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CALCULATED THERMODYNAMIC PROPERTIES OF REAL HYDROGEN UP TO 30,000 ATMOSPHERES AND 3500°K

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CALCULATED THERMODYNAMIC PROPERTIES OF REAL HYDROGEN UP TO 30,000 ATMOSPHERES AND 3500°K

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ABSTRACT: Isentropic data for real hydrogen are calculated in a range of pressures up to 30,000 atmospheres and temperatures up to 3500°K. The effects of ionization, excitation, and dissociation are considered negligible because of the relatively low temperatures and high densities involved. The effects of the intermolecular force are accounted for by fitting a virial coefficient equation to low temperature high density experimental data. These calculated data in turn are fitted to an empirical entropic equation of state. This particular equation of state is convenient for describing many thermodynamic processes.

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White Oak, Maryland

CALCULATED THERMODYNAMIC PROPERTIES OF REAL HYDROGEN UP TO 30,000 ATMOSPHERES AND 3500°K

Modern two-stage gun launchers use hydrogen as the propellant gas. The prediction of the performance of such launchers requires knowledge of the hydrogen gas thermodynamic data. This paper presents calculated thermodynamic data for hydrogen.

The authors acknowledge with gratitude the cooperation of Dr. Harold Woolley of the National Bureau of Standards. Dr. Woolley supplied the computer program with which the properties of hydrogen were calculated. The authors also thank Mrs. Louise Brown, who performed a great deal of the calculations for this report.

J. A. DARE
Captain, USN
Commander

R. Kenneth Lobb
R. KENNETH LOBB
By direction

CONTENTS

ILLUSTRATIONS

TABLES

REFERENCES

(1) Woolley, Harold W., Scott, Russell B., and Brickwedde, F. G., "Compilation of Thermal Properties of Hydrogen in its Various Isotopic and Ortho-Para Modifications, "National Bureau of Standards Research Paper RP1932, Volume 41, November 1948

(2) Seigel, A. E., "A Convenient and Accurate Semi-Empirical Entropic Equation for use in Internal Ballistic Calculations," NAVORD Report 2695, February 1953

(3) Seigel, A. E., "The Theory of High Speed Guns," Agardograph 91, May 1965

List of Symbols

p	pressure, in units of atmospheres
ρ	density, in units of amagat (at 1 amagat, $\rho = 5.60648 \times 10^{-3} \frac{lbs}{ft^3}$)
v	specific volume, in units of $\frac{ft^3}{lb}$
T	absolute temperature, in units of degrees Kelvin (^oK)
R	universal gas constant per pound of hydrogen ($R = 1381.35 \frac{ft}{^oK}$)
C_v	specific heat at constant volume
b	molecular volume, in units of $\frac{ft^3}{lb}$
β f K g	empirical constants for a given entropy
S	entropy, in units of $\frac{cal}{mole\ ^oK}$
U	internal energy
H	enthalpy
a	sound speed
B C	empirical constants for a given temperature

INTRODUCTION

Hydrogen gas is often used as the propellant in light gas guns. In the so-called "two stage guns" the hydrogen propellant may be compressed to densities as high as 2,000 amagats*. The temperature is increased relatively little, going from room temperature to as high as 3500°K. Under these conditions of high density, large intermolecular repulsive forces exist. The hydrogen gas no longer can be described by the ideal gas equation.

Unfortunately, there exists no reliable experimental data on the state properties of hydrogen at high pressures and temperatures. To approximate the behavior of the hydrogen gas at the high densities, the Abel-Noble or covolume equation of state is sometimes used. This equation is

$$p(v-b) = RT$$

With C_v taken to be a constant, the isentrope becomes

$$p(v-b)^{\gamma} = K$$

However, the Abel-Noble equation becomes a poor approximation at the high densities.

Therefore, a calculation of hydrogen gas data has here been made which attempts to better account for the intermolecular forces due to high density. The method involves first extending the calculation of Woolley, Scott, and Brickwedde, reference 1, for the thermal properties of real hydrogen, beyond the realm of experimental data as reported in reference 1. Secondly, the resulting theoretical data are fitted to the semi-empirical entropic equation of Seigel, reference 2:

$$p^{(\beta-2)/\beta}(v-f) = K$$

where β, f, and K are constants for any given entropy.**

---

*One amagat unit is the value of density at 1 atmosphere and 0°C.

**This equation has been fitted successfully to argon, nitrogen, and hydrogen data at temperatures below 430°K and pressures up to 4,000 atm.

It is seen that this equation is equivalent to the Abel-Noble equation for a given entropy if $\beta/(\beta-2)$ is replaced by γ, and if f is replaced by b; these constants, however, will change for each different entropy. The semi-empirical equation may be fitted to real gas data with much greater accuracy than the Abel-Noble equation because of the fact that the parameters β, f, and K may vary with entropy. In addition, the equation is convenient to use to describe gas dynamic processes such as occur in the two-stage gun.

