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STATE EQUATIONS AND MOLAR VOLUMES OF HYDROGEN AT SUPER HIGH PRESSURE

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Уравнения состояния и молярные объемы водорода
при сверхвысоких давлениях

Выполена интерполяция экспериментальных данных молярных объемов водорода с использованием логарифмического разложения и уравнения Тейта в интервале давлений от 3,0 до 7,0 кбар при четырех значениях температур. Показано, что в случае логарифмического уравнения для хорошей аппроксимации экспериментальных данных достаточно только трех параметров. Однако данное выражение для аппроксимации дает очень плохое фитирование для давлений $P < 3{,}0$ кбар.

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State Equations and Molar Volumes of Hydrogen
at Super High Pressure

Interpolations of hydrogen experimental molar volumes using logarithm expansion series and Tait equation in pressure interval from $P = 3.0$ kbar to $P = 7.0$ kbar for four experimental temperatures were carried out. It was shown that for good approximation of experimental values using logarithm expansion series only three parameters are necessary. Unfortunately, such an expansion gives very bad approximation at pressures $P < 3.0$ kbar.

INTRODUCTION

As it is well known, hydrides of metals attract huge attention since the discovery of palladium hydride in 1866 [1–3]. Firstly, hydrides of metals are very important materials for nuclear reactors such as decelerators, reflectors, radiation defenders as well as hydrogen accumulators for engines. One of the most important methods for the creation of metallic hydrides is the saturation of pure metals or metal alloys by hydrogen gas molecules at high and super high pressures [1–3]. As it is well known, concentration of hydrogen or its heavy isotopes in hydrides can be changed continuously up to $1 \, \mathrm{atom} \, H/\mathrm{atom} \, M$, and for some of them it is up to $3 \, \mathrm{atom} \, H/\mathrm{atom} \, M$ (as for uranium three hydride — UH_3). One of the methods for saturation of metals by hydrogen is the saturation at super high pressures in special high pressure chambers (pumps) [3].

Attempts of the authors of this article to find full experimental data for such important characteristics as molar volumes and atomic densities of hydrogen and its heavy isotopes and its behavior versus pressure or to use the existing calculations on the base of interpolation expressions presented in literary review (see as example [4] and references therein) did not allow one to carry out such estimations. The authors of this article tried to interpolate existing experimental data [4–6] using parameters presented in it but unfortunately without success.

The first purpose of this report is to consider the existing experimental data [4–8], to check the interpolations carried out of some of these dependences using the most popular theoretical expressions and models and to try to extrapolate dependences on wider temperature and pressure intervals. The second one is to extrapolate numerical expressions on wider intervals of pressures and temperatures, to estimate the atomic volumes of hydrogen (or deuterium, as they are practically the same) and to calculate the mean distances between the molecules and atoms. The third purpose is to compare the behavior of all extrapolated dependences under such extrapolations.

1. EXPERIMENTAL DATA

The smoothing molar volumes and compressibility of hydrogen versus the pressure in interval from $P_{\min} = 0.5$ kbar to $P_{\max} = 7.0$ kbar are presented in Tables 1 and 2 correspondingly for four temperatures: $T = 298.15, 323.15, 373.15$ and 423.15 K (see [4, 5]). The value of molar volume at $P = 4.5$ kbar and

Table 1. Experimental molar volumes of hydrogen (cm^3) [4, 5]

P, kbar	T, K				P, kbar	T, K			
	298.15	323.15	373.15	423.15		298.15	323.15	373.15	423.15
	Molar hydrogen volumes, cm^3					Molar hydrogen volumes, cm^3			
0.5	65.57	69.80	78.27	86.68	4.0	20.63	21.14	22.23	23.24
1.0	40.79	42.90	47.08	51.26	4.5	19.59*	20.14	21.13	22.02
1.5	32.31	33.71	36.50	39.27	5.0	18.91	19.31	20.21	21.01
2.0	27.91	28.96	31.05	33.13	5.5	18.24	18.60	19.43	20.15
2.5	25.16	25.99	27.68	29.33	6.0	17.65	17.98	18.75	19.70
3.0	23.22	23.91	25.33	26.70	6.5	17.13	17.43	18.15	18.75
3.5	21.77	22.37	23.59	24.76	7.0	16.66	16.94	17.62	18.17

Table 2. Experimental compressibilities ($Z = P \cdot V / R \cdot T$) of hydrogen (cm^3) [4, 5]

P, kbar	T, K				P, kbar	T, K			
	298.15	323.15	373.15	423.15		298.15	323.15	373.15	423.15
	Compressibility $Z = P \cdot V / R \cdot T$					Compressibility $Z = P \cdot V / R \cdot T$			
0.5	1.32	1.29	1.26	1.23	4.0	3.31	3.14	2.88	2.64
1.0	1.64	1.59	1.51	1.45	4.5	3.55	3.36	3.08	2.82
1.5	1.95	1.88	1.76	1.67	5.0	3.78	3.58	3.28	2.99
2.0	2.25	2.15	2.00	1.88	5.5	4.01	—	3.48	3.16
2.5	2.53	2.41	2.33	2.08	6.0	—	—	3.66	—
3.0	2.80	2.66	2.45	2.27	6.5	—	—	3.85	—
3.5	3.06	2.91	2.67	2.46	7.0	—	—	—	—

$T = 298.15$ K (with top symbol *) which was presented in [4] we changed to a more correct value from [6]. Interpolation of experimental data in Table 1 starting from the pressure $P = 3$ kbar was carried out in [4, 5] using the expansion:

$$\frac{P \cdot V}{R \cdot T} = Z = \sum_{i=0}^{4} \alpha_i \cdot (\ln P)^i. \tag{1}$$

Authors of [5, 6] carried out interpolation of experimental data (see Tables 1 and 2) and obtained the following expansion series parameters which are presented in Table 3. The parameters of the so-called Tait equation (see below) for description of experimental data are calculated too and presented in this table as well. The numerical calculations with various interpolating expressions (see below and the next articles) were carried out using experimental data massives from both Table 1 and 2.

