tion of the ammonium phosphomolybdate precipitate, solution of this in ammonium hydroxide, reduction to molybdenum trichloride by hydrochloric acid and zinc in an air-free atmosphere and titration to molybdenum pentachloride with a standard solution of methylene blue, on the assumption that the ammonium phosphomolybdate has the normal composition, $(NH_4)_3PO_4 . 12MoO_3 + nH_2O$.

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THE DISSOCIATION OF MOLECULAR HYDROGEN, FROM THE ENTROPIES OF DIATOMIC AND MONATOMIC HYDROGEN

BY GRAHAM EDGAR

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The extent of dissociation of the hydrogen molecule into atoms at high temperatures, and the heat of dissociation, are quantities of considerable interest, particularly from their bearing on the Bohr theory of the structure of the hydrogen molecule.

Langmuir, as the result of deductions from the behavior of hydrogen surrounding a heated tungsten filament, calculated[1] somewhat indirectly the heat of dissociation to be —136,000 cal. at 3000° K. at constant pressure, and the extent of dissociation to be about 2% at the same temperature and atmospheric pressure. Later,[2] as the result of a more extended study, he estimated —90,000 cal. as the heat of dissociation at 3000° K. and constant pressure, and the extent of dissociation to be 1.6% at atmospheric pressure and the same temperature.

The value of —90,000 cal. for the heat of dissociation at constant pressure (—84,000 at constant volume) seems to be rather generally accepted, and is in very good agreement with calculations made from the ionizing potential.[3]

Saha,[4] making use of a simplified form of the Nernst approximation formula, and using —82,000 cal. as the heat of dissociation, has calculated the degree of dissociation of hydrogen at various temperatures and pressures, obtaining results considerably higher than those estimated by Langmuir. His data have been confirmed by Duffendack,[5] who employed a more exact form of the Nernst formula, and obtained results very near to those of Saha and considerably higher than those of Langmuir. Duffendack also carried out experiments which indicated the presence of a con-

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[1] Langmuir, THIS JOURNAL, **34,** 860 (1912).

[2] Langmuir, *ibid.*, **37,** 417 (1915).

[3] Sommerfeld, "Atombau und Spectral-linien," 3rd ed., **1922.**

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

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

siderable amount of monatomic hydrogen at low pressures between 2000° K. and 2500° K.

It appears, therefore, that the heat of dissociation estimated by Langmuir is not altogether consistent with his estimate of the degree of dissociation, if the Nernst formula is approximately correct.

From the third law of thermodynamics we may assign definite values to the entropies of substances for which sufficient heat-capacity data are available, and this permits an approach to the problem differing somewhat from those cited above. A revised list[6] of the entropies of the elements at 25° and atmospheric pressure, contains the necessary data.

The entropy of diatomic hydrogen at 25° C. and atmospheric pressure is calculated from the most recent heat-capacity data (especially the results of Kammerlingh Onnes), and is given as

$$S_{298.1}\ \mathrm{H_2} = 29.44 \tag{1}$$

For higher temperatures, if we take[7] $C_p\mathrm{H_2} = 6.5 + 0.0009\ T$ we have

$$S_{\mathrm{H_2}} = 29.44 + \int_{298.1}^{T} C_p \frac{dT}{T} \tag{2}$$

or

$$S_{\mathrm{H_2}} = 29.44 + 6.5\ ln\ T/_{298.1} + 0.0009\ (T - 298.1) \tag{3}$$

For monatomic hydrogen the entropy may be calculated, following Lewis, Gibson and Latimer, from the formula

$$S_{\mathrm{H}} = R\ ln(T^{3/2}W^{3/2}V) - 11.39 \tag{4}$$

where W is the molecular weight, and V the volume (in cc.) occupied by one mole. This formula has been shown to hold accurately for a number of monatomic gases.

For the calculation of the degree of dissociation of hydrogen we make use of the following relationships,

$$K = \frac{P^2_{\mathrm{H}}}{P_{\mathrm{H_2}}} \tag{5}$$

$$\Delta F = -RT\ ln\ K \tag{6}$$

$$\Delta F = \Delta H - T\Delta S \tag{7}$$

where ΔF, ΔH, and ΔS, represent the respective increase in the free energy, heat content (essentially the heat absorbed at constant pressure), and entropy, when one mole of molecular hydrogen dissociates into atoms under given conditions, and P is the pressure in atmospheres.

ΔH at different temperatures is calculated from the Langmuir value at 3000 K. and from the heat capacities of molecular and atomic hydrogen ($C_pH = 4.97$) by the relation,

$$\Delta H = \Delta H_0 + 3.44T - 0.00045\ T^2 \tag{8}$$

Table I contains the values of the entropies, heats of reaction, and equilibrium constants calculated for several temperatures by the aid of Equations 3, 4, 5, 6, and 7.

