

5. Attention is called to the possible formation of acetic acid by reaction in the cold of liquid nitrogen peroxide with small amounts of higher hydrocarbons present in the methane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

SYMMETRICAL AND ANTISYMMETRICAL HYDROGEN AND THE THIRD LAW OF THERMODYNAMICS. THERMAL EQUILIBRIUM AND THE TRIPLE POINT PRESSURE

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The suggestion of Heisenberg¹ that hydrogen and other homopolar molecules exist in two forms, symmetrical and antisymmetrical, offers the most satisfactory explanation for the alternating intensity observed in the band spectra of these substances. This suggestion has been used by Dennison² to explain the heat capacity of hydrogen gas over the low temperature range in which it is taking up its rotational degrees of freedom. Dennison's theoretical curve is the first one of a large number offered by various authors which has agreed with the experimental heat capacity data within the limit of error.

A physical conception of symmetry and antisymmetry in the hydrogen molecule arises from the assumption of nuclei which may spin on their own axes. When the two spinning protons oppose each other, the molecule is symmetrical; when their angular momentum is additive, it is antisymmetrical. The statistical weight of the latter variety is increased by the factor three, since a total spin of $j = 1$, one-half unit for each proton, is assumed, and the *a priori* probability p is as usual taken equal to $(2j + 1)$. The symmetrical form takes up only the even rotation states $j = 0, 2, 4, 6, \dots$, while the antisymmetrical assumes the rotation states $j = 1, 3, 5, \dots$

In order to explain the heat capacity of hydrogen, Dennison found it necessary to assume that the transitions between symmetrical and antisymmetrical states are so rare that they do not occur appreciably during the experimental determination of heat capacity. Dennison's assumptions are supported by the band spectra data and interpretation of Hori.³ Birge⁴ has shown that Hori's data lead to a value of 0.480×10^{-40} g. cm.² for the moment of inertia of the hydrogen molecule in its normal state. Hori gave 0.467×10^{-40} as the value which the molecule would have if it lost its last half unit of vibration. This latter value should not be used

¹ Heisenberg, *Z. Physik*, **41**, 239 (1927).

² Dennison, *Proc. Roy. Soc.*, **115A**, 483 (1927).

³ Hori, *Z. Physik*, **44**, 834 (1927).

⁴ Birge, *Proc. Nat. Acad. Sci.*, **14**, 12 (1928); *Nature*, Jan. 28, 1928.

for heat capacity calculations. Dennison found 0.464×10^{-40} from the heat capacity data available to him. Cornish and Eastman⁵ found 0.475×10^{-40} from their own heat capacity measurements previously to the calculation of Birge. Condon⁶ has found from a purely theoretical calculation of the hydrogen molecule problem that 0.426×10^{-40} is a rough value of the moment of inertia and is definitely a lower limit. This would be increased to 0.44×10^{-40} g. cm.² when one-half unit of vibration in the normal state is considered.

Shortly after the publication of Dennison's paper, Dr. E. U. Condon communicated with this Laboratory in the hope that experimental work on the heat capacity of hydrogen gas carried out by Cornish and Eastman⁵ might be extended to include a very direct test of Dennison's idea. Condon's suggestion was based on the assumption that hydrogen gas, kept at the temperature of liquid air for sufficient time, might be expected to change from about one-fourth symmetrical to nearly all symmetrical. Subsequent determination of the heat capacity would, if the transition occurred, show a markedly different heat capacity, as may be seen from the computations in Dennison's paper. Unfortunately, the apparatus of Cornish and Eastman had been completely dismantled shortly before the arrival of Condon's letter. However, in connection with the study of the entropies of gases being carried out in this Laboratory, we have apparatus in which it is a comparatively easy matter to measure the vapor pressure of hydrogen. Also, the problem of keeping a considerable quantity of hydrogen gas at the temperature of liquid air for a long period presented little difficulty since large quantities of liquid air are always kept on hand. It seemed worth while to measure the vapor pressure of hydrogen which had been kept at a low temperature for a considerable period of time. The mean life of the transition has been estimated by Heisenberg at about three weeks. Condon suggested that two or three months at liquid air temperature might be expected to produce a considerable change.

Apparatus.—A steel container holding about ten moles of gas at a pressure of seventy-five atmospheres and a temperature of about 85°K. was filled with pure hydrogen, prepared by electrolysis and purified by means of a nickel catalyst until the oxygen present by diffusion was reduced to about 0.01%. The container was suspended in a Pyrex glass Dewar tube by means of a steel capillary tubing of very small bore and 45 cm. long which served as an inlet and outlet for the gas. The Dewar tube was approximately 90 cm. long and 11 cm. inside diameter. The liquid air required was about four liters every two days.