Tait equation is more often used for calculation of various compositions of compressed liquids and solids under high and super high pressures. This

Table 3. Values of interpolation polynomial (1) and Tait equation parameters for various temperatures are presented [4, 5]

T, K	α_0	α_1	α_2	α_3	α_4	B, kbar	C
278.15	8.98014	–5.58908	1.65154	–0.210079	0.01045140	–1.625	0.4771
323.15	8.13732	–5.27947	1.48478	–0.189566	0.00947049	–1.685	0.4804
373.15	7.48000	–4.79975	1.34959	–0.171887	0.00854293	–1.766	0.4852
423.15	6.42090	–4.04186	1.14436	–0.146734	0.00734177	–1.843	0.4922

Table 4. Square deviations of experimental data of molar volumes (Tables 1 and 2) using expansion (1) and Tait equation (2) with parameters from Table 3 [4, 5]

T, K	χ_i^2, expansion (1)	N — number of points, M — number of parameters	χ_i^2, Tait equation (2)	N — number of points, M — number of parameters
298.15	$1.065 \cdot 10^4$	$N = 9$, $M = 5$	$9.522 \cdot 10^3$	$N = 9$, $M = 2$
323.15	$1.019 \cdot 10^4$	$N = 9$, $M = 5$	$1.042 \cdot 10^4$	$N = 9$, $M = 2$
373.15	$9.479 \cdot 10^3$	$N = 9$, $M = 5$	$1.183 \cdot 10^4$	$N = 9$, $M = 2$
423.15	$8.899 \cdot 10^3$	$N = 9$, $M = 5$	$1.369 \cdot 10^4$	$N = 9$, $M = 2$

equation can be presented in logarithmical form (see as example [5, 10] and referred literature):

$$V(P,T) = V_0(P_0, T) \times \left[1 - C(T) \cdot \ln \frac{B(T) + P}{B(T) + P_0} \right]. \tag{2}$$

Here $C(T)$ and $B(T)$ are parameters of Tait equation, P_0 and V_0 are initial pressure and corresponding molar volume. Sometimes analogical form of such an equation is used [5]:

$$\rho(P,T) = \rho_0(P_0, T) + C(T) \cdot \ln \frac{B(T) + P}{B(T) + P_0}, \tag{3}$$

where ρ_0 is initial mass gas density (g/cm^3) at pressure [5].

We used the parameters presented in Table 3 for recalculation of the molar hydrogen volumes or compressibility coefficients (as the same) using the series of parameters $\alpha_i(T)$, $i = 1, \ldots, 5$ (expansion (1)) and Tait equation (2), (3). One can obtain the following values of square deviations χ_i^2 (these values are presented in Table 4), the so-called square function of deviations (see also the comment below to the least square method of approximations):

$$\chi_i^2 = \sum_{k=1}^{N} \left[\frac{Y_{k,\exp} - Y_{k,\text{calc}}[X_k, \alpha_i(i = 1, \ldots, K)]}{\Delta Y_{k,\exp}} \right]^2. \tag{4}$$

3

Here N and K are numbers of experimental points and numbers of parameters of numerical approximation, $Y_{k,\mathrm{exp}}$ and $Y_{k,\mathrm{calc}}$ are experimental and calculated values correspondingly, and $\Delta Y_{k,\mathrm{exp}}$ are the «experimental» mistakes of measured experimental values. Values $X_k(k = 1, \ldots, N)$ are the arguments of approximating function. As we do not know measured experimental mistakes of functions, we have taken all mistakes to be equal to $\Delta Y_{k,\mathrm{exp}} = 0.01 \cdot Y_{k,\mathrm{exp}}$.

All recalculations were carried out starting from pressure $P \geqslant 3.0$ kbar, because if anybody would approximate whole experimental data massive (from 0.5 to 7.0 kbar), the square deviations χ_i^2 should be much higher than those presented in Table 4. As one can see, the criterion of χ_i^2 does not allow one to conclude that the approximation carried out in [4, 5] is impossible to be estimated as a satisfactory one. This fact was the reason to carry out all the interpolations again!

2. INTERPOLATION OF EXPERIMENTAL DATA

For interpolation of experimental data we used the least square method, which assumes minimization of expression (4) [9, 10], i.e., calculates the parameters $\alpha_i(i = 1, \ldots, K)$ of approximating expression $Y_{k,\mathrm{calc}}[X_k, \alpha_i(i = 1, \ldots, K)]$ by minimization of functional (4). As we mean it is quite enough accuracy. It is well known that approximation is quite good, if $\chi_i^2 \approx N - K$. Here the value $N - K$ is the so-called number of freedom degrees. So, every time we calculated the accuracy of interpolations by comparing numbers of parameters and experimental points and corresponding value χ_i^2.

First of all, we tried to use most popular expressions, i.e., two types of practically similar expressions: with the linear member independent of pressure with $i = 0$ (Eq. (1)) and without such a member (Eq. (5)) for comparison:

$$\frac{P \cdot V}{R \cdot T} = Z(P, T) = \sum_{i=1}^{i=K} \alpha_i(T) \cdot [\ln P]^i. \tag{5}$$

It is clear that compressibility coefficients Z should depend on the temperature T and pressure P. And coefficients $\alpha_i(T)(i = 1, \ldots, 5)$ depend on temperature only. It will be used below for extrapolation of experimental values.

Our attempts showed that it is impossible to carry out good approximations using expressions (1) and (5) of whole experimental data from 0.5 to 7.0 kbar. It is necessary to exclude the interval from 0.5 to 2.5 kbar for not so bad interpolation. We will return to interpolation and extrapolation of wide whole molar volume dependences versus pressures in the following paper. The approximations of experimental data for $Z(P, T)$ or, similarly, for molar volumes $V(P, T)$ were carried out and the values χ_i^2 for three numbers of parameters $K = 3, 4, 5$ and

Table 5. Values of parameters χ_i^2 for two approximating functions (1) and (5) for different number of parameters