A BRIEF DESCRIPTION OF REFERENCE 1

In reference 1 the thermal properties of hydrogen are found for temperatures up to 5000°K, but at low densities where molecular interaction is negligible. These properties are then extended to somewhat higher densities by combining the low-density data with empirical real-gas data at intermediate densities. This is done by means of standard thermodynamic integrals taken along isotherms.

The empirical real-gas data of reference 1 were obtained in the following manner. The empirical equation

$$\frac{pv}{RT} = e^{(B\rho + C\rho^2)} \qquad (1)$$

was used to account for the intermolecular forces. The coefficients B and C were assumed to be functions of the temperature only. (When the above exponential is expanded, B is found to be the second virial coefficient.) The effects of excitation, ionization, and dissociation are assumed negligible because of the relatively high density and low temperature.* The constants B and C were fitted to experimental hydrogen data in the realm of temperatures from 273°K to 672°K and densities up to 500 amagat. The best overall fit by a weighted method of least squares was found to be in reference 1:

$$B = 0.0055478T^{-1/4} - 0.036877T^{-3/4} - .022004T^{-5/4}$$

$$C = 0.004788T^{-3/2} - 0.04053T^{-2}$$

---

*The ionization and excitation energies are very high (15.4 e.v. and 13.5 e.v., respectively) and, hence, the effects are negligible; the dissociation energy (4.5 e.v.) is negligible because of the high densities which exist.

EXTENDING THE CALCULATION OF REFERENCE 1

In figures 1 and 2 the coefficients B and C are plotted over a temperature range of 273°K to 3500°K. Reference 1 carried the calculation only to 600°K, for this is the extent of the realm of reliable experimental data. Here we have extended the curves for these coefficients to 3500°K. Values of p, v, and T obtained by using these curves with equation (1) are listed in Table 1. Values of S calculated by the method of reference 1 are listed also.

As indicated above, the effects of dissociation, ionization, and excitation of the hydrogen are assumed negligible in the calculation. This is probably a good assumption, because of the relatively low temperatures and high densities considered. The Seigel semi-empirical equation

$$p^{(\beta-2)/\beta}(v-f) = K \qquad (2)$$

was here fitted to the new high-pressure data which were calculated above. The fitting was done as outlined in reference 2 by making a three-point fit of equation (2) to the data along a given isentrope, thus obtaining the empirical constants, β, f, and K. Once this procedure was repeated for a number of isentropes, the constants β, f, and K were obtained as functions of entropy S. Thus, equation (2) was fitted to the data of Table 1 at temperatures from 273°K to as high as 3500°K and entropies of 20, 22, 24, 26, 28, 30, 32, 34, 36, and 38 $\frac{\text{cal}}{\text{mole}^\circ\text{K}}$. Figure 3 is a plot of the P-V data of Table 1. In nearly all regions of this plot, agreement between the data and the semi-empirical fit is so close that a comparison cannot be shown in this figure. The constants β, f, and K as obtained from this particular three-point fit are listed in Table 2. These same constants are plotted against entropy in figures 4 through 6. Other thermodynamic variables, such as internal energy U, enthalpy H, or sound speed a can be derived from equation (2). The following expressions (see reference 2 or 3) result:

$$U = \frac{\beta-2}{2} K p^{2/\beta} + g$$

$$H = \frac{\beta}{2} K p^{2/\beta} + fp + g$$

$$a = \frac{\beta}{\beta-2}\, p \, \frac{v^2}{v-f}$$

where g is a function of S only. The quantity g can be obtained in a manner similar to that of obtaining β, f, and K. Equation (2) is now an entropic or caloric equation of state from which all other thermodynamic variables can be derived in standard fashion. This procedure constitutes a rigorous method for describing the thermodynamics of a particular type of fluid.

In the case reported here, the empirical constants of equation (2) have been fitted to data in a region lacking experimental verification. Though this means of obtaining real hydrogen data does not have the desired experimental foundation, its virtue is in the fact that it continues the trend of the most accurately known hydrogen properties. In all likelihood its use yields a better approximation than previous techniques used to predict the behavior of this gas.

