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ON THE ENTROPY OF HYDROGEN*

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Abstract

The entropy difference between ordinary hydrogen and hydrogen in perfect equilibrium, both in the solid phase at the absolute zero, has been calculated to be $(3/4)R \log 3+R \log 4$. This value checks the result given by Giauque and Johnston. The method is the direct evaluation along a reversible path of $\int dQ/T$ under certain idealized assumptions, using partition functions. The thermodynamical and statistical aspects are examined.

In a recent paper[1] I have indicated a theoretical way, by which the entropy difference between ordinary hydrogen and hydrogen in perfect equilibrium may be calculated. In this study I shall consider the details. With Fowler[2] I assume, that ordinary hydrogen is a mixture of para- and ortho-hydrogen in the fixed ratio 1:3, that thus transitions between para- and ortho-hydrogen do not occur in the ordinary mixture, and further, that para- and ortho-hydrogen and its different mixtures always have the same vapor pressure and the same heat of transition, so that the ratio 1:3 persists unchanged, when ordinary hydrogen is liquified or solidified. Recent experiments[3] have shown that this last assumption is not exactly true. Calculations made on these assumptions must be regarded, therefore, only as first approximations.

All earlier investigations and measurements have shown that ordinary hydrogen, gaseous, liquid or solid, may behave like a substance in true equilibrium. We now must add, provided the experiments are not continued over too long a time. One may speak of reversible quasistatic changes of state, and thus, the entropy difference of ordinary hydrogen at higher and lower temperatures can be discussed.[4] Going to rather high temperatures (above 500°C) the transition velocity becomes measurable, but at sufficiently high temperature we have again the proportion 1:3 anyway. It seems to me that there is no objection against idealizing the theory. Thus I suppose that the necessary experiments can be performed in such a short time, that the transition velocity may be regarded as negligibly small over the whole range of temperature. This concerns ordinary hydrogen.

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[1] D. Mac Gillavry, Rec. trav. chim. **49**, 348 (1930).

[2] R. H. Fowler, Proc. Roy. Soc. **A118**, 52 (1928).

[3] K. F. Bonhoeffer and P. Harteck, Zeits. f. physik. Chem. Abt. B, **4**, 113 (1929); Naturwisscnschaften **17**, 182, 321 (1929). K. Clusius and K. Hiller, Zeits. f. physik. Chem. Abt. B, **4**, 158 (1929).

[4] P. Ehrenfest and V. Trkal, Verslag. Akad. Wetenschappen Amsterdam, **28**, 906 (1920).

On the other hand one can discuss also the entropy of hydrogen in ideal perfect equilibrium. In this second case care should be taken that the experiments are extended over such a long time, that the transition velocity may be considered as extremely rapid. Or one can take advantage of suitable catalysts accelerating this transition velocity.[5]

Now, the difference between para- and ortho-hydrogen resides only in the different rotational states. But the masses of all the hydrogen molecules are equal and the distribution of translational velocities is exactly the same. Further the total entropy can always be written as the sum of the translational and the rotational entropy, disregarding at first the vibrational states. If we take gaseous ordinary and gaseous ideal hydrogen at the same temperature (and pressure), then the difference in entropy must be a difference in rotational entropy only. Also, according to the assumptions already made by Fowler (l.c.), the difference in entropy between solid ordinary and solid ideal hydrogen must be rotational entropy only; for either form the rotations in the solid phase can be described by the same partition function, which holds good for the corresponding gas phase. The rotational entropy, therefore, should be unaffected by a change in phase, if it were rigorously true, that the ratio of ortho- and para-hydrogen is not altered by a change of phase, in the case of ordinary, as well as in the case of ideal hydrogen.