Number of parameters, K	T, K χ_i^2, computer code «FUMILI», method of least squares [9, 10]				T, K χ_i^2, computer code «LINEAR», method of inversion of mistake matrix			
	298.15	323.15	373.15	423.15	298.15	323.15	373.15	423.15
$K = 3$ (1)	0.2379	0.03539	0.02175	1.759	0.2377	0.04357	0.02291	1.759
$K = 3$ (5)	0.6426	0.3674	0.4408	2.926	0.6471	0.3889	0.4420	2.932
$K = 4$ (1)	18.18	23.95	22.50	22.72	0.9932	263.9	13.83	11.69
$K = 4$ (5)	0.6397	0.3637	0.4349	2.911	Bad approximation			
$K = 5$ (1)	0.4866	0.3545	0.3435	1.693	Bad approximation			
$K = 5$ (5)	0.4381	0.04217	0.05849	1.921	Bad approximation			

for both expansions (1) and (5) are presented in Table 5 for various experimental temperatures beginning from the pressure $P = 3.0$ kbar to $P = 7.0$ kbar. One can conclude from Table 5 that interpolation of experimental data (for pressures $P \geqslant 3.0$ kbar) using the method of least squares with expression (5), i.e., without independent of pressure member α_0 is better approximated experimental data than expression (1), because the values of χ_i^2 are lower for all numbers of parameters $K = 3, 4, 5$.

For interpolation we used two methods for minimization of functional (4): direct least square method (computer code «FUMILI», Dubna) and our own computer code «LINEAR» which uses the inversion of mistake matrix. The last method is quite good for approximation of smooth experimental data by interpolating polynomials. One can see from Table 5 that interpolation of experimental molar volumes versus pressure is really good with only two or three parameters. Here the number of points and parameters are $N = 9$ and $K = 3, 4, 5$, respectively.

If we would decrease the number of parameters from three to two, the values of χ_i^2 would begin to grow very quickly. The same situation would occur if we would increase the number of approximation parameters from three to four. χ_i^2 is very small again only at $K = 5$ (Eq. (1)).

Below the values of χ_i^2 and the calculated parameters of expansion (1) (see Table 6) and expansion (5) (see Table 7) are presented versus the temperature for different numbers of parameters of expansions. The corresponding values of χ_i^2 and calculated parameters of expansion (1) for more obvious comparison of our calculations and previous interpolations (see [5, 6]) are presented in Table 6 too.

It was proved that the critical value of the number of approximating parameters exists (see [9, 10]), i.e., such a critical value $K = K_{\text{critical}}$ determines optimal approximation. If anybody spends approximation by polynomials with degree $K > K_{\text{critical}}$, it will be possible to approach calculated data to exper-

Table 6. Parameters of approximating expansion (1) and corresponding χ_i^2 for interpolation of molar volumes $V(P)$ (see Table 1) or compressibility coefficients Z (see Table 2) [4,5]

Parameters/ temperatures	χ_i^2	α_0	α_1	α_2	α_3	α_4
298.15 K, $\quad K=3$	0.2379	2.1207	–0.27430	0.82330	—	—
298.15 K, $\quad K=4$	18.18	3.6056	–2.1296	1.2871	0.5975	—
298.15 K, $\quad K=5$	1.977	3.6056	–2.1296	0.46149	1.1349	–0.34083
298.15 K (see Table 3)	$1.065 \cdot 10^4$	8.98014	–5.589080	1.65154	–0.210079	0.0104514
323.15 K, $\quad K=3$	0.03539	1.9647	–0.15140	0.72360	—	—
323.15 K, $\quad K=4$	23.95	3.4952	–2.0105	1.10250	0.10119	—
323.15 K, $\quad K=5$	1.895	3.4061	–2.0105	0.49545	1.01174	–0.31191
323.15 K (see Table 3)	$1.019 \cdot 10^4$	8.13732	–5.27947	1.48478	–0.189566	0.00947049
373.15 K, $\quad K=3$	0.02175	1.8413	–0.14640	0.63807	—	—
373.15 K, $\quad K=4$	22.50	3.2572	–1.9206	1.0633	0.068838	—
373.15 K, $\quad K=5$	1.712	3.1530	–1.9206	0.59789	0.81491	–0.25964
373.15 K (see Table 3)	$9.479 \cdot 10^3$	7.48000	–4.79975	1.34959	–0.171887	0.00854293
423.15 K, $\quad K=3$	1.759	1.7404	–0.13550	0.56750	—	—
423.15 K, $\quad K=4$	22.72	3.0552	–1.8286	1.0251	0.043056	—
423.15 K, $\quad K=5$	2.241	2.9392	–1.8286	0.65421	0.67673	–0.22561
423.15 K (see Table 3)	$8.899 \cdot 10^3$	6.42090	–4.04186	1.14436	–0.146734	0.00734177

imental ones and obtain much better harmony (agreement), but unfortunately it is inevitable to get worse consent with true curve, which all specialists try to estimate ([9], p.165).

Taking into account the short remark above, one can conclude that approximations of experimental data with only three parameters (see Tables 5, 6, 7) allow one to get very good accuracy. So, there is no necessity to take more parameters for determination of true curve than $K = 3$!

So, we approximated experimental values of molar volumes (see Table 1) using Tait equation (2) and its modification (3). It is necessary to note that it is better to use χ_i^2 criteria equation (2) than Eq. (3) for approximations. We interpolated experimental data by the least square method beginning at the minimum pressure $P_0 = 3$ kbar and taking the corresponding volume $V_0(T)$. Parameters of Tait equations $C(T)$ and $B(T)$ and following χ_i^2 together with the analogical quantities from Table 3 [5,6] for comparison are presented in Table 8.