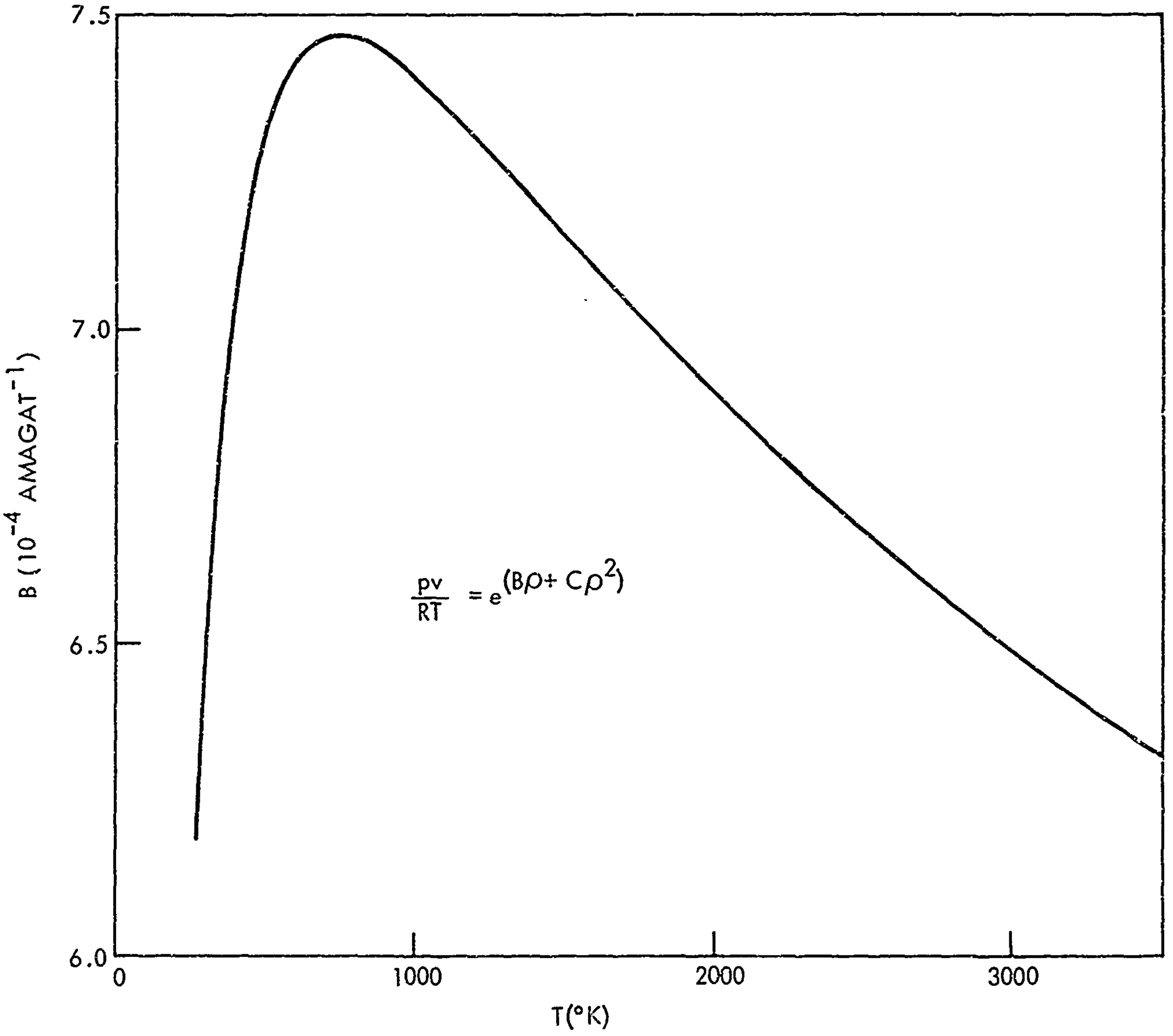

FIG. 1 EMPIRICAL CONSTANT B VS T (REFERENCE 1)

