THE ENTROPY OF HYDROGEN AND THE THIRD LAW OF THERMODYNAMICS
THE FREE ENERGY AND DISSOCIATION OF HYDROGEN

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The band spectrum data of the hydrogen molecule have recently been considered by Birge, Hyman and Jeppesen.[1] They have shown that the observed rotational energies associated with the vibrational levels may be represented with a very high degree of accuracy by means of simple equations for which they give the constants. Accepting their representation of the observed behavior of the molecule, we will illustrate the application of such data in the exact calculation of several thermodynamic properties. The equations required for this purpose have been given in the preceding paper.[2] These eliminate the necessity of such assumptions as molecular rigidity and other approximations.

These calculations will serve not only in making available important and very accurate thermodynamic properties of the hydrogen molecule, but will furnish an introduction to an extended series of papers in which similar data will be given for the elements and simpler molecules. At the present time calculations have been made on about one-third of the elements and a number of other substances.

A second purpose of this paper is to clear up the numerous misunderstandings which have arisen concerning the effect of nuclear spin on the entropy of hydrogen and the use of this entropy in conjunction with the entropies obtained from the third law of thermodynamics.

The situation existing in hydrogen has been correctly stated in the paper of Giauque and Johnston[3] and the use of the entropy of hydrogen in connection with the third law has been discussed by Kelley[4] as a personal communication from this author. Following this, a paper by Rodebush[5]

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[1] (a) Personal Communication; (b) Hyman and Jeppesen, *Nature*, (March, 1930); (c) Birge and Jeppesen, *ibid.*, (March, 1930).

[2] Giauque, THIS JOURNAL, **52**, 4808 (1930).

[3] Giauque and Johnston, *ibid.*, **50**, 3221 (1928). Also see Fowler, *Proc. Roy. Soc.*, (London), **118A**, 52 (1928). Fowler's treatment led to an incorrect result.

[4] (a) Kelley, *Ind. Eng. Chem.*, **21**, 353 (1929); THIS JOURNAL, **51**, 1145 (1929).

[5] Rodebush, *Proc. Nat. Acad. Sci.*, **15**, 678 (1929). A paper [*Phys. Rev.*, **36**, 1398 (1930)] has recently appeared in which D. MacGillavry, who did not know of the paper by Rodebush, has raised the same objection, although he agrees with our result. This objection, which concerns the reliability of an *a priori* calculation of the entropy of a system when molecules such as ortho and para hydrogen are not in complete equilibrium, has been answered more specifically by Giauque and Johnston [*Phys. Rev.*, **36**, Nov. 15, (1930)].

We add here for the sake of completeness that most, if not all, of the systems

has criticized not only our method of considering the problem, but also the numerical result, although his value is identical with ours. However, confusion has arisen since the paper by Rodebush, while giving the correct value for the absolute entropy of hydrogen, leaves the impression that this value should be used in conjunction with values obtained for other substances from the $\int_0^T C_p \, d \ln T$ with the assistance of the usual extrapolation methods at very low temperatures. The papers of Giauque and Johnston and of Kelley make a very specific point of the fact that this cannot be done. We have learned from a number of personal communications and also from criticism of Kelley for using our correct values, which we have recently noticed, that it is desirable to restate this problem which has implications relating not alone to hydrogen, but to all the elements excepting a few which are without nuclear spin. We will return to this problem later in this paper.

The results of Birge, Hyman and Jeppesen for the normal electronic state of the hydrogen molecule may be represented by the equation

$$E = E_v + B_v m^2 + D_v m^4 + F_v m^6$$

where m has the values $\dfrac{1}{2}, \dfrac{3}{2}, \dfrac{5}{2}, \ldots \ldots \ldots$; $m = j + \dfrac{1}{2}$ where j represents the number of units of rotational momentum; v refers to the number of units of vibration in addition to the half unit of zero point vibration. The values of the constants of the above equation are given in Table I.

TABLE I

CONSTANTS IN THE ENERGY EQUATION OF THE HYDROGEN MOLECULE IN CM.$^{-1}$

v	E_v	B_v	v	E_v	B_v
0	0	59.354	7	24281	39.209
1	4161.96	56.404	8	26823	36.121
2	8083	53.630	9	29117	32.930
3	11778.5	50.834	10	31148	29.53
4	15247.5	48.008	11	32883	25.7
5	18489	45.138		$D_v = -0.0465 + 0.00135 \left(v + \tfrac{1}{2}\right)$	
6	21501	42.210		$F_v = 5.18 \times 10^{-5}$	

considered by means of thermodynamics or statistics are not in complete equilibrium. Not only "stable" molecules but even the elements are potentially unstable with respect to others.

If we knew the absolute entropies of two organic isomers we believe that no criticism would be made if the total entropy of a system consisting of an isomeric mixture was calculated by adding the entropy of mixing to that of the pure constituents. However, when this generally accepted method is applied to the identical case of the recently discovered hydrogen isomers, the method is considered not plausible.

The calculation of absolute entropy is not appreciably complicated by the coexistence of some non-equilibrium states. The substitution of a lengthy calculation along a reversible path through limiting high temperatures for the simple and direct isothermal reversible path usually used in such cases, does not increase the certainty of the result. In most cases the former method would require information not yet available.