Using the so-called χ_i^2 criteria of the least square method with $N = 9$ and $K = 2$, i.e., with $N-K = 7$ — numbers of freedom degrees, one can

Table 7. Parameters of approximating function (5) and corresponding χ_i^2 for interpolation of molar volumes $V(P)$ (see Table 1) or compressibility coefficients Z (see Table 2) [4,5]

Parameters/ temperatures	χ_i^2	α_1	α_2	α_3	α_4	α_5
298.15 K, $K=3$	0.6426	4.1058	–2.1296	0.65061	—	—
298.15 K, $K=4$	0.6397	4.0987	–2.1296	0.65984	–0.0039721	—
298.15 K, $K=5$	0.4381	4.1718	–2.1296	0.45090	0.18233	–0.045785
323.15 K, $K=3$	0.3674	3.9055	–2.0105	0.60227	—	—
323.15 K, $K=4$	0.3637	3.8997	–2.0105	0.60991	–0.0032185	—
323.15 K, $K=5$	0.04217	4.0835	–2.0105	0.10250	0.44177	–0.10781
373.15 K, $K=3$	0.4408	3.6530	–1.9206	0.56330	—	—
373.15 K, $K=4$	0.4349	3.6471	–1.9206	0.57101	–0.0032798	—
373.15 K, $K=5$	0.05849	3.8312	1.9206	0.063300	0.44168	–0.10773
423.15 K, $K=3$	2.926	3.4389	–1.8286	0.52509	—	—
423.15 K, $K=4$	2.911	3.4291	–1.8286	0.53807	–0.0055262	—
423.15 K, $K=5$	1.921	3.6130	–1.8286	0.025100	0.44640	–0.10991

Table 8. Parameters of Tait equation (2) and χ_i^2 for various temperatures. Initial parameters are equal $P_0 = 3$ kbar and $V_0 = V(P_0)$

T, K	χ_i^2	V_0, cm^3	$C_{\text{calc}}^{\text{our}}$	χ_i^2	C [5]	B [5], kbar
298.15	0.2434	23.231	0.20762	$9.522 \cdot 10^3$	0.4771	–1.625
323.15	0.0776	23.955	0.20970	$1.042 \cdot 10^4$	0.4804	–1.685
373.15	0.1058	25.388	0.21176	$1.183 \cdot 10^4$	0.4852	–1.766
423.15	1.850	26.769	0.21320	$1.369 \cdot 10^4$	0.4922	–1.843

conclude that interpolation with Tait equation is really very good. One can see that our direct interpolation in distinction to previous results gives another value of parameters $C(T)$ conserving the same values of parameters $B(T)$. *The ratios between old parameters ($C_{[5]}(T)$) and our parameters ($C_{\text{calc}}^{\text{our}}(T)$) are about $C_{[5]}(T)/C_{\text{calc}}^{\text{our}}(T) = 2.302585$.* It means that there is a mistake in Tait equation in the book [5]: mixing up of natural logarithm and tenth logarithm. So, this is the reason for such high values of $\chi_i^2(T)$ at the approximation with Tait equation.

By the way, we recalculated the approximation of experimental data (see Tables 1 and 2) with fifth parameters presented in Table 3 with exchange in Eq. (1) of natural logarithm on tenth logarithm, but results were practically the same as presented in Table 4.

Besides that, we used Tait equation in the form (3) for interpolation of experimental data (Table 1) too. The interpolation results and values $\chi_i^2(T)$

Table 9. Parameters of interpolation with Tait equation in the form (3) of experimental data (Table 1) at two numbers of parameters $K = 2$ and $K = 3$

T, K	K	χ_i^2	$\rho_0(P,T)$, g/cm^3	$C(T)$, g/cm^3	$B(T)$, kbar
298.15	2	10.45	0.0861 Eq. (6)	0.0240 ± 0.00041	-1.625
298.15	3	9.179	0.0854 ± 0.00065	0.0248 ± 0.00077	-1.625
323.15	2	14.25	0.0836 Eq. (6)	0.0236 ± 0.00039	-1.685
323.15	3	12.18	0.0827 ± 0.00064	0.0245 ± 0.00074	-1.685
373.15	2	18.18	0.0790 Eq. (6)	0.0228 ± 0.00036	-1.766
373.15	3	15.33	0.0779 ± 0.00061	0.0238 ± 0.00068	-1.766
423.15	2	24.60	0.0749 Eq. (6)	0.0220 ± 0.00033	-1.843
423.15	3	20.96	0.07379 ± 0.00058	0.02302 ± 0.00063	-1.843

with two parameters of approximation $B(T)$ and $C(T)$ ($K = 2$) and with three parameters of approximation $\rho_0(T)$, $B(T)$ and $C(T)$ are presented in Table 9.

For two parameters of interpolation the value $\rho_0(P_0,T)$ is taken for pressure beginning at $P_0 = 3$ kbar and can be written as

$$\rho_0(P_0,T) = M_{H_2} \cdot N_A / V(P_0,T), \tag{6}$$

where $M_{H_2} = 3.345 \cdot 10^{-24}$ g is the mass of hydrogen molecule, and $N_A = 6.02214199 \cdot 10^{23}$ molecules/mole is Avogadro number [11–13], $V(P,T)$ is molar volume at pressure P. At normal pressure, it is well known that $V_A(P = 1 \text{ atm}, T = 293.15 \text{ K}) = 2.24141 \cdot 10^4$ cm^3/mole is the volume of one mole.

By comparing Tables 8 and 9 using criteria χ_i^2, one can conclude that original Tait equation (2) is better for approximations of experimental data than the modification equation (3).

2.1. Extrapolation of Experimental Data for Super High Pressures. Taking into consideration all the remarks about accuracy of extrapolation of theoretical expressions on wide intervals of temperature and pressure, we calculated molar volumes versus pressure for two temperatures (these temperatures were used in experimental studies [4, 5]) on the basis of two expressions (maybe the best ones at this moment, we will return to this point of view later, in the next article) — expansion (1) with only three parameters and Tait equation (3). The calculated values of molar volumes are presented in Table 10.

For better presentation of both massives of calculated data we introduced square deviations of calculated molar volumes with the use of two expressions:

$$\Delta_1(T) = \sum_{i=1}^{i=N} \left(\frac{V_{\text{calc}}^{\text{Eq.}(1)}(P_i,T) - V_{\text{calc}}^{\text{Eq.}(2)}(P,T)}{0.01 \cdot V_{\text{calc}}^{\text{Eq.}(2)}(P,T)} \right)^2, \tag{7.1}$$

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Table 10. Molar volumes of hydrogen versus pressure for two temperatures $T = 298.15$ K and $T = 423.15$ K. The $\chi_i^2(T)$ parameters of interpolation for experimental [4, 5] pressure interval $(3.0 \leqslant P \leqslant 7.0$ kbar) are written too (right values)

