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EQUATION OF STATE FOR HYDROGEN

By

V. A. Rabinovich



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PREPARED BY:

TRANSLATION SERVICES BRANCH
FOREIGN TECHNOLOGY DIVISION
WP-APB, ONR.

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ANALYSIS OF EXPERIMENTAL THERMAL VALUES AND
EQUATION OF STATE FOR HYDROGEN

V. A. Rabinovich

Detailed analysis is made of the $p - v - T$ data of various experimenters and this is used to derive a grid of reference values for thermal quantities. An equation of state is set up for hydrogen and the feasibility of extrapolating it into the high-temperature region while allowing for the dissociation of hydrogen molecules is demonstrated.

The majority of experimental data on the thermal properties of substances are obtained in the best case from the curve of saturation up to a temperature on the order of 600°C . The experimental caloric values in the literature are relatively scanty and in the majority of cases are completely lacking.

The problem of the present work was to derive an accurate equation of state for hydrogen, correct in the gaseous phase in a broad interval of change in temperature and pressure.

Analysis and Concordance of Experimental and Thermal Data

It is necessary to create a network of grid reference data on existing thermal values in order to set up an equation of state and

to disclose the patterns and peculiarities of the thermodynamic behavior of a substance.

The initial values were graphically conformed in dimensionless coordinates along the isotherms $\sigma - \tau = f(\omega)$ and the isochores $\sigma - \tau = f(\tau)$, where $\sigma = pv/RT_K$, $\omega = v_K/v$, and $\tau = T/T_K$.

As a result of this concordance of a large number of experimental $p - v - T$ data [1-9] we were successful in analyzing and estimating the accuracy of the initial values.

In the analysis it was discovered that the data in Bartlett [1] and Wiebe and Gaddy [2] differ from each other by up to 1%, but their average values link up well with the experiment in Michels et al. [3] which is distinguished by a high accuracy noted by the authors themselves and confirmed on constructing isothermal and isochoric cross-sections. The data in Holborn and Otto [4] are slightly inferior in accuracy to the thermal values in Michels et al. [3], but within limits of 0.25% they may be smoothly linked with the latter. The experimental values in Witkowski [5] and Onnes and Braak [7] are excessive and with the growth of ω the deviations from Michels et al. [3] and Holborn and Otto [4] reach 0.5%. The data in Onnes and Pening [6] also completely satisfactorily conform in the low-temperature regions; at temperatures near the critical, however, noticeable discrepancies, reaching 2% close to the critical point, are observed. The supercritical point was therefore the object of the especially careful processing of the experimental data.

The graphic concordance of the experimental $p - v - T$ data enabled us to create a grid of thermal reference values; with this as a basis we were successful in disclosing several patterns in the thermodynamic behavior of hydrogen comprised in the following.

1. All the isochores in the experimental interval of temperature change $\tau = 0.6$ to 20 with $\omega < 1$ have an upward-directed convexity, i.e., $(\partial^2 \sigma / \partial \tau^2)_{\omega} < 0$. The curvature of the isochores increases $\omega = 0.4$ to 0.6, but then drops anew as the density approaches the critical.

2. In the range $\omega = 1$ to 1.8 all the isochores have a double curvature and the point of inflection is the region of change $\tau = 1.7$ to 2.1. When $\omega > 1.8$ and $\tau > 2.1$ the inequality $(\partial^2 \sigma / \partial \tau^2)_{\omega} < 0$ again becomes true for all isochores.

3. When we examined the isochoric cross-sections we discovered no straight-line isochores. The critical isochore is a curved line, the curve of which decreases as it approaches the critical point.

We must note that all these conclusions are in complete concordance with those of A. Ye. Sheyndlin [10] derived from the presence of maximums of c_p on the isobars and the anomalous transitions connected with them in pure substances.

Equation of State for Hydrogen

The best known equations of state for practicable gases (Beatty-Bridgeman, Benedict-Webb-Rubin, Vukalovich-Novikov, and the one set up by Ya. Z. Kazavchinskiy's method [11]) define pressure p as a function of specific volume v and temperature T . In the general case all these equations may be written in the form

$$p = f_1(v) + f_2(v)T + F(T, v). \quad (1)$$

This form of the equation, consisting of the linear portion $f_1(v) + f_2(v)T$ and of a function composed of two variables $F(T, v)$ caused by the distortion of the isochores, proceeds from the general thermodynamic relationships. As investigations on a whole series of

substances have shown, function $F(T, v)$ is small in comparison with the linear portion of Eq. (1) and monotonically decreases with temperature increase.