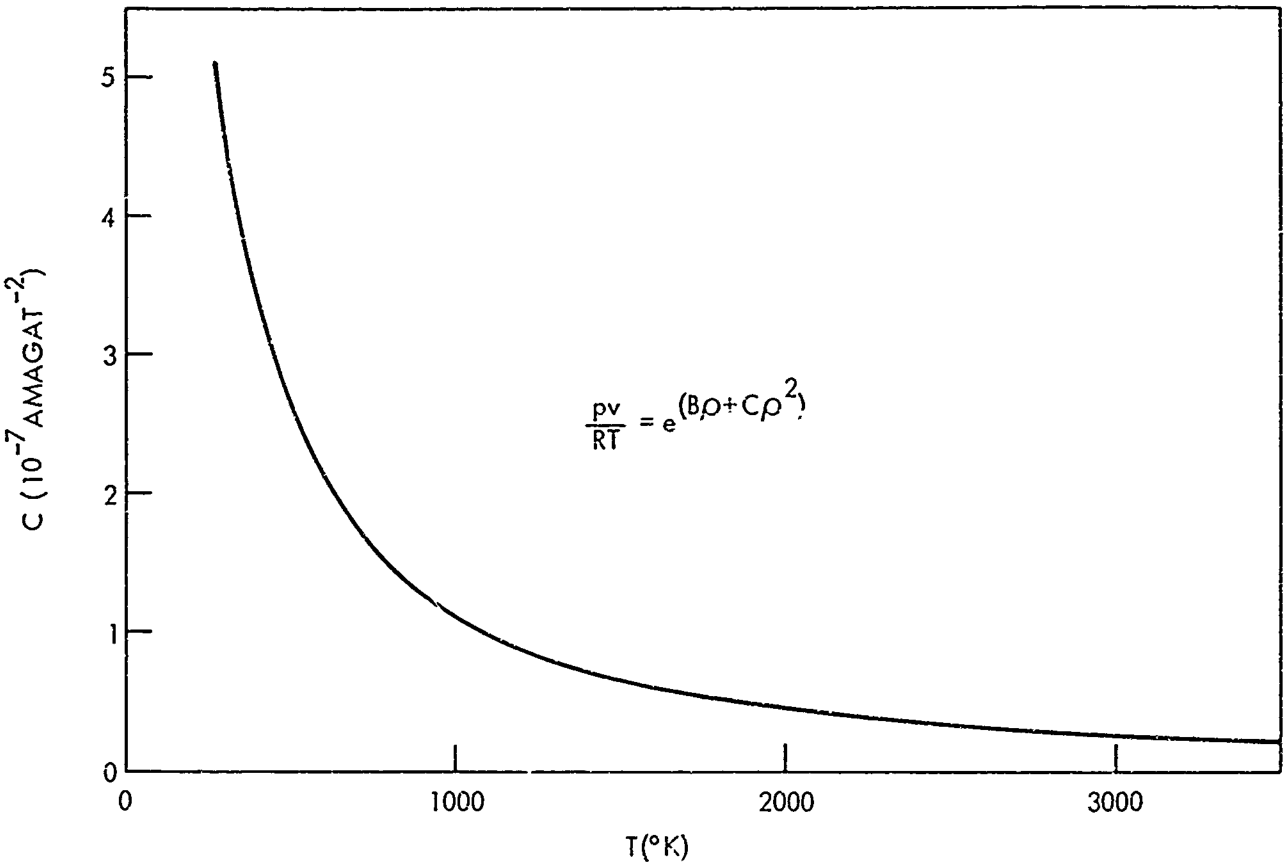

FIG. 2 EMPIRICAL CONSTANT C VS T (REFERENCE 1)

