABLE VII.

T°K	0	298.1	400	575	700
$-F$	−82.46	90.1	153.1	239.9	278.9
K_1/K_2	0.0	1.164	1.212	1.234	1.222

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[15] M. Czerny, Zeits. f. Physik **44**, 235 (1927).

[16] E. O. Salant and A. Sandow, Phys. Rev. **37**, 373 (1931).

[17] Private communication.

700°K. Finally we may estimate the effect of the use of $J(J+1)$ instead of $(J+1/2)^2$ in our equations. The use of the latter dependence on J would increase these constants by $10^{3.67/T}$ which amounts to 2.6 percent at 298.1° and 1.2 percent at 700°.

The ratio of K_1/K_2 of the H^1Cl and H^2Cl reactions is thus quite different from that of the H^1I and H^2I reactions. This difference is due to the difference in zero point energies largely; this energy difference in the case of reaction (13) is 579.1 calories and in that of reaction (19) is 82.46 calories. The term of Eq. (14) containing the masses is largely cancelled by that containing the Q's, so that the zero point energy is relatively important.

The ratio K_1/K_2 of the H^1I and H^2I reactions is sufficiently large at 575–700°K to permit test of these calculations, if rather high concentrations of $H_2{}^2$ can be secured. In any such sample the molecules $H_2{}^1$, H^1H^2 and $H_2{}^2$ must all be present. The concentration of H^1H^2 is determined by Eq. (8) and the calculated values of Table II, and thus for a sample containing a given ratio of H^1 to H^2 the concentration of hydrogen, hydrogen iodide and iodine can be calculated and compared with experiment.

The reactions (11) and (12) cannot be investigated readily since the equilibria are so far toward the hydrogen chloride side, but reaction (13) can probably be studied, if sufficiently high concentrations of H^2 can be secured. The various methods developed for concentrating H^2 are so promising that we believe that such tests of the theoretical calculations will be possible.

THE ELECTRODE POTENTIALS OF $H_2{}^1$ AND $H_2{}^2$

The free energy change of the reaction between hydrogen and chlorine in an electrolytic cell differs from that considered above by the free energy of solution of gaseous hydrogen chloride in a water solution at the concentration used in the cell. Thus differences in the free energy of solution of H^1Cl and H^2Cl molecules, i.e., the solubilities of these two hydrogen chloride molecules, may exist and thus no prediction of electrode potentials can be made. It seems, though, that the free energy differences calculated above for these hydrogen-hydrogen halide reactions should give the order of magnitude of the electrode potential differences. These electrode potential differences at 298.1° are 0.00886 and 0.00195 volts in the cases of the hydrogen chloride and hydrogen iodide reactions respectively.

These differences are so small that no separation of the hydrogen isotopes can be expected by fractional electrolysis insofar as this fractionation depends on the differences of electrode potentials. The discovery by Washburne and Urey[18] that such fractionation does occur in commercial hydrogen-oxygen electrolytic cells with KOH solutions as electrolyte and nickel electrodes is probably due to other causes than the electrode potential differences, perhaps the rates of diffusion to the electrode surface or the rates of recombination of hydrogen atoms on the electrodes.

Though these calculations have not been experimentally confirmed, they are based on well established methods. They show that rather appreciable differences in thermodynamic properties of the compounds of H^1 and H^2 are to be expected. The differences of the vapor pressures of $H_2{}^1$ and H^1H^2 required by thermodynamic reasoning previously presented and demonstrated by Urey, Brickwedde and Murphy[2] is another marked variation in properties due to the large ratio of masses of the two isotopes of hydrogen. These differences as well as differences in reaction velocities, of which the electrolytic fractionation of the hydrogen isotopes is probably an example, are so great that had the abundance of H^2 been about equal to that of H^1, very marked variations of the atomic weight of hydrogen would certainly have been observed many years ago, with a considerable change in the historical development of chemistry.

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[18] E. W. Washburne and H. C. Urey, Proc. Nat. Acad. Sci. **18**, 496–498 (1932).