We selected Kazavchinskiy's equation [11], which derived its theoretical basis from Kessel'man [12] and in the general case is written in dimensionless parameters as follows:

$$\sigma = a_0(\omega) + a_1(\omega)\tau + \beta(\omega)\psi(\tau) + \gamma(\omega)\psi^2(\tau) + \dots \quad (2)$$

to describe the thermodynamic properties of hydrogen. Differentiating Eq. (2) twice with respect to τ we obtain

$$\left(\frac{\partial^2 \sigma}{\partial \tau^2}\right)_\omega = \beta(\omega)\psi'' + \gamma(\omega)(\psi^2)'' + \dots \quad (3)$$

Rabinovich [14] has shown that if we use reliable values of the curvilinear portion we may set up an equation of state which very accurately describes not only the thermal values, but also the caloric.

A reference grid of thermal values, from which ten basic isochores were selected, was used for separating the curvilinear part of equation of state (2).

The entire curvilinear portion in the experimental range of hydrogen parameter change was obtained in tabular form as a result of twofold graphic differentiation with intermediate and final flattening of the isochores.

As was ascertained, all the isotherms of $(\partial^2 \sigma / \partial \tau^2) = f(d_A)$ (Fig. 1) above the Boyle temperature $T > T_B$ comply with a simple proportional law, i.e., the ratio $\partial^2 \sigma / \partial \tau^2$ on any two isotherms remains unchanged when d_A is the same.

The calculations confirmed that the entire curvilinear portion of the equation of state for temperatures above that of Boyle may be

described by an analytical expression of the form

$$\frac{\partial^2 \sigma}{\partial \tau^2} = \beta(\omega) \psi''. \quad (4)$$

The method of determining the elementary functions of β and ψ'' in the presence of the tabular values of $\partial^2 \sigma / \partial \tau^2$ is shown in Rabinovich [14].

It proved to be insufficient to limit ourselves to one term in the curvilinear portion when passing into the temperature region below Boyle's temperature. Therefore on seven isotherms ($T = 33.26; 43.16; 53.16; 63.16; 73.16; 83.16; 93.16$) were constructed the differences

$$\frac{\partial^2 \sigma}{\partial \tau^2} - \beta(\omega) \psi''.$$

Analysis of these differences on the listed isotherms showed that in the interval of change of the cited densities $\omega = 0$ to 1 ($d_A = 0$ to 345) they may all be determined by adding one more member to the curvilinear portion of the equation of state, i.e.,

$$\frac{\partial^2 \sigma}{\partial \tau^2} - \beta(\omega) \psi'' = \gamma \varphi''. \quad (5)$$

In order acceptably to satisfy the initial values of $\partial^2 \sigma / \partial \tau^2$ in the relatively simple expression of the curvilinear portion for temperatures $T > T_B$ the interval of change in the cited densities was limited to $\omega = 1$, since the substantial complications caused in the analytical expression in order to extend the interval with respect to ω are unjustified.

We set up equations for the two isotherms $+50$ and -50°C reflecting the experimental data with an accuracy of up to 0.1% in order to determine the linear portion of equation of state (2).

After the substitution of the derived expressions of the elementary functions in Eq. (2) the equation of state for hydrogen assumes the final form

$$\begin{aligned} \sigma = & 0,48374 \omega + 0,95074 \omega^2 - 0,90968 \omega^3 + 0,91770 \omega^4 - 0,19778 \omega^5 + \\ & + (1 + 0,23510 \omega + 0,01394 \omega^2 + 0,07029 \omega^3 - 0,05824 \omega^4 + 0,01273 \omega^5) \tau + \\ & + (-1,90330 \omega - 0,77848 \omega^2 + 0,71110 \omega^3 - 0,66808 \omega^4 + 0,09700 \omega^5 + \\ & + 0,02043 \omega^6) \exp(-0,127 \tau) + (-0,65566 \omega - 0,14624 \omega^2 + 3,27170 \omega^3 - \\ & - 3,44870 \omega^4 + 1,18672 \omega^5 - 0,12090 \omega^6) \exp(-1,905 \tau). \end{aligned} \quad (6)$$

Equation of state (6), true when $T > T_B$ in the range of the cited densities of $\omega = 0$ to 2.4 (to $p_{\max} = 3000 \text{ kg/cm}^2$) and when $T < T_B$ in the change interval of ω from 0 to 1, was used to calculate the thermal and caloric values with the aim of comparing them with the experimental data.