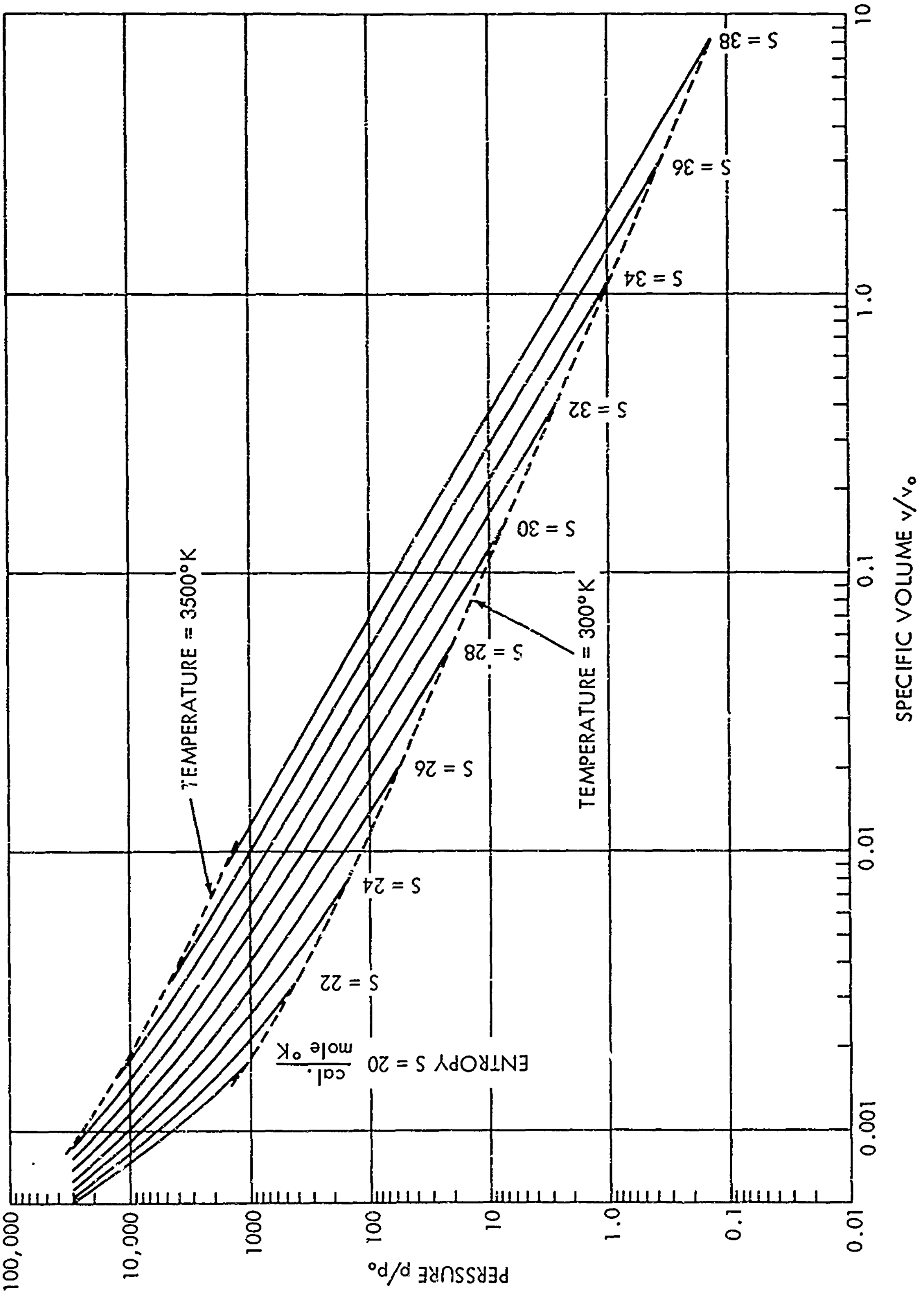

FIG. 3 P V DIAGRAM FOR REAL HYDROGEN

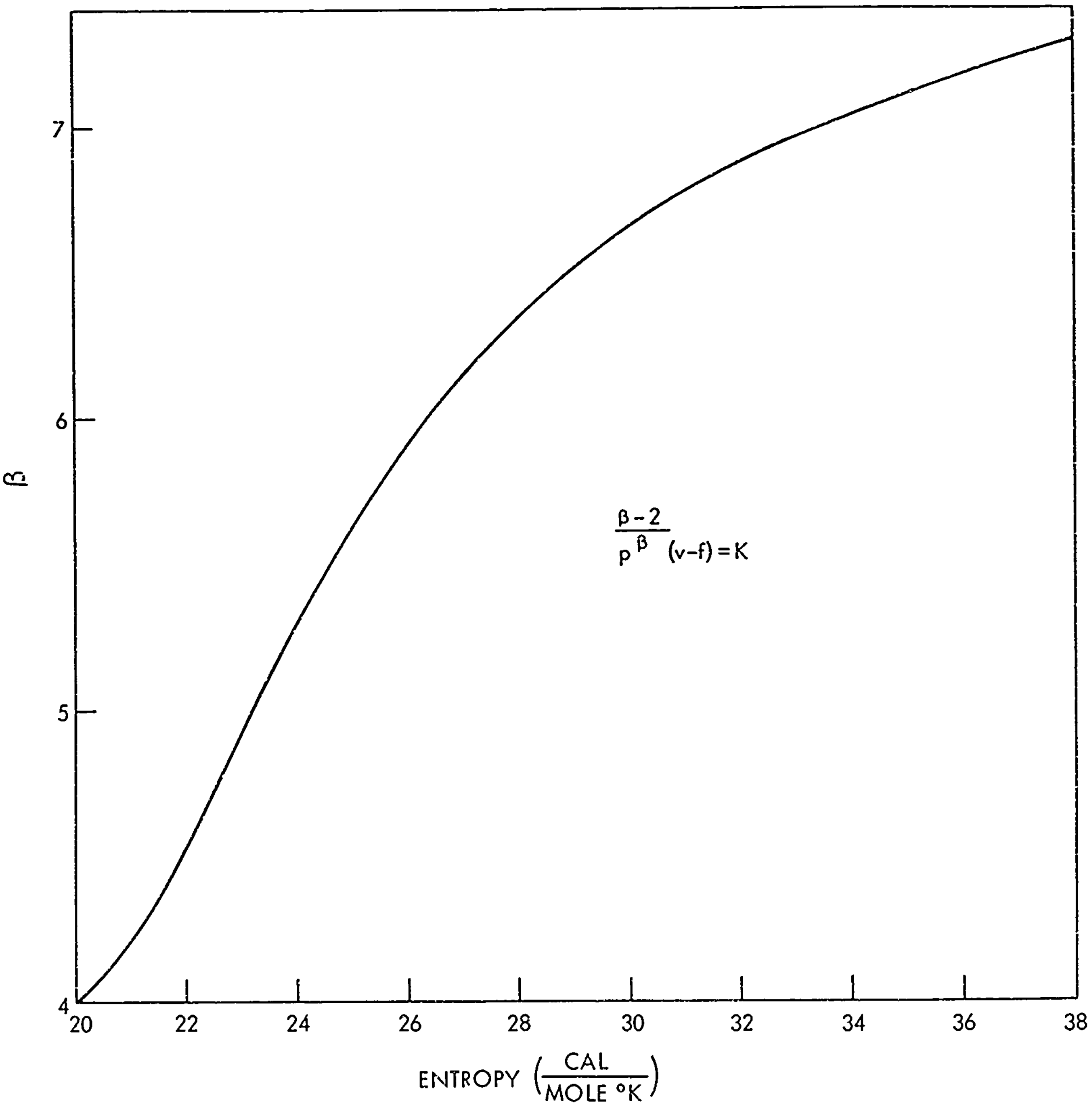

FIG 4 FIG. 4 EMPIRICAL CONSTANT β VS ENTROPY

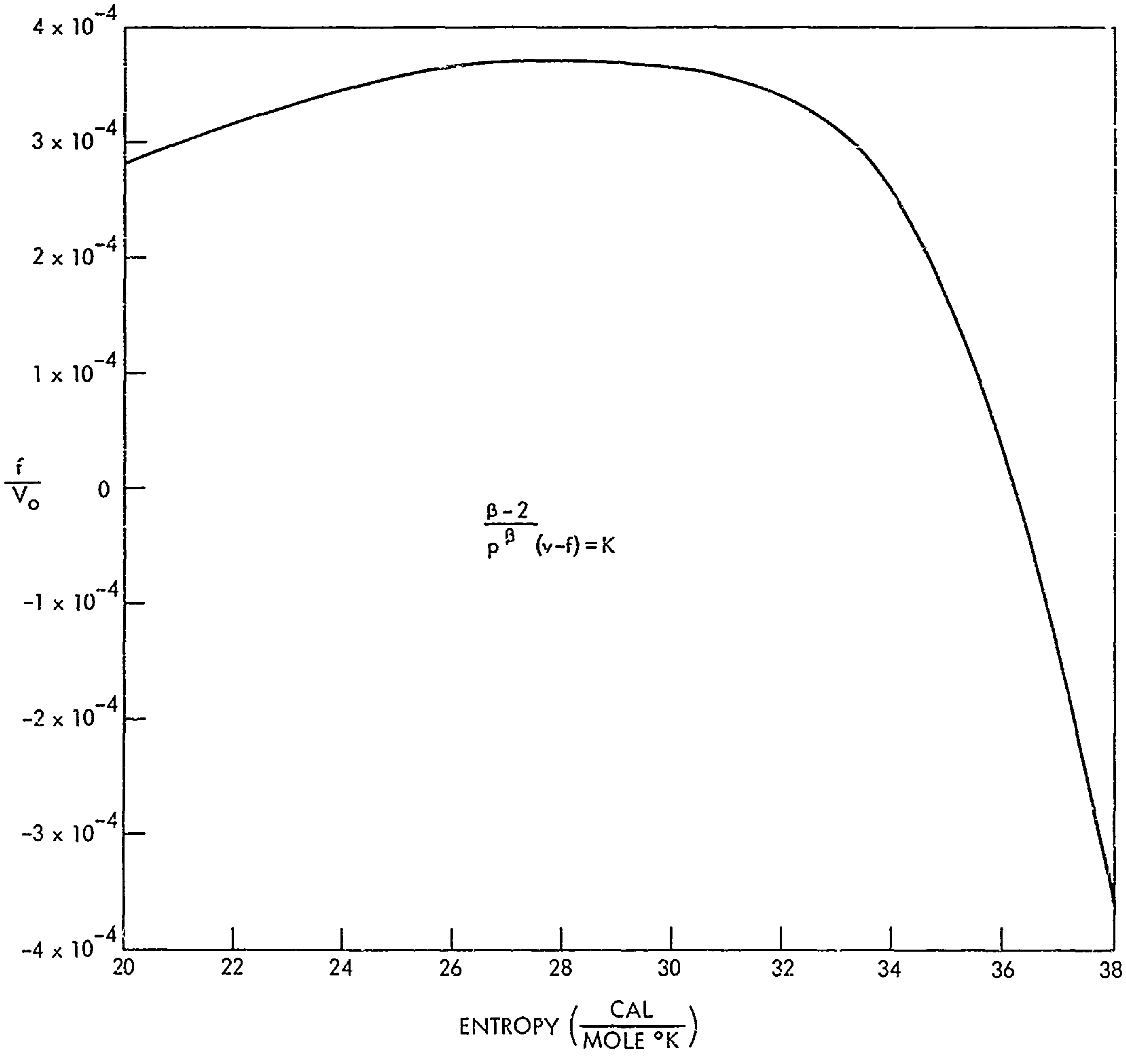

FIG. 5 EMPIRICAL CONSTANT $\frac{f}{V_o}$ VS ENTROPY

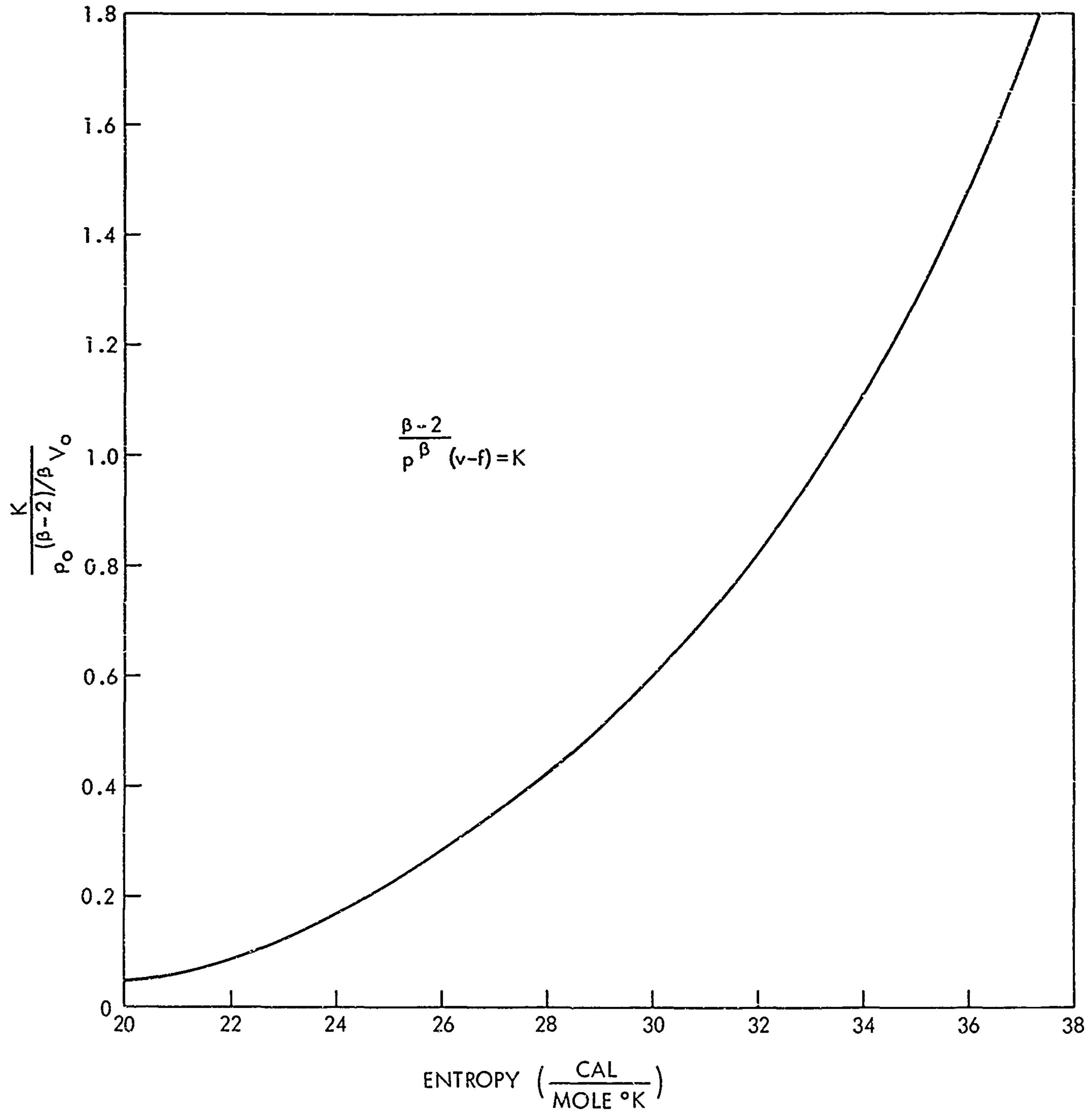

FIG. 6 EMPIRICAL CONSTANT $\frac{K}{P_o^{(\beta-2)/\beta} V_o}$ VS ENTROPY

TABLE I