The conclusion of Heisenberg,[6] on the basis of wave mechanics, that two general classes of hydrogen molecules exist has been amply substantiated by experiment. In the normal electronic state the para form, which has the nuclear spins opposed in the molecule can have only the even molecular rotational levels, $j = 0, 2, 4, 6, \ldots\ldots\ldots$, or $m = \dfrac{1}{2}, \dfrac{5}{2}, \dfrac{9}{2}, \dfrac{13}{2}\ldots\ldots\ldots$, while the ortho form can have only the odd rotational levels. The ortho hydrogen has three times the statistical weight which it would have in the absence of nuclear spin since the additive coupling of the two half-unit nuclear spins leads to $j_s = 1$ and an *a priori* probability $p_s = 2j_s + 1 = 3$. The para hydrogen with the canceling coupling has $j_s = 0$, $p_s = 2j_s + 1 = 1$. Thus at high temperatures a ratio of 1:3 between para and ortho states is found. The first definite experimental evidence for this ratio was given by Hori[7] from his measurements on the relative intensities of the lines in the band spectrum of hydrogen. Dennison[8] then showed that the long unexplained shape of the rotational heat capacity curve, first obtained experimentally by Eucken,[9] was in complete agreement with the above conditions. It was assumed that the rate of conversion of ortho and para hydrogen into each other is so slow as to be negligible under the conditions of experiment. At the suggestion of E. U. Condon, Giauque and Johnston[3] kept hydrogen at the temperature of liquid air to study the rate of conversion. A bomb containing about 10 moles of hydrogen at a pressure of 75 atmospheres was kept at about 85°K. for 197 days. On liquefying some of this hydrogen the vapor pressure when solid and liquid phases were present was found to have been lowered. Smits[10] has called attention to the fact that ordinary hydrogen has no triple "point" since the solid is in reality a solid solution.

The observed lowering of the vapor pressure, while small, was beyond the limit of experimental error and thus indicated the predicted readjustment of the relative proportions of ortho and para hydrogen. The further experiments promised by these authors were discontinued following the publication of the excellent work of Bonhoeffer and Harteck,[11] who carried out further investigations of the vapor pressure and made quantitative measurements of the rate of conversion with the assistance of a charcoal catalyst and an analytical method depending on the different thermal conductivities of the ortho and para forms. MacLennan and MacLeod[12]

[6] Heisenberg, *Z. Physik*, **41**, 239 (1927).

[7] Hori, *ibid.*, **44**, 834 (1927).

[8] Dennison, *Proc. Roy. Soc.* (London), **115A**, 483 (1927).

. [9] (a) Eucken, *Sitzb. preuss. Akad. Wiss.*, 144 (1912); (b) *Ber. deut. physik. Ges.*, **18**, 4 (1916).

[10] Smits, *Koninklijke Akad. Wetenschappen Amsterdam*, **32**, 603 (1929).

[11] (a) Bonhoeffer and Harteck, *Sitzb. preuss. Akad. Wiss.*, 103 (1929); (b) *Naturwiss.*, **17**, 182, 321 (1929); (c) *Z. physik. Chem.*, **4B**, 113 (1929).

[12] McLennan and MacLeod, *Nature*, **113**, 152 (1929).

have shown from measurements of Raman spectra on liquid hydrogen that the two forms exist under this condition. Further substantiation from heat capacity and heat content measurements will be considered later.

The Equilibrium Composition of Hydrogen.—From Equation 1 of the previous paper

$$N = p_0 A + p_1 A e^{-\epsilon_1/kT} + p_2 A e^{-\epsilon_2/kT} + \ldots\ldots = AQ$$

where N is Avogadro's number and A the number of molecules in the lowest energy state, we have calculated the ratio of ortho and para molecules existing at various temperatures under equilibrium conditions. In place of the usual rotational a priori weights 1, 3, 5, 7, 9, ..., the weights 1, 9, 5, 21, 9, ..., must be used.

The fraction of the molecules in the para states is given by

$$\frac{p_0 + p_2 e^{-\epsilon_2/kT} + p_4 e^{-\epsilon_4/kT} + \ldots\ldots}{p_0 + p_1 e^{-\epsilon_1/kT} + p_2 e^{-\epsilon_2/kT} + p_3 e^{-\epsilon_3/kT} \ldots\ldots} = \frac{Q_{\text{para}}}{Q}$$

The energies used in calculating the exponents are the actual energy levels of the molecule and, of course, include such effects as work done in the stretching of the molecule with increasing rotation and the change in the moment of inertia due to the same cause. The results are given in Table II.

TABLE II

EQUILIBRIUM DISTRIBUTION OF HYDROGEN MOLECULES IN ORTHO AND PARA ROTATION STATES

T, degrees absolute	Percentage para	T, degrees absolute	Percentage para	T, degrees absolute	Percentage para
0	100	75	51.776	250	25.257
15	99.989	100	38.461	273.1	25.141
20	99.814	125	31.871	298.1	25.074
25	98.996	150	28.544	It will be seen that the	
30	96.951	175	26.836	1:3 ratio is closely ap-	
40	88.547	200	25.953	proximated at room	
50	76.798	225	25.495	temperature	

The Energy Content of Hydrogen.—From Equations 1 and 2 of the previous paper the total energy of the system (excluding translation) with reference to the zero state may be calculated.

$$E^\circ - E_0^\circ = \frac{N\Sigma p e e^{-\epsilon/kT}}{\Sigma p e^{-\epsilon/kT}}$$

The calculations have been made for four conditions, pure para hydrogen, pure ortho hydrogen, for the equilibrium mixture of the two, and for the 1:3 mixture. The first, third and fourth cases are easily realizable experimentally, while the data on ortho hydrogen are useful for the calculation of the wide range of realizable systems intermediate between pure para hydrogen and the equilibrium mixture. The values are given in Table

III. The amount $3/2RT = 2.9804\ T$ cal./deg. per mole should be added for translational energy if the total energy is required.

