THE ENTROPY OF HYDROGEN

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If the entropy of hydrogen is calculated directly from the thermal data a value of slightly less than 15.0 is obtained for the entropy of $^1/_2$ H_2. The value obtained indirectly from the equilibrium between hydrogen, oxygen and water is between 15 and 16 entropy units. The discrepancy between these two values has not caused much concern because it could be easily accounted for by uncertainties in the thermal data at low temperatures.

Now that it has been demonstrated by Bonhoeffer and Harteck[1] and by Eucken[2] that hydrogen is a mixture of two kinds of molecules which transform into each other so slowly that equilibrium will only be attained after a long period at low temperatures, the problem takes on a new aspect. It is obvious that the thermal data previously obtained at low temperature apply to a non-equilibrium mixture and that a higher value would in all probability be obtained for the entropy if the specific-heat measurements were made upon hydrogen which had been kept at low temperatures for a long time. R. H. Fowler[3] and Giauque and Johnston[4] have speculated at some length on the question. Fowler questions the applicability of the third law to what he calls a metastable state of hydrogen. The term metastable does not seem to be appropriate here. Monoclinic sulfur at 0°K. is metastable and presumably has zero entropy, but hydrogen is a mixture of two kinds of molecules which approach statistical equilibrium slowly.

Giauque and Johnston consider that there are ten varieties of molecules present at low temperatures and that the entropy should be increased by the entropy of mixing these varieties. It seems doubtful if the entropy of a system of molecules which is not in statistical equilibrium can be calculated from *a priori* considerations.

The important point is, however, that from the standpoint of thermodynamics there are not ten varieties or even two varieties of hydrogen molecules so long as we deal with an equilibrium mixture of hydrogen. It is not necessary to take account of this equilibrium, any more than it is necessary to consider the various kinds of molecules present in liquid water, when we calculate the thermodynamic properties of that substance. It is only necessary to be sure that the equilibrium is attained. Fowler appears to think that this condition offers practical difficulties but as a matter of fact all of the reactions of hydrogen take place with the equilibrium mixture and it is only in the measurement of the thermal properties at low temperatures that precautions must be taken to obtain equi-

librium. The two kinds of molecules differ presumably only in the possession of even and odd states of rotational energy, the odd states having a common weight factor of three as compared to the even states. This difference may be due to the orientation of nuclear spins but the coupling of the nuclear spins is presumably so weak that no differences would be observed in the thermodynamic properties of the two kinds of hydrogen, except, of course, the difference in the rotational heat capacities at low temperatures. We should, therefore, need only to determine the heat capacity of hydrogen gas under equilibrium conditions in order to calculate the correct value of the entropy, since the stable phase at low temperature consists entirely of molecules in the zero rotational state with unit weight, so that no difficulties will be encountered in the application of the third law. This, of course, is true only on the assumption that the thermodynamic properties of the condensed phases will show only "second order" effects with the change in relative amounts of the two varieties of molecule. The measurements of Eucken on the heat capacity of the gas which has been held for a time at low temperature indicate that a considerably higher value will be obtained for the entropy from these measurements.

However, it should not be necessary to make any heat capacity measurements at all, or any assumptions as to the thermal properties of the solid and liquid states in order to calculate the correct value for the entropy of hydrogen. Since hydrogen gas at low temperatures consists entirely of molecules in the zero rotational state, its entropy will be that of a monatomic gas of atomic weight 2.016. The entropy at 298°K. will be obtained by adding the integral $\int C_p d \ln T$ over the proper temperature range. The heat capacity may be separated into a constant term $5/2R$ and the rotational term C_r.

The integral $\displaystyle\int_0^T C_r d \ln T$ is $\dfrac{E_r}{T} + R \ln \sum$.

Where E_r is the total rotational energy per mol and $\sum$ is the series

$$1 + 9e^{-2\sigma} + 5e^{-6\sigma} + 21e^{-12\sigma} + \ldots.$$

$$\text{Where } \sigma = \frac{h^2}{8\pi^2 I k T}$$

C_r is the heat capacity that would be obtained experimentally by heating the equilibrium mixture of hydrogen very slowly or in the presence of a catalyst. Using the value $I = 0.480 \times 10^{-40}$ we obtain for the entropy of $^1/_2$ H_2 at 298 the value 17.0.

Apparently the integral $\displaystyle\int_0^T C_r d \ln T$ contains all of the "symmetry" factors[5] that need to be considered since it leads at high temperatures to the formula given by Fowler[6] for the chemical constant of a diatomic

gas. This comes about because for an elementary diatomic molecule half the rotational levels are missing so that while the energy and heat capacity at high temperatures are not affected, the term $\sum$ contains the factor $1/2$ which is usually designated as the symmetry factor. The value 17.0 is somewhat higher than the values obtained by Fowler and by Giauque and Johnston from their considerations of the 3 to 1 mixture.

It remains to be considered whether this value can be brought into agreement with the equilibrium data for reactions in which hydrogen takes part. Fowler assumes that agreement can be obtained only by adding hitherto unsuspected weight terms to the entropies of hydrogen compounds. This may very well be, but the prediction may be hazarded that these added terms will turn out to be corrections in the thermal data.

As a matter of fact there are no reactions involving hydrogen in which the equilibrium data and all of the thermal quantities are known with sufficient exactness to determine the entropy of hydrogen with an uncertainty of less than one or two entropy units. It is not certain as yet that the third law as stated by Lewis and Gibson[7] fails in the case of hydrogen.

[1] Bonhoeffer and Harteck, *Naturwissenschaften*, **11**, 182, 1929.

[2] Eucken, *Ibid.*, **11**, 182, 1929.

[3] R. H. Fowler, *Proc. Roy. Soc.*, **118A**, 52, 1929.

[4] Giauque and Johnston, *J. Am. Chem. Soc.*, **50**, 3221, 1928.

[5] Gibson and Heitler, *Zeit. Physik*, **49**, 465, 1928.

[6] *Statistical Mechanics*, 147 Cambridge Press, 1929.

[7] Lewis and Gibson, *J. Am. Chem. Soc.*, **42**, 1529, 1920.

IRREVERSIBLE TRANSFORMATIONS OF ORGANIC COMPOUNDS UNDER HIGH PRESSURES

(*Preliminary Paper*)

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The observation was made some years ago that egg white was coagulated by the application of a pressure of 5000–7000 atm. for 30 minutes.[1] The present investigation was undertaken in order to discover what other types of essentially irreversible organic transformations could be brought about by the application of pressures greater than 3000 atmospheres, and to study in more detail the effect of pressure on protein solutions. We have as yet tried but relatively few of the many substances and mixtures