Properties of Hydrogen from Extended Calculation of Woolley, Scott, and Brickwedde of NBS (ref. 1)

$P_o = 14.7$ psi.
$v_o = 178.365\ ft^3/lb.$

S $\frac{cal}{mole\,^\circ K}$	P/P_o	v/v_o	T ($^\circ K$)
20	1066.42	1.741×10^{-3}	300
	3000	1.154×10^{-3}	395.570
	3130.29	1.136×10^{-3}	400
	6000	9.074×10^{-4}	473.285
	30,000	5.617×10^{-4}	694.486
22	397.050	3.464×10^{-3}	300
	1000	2.135×10^{-3}	388.616
	1110.28	2.029×10^{-3}	400
	3000	1.304×10^{-3}	524.577
	6000	9.958×10^{-4}	632.060
	30,000	5.856×10^{-4}	963.957
24	149.060	8.037×10^{-3}	300
	408.842	4.297×10^{-3}	400
	1000	2.593×10^{-3}	514.004
	3000	1.506×10^{-3}	696.100
	6000	1.117×10^{-3}	840.715
	30,000	6.212×10^{-4}	1289.86
26	55.4093	2.047×10^{-2}	300
	100	1.370×10^{-2}	355.417
	151.355	1.038×10^{-2}	400
	1000	3.202×10^{-3}	681.047
	3000	1.776×10^{-3}	921.428
	6000	1.277×10^{-3}	1109.88
	30,000	6.677×10^{-4}	1682.07

TABLE I (CONT.)