TABLE III

ENERGY OF HYDROGEN GAS WITH REFERENCE TO THE ZERO STATE

(Translational Energy is not Included)

T, degrees absolute	Pure para hydrogen	Pure ortho hydrogen	Equilibrium mixture	$^1/_4$ Para $^3/_4$ Ortho
0	0.00	337.17	0.00	252.88
15	.00	337.17	.04	252.88
20	.00	337.17	.63	252.88
25	.00	337.17	3.39	252.88
30	.00	337.17	10.28	252.88
40	.05	337.17	38.63	252.89
50	.20	337.18	78.38	252.94
75	5.77	337.22	165.61	254.36
100	30.56	338.59	219.78	262.17
125	80.09	341.83	258.41	276.39
150	146.61	351.40	292.94	300.20
175	219.09	368.54	328.44	331.17
200	290.22	393.59	366.76	367.75
225	357.04	425.69	408.19	408.53
250	419.27	463.46	452.30	452.41
273.1	473.34	502.16	494.84	494.91
298.1	529.12	546.92	542.46	542.47

Elbe and Simon[13] have calorimetrically determined the difference in energy content of the 1:3 mixture and the equilibrium state by means of adsorption of each on charcoal. At 77.5°K. the difference found was 74 calories per mole. By interpolation we find the value of 83 calories per mole at this temperature. At 20.4°K. the difference was 241 calories against 252 calories from Table III. Considering the difficulty of experiment, this is good agreement and is well within the limits of error indicated by Elbe and Simon, who made a similar comparison.

The Heat Capacity of Hydrogen.—The heat capacity for several conditions of hydrogen was calculated from Equation 6 of the previous paper.

$$\frac{dE^\circ}{dT} = \frac{N}{kT^2}\left[\frac{\Sigma\epsilon^2 pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}} - \left(\frac{\Sigma\epsilon pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}}\right)^2\right]$$

For example, in making this calculation for pure para hydrogen, only the even terms are considered in the summations. The method of using the actual energy levels of the molecules gives the heat capacity with an accuracy exceeding that of any direct experimental measurement. The values are given in Table IV. The value of $3/2\ R = 2.9804$ cal./deg. per mole should be added to these values on account of translation if the total heat capacity at constant volume is required.

13 Elbe and Simon, Z. physik. Chem., 6B, 79 (1929).

TABLE IV

HEAT CAPACITY OF HYDROGEN GAS (EXCLUDING TRANSLATION)

T, degrees absolute	Pure para hydrogen	Pure ortho hydrogen	Equilibrium mixture	$^1/_4$ Para $^3/_4$ Ortho
0	0.0000	0.0000	0.0000	0.0000
15	.0000	.0000	.0028	.0000
20	.0000	.0000	.2649	.0000
25	.0000	.0000	.9196	.0000
30	.0001	.0000	1.8795	.0000
40	.0049	.0000	3.4465	.0012
50	.0399	.0000	4.1042	.0100
75	.5177	.0079	2.7263	.1353
100	1.5041	.0731	1.7498	.4309
125	2.3981	.3131	1.4138	.8343
150	2.8451	.5271	1.3801	1.1066
175	2.9046	.8464	1.4708	1.3610
200	2.7674	1.1512	1.5965	1.5553
225	2.5777	1.3023	1.7148	1.6211
250	2.4056	1.6049	1.8101	1.8051
273.1	2.2819	1.7378	1.8756	1.8738
298.1	2.1862	1.8377	1.9254	1.9248

Calories per degrees per mole

Similar calculations were given by Dennison[8] and by Beutler[14] both of whom assumed the molecule to be rigid. Their results are expressed in terms of the variable B/kT, where B is the same as in the first term of the equation used above to represent the energy levels of the molecule. This can be done only when the condition of rigidity is imposed. By interpolation of Dennison's values it is found that the neglect of molecular stretching leads to results about 1% too low at 200°K. and about 1.3% too low at 298.1°K. The necessity of considering molecular stretching in this connection was pointed out by Kemble and Van Vleck.[15]

The various experimental measurements on the rotational heat capacity of hydrogen have been summarized by Eucken and Hiller,[16] who have carried out a very interesting series of experiments on hydrogen with 95, 43.1, 36.4 and 31.1%, respectively, of the para variety in addition to ordinary hydrogen with 25%. It is interesting to note that when we consider the effect of molecular stretching, the good agreement of the results of Cornish and Eastman[17] with the theoretical curve is further improved.

The Entropy of Hydrogen.—The important and much misunderstood value of the entropy of hydrogen may be calculated from Equation 14 of the previous paper.

$$S° = R\left[\ln \Sigma pe^{-\epsilon/kT} + \frac{1}{kT}\frac{\Sigma p\epsilon e^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}}\right]$$

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[14] Beutler, *Z. Physik*, **50**, 581 (1928).

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

[16] Eucken and Hiller, *Z. physik. Chem.*, **4B**, 142 (1929).