[6] Lewis, Gibson and Latimer, This Journal, **44,** 1008 (1922).

[7] Lewis and Randall, *ibid.*, **34,** 1128 (1912).

TABLE I

T °K	$2S_{H}$	S_{H_2}	ΔH	ΔF	K
0	...	...	83730	....	....
298.1	51.44	29.44	84715	78160	....
1500	67.52	31.02	87878	48140	0.0798
2000	70.36	43.34	88810	34770	0.0316
2500	72.58	45.24	89518	21170	0.0141
3000	74.40	46.88	90000	7470	0.286

Table II shows the fraction of hydrogen dissociated (X) at several temperatures and pressures, calculated from the equilibrium constants of Table I by the equation,

$$X = \sqrt{\frac{K}{4P + K}} \tag{9}$$

TABLE II

FRACTION OF HYDROGEN DISSOCIATED AT VARIOUS TEMPERATURES AND PRESSURES. (X)

X	$T = 1500°$			$T = 2000°$		
	$P = 1$	$P = 0.1$	$P = 0.001$	$P = 1$	$P = 0.1$	$P = 0.001$
Edgar	0.0316	0.035	0.0049	0.0063	0.020	0.19
Langmuir	0.0438	...	....	0.0017	...	...
Duffendack[8]	0.0325	0.379	0.0078	0.0102	0.032	0.306
Saha	...	...	....	0.01	0.03	0.29

	$T = 2500°$			$T = 3000°$		
	$P = 1$	$P = 0.1$	$P = 0.001$	$P = 1$	$P = 0.1$	$P = 0.001$
Edgar	0.0595	0.185	0.883	0.26	0.62	0.993
Langmuir	0.016	...	...	0.07	...	...
Duffendack[8]	0.095	0.29	0.95	0.40	0.825	0.997
Saha	0.11	0.35	0.97	0.46	0.85	...

where P is the total pressure. For purposes of comparison the results of Langmuir, Saha, and Duffendack are also included.

It may be noted that instead of making the calculation as indicated above we may make use of the familiar free energy equation

$$\Delta F = \Delta H_0 - 3.44\, T \ln T + 0.00045\, T^2 + IT \tag{10}$$

where ΔH_0 is 83730, and I (= 0.768) is the integration constant obtained by substituting in the general equation (10) the value of $\Delta F_{298.1}$ obtained from the entropies at 298.1°. Equation 10, of course, gives values for ΔF at the various temperatures identical with those in Table I.

The data presented in Table II show that the Langmuir value of the heat of dissociation is not consistent with the low degree of dissociation estimated by him, if the data for the entropies of monatomic and diatomic hydrogen are correct. The calculations made from the entropies give values for the dissociation somewhat lower than those made from the

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[8] Duffendack's data have been recalculated to make them consistent with the heat values selected for the calculations made in this paper. The results differ slightly from those given by Duffendack.

Nernst approximation formula, but the values are certainly of the same order.

It should be noted that the largest factor in any case in determining the extent of dissociation is the *heat* of dissociation, and this seems to be more uncertain than any other factor. However, the method of calculation employed above should always permit the calculation of the degree of dissociation from any value of the heat of dissociation which may finally be selected, and conversely the heat of dissociation should be accurately calculable when more accurate data for the degree of dissociation become available.

Summary

1. The free energy of dissociation, the dissociation constant, and the degree of dissociation, of molecular hydrogen into atomic hydrogen, have been calculated from the entropies of the substances and published data for the heat of dissociation.
2. The results indicate, in accordance with the conclusions of Duffendack and of Saha, that hydrogen is much more highly dissociated at high temperatures than earlier calculations had indicated.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE SEPARATION OF IRON AND ALUMINUM FROM MANGANESE AND CERTAIN OTHER ELEMENTS[1]

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Introduction

It is generally stated that the separation of iron and aluminum from manganese is not satisfactory when ammonia is used as the precipitant, and that special procedures, such as the basic acetate method or precipitation with barium carbonate, are necessary. There is no denial that these methods perform their function and are desirable in special cases; the question is as to their necessity in the analysis of such materials as silicate and carbonate rocks. All of the special procedures entail extra work, complications, and sometimes uncertainties, as in the basic acetate separation with its tedious neutralization, its uncertain precipitation of aluminum, and its non-precipitation of certain of the rare earths.[2] As to the necessity, in the case of manganese, for such methods, one of us has long entertained doubts. It seemed reasonable to expect that precipitations carried out under the conditions prescribed by Blum[3] for the

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Hillebrand, U. S. Geol. Surv., *Bull.*, **700**, 109 (1919).

[3] Blum, Bur. Standards, *Sci. Paper*, **286** (1916); THIS JOURNAL, **38**, 1282 (1916).