P, kbar	$T = 298.15$ K Tait equation (2) $\chi_i^2 = 0.2434$	$T = 298.15$ K Expansion (1), $K = 3$ $\chi_i^2 = 0.2377$	$T = 423.15$ K Tait equation (2) $\chi_i^2 = 1.850$	$T = 423.15$ K Expansion (1), $K = 3$ $\chi_i^2 = 1.759$
	Molar hydrogen volumes, cm³/mol			
3.0	23.2149/23.22	23.244/23.22	26.7474/26.70	26.697/26.70
4.0	20.5748/20.63	20.592/20.63	23.1978/23.24	23.248/23.24
5.0	18.8784/18.91	18.899/18.91	21.0268/21.01	21.055/21.01
6.0	17.6259/17.65	17.652/17.65	19.4583/19.70	19.464/19.70
7.0	16.6326/16.66	16.660/16.66	18.2295/18.17	18.222/18.17
8.0	15.8094	15.835	17.2192	17.206
9.0	15.1064	15.3530	16.3613	16.349
10.0	14.4930	14.512	15.6157	15.611
11.0	13.9489	13.965	14.9565	14.963
12.0	13.4600	13.475	14.3656	14.389
13.0	13.0161	13.031	13.8303	13.873
14.0	12.6097	12.626	13.3409	13.407
15.0	12.2348	12.255	12.8903	12.982
16.0	11.8871	11.913	12.4727	12.593
17.0	11.5627	11.596	12.0836	12.234
18.0	11.2588	11.301	11.7194	11.903
19.0	10.9728	11.026	11.3770	11.594
20.0	10.7030	10.768	11.0540	11.306

$$\Delta_2(T) = \sum_{i=1}^{i=N} \left(\frac{V_{\text{calc}}^{\text{Eq.(1)}}(P_i, T) - V_{\text{calc}}^{\text{Eq.(2)}}(P, T)}{0.01 \cdot V_{\text{calc}}^{\text{Eq.(1)}}(P, T)} \right)^2. \tag{7.2}$$

Using numerical calculations it was obtained that such square deviations have the following values:

$$\Delta_1(T = 298.15 \text{ K}) = 0.3644; \quad \Delta_2(T = 298.15 \text{ K}) = 0.3688,$$

$$\Delta_1(T = 423.15 \text{ K}) = 5.197; \quad \Delta_2(T = 423.15 \text{ K}) = 4.968.$$

The number of calculated molar volume values is $N = 18$ and the number of parameters is $K = 3$. One can conclude that expressions (1) and (2) can be used for extrapolation of pressure dependences of molar volumes with not so low probability of such an extrapolation. In spite of the significant distinctions of mathematical forms of these expressions at high pressures they give very low deviations from one another.

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Calculations of molar volumes using expansions (1) and (5) with four ($K = 4$) and five parameters ($K = 5$) give much stronger square deviations (7) at high pressures.

3. EXTRAPOLATIONS OF EXPERIMENTAL DATA ON WIDE TEMPERATURE AND PRESSURE INTERVALS (EXPANSION (1) AND TAIT EQUATION (2))

Let us try to extrapolate the parameters of Tait equation on a wider temperature area and pressure interval. For that purpose let us find the coefficients of the simplest approximation of all Tait equation parameters using the polynomial functions:

$$V_0(T) = \alpha_{V1} + \alpha_{V2} \times T + \alpha_{V3} \times T^2, \tag{8.1}$$

$$B(T) = \alpha_{B1} + \alpha_{B2} \times T + \alpha_{B3} \times T^2, \tag{8.2}$$

$$C(T) = \alpha_{C1} + \alpha_{C2} \times T + \alpha_{C3} \times T^2, \tag{8.3}$$

where T is temperature in the absolute scale of temperatures.

It is necessary to note here that extrapolation signifies that the expansion of the experimentally found functional dependence, which exactly takes place for a limited branch of argument values, changes in a wider area, i.e., propagation (prolongation) is carried out in these area limits. In such a way one can obtain data, which are impossible to get by immediate measurements or when such data are absent (see [10], p.156).

From the physical point of view, extrapolation is of course not a very legitimate operation, because we assume that functional dependence would be kept as well over the boundaries of studied interval of arguments. Sometimes there are not enough foundations to confirm such an assumption. Only one foundation can be suggested, the physical nature of phenomenon does not change. So, in many cases extrapolation is very useful and is a unique method of obtaining new data [14].

The values of temperature-independent coefficients α_{Vi}, α_{Vi} and α_{Vi} at $i = 1, 2, 3$ and χ_i^2 obtained at the interpolation of temperature dependences of parameters in Table 8 by expressions (8) using computer code «LINEAR» are written in Table 11.

One can use the obtained temperature-independent coefficients α_{Vi}, α_{Vi} and α_{Vi} at $i = 1, 2, 3$ for determination of extrapolated parameters of Tait equation (2) on wide temperature interval, taking into consideration the remark made above. Of course, the accuracy of such an approximation is very difficult to estimate without experimental measurements. The calculated parameters of Tait equation (2) for experimental temperatures are presented in Table 12.

Table 11. Coefficients α_{Vi}, α_{Vi} and α_{Vi} at $i = 1, 2, 3$ and χ_i^2 obtained at the interpolation of expressions (8)

Tait parameter $V_0(T)$	$\chi_i^2 = 0.02046$	$\alpha_{V1} = 13.686$	$\alpha_{V2} = 0.03457$	$\alpha_{V3} = -10^5$
Tait parameter $B(T)$	$\chi_i^2 = 0.1839$	$\alpha_{B1} = -0.65026$	$\alpha_{B2} = -0.00438$	$\alpha_{B3} = 0.0$
Tait parameter $C(T)$	$\chi_i^2 = 0.02465$	$\alpha_{C1} = 0.16333$	$\alpha_{C2} = 0.00022$	$\alpha_{C3} = 0.0$

Table 12. Parameters of Tait equation (2) for various experimental temperatures [4]

T, K	V_{0calc}, cm^3	V_{0exp} [5], cm^3	B_{calc}, kbar	B_{exp} [5], kbar	C_{calc}	C_{exp}
298.15	23.215	23.22	−1.62804	−1.625	0.20773	0.20762
323.15	23.943	23.91	−1.68015	−1.685	0.20943	0.20970
373.15	25.367	25.33	−1.77049	−1.766	0.21191	0.21176
423.15	26.747	26.70	−1.84234	−1.843	0.21315	0.21320

The calculated values of Tait equation parameters extrapolated on wide temperature interval are presented in Figs. 1 and 2.