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

$$= 4.5750 \left[\log 7.7533 + \frac{3.0839}{7.7533} \right] = 5.889 \text{ E.U.}$$

when $T = 298.1°\text{K}$. To this must be added the entropy due to translation, namely 28.090 E.U. This is obtained from the Sackur equation given as Equations 20 and 21 in the previous paper.

$$S° \text{ Translation} = 3/2\, R \ln M + 5/2\, R \ln T - 7.267$$

where M is the molecular weight and the pressure of the gas is one atmosphere.

. The absolute entropy of hydrogen is thus found to be 33.98 calories per degree per mole, in agreement with our previous value mentioned above. However, we hasten to add that this is not the value which should be used as the entropy of hydrogen in combination with $\int C_p\, d \ln T$ for other substances.

This can perhaps best be made clear by discussing the application of the third law of thermodynamics to hydrogen. It was shown by Giauque and Johnston[3] that ordinary solid hydrogen had an entropy of 4.39 E.U. above the vibrational entropy. This is due to the existence of ten kinds of molecules within the solid state. These kinds of molecules are distinguished only in that each has a different rotational or nuclear spin quantum specification. Of these one-fourth are para hydrogen with $j = 0$ and three-fourths are equally divided between nine kinds of ortho hydrogen, with $j_{\text{rot.}} = 1$ and $j_s = 1$, each of the latter therefore making up one-twelfth of the total amount. This can be considered by the usual expression for the entropy of mixing

$$\Delta S = -1/4\, R \ln 1/4 - 9/12\, R \ln 1/12 = 4.39 \text{ E.U.}$$

The best determinations of the heat capacity of condensed hydrogen are due to Simon and Lange,[18] who also directly determined the heat of vaporization. They found that their results on solid hydrogen could be represented by a Debye function with an $h\nu/k = 91$. The most accurate determinations of the heat capacity of hydrogen gas are those of Cornish and Eastman,[17] who used the velocity of sound method at low temperatures. The greatest uncertainty in calculating entropy from the experimental measurements lies in the estimation of the correction of the actual hydrogen gas to the ideal gas at low temperatures, since the heat capacity of the actual hydrogen gas has not been measured at the temperatures of condensed hydrogen. For this reason we have used the heat of vaporization at the melting "point(?)" of hydrogen but even here where the pressure is but 5.38 cm., the correction obtained by combining the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ with the equation of Berthelot is 0.13 E.U., while that obtained from the equation of van der Waals is 0.03 E.U. A summary of the calculation is given in Table V.

[18] Simon and Lange, *Z. Physik*, **15**, 312 (1923).

TABLE V

CALCULATION OF THE ENTROPY OF HYDROGEN

Solid	Cal./deg. per mole
$0-13.95°K.$, $h\nu/k = 91$	0.52
Fusion, $28.0/13.95$	2.01
Vaporization at 5.38 cm. pressure, $217.8/13.95$	15.61
Correction to ideal gas	0.13 Berthelot, or
	.03 van der Waals
Compression from 5.38 cm. to 76.0 cm.	-5.26
$\int_{13.95}^{298.1} C_p \, d \ln T$	16.73
	29.74 Berthelot gas, or
	29.64 van der Waals gas

Subtracting the entropy of mixing referred to above from the absolute entropy, the value $33.98 - 4.39 = 29.59$ E.U. is found to be in excellent agreement with the observed value. This is a very interesting confirmation, not only of the truth of the third law, but also of the correctness of the situation assumed to exist in solid hydrogen.

Recently Simon, Mendelssohn and Ruhemann[19] have published a preliminary report of an investigation of the heat capacity of solid hydrogen at the temperatures of liquid helium. They have found that the heat capacity fails to follow the Debye curve and at about 2°K. is increasing with decreasing temperature. For the ordinary mixture this additional loss of entropy amounts roughly to 0.7 E.U. to 2°K. and shows that hydrogen is beginning to dispose of the 4.39 E.U. referred to above.

In a recent paper Pauling[20] gives convincing reasons for believing that not only hydrogen but many other molecules containing hydrogen are rotating in the solid state. Pauling supports the conclusions of Giauque and Johnston and predicts that the process of losing the 4.39 E.U. will not approximate completion until temperatures below 0.001°K. are reached.

From the above results it will be evident that it is not practical to obtain the absolute entropy of hydrogen from heat capacity measurements alone. It is equally certain that in the case of other substances with nuclear spin, and this includes nearly all substances, heat capacity measurements over the attainable temperature range will not suffice to give the absolute entropy. This situation which would at first sight seem fatal to the exact practical application of the third law of thermodynamics is by no means so serious since there is reason for believing that hydrogen may be the only substance which does not cause a very simple type of deviation for which a correction may be applied.

To make this clear we will consider an important observation of Gibson

[19] Simon, Mendelssohn and Ruhemann, *Naturwiss.*, **18**, 34 (1930).

[20] (a) Pauling, *Phys. Rev.*, **36**, 430 (1930); (b) Personal communication.

and Heitler,[21a] who carried out, from spectroscopic data, the calculation of the dissociation of gaseous iodine into its atoms. They show with the assistance of wave mechanics that in reactions involving diatomic and monatomic substances that nuclear spin contributes equally to the absolute entropy of the reactants and to the products. Using this fact Gibson and Heitler were able to make a very accurate calculation of the dissociation constant even though the nuclear spin of the iodine atom is unknown. Gibson[21b] has expressed the opinion that cancellation will occur in reactions involving polyatomic molecules.