Good correspondence of the experimental and calculated values is observed in the whole temperature range; the maximum deviations in the individual points do not exceed the errors of the experiment itself. The isotherms 200 and 300°C, where the experimental values of σ_{exp} lie along both sides of the calculation curves and reach ± 0.5 , are exceptions. The discrepancy of the experimental data on these isotherms was noted even in analysis of the initial values.

On the -150°C and 0°C isotherms (Table 1) the coincidence of calculated values of internal energy with the data in Michels et al. [15] is completely satisfactory; a somewhat poorer coincidence of values is observed on the 150°C isotherm. Only that the 150°C isotherm was the last one on the isochores and that in differentiation in that work [15] inaccurate derivative values might have been obtained can explain the foregoing.

Table 2 compares the calculated values of isochoric specific heats with the data in Michels et al. [15]. The average deviations do not exceed 2% and this is completely permissible in specific heat values.

The results of the comparison enable us to draw the following conclusion. Separating the curvilinear portion of the equation of state by twofold differentiation of the isochores and on this basis determining the volumetric and temperature functions enable us, without deviating from the basic requirement that the thermal properties of the substances ultimately be accurately described, to analyze and describe the derivatives which considerably influence the caloric values and also reliably to extrapolate the equation of state into the high temperature region.

In the calculation of the thermodynamic values the following values of the constants were adopted:

$$p_K = 13.225 \text{ kg/cm}^2; T_K = 33.26^\circ \text{ K}; v_K = 32.248 \text{ l/kg}; M = 2.156; \\ R = 420.634 \text{ kg-m/kg} \cdot \text{deg}; A = 426.94^{-1} \text{ kcal/kg-m.}$$

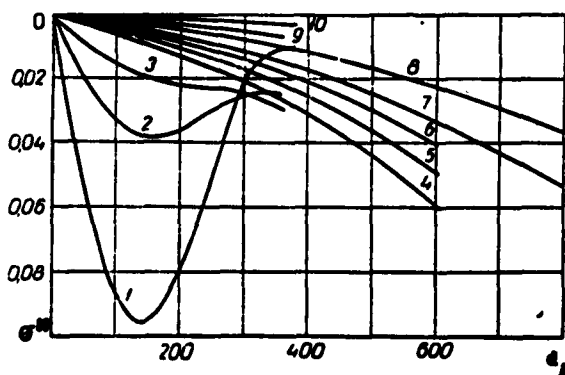


Fig. 1. Isotherms of second derivatives of $\sigma'' = (\partial^2 \sigma / \partial \tau^2) = f(d_A)$ for the following temperatures: 1) -239°C ; 2) -220° ; 3) -200° ; 4) -150° ; 5) -100° ; 6) -50° ; 7) 0° ; 8) 100° ; 9) 200° ; 10) 400°C .

Extrapolating the Equation of State into the High-Temperature Region

In the high-temperature region the thermodynamic properties of substances even at high pressures are chiefly described by the second and more rarely by the third virial coefficients, therefore the trustworthiness of their extrapolation determines the

reliability of the extrapolation of the equation of state as a whole.

If we collect all the members of equation of state (6) which stand in front of ω we may derive the analytical expression for the second virial coefficient

$$B = 0,48374 + 0,23510\tau - 1,90337 \exp(-0,127\tau) - 0,65566 \exp(-1,905\tau). \quad (7)$$

The values of the second virial coefficient in the temperature range from -253°C to $+4000^{\circ}\text{C}$ were calculated by this formula. In order to test the truth of the values of B in the experimental range of temperature change the data of various authors on the second virial coefficient were plotted on the calculated curve $B = f(t)$ (Fig. 2). As is evident from this figure the calculated curve passes in the very neatest way through the points taken from Michels et al. [3], Holborn and Otto [4], Nijhoff and Keesom [9], Michels and Goudekot [16]. We determined the values of B at the temperatures of 300 and 400°C from data on hydrogen compressibility on those isotherms in Bartlett [1] and Wiebe and Gaddy [2].