In this paper I shall calculate the entropy difference at the absolute zero between the two solid forms of hydrogen (ordinary and ideal). The problem may be solved in this way. One calculates at first the rotational entropy difference between ordinary hydrogen at a very high temperature and at the absolute zero. One calculates in the same way the rotational entropy difference of ideal hydrogen at the same very high temperature and at the absolute zero. Finally one goes to the limit of infinitely high temperature. But at infinitely high temperature there is no difference between ordinary and ideal hydrogen. The distribution of energy over the rotational states becomes exactly the same at extremely high temperatures. *Therefore, the desired difference of entropy is obtained by simply subtracting the two indicated differences.* At the same time it is obvious, that one may disregard complications caused by vibrations and other mechanisms. In the neighborhood of absolute zero rotational states only are excited.

For the actual calculation we can best make use of the methods developed by Fowler. Although ordinary hydrogen is a mixture, we can omit at once the paradox term, for the ratio of the two constituents is assumed to remain exactly constant. The entropy η is related to the partition function F by the equation:[6]

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[5] K. F. Bonhoeffer and P. Harteck, reference 3. It is interesting to mention, that the catalysts, which catalyze the transitions between ortho- and para-hydrogen, also catalyze the combination of hydrogen and chlorine. Mellor in his Comprehensive Treatise on Inorganic and Theoretical Chemistry (Vol. II, page 159 top) says: "the mixed gases can be exploded by a piece of brick at 150°, while platinum black or charcoal may produce an explosion at ordinary temperature in the dark; in any case, they start the gases reacting—presumably by catalysis." Cf. Rec. trav. chim. **49,** 348 (1930).

[6] R. H. Fowler, Phil. Mag. **44,** 823 (1922).

$$\eta_2 - \eta_1 = \left| \left(R + RT\frac{d}{dT} \right) \log F \right|_1^2 . \tag{1}$$

The indices 1 and 2 indicate two states with temperature T_1 and T_2; the pressure does not influence the rotational properties of perfect gases. The partition function of ideal hydrogen is:

$$F_i = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \cdots + 3.3e^{-2\sigma} + 3.7e^{-12\sigma} + \cdots = \phi_p + \phi_o, \tag{2.1}$$

and the partition function of ordinary hydrogen is:

$$F_c = (1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \cdots)^{1/4}$$
$$\times (3.3e^{-2\sigma} + 3.7e^{-12\sigma} + \cdots)^{3/4} = \phi_p^{1/4} \cdot \phi_o^{3/4}; \tag{2.2}$$

and where ϕ_p is the partition function for para-hydrogen:

$$\phi_p = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \cdots \tag{3.1}$$

and ϕ_o is the partition function for ortho-hydrogen:

$$\phi_o = 3(3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-30\sigma} + \cdots). \tag{3.2}$$

$$\sigma = h^2/8\pi^2 IkT.$$

where h is the constant of Planck, k the constant of Boltzmann, I the moment of inertia. Thus, we have to form the expression:

$$\eta_c^* - \eta_i^* = \{\eta_c(0) - \eta_c(\infty)\} + \{\eta_i(\infty) - \eta_i(0)\}$$
$$= \lim_{T_2=\infty} \lim_{T_1=0} \left\{ - \left| R\left(1 + T\frac{d}{dT}\right) \log F_c \right|_1^2 + \left| R\left(1 + T\frac{d}{dT}\right) \log F_i \right|_1^2 \right\}. \tag{4}$$

The indices c and i indicate ordinary and ideal hydrogen respectively.