However, it must be pointed out that the nuclear spin cancellation is only a limiting approximation which is valid when the temperature is high enough. For gas reactions there is little reason for doubting that room temperature is always sufficient. As an example the equilibrium reaction $H_2 = 2H$ would approximate an error of $2\,R\ln 2 = 2.75$ E.U. at 20°K. where, at equilibrium, nearly all of the diatomic hydrogen would be in the zero state of the para form which has unit weight, whereas the monatomic hydrogen still retains equal distribution among its spin multiplets. At 100°K. the discrepancy has been reduced to 0.88 E.U., while at room temperature it is negligible. It may also be added that hydrogen shows this effect to a much greater degree than is possible in any other diatomic molecule at the same temperatures and almost certainly to a greater degree than will be found possible in polyatomic molecules. If solid substances always retain the high temperature multiplicity due to nuclear spin over the experimental range used in connection with the third law of thermodynamics, it is obvious that it will be unnecessary to consider it. Very probably this is nearly always true, the one known exception being hydrogen, with some compounds containing hydrogen being somewhat uncertain.

On the experimental side the results of Giauque and Wiebe[22] on hydrogen chloride, hydrogen bromide and hydrogen iodide all prove that the limiting entropy due to spin persists to temperatures below 15°K. They showed that the entropy given by the third law agreed with that obtained from spectroscopic data when nuclear spin was ignored in the calculation. This author will soon publish a paper showing that the available data on iodine lead to the same result. This is particularly important since, in distinction from the polar hydrogen halides, the symmetry of the iodine molecule must lead, as in all such cases, to ortho and para molecular species. Pauling, in the paper referred to above, indicates that this is due to the fact that a molecule like iodine cannot rotate in the solid state, whereas

[21] (a) Gibson and Heitler, Z. Physik, **49**, 465 (1928); (b) Gibson, personal communication.

[22] (a) Giauque and Wiebe, This Journal, **50**, 101 (1928); (b) **50**, 2193 (1928); (c) **51**, 1441 (1929).

hydrogen can. Experimental work on nitrogen and methane is in progress in this Laboratory in order to decide this question.

From the above it is concluded that all polar molecules which do not have the possibility of ortho and para rotational series of the type illustrated by hydrogen, will retain their high temperature nuclear spin entropy to temperatures far below 1°K. In the case of molecules having two or more similar atoms symmetrically placed within the molecule, all those containing such symmetrically placed atoms other than hydrogen will probably retain their limiting spin entropy to temperatures below 1°K. In the case of hydrogen it must be considered that the size of the proton places it in a class far removed from the other atoms whose "size" depends on the electron configuration about them. Many organic compounds undoubtedly have symmetrically placed hydrogen atoms. This does not necessarily mean that nuclear spin cancellation does not occur, since these molecules differ from hydrogen in that they condense at temperatures where the high temperature nuclear spin entropy is established, whereas the hydrogen molecules are frozen out at temperatures greatly below this point.

In many recent references to the use of the third law in connection with reactions involving hydrogen, the authors seem to feel that the entropy of hydrogen is in doubt. We hope it has been made clear that the entropy of hydrogen is definitely established and that the remaining doubt concerns other molecules which contain hydrogen. Since the effects discussed are of primary importance in connection with the use of the third law of thermodynamics in organic chemistry, it is interesting to note that the predominant isotopes carbon 12 and oxygen 16 are without nuclear spin.

The value of the entropy of hydrogen which should be used in conjunction with data obtained from the third law of thermodynamics is 31.23 E.U. This is the value which has been used by Kelley[4] at our suggestion. It is obtained by subtracting the high temperature nuclear spin entropy $R \ln 4 = 2.75$ E. U. from the absolute entropy of hydrogen $33.98 - 2.75 = 31.23$ E. U. This places hydrogen on the same basis as other molecules in most of which, and perhaps in all of which, the subtraction is taken care of by the fact that heat capacities are not usually measured below temperatures of a few degrees absolute.

The Dissociation of Hydrogen.—Langmuir and Mackay[23] have determined the heat of dissociation of hydrogen and the equilibrium constant over a range of temperatures. They utilized measurements of the energy conducted away from a heated filament operating in hydrogen gas at various pressures. As is well known, the evaluation of the heat of reaction

[23] (a) Langmuir, THIS JOURNAL, 34, 860, 1310 (1912); (b) 37, 417 (1915); (c) Langmuir and Mackay, ibid., 36, 1708 (1914).

and dissociation constant from data where both occur as unknowns is very difficult and for this reason no very high accuracy has been claimed for the values obtained. However, with the assistance of the data and methods discussed above it is possible to show that the values of the dissociation of hydrogen given by Langmuir over the temperature range where his method was considered to be reliable are very satisfactory even though their temperature coefficient is somewhat in error.

From Equation 27 of the previous paper we have

$$\frac{F^\circ - E_0^\circ}{T} = -3/2\,R \ln M - 5/2\,R \ln T + R \ln P - R \ln Q + 7.267$$

$$R = 1.9869 \text{ calories per degree per mole.}$$

From the energy equations of Birge, Hyman and Jeppesen[1] the values of the absolute $Q = \Sigma p e^{-\epsilon/kT}$ for the hydrogen molecule have been calculated. The values of $(F^\circ - E_0^\circ)/T$ are given in Table VI.