The laws of statistical physics were adduced to estimate the reliability of the calculated values of the second virial coefficient in the temperature region beyond the limits of the experiment.

Statistical physics gives this expression for the second virial coefficient:

$$B_{\text{theor.}} = 2\pi N \int_0^{\infty} (1 - e^{-\frac{u}{kT}}) r^2 dr. \quad (8)$$

If we use the Lennard-Jones potential [6, 12] as a function of the reciprocity between the molecules $u(r)$ then we may integrate

TABLE 1

Comparison of Calculated Values of Internal Energy Δu_p
(kcal/mole) with Data in Michels et al. [15].

$d_A = \frac{d}{d_0}$	w	Temperature, °C					
		-150		0		150	
		Δu_p	Δu	Δu_p	Δu	Δu_p	Δu
0	0,000000	0	0	0	0	0	0
40	0,115974	- 9,69	- 9,60	- 6,68	- 7,13	- 3,68	- 4,67
80	0,231948	- 19,21	- 19,13	- 13,07	- 13,90	- 6,95	- 8,83
120	0,347922	- 28,58	- 28,56	- 19,22	- 20,33	- 9,88	- 12,47
160	0,463896	- 37,81	- 37,87	- 25,15	- 26,42	- 12,49	- 15,61
200	0,579870	- 46,88	- 47,04	- 30,84	- 32,16	- 14,77	- 18,25
240	0,695844	- 55,80	- 56,04	- 36,29	- 37,56	- 16,72	- 20,35
280	0,811818	- 64,55	- 64,86	- 41,45	- 42,62	- 18,27	- 21,91
320	0,927792	- 73,09	- 73,48	- 46,28	- 47,32	- 19,38	- 22,87
360	1,043766	- 81,37	- 81,87	- 50,73	- 51,58	- 19,95	- 23,17
400	1,159740	- 89,26	- 90,01	- 54,74	- 55,38	- 19,92	- 22,74
440	1,275714	- 96,94	- 97,87	- 58,24	- 58,65	- 19,20	- 21,56
480	1,391688	- 104,27	- 105,41	- 61,18	- 61,33	- 17,71	- 19,56
520	1,507662	- 111,18	- 112,59	- 63,48	- 63,38	- 15,34	- 16,71
560	1,623636	- 117,56	- 119,32	- 64,99	- 64,71	- 11,95	- 12,97
600	1,739610	- 123,51	- 125,56	- 65,87	- 65,25	- 7,69	- 8,33
640	1,855584			- 65,82	- 64,84	- 2,25	- 2,80
680	1,971558			- 64,85	- 63,48	+ 4,34	+ 3,76
720	2,087532			- 62,91	- 61,13	+ 12,14	+ 11,43
760	2,203506			- 59,89	- 57,70	+ 21,19	+ 20,30
800	2,319480			- 55,38	- 53,14	+ 32,02	+ 30,43
840	2,435454			- 50,43	- 47,39	+ 43,11	+ 41,89
Average differences		± 0,66		± 1,43		± 1,98	

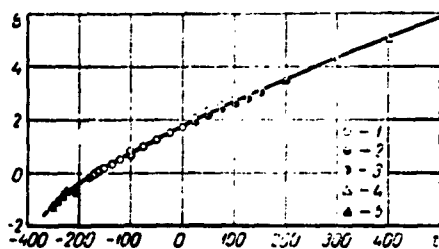


Fig. 2. Dependence of second virial coefficient B on temperature $t(^{\circ}\text{C})$ according to: 1) Michels et al. [3]; 2) Holborn and Otto [4]; 3) Michels et al. [16]; 4) Bartlett [1] and Wiebe and Gaddy [2]; 5) Nijhoff and Keesom [9].

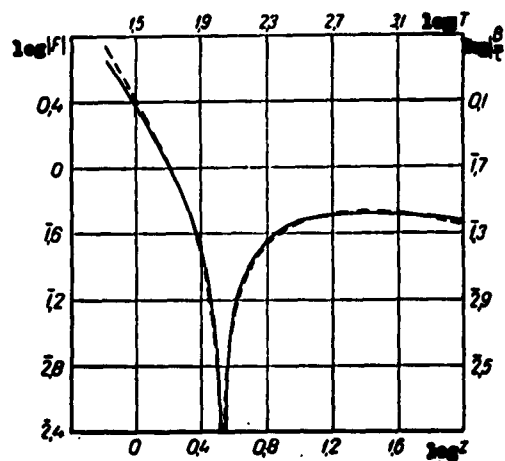


Fig. 3. Comparison of calculated and the theoretical values of second virial coefficients and of function $F(z)$. Solid line) calculated; dashed line) theoretical.