There are good interpolations of experimental data in temperature interval $298.15 \leqslant T \leqslant 423.15$ K, and there are extrapolations in temperature intervals: 1) from liquid nitrogen temperature $T_{liquid} = 77.15$ K to $T = 273.15$ K, and 2) from $T = 473.15$ K to quite high temperature $T = 1273.15$ K. Parameters $V_{0\,exp}$, B_{exp} and C_{exp} have bottom symbol «exp», because they were calculated using experimental values of molar volumes. It is clear that extrapolation of temperature dependences (6) on wide temperature interval is really unproved. It is necessary to check up such dependences in experiments. Our calculations showed that such an extrapolation causes the change of sign of both parameters B_{exp} and C_{exp} at temperatures $T > 1273.15$ K.

Of course, it is impossible to use Tait equation for pressures below $P < 3.0$ kbar. But one can believe that this equation provides not so bad approximations for high pressures — $P > 7.0$ kbar, as an example.

The calculated molar volumes of hydrogen versus pressures up to super high pressures are presented in Figs. 3–5. We used the calculated values parameters $V_{0calc}(T)$, $B_{calc}(T)$ and $C_{calc}(T)$ of Tait equation (2) from Table 12 and Figs. 1, 2 for such interpolations (at following intervals: $3.0 \leqslant P \leqslant 7.0$ kbar and temperatures $T = 298.15-423.15$ K (see Table 1)) and approximations (at following intervals: $7.0 < P \leqslant 20.0$ kbar and temperatures from liquid nitrogen to 1473.15 K).

The calculated and experimental values of molar hydrogen volumes are presented in Table 13, because it is impossible to show so small differences by corresponding curves in Fig. 2.

11
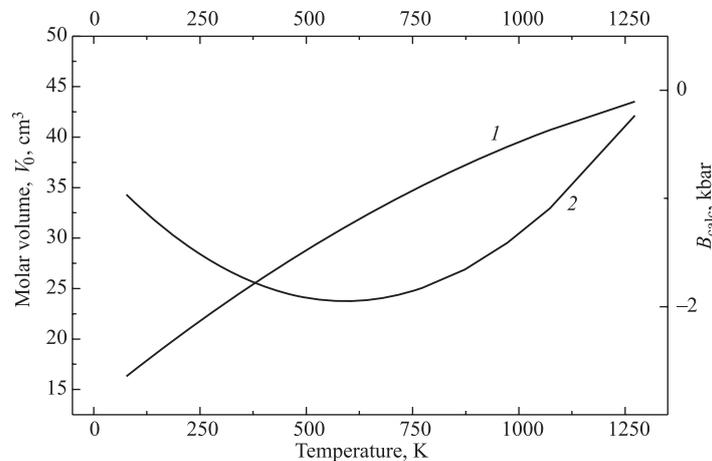
Fig. 1. Calculated temperature dependences of initial molar volumes $V_{0\text{calc}}$ (curve *1*) and B_{calc} (curve *2*)
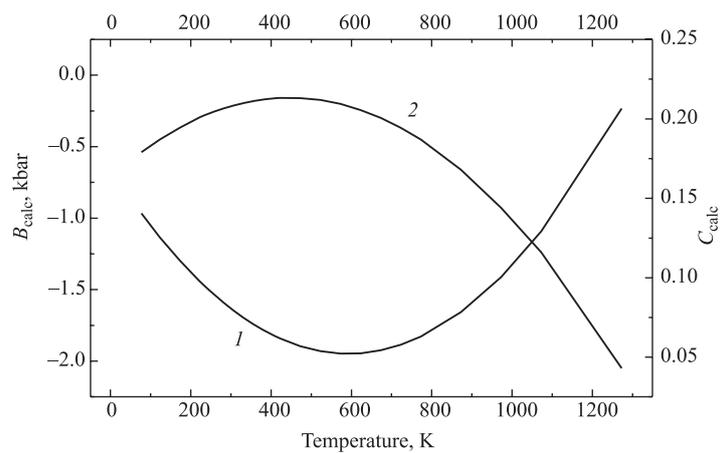
Fig. 2. Calculated temperature dependences of initial molar volumes B_{calc} (curve *1*) and C_{calc} (curve *2*)

It is necessary to note that the calculated Tait equation parameters B_{calc} and C_{calc} change the signs at temperatures $T > 1273.15$ K. Curves of molar volumes versus pressure at such temperatures begin to grow with the increase in pressure. Such a behavior is an unreadable (unphysical) one. So, it is senseless to carry out extrapolations for such a temperature interval.

12
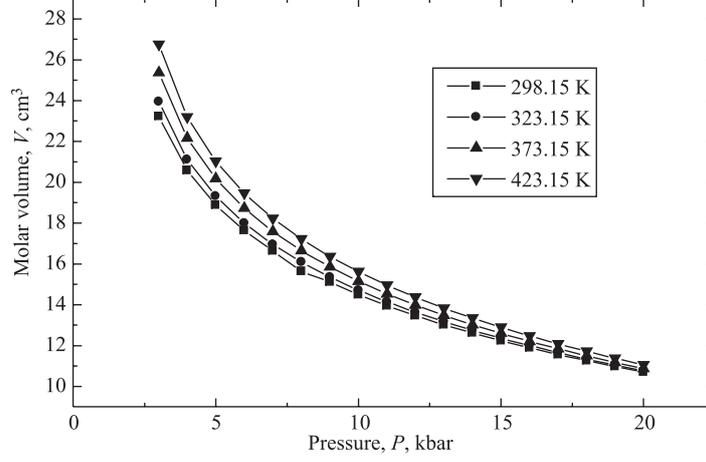
Fig. 3. Interpolation of experimental data (at pressure interval $3.0 \leqslant P \leqslant 7.0$ kbar) and extrapolation (at pressure interval $7.0 < P \leqslant 20.0$ kbar) of hydrogen molar volumes versus pressure on the base of Tait equation (2)
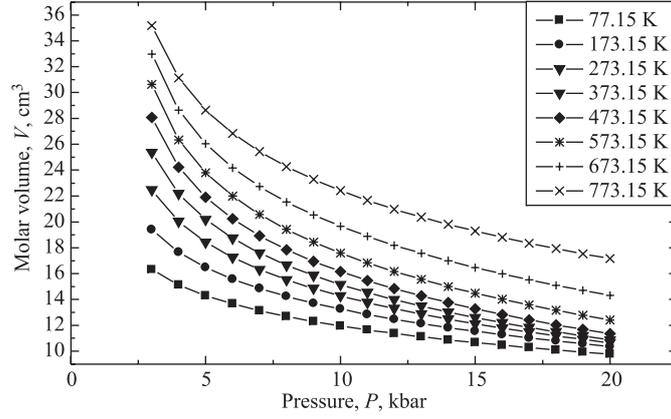
Fig. 4. Interpolation of hydrogen molar volumes versus pressure on the base of Tait equation (2) in temperature interval from 77.15 to 773.15 K with step 100 K