TABLE VI

ABSOLUTE $(F^\circ - E_0^\circ)/F$ FOR THE HYDROGEN MOLECULE

T	$-\dfrac{F^\circ - E_0^\circ}{T}$	T	$-\dfrac{F^\circ - E_0^\circ}{T}$	T	$-\dfrac{F^\circ - E_0^\circ}{T}$
298.1	27.191	1250	37.069	3200	44.018
300	27.235	1300	37.344	3300	44.259
350	28.285	1400	37.868	3400	44.493
400	29.193	1500	38.360	3500	44.720
450	29.999	1600	38.825	3600	44.941
500	30.720	1700	39.264	3700	45.157
550	31.374	1800	39.678	3800	45.368
600	31.973	1900	40.069	3900	45.574
650	32.524	2000	40.440	4000	45.776
700	33.035	2100	40.795	4100	45.973
750	33.512	2200	41.137	4200	46.166
800	33.959	2300	41.468	4300	46.355
850	34.379	2400	41.789	4400	46.540
900	34.775	2500	42.100	4500	46.721
950	35.150	2600	42.402	4600	46.899
1000	35.507	2700	42.694	4700	47.074
1050	35.847	2800	42.977	4800	47.246
1100	36.172	2900	43.250	4900	47.416
1150	36.483	3000	43.514	5000	47.584
1200	36.782	3100	43.770		

The values given in heavy type have been directly calculated, the others have been carefully interpolated.

In calculating the values in Table VI the effect of nuclear spin has been included. However, if these values are to be combined with similar data for substances where the nuclear spin is unknown, and thus is conveniently ignored, the amount of $R \ln 4 = 2.755$ should be added to $(F^\circ - E_0^\circ)/T$. For example, the value of $-(F^\circ - E_0^\circ)/T$ for $298.1°$K. becomes 24.436 calories per degree per mole.

For monatomic hydrogen the absolute $Q = 4$ per atom, a multiplicity of 2 arising from nuclear spin with an additional factor of 2 due to the electron spin in this atom. Thus the absolute

$$\frac{F° - E_0°}{T} = -3/2\, R \ln 1.0076 - 5/2\, R \ln T - R \ln 4 + 7.267$$

In Table VII the values of $+5/2\, R \ln T - 7.267$ are given instead of the whole function because these values are necessary in connection with all other gaseous substances. The constant amount $3/2\, R \ln 1.0076 + R \ln Q = 2.784$ must be added to the values in Table VII to give $-(F° - E_0°)/T$ for atomic hydrogen. For example, the value for 298.1°K. is 23.818 calories per degree per mole.

To eliminate the contribution of nuclear spin the amount $R \ln 2 = 1.378$ should be subtracted, thus giving 22.440 at 298.1°K.

<div align="center">TABLE VII</div>

<div align="center">VALUES OF $\dfrac{5}{2} R \ln T + R \ln \dfrac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + R \ln R$</div>

T	$\frac{5}{2} R \ln T - 7.267$	T	$\frac{5}{2} R \ln T - 7.267$	T	$\frac{5}{2} R \ln T - 7.267$
298.1	21.034	1250	28.154	3200	32.823
300	21.065	1300	28.349	3300	32.976
350	21.831	1400	28.717	3400	33.124
400	22.494	1500	29.060	3500	33.268
450	23.079	1600	29.380	3600	33.408
500	23.603	1700	29.681	3700	33.544
550	24.076	1800	29.965	3800	33.677
600	24.508	1900	30.234	3900	33.806
650	24.906	2000	30.489	4000	33.932
700	25.274	2100	30.731	4100	34.054
750	25.617	2200	30.962	4200	34.174
800	25.937	2300	31.183	4300	34.291
850	26.238	2400	31.394	4400	34.405
900	26.522	2500	31.597	4500	34.517
950	26.791	2600	31.792	4600	34.626
1000	27.046	2700	31.979	4700	34.733
1050	27.288	2800	32.160	4800	34.837
1100	27.519	2900	32.334	4900	34.940
1150	27.740	3000	32.503	5000	35.040
1200	27.951	3100	32.665		

For the reaction $H_2 = 2H$, values of $\Delta(F° - E_0°)/T$ may be obtained from the above tables.

$$\frac{\Delta F°}{T} = -R \ln K = \Delta\left(\frac{F° - E_0°}{T}\right) + \Delta E_0°$$

where $K = [H]^2/[H_2]$.

$\Delta E_0°$ has been evaluated by a number of authors from vibration bands which have been observed to dissociate in the case of one of the higher electronic levels. A knowledge of the molecular and atomic excitation

energy completes the necessary information. The basis of such calculations has been discussed by Birge and Sponer[24] and a summary of recent work has been given by Birge.[25]

The most reliable value is that given by Richardson and Davidson,[26] namely, 4.46 ± 0.04 volt electrons or since 1 volt electron = 23,059 calories per mole, $\Delta E_0^\circ = 102,800 \pm 1000$ calories per mole.

Bichowsky and Copeland[27] have calorimetrically determined the ΔH of the above reaction to be $105,000 \pm 3500$ calories per mole at room temperature. With the assistance of Table III it is found that this should be decreased by 940 calories in order to obtain ΔE_0°. Thus $\Delta E_0^\circ = 104,000 \pm 3500$ calories in satisfactory agreement with the spectroscopic value.

Using the value $\Delta E_0^\circ = 102,800 \pm 1000$ calories per mole with Tables VI and VII, the values given in Table VIII have been computed.