The vapor pressure measurements were carried out in the apparatus previously used by Giauque, Johnston and Kelley⁷ for measurements of the vapor pressure of hydrogen and of oxygen. The description of this apparatus has been given by Giauque and

⁵ Cornish and Eastman, *THIS JOURNAL*, 50, 627 (1928).

⁶ Condon, *Proc. Nat. Acad. Sci.*, 13, 466 (1927).

⁷ Giauque, Johnston and Kelley, *THIS JOURNAL*, 49, 2367 (1927).

Wiebe.⁸ The hydrogen was withdrawn from the container through a sensitive needle valve.

Vapor Pressure of Hydrogen.—It was thought desirable to measure the vapor pressure of ordinary hydrogen shortly before making the measurements on the material which had been kept cold, so this was done. While it seemed improbable that the process of crystallization would in any way affect the relative amounts of symmetrical and antisymmetrical molecules, this was investigated by measuring the vapor pressure of the liquid both before and after solidification. The measurements, made at 53.7 cm. pressure, agreed to better than 0.01°. The triple point pressure of the ordinary hydrogen measured on May 1, 1928, was 5.383 international cm., while the reading on the gold resistance thermometer was 83.417 ohms.

The special hydrogen was kept at the temperature of liquid air from October 19, 1927, to May 3, 1928, a total of 197 days. In order to introduce the hydrogen into the apparatus, it was necessary to pass through a section of tubing at room temperature. The rate of transfer of the gas was such that it was kept at room temperature for approximately fifteen seconds. It was immediately obvious during the course of the observations that any difference which might exist was extremely small, so further efforts were concentrated on the triple point pressure.

The measurements on the special hydrogen are given in Table I. In the first column, the approximate percentage of the material melted is given. It will be noticed that the pressure was higher when a large amount of liquid was present. The reason appeared to be superheating of the liquid

TABLE I
TRIPLE POINT PRESSURE OF SPECIAL HYDROGEN
May 3, 1928

Percentage melted	Pressure, international cm. of Hg	Resistance thermometer, ohms
15	5.338	83.411
50	5.334	83.411
70	5.360	83.412
95	5.392	83.414
Melted, then cooled below triple point. Heated		
15	5.344	83.413
50	5.344	83.413
85	5.380	83.412
Melted, then cooled below triple point. Heated		
90	5.364	83.411
Increased heat leak by 150%		
90	5.408	83.412
Accepted values	5.34	83.412

⁸ Giauque and Wiebe, *THIS JOURNAL*, 50, 101 (1928).

near the surface, due to heat leak from above. The last two observations listed in Table I were designed to decide this question. With most of the material melted, a measurement was made; then with no other change the heat leak was increased about 150% by raising the temperature of the surroundings a few degrees. The next measurement showed the expected increase in pressure. It appears to be very difficult to avoid a slight superheating of the hydrogen and we suspect that the deviations of various previous observers may be due largely to this effect. The heavy gold walls of the container with the interior gold vanes were apparently unable to prevent a surface heating effect of the order of one-hundredth of a degree necessary to explain the increase in pressure. For this reason we have not considered any measurements where more than half of the hydrogen was melted and take the triple point pressure of the special hydrogen as 5.34 cm.

The surface heating effect made it desirable to repeat the measurements on ordinary hydrogen with greater care, especially since we had not recorded the percentage melted in that case. The results of these measurements are given in Table II. The third and fourth measurements were designed to demonstrate the surface heating in a second manner. With about 85% of the material melted, some of the hydrogen was evaporated from the surface by means of a pump. A reading taken immediately after this agreed with the previous results, but on standing for fifteen minutes the pressure had risen to a considerably higher value.

TABLE II
TRIPLE POINT PRESSURE OF ORDINARY HYDROGEN
May 30, 1928

Percentage melted	Pressure, international cm. of Hg	Resistance thermometer, ohms
<1	5.391	83.417
15	5.394
Melted 85% and evaporated some by reduced pressure		
85	5.390	83.417
Fifteen minutes after the surface evaporation		
85	5.440
Accepted values	5.39	83.417

The value previously obtained by Giauque, Johnston and Kelley⁷ was 5.37 cm. The present determinations of 5.38 and 5.39 cm. seem to indicate that the triple point pressure of ordinary hydrogen is 5.38 ± 0.01 cm. This is in good agreement with the 5.382 cm. value of Onnes and Braak⁹ and the 5.38 cm. value of Simon and Lange.¹⁰ Henning¹¹ has recently ob-

⁹ Onnes and Braak, *Comm. Phys. Lab. Univ. Leiden*, 1926, 184.