Eq. (8) using the known H-function and obtain a convenient formula for calculating the second virial coefficient

$$B_{\text{theor}} = b_0 F(z)$$

where

$$b_0 = \frac{2}{3} \pi N r_0^3, \quad z = \frac{kT}{u}. \quad (9)$$

The function $F(z)$ with a complicated analytical form was tabulated by Hirschfelder [17] for different values of argument z .

TABLE 2

Comparison of Calculated Values of Specific Heats $c_{v,p}$
(kcal/mole · deg) with Data in Michels et al. [15].

$d_A = \frac{d}{d_0}$	ω	Temperature, °C					
		-150		0		150	
		$c_{v,p}$	c_v	$c_{v,p}$	c_v	$c_{v,p}$	c_v
0	0.000000	3.736	3.736	4.852	4.852	4.994	4.994
40	0.115974	3.755	3.751	4.873	4.869	5.012	5.013
80	0.231948	3.773	3.769	4.893	4.886	5.031	5.032
120	0.347922	3.793	3.788	4.917	4.904	5.051	5.053
160	0.463896	3.812	3.807	4.940	4.920	5.071	5.079
200	0.579870	3.831	3.829	4.964	4.941	5.092	5.104
240	0.695844	3.852	3.850	4.988	4.962	5.113	5.131
280	0.811818	3.872	3.873	5.013	4.985	5.135	5.158
320	0.927792	3.896	3.895	5.039	5.009	5.158	5.189
360	1.043766	3.913	3.918	5.066	5.033	5.181	5.220
400	1.159740	3.930	3.946	5.094	5.059	5.206	5.254
440	1.275714	3.953	3.976	5.124	5.086	5.231	5.291
480	1.391688	3.983	4.004	5.155	5.113	5.258	5.330
520	1.507662	4.004	4.036	5.187	5.144	5.286	5.369
560	1.623636	4.031	4.071	5.221	5.176	5.316	5.410
600	1.739610	4.060	4.112	5.257	5.210	5.348	5.454
640	1.855584			5.294	5.244	5.380	5.494
680	1.971558			5.331	5.272	5.415	5.534
720	2.087532			5.374	5.302	5.450	5.578
760	2.203506			5.416	5.338	5.487	5.624
800	2.319480			5.460	5.374	5.527	5.665
840	2.435454			5.503	5.406	5.563	5.711
Average error, %		± 0.4		+0.8		+1.2	

We succeeded in obtaining almost complete coincidence of the curves compared not by only parallel transfer of the coordinate system but also by turning it, cp. Kazavchinskiy et al. [19]. The

angle of turning for this case proved to be very small and did not substantially ameliorate the coincidence of the curves. In the very low-temperature region of $T = 20$ to 45° K the curves deviate considerably. This can be explained by the fact that the theoretical assumptions get experimentally confirmed for hardly any substances at temperatures close to the critical.

The good agreement of the theoretical and calculated curves in the experimental temperature range $T = 45^\circ$ to 673.16° K and also in the temperature beyond the bounds of the experiment allows us to figure that the calculated values of the second virial coefficient are reliable and may be used to determine the thermodynamic properties of hydrogen at high temperatures.

In conclusion let us note that in the cited equation of state the detailed tables of the thermodynamic properties of hydrogen in the temperature interval $t = -253^\circ$ to $+4000^\circ \text{ C}$ at pressures $p = 1$ to 500 kg/cm^2 were calculated without allowing for dissociation of molecules at high temperature; and the $i - s$ diagram was thus constructed.

Nomenclature

$\alpha_1(\omega), \alpha_2(\omega), \beta(\omega), \gamma(\omega), \dots$ are the functions of the cited density ω ; $\psi(\tau)$ is the monotonically decreasing function of the cited temperature; N is the Avogadro number; k is Boltzmann's constant; $u = u(r)$ is the potential energy of reciprocity between two molecules at distance $\underline{r}$ from each other.

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