That the substitution of F_i for ideal hydrogen and of F_c for ordinary hydrogen in formula (1) gives correct results, can be proved also with the general theorems given by Fowler in his monograph on "Statistical Mechanics." One finds on page 129 the theorem: that any particular species of free molecule contributes to the characteristic function of Planck:

$$k\overline{M}\left\{ \log \frac{F(T)}{\overline{M}} + 1 \right\}, \tag{5}$$

where $\overline{M}$ is the average number present in the specified equilibrium state.[7] One gets the entropy from Planck's characteristic function by applying the operator $(1 + T\, d/dT)$. Thus any entropy difference of ideal hydrogen, for instance, is given by:

$$\frac{\eta_{i_2} - \eta_{i_1}}{R} = \left| \left(1 + T\frac{d}{dT}\right) \left(\log \frac{F_i}{N} + 1 \right) \right|_1^2$$

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[7] Combination of the two theorems on page 128 and 129.

$$= \left|\left(1 + T\frac{d}{dT}\right)\log F_i\right|_1^2 + \left|\log\frac{1}{N} + 1\right|_1^2$$

$$= \left|\left(1 + T\frac{d}{dT}\right)\log F_i\right|_1^2, \tag{1}$$

then $\overline{M}$ here equals N, Avogadro's number, if we employ molar entropies.

It may be instructive to interpret ideal hydrogen also as a mixture of para- and ortho-hydrogen, between which two forms equilibrium has been established. One verifies easily that:[8]

$$\overline{M}_{pi} = \frac{\phi_p}{\phi_p + \phi_o} \times N \quad \text{and} \quad \overline{M}_{oi} = \frac{\phi_o}{\phi_p + \phi_o} \times N. \tag{6}$$

We first get:

$$\frac{\eta_{i_2} - \eta_{i_1}}{R} =$$

$$\left|\left(1 + T\frac{d}{dT}\right)\left\{\frac{\phi_p}{\phi_p + \phi_o}\left(\log\frac{\phi_p}{\overline{M}_{pi}} + 1\right) + \frac{\phi_o}{\phi_p + \phi_o}\left(\log\frac{\phi_o}{\overline{M}_{oi}} + 1\right)\right\}\right|_1^2,$$

which becomes:

$$\left|\left(1 + T\frac{d}{dT}\right)\left\{\frac{\phi_p}{\phi_p + \phi_o}\log F_i + \frac{\phi_o}{\phi_p + \phi_o}\log F_i\right\}\right|_1^2$$

$$+ \left|\left(1 + T\frac{d}{dT}\right)\left\{\frac{\phi_p}{\phi_p + \phi_o}\left(\log\frac{1}{N} + 1\right) + \frac{\phi_o}{\phi_p + \phi_o}\left(\log\frac{1}{N} + 1\right)\right\}\right|_1^2$$

$$= \left|\left(1 + T\frac{d}{dT}\right)\log F_i\right|_1^2. \tag{1}$$

The functions ϕ_p and ϕ_o depend on the temperature T.

I leave it to the reader to derive in an analogous way the formula for the entropy differences of ordinary hydrogen. I recall only that the concentrations of the para- and the ortho-forms now have the constant values:

$$(\overline{M}_p)_c = \lim_{T=\infty}(\overline{M}_p)_i = \lim_{T=\infty}\frac{\phi_p}{\phi_p + \phi_o}N = \frac{1}{4}N, \tag{7.1}$$

$$(\overline{M}_o)_c = \lim_{T=\infty}(\overline{M}_o)_i = \lim_{T=\infty}\frac{\phi_o}{\phi_p + \phi_o}N = \frac{3}{4}N. \tag{7.2}$$

The omission of the paradox terms from the two terms of equation (4) is legitimate, since they cancel if they are not omitted.

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[8] Cf. R. H. Fowler, Statistical Mechanics, p. 30 formula (51), or p. 106 formulae (310) and (311).

Equation (4) represents exactly

$$\int \frac{dQ}{T} = \int d\eta = \int \frac{c_r}{T} dT,$$

the integral taken along the reversible way examined in this study. It must be possible to check the theory experimentally step by step, measuring heat capacities, as is always done. From the thermodynamical arguments used thus far it is evident, that no further term has to be added to the two terms of equation (4).