TABLE VIII

FREE ENERGY OF DISSOCIATION OF HYDROGEN

T, degrees absolute	$-\Delta\left(\dfrac{F^\circ - E_0^\circ}{T}\right)$ Calories per degree	$\dfrac{\Delta F}{T}$	$K = e^{-\Delta F/RT} = [\mathrm{H}]^2/[\mathrm{H}_2]$
298.1	20.445	324.406	$(1.2 \pm 4.7) \times 10^{-71}$
500	22.054	183.546	$(7.6 \pm 12) \times 10^{-41}$
1000	24.153	78.647	$(6.4 \pm 3.8) \times 10^{-18}$
1500	25.328	3.205	$(3.6 \pm 1.3) \times 10^{-10}$
2000	26.106	25.294	$(2.96 \pm 0.77) \times 10^{-6}$
2500	26.662	14.458	$(6.92 \pm 1.4) \times 10^{-4}$
3000	27.060	7.207	$(2.66 \pm 0.45) \times 10^{-2}$
3500	27.384	1.987	$(3.68 \pm 0.52) \times 10^{-1}$
4000	27.656	-1.956	2.68 ± 0.32
5000	28.064	-7.504	43.7 ± 4.4

Additional values may be calculated similarly from the data given in Tables VI and VII. The estimate of the accuracy is based on the assumption that the ΔE_0° is reliable to 0.04 volt electrons. When a more accurate value of ΔE_0° becomes available, a very simple correction may be applied.

In Table IX the values of the percentage dissociation at one atmosphere pressure are given: percentage dissociation = $100 \sqrt{K/(K + 4P)}$, where P = total pressure. The values given by previous authors have been included for comparison.

We have previously mentioned the good agreement between the calculated values and those obtained by Langmuir. This would not be so if the spin effects were not properly considered. For example, neglect of the electron spin multiplicity in the hydrogen atom would decrease all the

[24] Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).
[25] Birge, *Trans. Faraday Soc.*, **25**, 707 (1929).
[26] Richardson and Davidson, *Proc. Roy. Soc.*, (London), **123A**, 466 (1929).
[27] Bichowsky and Copeland, THIS JOURNAL, **50**, 1315 (1928).

TABLE IX

PERCENTAGE OF HYDROGEN DISSOCIATED AT A TOTAL PRESSURE OF ONE ATMOSPHERE

T, degrees absolute	This author	Lang-muir[23b] 1915	Saha[28] 1920	Duffendach[29] 1922	Edgar[30] 1923	Lewis and Randall,[31] 1923	Wohl[32] 1924
298.1	$(1.8 \pm 6.6) \times 10^{-34}$	..	..	....	..	..	..
500	$(4.4 \pm 6.7) \times 10^{-19}$	..	..	....	..	..	..
1000	$(1.3 \pm 0.8) \times 10^{-7}$	..	..	....	..	..	..
1500	$(9.5 \pm 3.4) \times 10^{-4}$	..	..	1900×10^{-4}	..	..	..
2000	0.086 ± 0.011	0.17	1	6.5	0.63	0.89	0.83
2500	1.31 ± 0.13	1.6	11	59	5.95	..	..
3000	8.1 ± 0.65	7.2	46	....	26	..	..
3500	29.7 ± 1.1	21	85	....	..	70	..
4000	63.3 ± 2.2	..	96.5	....	..	..	..
5000	95.7 ± 0.1	..	100	....	..	..	..

calculated dissociation constants by a factor of four. This same effect has been even more definitely demonstrated by Gibson and Heitler[21] in the case of the dissociation of iodine.

The agreement also supports the statement of Gibson and Heitler that nuclear spin effects cancel in chemical reactions and can thus be ignored. Although this factor was not ignored in the above calculation, the results above ordinary temperatures would be identical if it had been, since the limiting contribution to the free energy of both reactant and product is $-RT \ln 4$.

It is evident that the results of spectroscopy will permit the determination of chemical equilibria involving simple molecules with an accuracy not attainable by previous experimental methods.

Summary

The band spectrum data of the hydrogen molecule have been used to illustrate the exact calculation of several thermodynamic properties.

The relative amounts of ortho and para hydrogen molecules under equilibrium conditions have been given over the significant temperature range with high accuracy.

The energy contents and heat capacities of pure para hydrogen, pure ortho hydrogen, the equilibrium mixture and the mixture consisting of one part para to three parts of ortho hydrogen have been calculated over the range from 0° to 298.1°K.

The free energy of the reaction $H_2 = 2H$ has been calculated at various temperatures up to 5000°K. The equilibrium constants and percentage

[28] Saha, *Phil. Mag.*, **40**, 472 (1920).

[29] Duffendach, *Science*, **55**, 210 (1922); *Phys. Rev.*, **20**, 665 (1922).

[30] Edgar, THIS JOURNAL, **45**, 673 (1923).

[31] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 471.

[32] Wohl. *Z. Elektrochem.*, **30**, 49 (1924).

dissociation have been given and comparison has been made with the results published by others. The fractions dissociated as obtained from band spectrum data alone are shown to be in good agreement with those given by Langmuir on the basis of the amount of heat conducted from a hot filament in an atmosphere of hydrogen.

Tables of the free energy function for hydrogen have been given for temperatures up to 5000°K. These will be useful in connection with chemical reactions in which hydrogen takes part, and will be followed by the publication of similar tables for other substances.