Let us introduce mean distance between hydrogen molecules at pressure P and temperature T:

$$\overline{L}_{\mathrm{H_2-H_2}}(P,T) = [\rho_{\mathrm{H_2}}(P,T)]^{-1/3}, \tag{9.1}$$

13
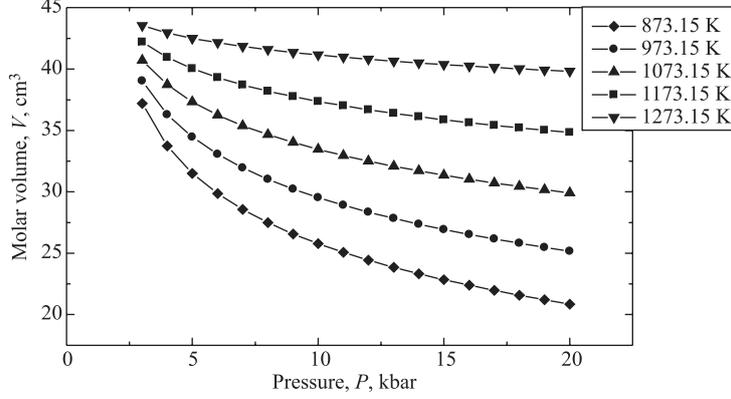
Fig. 5. Interpolation of hydrogen molar volumes versus pressure on the base of Tait equation (2) in temperature interval from $T = 873.15$ K up to $T = 1273.15$ K with step 100 K

Table 13. Calculated and experimental hydrogen volumes versus pressure from $P = 3.0$ kbar to $P = 20.0$ kbar for four temperatures which were used in experimental studies [4, 5]

P, kbar	Temperature, K			
	$T = 298.15$ K	$T = 323.15$ K	$T = 373.15$ K	$T = 423.15$ K
	Molar hydrogen volumes, cm³/mol			
3.0	23.2149/23.22	23.9432/23.91	25.3672/25.33	26.7474/26.70
4.0	20.5748/20.63	21.1151/21.14	22.1678/22.23	23.1978/23.24
5.0	18.8784/18.91	19.3179/19.31	20.1758/20.21	21.0268/21.01
6.0	17.6259/17.65	17.9975/17.98	18.7257/18.75	19.4583/19.70
7.0	16.6326/16.66	16.9534/16.94	17.5849/17.62	18.2295/18.17

or, as what is practically the same, between hydrogen atoms:

$$\overline{L}_{\mathrm{H-H}}(P,T) = [\rho_{\mathrm{H}}(P,T)]^{-1/3} =$$
$$= [2 \cdot \rho_{\mathrm{H_2}}(P,T)]^{-1/3} \approx 0.794 \cdot \overline{L}_{\mathrm{H_2-H_2}}(P,T). \quad (9.2)$$

Here $\rho_{\mathrm{H}}(P,T)$ and $\rho_{\mathrm{H_2}}(P,T)$ are atomic and molecular densities of hydrogen, correspondingly. One of the purposes of this article is to calculate this parameter versus pressure P and temperature T. The value of molecular density of hydrogen can be written in the form:

$$\rho_{\mathrm{H_2}} = N_A/V(P,T), \quad (10)$$

14
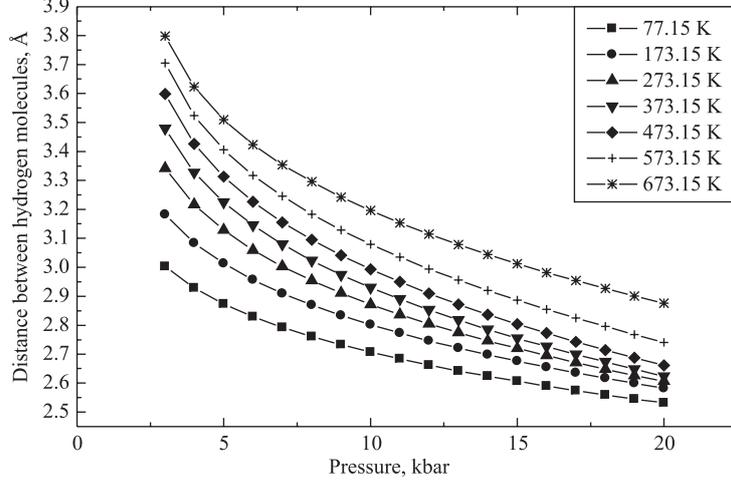
Fig. 6. The mean distances between hydrogen molecules $\overline{L}_{H_2-H_2}(P,T)$ versus the pressure. Curves correspond to temperatures from $T = 77.15$ K up to $T = 673.15$ K with step 100 K

where $N_A = 6.02252 \cdot 10^{23}$ molecules/mole is Avogadro number [10, 15] and $V(P,T)$ is in cm^3.