S $\frac{\text{cal}}{\text{mole}^{o}\text{K}}$	P/P_o	V/V_o	T (^{o}K)
28	20.4089	5.443×10^{-2}	300
	55.7425	2.696×10^{-2}	400
	100	1.801×10^{-2}	472.335
	1000	4.004×10^{-3}	901.583
	3000	2.124×10^{-3}	1211.63
	6000	1.480×10^{-3}	1449.26
	30,000	7.253×10^{-4}	2153.86
30	7.48250	1.473×10^{-1}	300
	10	1.200×10^{-1}	326.090
	20.4426	7.230×10^{-2}	400
	100	2.371×10^{-2}	627.815
	1000	5.038×10^{-3}	1186.74
	3000	2.560×10^{-3}	1575.86
	6000	1.731×10^{-3}	1868.39
	30,000	7.951×10^{-4}	2722.17
32	2.73810	4.015×10^{-1}	300
	7.48178	1.963×10^{-1}	400
	10	1.597×10^{-1}	434.442
	100	3.123×10^{-2}	833.362
	1000	6.336×10^{-3}	1545.34
	3000	3.097×10^{-3}	2023.77
	6000	2.036×10^{-3}	2379.57
	30,000	8.788×10^{-4}	3406.82
34	1.00124	1.097	300
	2.73602	5.356×10^{-1}	400
	10	2.123×10^{-1}	578.167
	100	4.099×10^{-2}	1100.39
	1000	7.934×10^{-3}	1986.51
	3000	3.748×10^{-3}	2568.45
	6000	2.405×10^{-3}	2998.87
	30,000	9.785×10^{-4}	4229.22

TABLE I (CONT.)

S $\frac{cal}{mole^oK}$	P/P_o	V/V_o	T (^oK)
36	0.36602	2.999	300
	1	1.464	399.974
	10	2.819×10^{-1}	768.423
	100	5.333×10^{-2}	1438.10
	1000	9.878×10^{-3}	2522.81
	3000	4.537×10^{-3}	3226.76
	6000	2.850×10^{-3}	3745.12
38	0.13379	8.204	300
	0.36562	4.003	400
	1	1.949	532.505
	10	3.728×10^{-1}	1016.94
	100	6.857×10^{-2}	1855.11
	1000	1.223×10^{-2}	3170.76
	3000	5.486×10^{-3}	4017.95

TABLE II

Empirical Constants of Equation (2) vs. Entropy S as Obtained from Three-Point Fits to Curves of Figure 3

S $\frac{\text{cal}}{\text{mole}^{\circ}\text{K}}$	β	$\frac{f}{v_o}$	$\frac{K}{p_o^{(\beta-2)/\beta} v_o}$
20	3.990	2.81×10^{-4}	0.04735
22	4.519	3.15×10^{-4}	0.08691
24	5.286	3.44×10^{-4}	0.1677
26	5.900	3.65×10^{-4}	0.2798
28	6.338	3.71×10^{-4}	0.4211
30	6.646	3.65×10^{-4}	0.5950
32	6.866	3.41×10^{-4}	0.8166
34	7.025	2.60×10^{-4}	1.100
36	7.168	4.00×10^{-5}	1.464
38	7.293	-3.53×10^{-4}	1.949

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13 ABSTRACT

Isentropic data for real hydrogen are calculated in a range of pressures up to 30,000 atmospheres and temperatures up to 3500°K. The effects of ionization, excitation, and dissociation are considered negligible because of the relatively low temperatures and high densities involved. The effects of the intermolecular forces are accounted for by fitting a virial coefficient equation to low temperature high density experimental data. These calculated data in turn are fitted to an empirical entropic equation of state. This particular equation of state is convenient for describing many thermodynamic processes.

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Naval Ordnance Laboratory, White Oak, Md.
(NOL technical report 65-209)
CALCULATED THERMODYNAMIC PROPERTIES OF REAL HYDROGEN UP TO 30,000 ATMOSPHERES AND 3500°K, by D. N. Bixler and others. 1 Dec. 1965. 4p. charts, tables. (Ballistics research report 153) NOL task 364. UNCLASSIFIED

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2. Gun launchers
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