¹⁰ Simon and Lange, *Z. Physik*, 15, 312 (1923).

¹¹ Henning, *ibid.*, 40, 775 (1926).

tained a value of 5.486 cm. as a result of four experiments varying from 5.480 to 5.495 cm. The 5.34 cm. value of the triple point pressure of the special hydrogen is lower than any value obtained for ordinary hydrogen. The 0.005-ohm difference on the resistance thermometer, which is not very sensitive at this temperature, indicates that the triple point temperature of the special hydrogen was 0.04° lower than that of ordinary hydrogen. We do not feel that we can claim with certainty that a difference exists but the apparent difference is beyond the limit of any error of which we are aware. The greater part of the hydrogen remains and is being kept cold. We hope to make further observations on its properties at a considerably later date.

The Entropy Effect Due to Symmetrical and Antisymmetrical Hydrogen

Heisenberg¹ in suggesting the presence of more than one kind of hydrogen mentioned an effect on the entropy as a consequence. Fowler¹² has recently considered the manner in which the statistical calculation of the entropy of hydrogen gas must be modified by the recognition of the two forms. However, in making this same calculation we are unable to arrive at the same result. It appears that Fowler's calculation amounts to having considered the entropy of symmetrical and of antisymmetrical hydrogen individually, but has omitted the entropy of mixing of the two. We cannot be sure from his statements that this has not been done intentionally, but, if so, we can see no reason for it.

We consider the matter as follows. Let us assume that the ratio of symmetrical to antisymmetrical molecules is one to three and that the gas has been cooled to a temperature at which it is acting in the manner of a monatomic gas. The statistical weight of the symmetrical variety is unity while the weight of the antisymmetrical molecules is nine; that is, one-quarter of the gas consists of one kind of molecules and the other three-quarters is divided between nine varieties which arise from the consideration that the unit of momentum of the combined nuclei gives rise to three orientations which are themselves distributed between the three additional orientations arising from the molecular rotation which the antisymmetrical variety retains in its lowest rotation state. The entropy of such a mixture should exceed the entropy of a monatomic gas merely by the entropy of mixing of the ten varieties. Therefore, $\Delta S = -\frac{1}{4} R \ln \frac{1}{4} - \frac{3}{4} R \ln \frac{1}{12} = 4.39$ cal./deg. per mole. Thus 4.39 E. U. must be added to the value obtained from the Sackur equation. Fowler found $\frac{3}{2} R \ln 3 = 3.27$ E. U.

The assumption of an exact one-to-three ratio between the two forms of hydrogen is open to question on two grounds: first, the true equilibrium at room temperature would favor the symmetrical form by several per

¹² Fowler, *Proc. Roy. Soc.*, **118A**, 52 (1928).

cent. if the various rotational energy levels represent the only energy differences between the two forms; second, it is not known that there is not an energy difference between the two forms in addition to that accompanying the rotation change. The alternating lines of the band spectra fall in a smooth series, showing as would be expected that the molecular dimensions are not appreciably different; however, this does not, in itself, eliminate the possibility of a sufficient energy of transition to modify the one-to-three ratio considerably. The band spectra intensity determinations are not very accurate. Dennison's² limits of 1:3.5 and 1:2.7 obtained from the heat capacity data are the best experimental indication that the coupling energy is small. The entropy effect corresponding to the above limits is 4.45 E. U. and 4.34 E. U., respectively. Therefore, if Dennison's interpretation of the behavior of hydrogen is correct, we must add 4.39 ± 0.06 cal./deg. per mole to the entropy as given by the Sackur equation or by the ordinary application of the third law.

It has long been generally recognized that the entropy of hydrogen, as given by the direct application of the third law of thermodynamics in the ordinary manner, is lower than the value obtained indirectly from this law. Fowler notes that his 3.27 E. U. increase is rather too large an addition. We agree with this and our calculated amount of 4.39 E. U. is no improvement from this point of view. The only apparent alternative to assuming the non-existence of antisymmetrical hydrogen is to adopt the suggestion of Fowler that the products of reactions in which hydrogen is consumed must also have the antisymmetrical property.

Fowler calls attention to the failure of the Nernst heat theorem for such a substance as hydrogen, but states that the theorem would be true in this case if true equilibrium were attained since there is but one form of the symmetrical state. This question of true equilibrium between the various molecular species of a pure substance was the principal point which led Lewis and Gibson¹³ to question the Nernst heat theorem and to make a restatement of the entropy principle which they have called the third law of thermodynamics. We believe that true equilibrium in any system must lead to an ordered crystalline state at the absolute zero of temperature and it is only to this perfect crystalline state, "lacking any sort of randomness," that Lewis and Gibson have assigned zero entropy.