The absolute entropy of hydrogen was found to be 33.98 calories per degree per mole. The entropy which should be given by the ordinary application of the third law of thermodynamics, including the usual Debye extrapolation below the temperatures of liquid hydrogen, is shown to be 29.59 E.U. This is in close agreement with the experimental value 29.7 or 29.6 depending on whether the equation of Berthelot or that of van der Waals, is used in correcting for gas imperfection. The theoretical value of 29.59 E.U. is obtained from the assumption that the lowest levels of ortho and para hydrogen, with their combined total of ten quantum species, are present in the solid state as a perfect solution. The relative amounts are those determined by the room temperature equilibrium of ortho and para hydrogen. This is one of the best proofs of the third law of thermodynamics.

The effect of nuclear spin on the entropies obtained from the third law has been discussed. This question is of first importance in the practical application of the third law since nearly all elements have a nuclear spin and it contributes a considerable amount of entropy. It is concluded that the portion of the absolute entropy resulting from nuclear spin will usually persist to temperatures below those at which measurements are ordinarily made. There is reason to believe that hydrogen will prove to be the one exception to the above statement but further experiments are necessary to lend weight to this.

Gibson and Heitler have shown that the effect of nuclear spin, like the isotope effect, cancels in reactions. While this is a high temperature approximation, the sense of our above statements is that a few degrees absolute is usually a sufficiently high temperature to effect cancellation. This being so the ordinary method of applying the third law automatically corrects for the neglect of nuclear spin entropy through cancellation in the chemical reaction concerned. This explains the previous successful tests of the third law.

In the case of hydrogen a few degrees or even a hundred degrees absolute is not sufficient to approach the limiting case. Thus in order to obtain an entropy value for hydrogen which may be used in combination with those obtained by the ordinary application of the third law to other substances, we may adopt the artifice of subtracting the limiting spin

entropy from the known absolute entropy, giving the value $33.98 - R \ln 4$ = 31.23 E.U.

This is in agreement with the fact that the ordinary, and incorrect, application of the third law to hydrogen has, in general led to discrepancies which would be reduced by the use of this value.

We wish to emphasize that while some uncertainty may remain as to the effect of nuclear spin on other substances, no reasonable doubt exists as to the value of the entropy of hydrogen.

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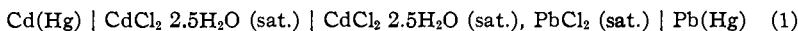[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

A STUDY OF THE CADMIUM–LEAD CHLORIDE VOLTAIC CELL[1]

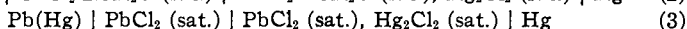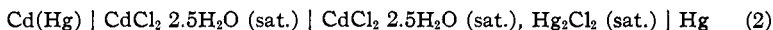BY RUDOLF J. PRIEPKE AND WARREN C. VOSBURGH

The difference between two values reported for the electromotive force of the cell

$$Cd(Hg) \mid CdCl_2 \; 2.5H_2O \; (sat.) \mid CdCl_2 \; 2.5H_2O \; (sat.), \; PbCl_2 \; (sat.) \mid Pb(Hg) \quad (1)$$

namely 0.1408 v.[2] and 0.13859 v.[3] at 25°, respectively, is too great to be attributed to experimental error.

The value for Cell 1 can be calculated from the values of the cells

$$Cd(Hg) \mid CdCl_2 \; 2.5H_2O \; (sat.) \mid CdCl_2 \; 2.5H_2O \; (sat.), \; Hg_2Cl_2 \; (sat.) \mid Hg \quad (2)$$

$$Pb(Hg) \mid PbCl_2 \; (sat.) \mid PbCl_2 \; (sat.), \; Hg_2Cl_2 \; (sat.) \mid Hg \quad (3)$$

Lipscomb and Hulett[4] found for Cell 2 the value $E_{25} = 0.67080$ v. For Cell 3 Gerke[5] found the value $E_{25} = 0.5299$ v. Calculating the electromotive force of Cell 1 from these values gives a result which agrees well with the value found by Obata. Cell 3 and the similar cell with a solid lead electrode have been studied by numerous other investigators.[6] Values calculated for Cell 1 from the results for Cell 3 obtained by some of these investigators are in better agreement with Vosburgh's value. Cells 1 and 3 have therefore been studied further.

The electromotive force–temperature curve of Vosburgh's cell shows a transition point at 26° which does not correspond to the transition point of cadmium chloride. An explanation of this was sought also.

[1] Taken from a thesis presented by Rudolf J. Priepke in partial fulfilment of the requirements for the degree of Master of Arts at Duke University in June, 1930.

[2] Obata, *Proc. Phys. Math. Soc. Japan*, [3] 3, 64, 136 (1921).

[3] Vosburgh, THIS JOURNAL, 49, 2222 (1927).

[4] Lipscomb and Hulett, *ibid.*, 38, 20 (1916).

[5] Gerke, *ibid.*, 44, 1698 (1922).

[6] (a) Babinski, Dissertation, Leipzig (1906); (b) Timofejew, *Z. physik. Chem.*, 78, 310 (1912); (c) Brönsted, *Z. Electrochem.*, 19, 754 (1913); (d) Lewis and Brighton, THIS JOURNAL, 39, 1906 (1917); (e) Günther, *Z. Electrochem.*, 23, 197 (1917); (f) Krahmer, *ibid.*, 26, 97 (1920); (g) Getman, THIS JOURNAL, 40, 611 (1918).