Now, we regroup the terms of expression (4) in a more convenient way, omitting the indices 1 and 2:

$$\frac{\eta_c^* - \eta_i^*}{R} = \lim_{T=0}\left(1 + T\frac{d}{dT}\right)\log\frac{F_c}{F_i} - \lim_{T=\infty}\left(1 + T\frac{d}{dT}\right)\log\frac{F_c}{F_i}\cdot \qquad (4a)$$

We introduce two new functions, defined by the equations:

$$\phi_o = e^{-2\sigma}\phi_o',$$

$$F_c = (e^{-2\sigma})^{3/4}F_c' = e^{-3\sigma/2}F_c';$$

and we substitute F_c' in the first term of (4a), noticing that always:

$$\left(1 + T\frac{d}{dT}\right)\log e^{-a/T} = \left(1 + T\frac{d}{dT}\right)\left(-\frac{a}{T}\right) = -\frac{a}{T} + \frac{a}{T} = 0;$$

thus:

$$\frac{\eta_c^* - \eta_i^*}{R} = \lim_{T=0}\left(1 + T\frac{d}{dT}\right)\log\frac{F_c'}{F_i} - \lim_{T=\infty}\left(1 + T\frac{d}{dT}\right)\log\frac{F_c}{F_i}\cdot$$

I will give the results at once:

$$\lim_{T=0}\log\frac{F_c'}{F_id} = \log 1^{1/4}\cdot 9^{3/4} = \log 9^{3/4}; \qquad (8.1)$$

$$\lim_{T=0} T\frac{d}{dT}\log\frac{F_c'}{F_i} = 0; \qquad (8.2)$$

$$\lim_{T=\infty}\log\frac{F_c}{F_i} = \log\left(\frac{1}{4}\right)^{1/4}\left(\frac{3}{4}\right)^{3/4}; \qquad (8.3)$$

$$\lim_{T=\infty} T\frac{d}{dT}\log\frac{F_c}{F_i} = 0. \qquad (8.4)$$

Thus:

$$\eta_c^* - \eta_i^* = R\log 9^{3/4} - R\log\left(\frac{1}{4}\right)^{1/4}\left(\frac{3}{4}\right)^{3/4} = \frac{3}{4}R\log 3 + R\log 4. \qquad (9)$$

The mathematical material, necessary for the justification of equations (8), has already been furnished by Fowler.[9]

This analysis is sound from a thermodynamical standpoint. However, a statistician may ask, does expression (4) really represent the desired entropy difference? Should not a third term be added? At higher temperatures ordinary and ideal hydrogen have the same internal energy and the same specific heat of rotation. At one time it has been supposed that transitions were prohibited, and at a later time it has been supposed that transitions do occur. Does not this different viewpoint necessitate a third term? Let us now add a third term, representing the entropy difference arising from those two viewpoints:

$$\eta_c(\infty) - \eta_i(\infty),$$

using again the most general theorems; then the operator

$$\mathrm{Lim}_{T=\infty} R(1 + T d/dT)$$

has to work on the expression:

$$\frac{1}{4}\left(\log\frac{\phi_p}{N/4} + 1\right) + \frac{3}{4}\left(\log\frac{\phi_o}{3N/4} + 1\right) - \left(\log\frac{F_i}{N} + 1\right)$$

$$= \log \phi_p{}^{1/4}\phi_o{}^{3/4} - \log\left(\frac{1}{4}\right)^{1/4}\left(\frac{3}{4}\right)^{3/4} + \left(\log\frac{1}{N} + 1\right) - \log F_i - \left(\log\frac{1}{N} + 1\right)$$

$$= \log\frac{F_c}{F_i} - \log\left(\frac{1}{4}\right)^{1/4}\left(\frac{3}{4}\right)^{3/4}.$$

The application of the operator $\lim_{T=\infty} R(1 + T\, d/dT)$ yields zero,[10] in accordance with the thermodynamical considerations.