We should like to call attention to a point that has apparently not previously been recognized, namely, that true equilibrium, even in a solution of isotopes, would, in the absence of any specific effect due to nuclear differences, lead to complete separation of the various components at the absolute zero, as may be shown by the thermodynamic equation¹⁴

¹³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, Chapter XXXI.

¹⁴ Ref. 13, page 244.

$$\frac{dN_1}{dh} = \left(\frac{W\bar{V}_1}{V} \right) - W_1 \frac{N_1 g}{RT}$$

obtained for a perfect solution. h is the height, g the acceleration of gravity; W and V the molal mass and volume, respectively, of the solution, and N_1 , W_1 and \bar{V}_1 the mole fraction, molal mass and partial molal volume, respectively, of component one. The existence of some specific force due to nuclear differences would, of course, in itself, suffice to eliminate randomness either by separation into phases or specific combination as the temperature approached the absolute zero. The above-described processes are, of course, experimentally unrealizable, but we wish to clearly distinguish between the truth of the third law of thermodynamics and our experimental difficulties in using it directly.

It is becoming apparent that there are, perhaps, many substances in which the attainment of equilibrium is so slow as to interfere with the practical application of the third law without recognition of sources of entropy which do not appear from the measurement of heat capacity alone.

The entropy effect due to orientations arising from unbalanced angular momentum of electronic systems has been discussed by Schottky,¹⁵ and by one of us.¹⁶

In the case of this large group of substances, the practical difficulty in obtaining the entropy from heat capacity measurements alone may be due not only to lack of equilibrium but to the fact that transformation to a single orientation by existing magnetic and electrical fields would occur at temperatures below those experimentally practicable. The behavior of pure antisymmetrical hydrogen, could it be obtained, would be analogous to the above case.

Summary

The triple point pressure of ordinary hydrogen has been found to be 5.38 ± 0.01 cm.

The triple point pressure of hydrogen which had been kept at the temperature of liquid air for 197 days was 5.34 cm. The difference between the two values is small, but we know of no source of experimental error that would account for it.

The experiment was carried out to obtain information concerning the existence of symmetrical and antisymmetrical hydrogen and the extremely slow transition rate believed to exist between the two forms. No large difference in pressure was anticipated. We have regarded the experiment as one that could give evidence for but not against the existence of the two forms.

¹⁵ Schottky, *Physik. Z.*, **22**, 1 (1921); **23**, 9 (1922).

¹⁶ Giauque, *THIS JOURNAL*, **49**, 1870 (1927).

It has been calculated that the entropy effect due to the existence of the two forms of hydrogen would be 4.39 ± 0.06 cal./deg. per mole. This amount must be added to that given by the Sackur equation or to that given by the ordinary application of the third law of thermodynamics. It does not appear possible to reconcile this addition with third law data unless a similar consideration, not necessarily leading to the same amount, is applied to molecules containing hydrogen. These effects may be expected in many, if not most, of the other elements.

We believe that any system approaches zero entropy as the absolute zero of temperature is approached when true equilibrium exists in the distribution of energy between such energy states as are actually occupied by the system. As a particular example, the cooling of a solution of isotopes is considered. Our conclusions are in complete agreement with the third law of thermodynamics as stated by Lewis and Gibson, although we recognize additional difficulties in the application of this law.

We wish to emphasize the distinction between the exactness of the third law of thermodynamics and our experimental inadequacy in using it directly.

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EQUILIBRIUM BETWEEN ALUMINUM CARBIDE AND NITROGEN AT HIGH TEMPERATURES

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Plan of the Investigation

The present work is a continuation of a program of research in the field of high-temperature equilibria involving the extension of our previous methods to cover a region of very low pressures. Measurements have been made of equilibrium pressures from 0.0016 mm. to 0.017 mm. at temperatures from 1774°K. to 1909°K. The McLeod gages now in use would cover the range up to 5 mm. The manometer technique previously devised has been used at pressures from 3 cm. to 2.3 atmospheres and at temperatures up to 2500°K. So the combined methods seem applicable to pressures differing by a factor of a million and at temperatures from 1000°K. to 2500°K. The most significant region probably lies above 1500°K. where more conventional technique is inapplicable.

The subject of the present work is the equilibrium of the system aluminum carbide, nitrogen, aluminum nitride and carbon. The equilibrium pressure of nitrogen may be approximately predicted by combining the

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