We may consider hydrogen as a mixture, if the experiments do not take much time, and we may consider hydrogen as a single gas, if we always wait a sufficiently long time. The entropy of hydrogen in equilibrium at higher temperatures can not depend on the length of time we keep it in a vessel. The equality can only be obtained in statistics by inserting the appropriate paradox terms (logarithmic terms), and for hydrogen considered as a mixture, and for hydrogen considered as a single gas; then the term representing the difference vanishes. Here we have a case, that a mixed gas has the same entropy as a single gas (see below).

Let us now consider the analysis more carefully. From thermodynamical considerations two terms have arisen:

$$\eta_c(0) - \eta_c(\infty) \quad \text{and} \quad \eta_i(\infty) - \eta_i(0).$$

To complete the argument from a statistical standpoint a third term has been added:

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[9] One may refer concerning the limits (8.1) and (8.2) to Proc. Roy. Soc. **A118**, 52 (1928), and concerning the limits (8.3) and (8.4) to Statistical Mechanics p. 52, 53, and also Phil. Mag. **45**, 11 (1923).

[10] See equations (8.3) and (8.4).

$$\eta_c(\infty) - \eta_i(\infty).$$

In this way we have come to the equation:

$$\eta_c^* - \eta_i^* = \eta_c(0) - \eta_i(0) = \{\eta_c(0) - \eta_c(\infty)\} + \{\eta_c(\infty) - \eta_i(\infty)\} + \{\eta_i(\infty) - \eta_i(0)\},$$

which is trivial mathematically. It is obvious, that the mathematical calculation can at once be shortened in just this way, provided the general theorems are applied throughout. Therefore, we get:

$$\frac{\eta_c(0) - \eta_i(0)}{R} = \lim_{T=0}\left(1 + T\frac{d}{dT}\right)\left\{\frac{1}{4}\left(\log\frac{\phi_p}{N/4} + 1\right) + \frac{3}{4}\left(\log\frac{\phi_o}{3N/4} + 1\right) - \left(\log\frac{F_i}{N} + 1\right)\right\}$$

$$= \lim_{T=0} \log\frac{F_c'}{F_i} - \frac{1}{4}\log\frac{1}{4} - \frac{3}{4}\log\frac{3}{4} \cdot \qquad (10)$$

Giauque and Johnston[11] give for this quantity

$$\eta_c^* - \eta_i^* = R\left(-\frac{1}{4}\log\frac{1}{4} - \frac{3}{4}\log\frac{1}{12}\right) = \frac{3}{4}R\log 3 + R\log 4, \qquad (9a)$$

which is exactly our value. They consider ordinary hydrogen at the absolute zero as a mixture of para-hydrogen and of nine species of ortho-hydrogen, in accordance with the weight factor 3×3 of the lowest ortho-state. Although our final result is the same, Giauque and Johnston's interpretation of quantity (9a) as a paradox term does not seem *a priori* plausible. We do not compare ordinary hydrogen with the total of the separated constituents, but with 100% para-hydrogen. The conception of nine species of ortho-hydrogen is confined to the absolute zero, whereas our analysis, following Fowler, is generally applicable.

Fowler[12] gives the quantity $(3/4)R \log 9$, which value is not confirmed by the above given analysis. In fact, only the first term of expression (9) is given by Fowler. The second term, a paradox term, has resulted from our general *uniform* analysis. *This paradox term is intrinsic to entropy.* Its significance for diffusion problems constitutes only a special case.

In the monograph on Statistical Mechanics, page 163, one weight factor 3 is retained as an experiment, i.e., a correction $(3/4)R \log 3$ is used. The argument is, that nuclear weights must pursue hydrogen through all its combinations. If a nuclear spin accompanies hydrogen in all compounds, then I prefer to apply the full correction (9) to hydrogen and separate corrections to its combinations.

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[11] W. F. Giauque and H. L. Johnston, J. Am. Chem. Soc. **50**, 3221 (1928).

[12] R. H. Fowler, Proc. Roy. Soc. **A118**, 52 (1928).