One can estimate the correlation between mistakes in measurements (or calculations) of molar volume $(V(P,T))$ and mean distance between hydrogen molecules, using the following simple expression:

$$\delta L_{H_2-H_2} \equiv \frac{\Delta L_{H_2-H_2}(P,T)}{L_{H_2-H_2}(P,T)} = \frac{1}{3} \cdot \frac{\Delta V(P,T)}{V(P,T)}. \tag{11}$$

Here $\Delta L_{H_2-H_2}(P,T)$ and $L_{H_2-H_2}(P,T)$ are absolute mistake and value of mean distance between hydrogen molecules. So, relative mistakes of mean distance between hydrogen atoms or molecules $(\delta L_{H_2-H_2})$ are three times less than those of molar volumes. The pressure dependences of mean distances between hydrogen molecules $\overline{L}_{H_2-H_2}(P,T)$ are presented in Fig. 6.

As one can see, mean distances in temperature interval from 77.15 to 673.15 K at pressure $P = 3.0$ kbar change in area $3.003 \leqslant \overline{L}_{H_2-H_2}(P,T) \leqslant 3.798$ Å and at $P = 20.0$ kbar — in interval $2.532 \leqslant \overline{L}_{H_2-H_2}(P,T) \leqslant 2.876$ Å. It means that the saturation of any samples of metals for production of metal hydrides should be carried out at low temperatures and at higher molecular hydrogen densities.

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Below we will estimate the mean distances between hydrogen or deuterium molecules in some metal hydrides [1].

As it is well known, the so-called metallic hydrides are created by transition metals. Such hydrides have some properties which usually occur in metals: high heat and electrical conductivity, hardness, shine, satisfactory mechanical properties. However, hydrides unlike metals are very brittle. The parameters of more interesting metal hydrides are presented in Table 14.

In Table 14 we presented the calculated minimum mean distances between hydrogen atoms in metallic lattices of hydrides using the simplest estimations, such as:

$$\overline{L}_{\text{H−H}}^{\text{Hydride}} = [K \times N]^{-1/3}. \tag{12}$$

Here K is the number of H molecules (see the fourth column in Table 14) in a hydride molecule and N is the atomic density of metal in initial metal without hydrogen. It is clear that the absorption of hydrogen by metals under the process of its saturation should increase the interstitial volume which usually occupies hydrogen atom and in such a manner the parameter of metal lattice in a hydride is increased too (see the fifth column in Table 14 for Ni and Pd, as an example). The known values of Roentgen densities (see the sixth column) prove this conclusion as well. Such a value for UH_3 is decreased drastically from density $\rho_U = 19.04$ g/cm^3 to $\rho_{\text{Hydride}} = 10.91$ g/cm^3. Consequently, expression (12) will give minimum values of mean distances between hydrogen atoms (see the seventh column). More detailed calculations with the original forms of lattices and interstitial positions in lattice will be presented in our next article, which will be dedicated to metal hydrides.

The mean distances between hydrogen atoms $\overline{L}_{\text{H−H}}(P,T)$ in hydrogen gas at not recorded pressures $P = 10$ kbar and $P = 20.0$ kbar and liquid nitrogen and room temperatures $T = 77.15$ K and $T = 298.15$ K are presented in the eighth column for comparison (Table 14)).

One can conclude that mean distances between hydrogen atoms in dense hydrogen gas are lower than such values in any hydrides and for saturation of metals by hydrogen they are better to be used to carry out such saturation (hydride method production high pressures vessels at temperatures less than the room temperatures (see Fig. 4 and Table 14)).

Let us make one short remark at the end of this section. Let us write the same parameters of liquid hydrogen [11–13]: evaporation hydrogen temperature is $T_{\text{evap}} = 20.38$ K, mass density of hydrogen at this temperature is $\rho = 0.0709$ g/cm^3, mass of hydrogen atom is $m_{\text{H}} = 1.67252 \cdot 10^{-24}$ g, atomic density of hydrogen is $N_{\text{H}} \equiv \rho_{\text{H}}/m_{\text{H}} = 4.226 \cdot 10^{22}$ atom/cm^3, so that distances between hydrogen atoms in liquid hydrogen are equal to $\overline{L}_{\text{H−H}}^{\text{Liquid}} = 2.8709$ Å.

Table 14. Parameters of metal hydrides with high hydrogen concentrations

Metal	Metal structure, lattice type and lattice parameter value	N, atom/cm³; ρ, g/cm³	Formula of hybrid	Structure of metal sublattice	Roentgen density, g/cm³	Relative distance between H–H atoms, $\overline{L}_{H-H}^{Hydride}$, Å	P, kbar; T, K; $\overline{L}_{H-H}^{Gas}$, Å
Ti	H.C.P. $a_0 = 0.360$ nm	$5.681 \cdot 10^{22}$ / 4.505	TiH₂	F.C.C.	—	> 2.064	10 kbar 298.15 K 2.292 Å
Zr	H.C.P. $a_0 = 0.323$ nm	$4.284 \cdot 10^{22}$ / 6.45	ZrH₂	F.C.T.	5.61 [1]	> 2.268	
V	B.C.C. $a_0 = 0.303$ nm	$7.045 \cdot 10^{22}$ / 5.96	VH, VH₂	B.C.T, F.C.C.	—	> 2.421, > 1.922	20 kbar 298.15 K 2.072 Å
Cr	B.C.C. $a_0 = 0.288$ nm	$8.338 \cdot 10^{22}$ / 7.2	CrH, CrH₂	H.C.P., F.C.C.	—	> 2.289, > 1.817	
Ni	F.C.C. $a_0 = 0.352$ nm	$9.127 \cdot 10^{22}$ / 8.91	NiH	F.C.C. $a_0 = 0.372$ nm	≈ 7.55*	> 2.221	10 kbar 77.15 K 2.149 Å
Nb	B.C.C. $a_0 = 0.330$ nm	$5.554 \cdot 10^{22}$ / 8.57	NbH, NbH₂	B.C.T., F.C.C.	—	> 2.623, >2.082	
Pd	F.C.C. $a_0 = 0.389$ nm	$6.803 \cdot 10^{22}$ / 12.02	PdH	F.C.C. $a_0 = 0.403$ nm	≈ 9.17*	>2.4496	20 kbar 77.15 K 2.010 Å
U	Orthorhombic 0.285 nm 0.2056 nm	$4.816 \cdot 10^{22}$ / 19.04	β–UH₃, α–UH₃, UD₃	β–W (cubic), B.C.C.	10.91 [1], 10.91 [1], 11.11 [1]	> 1.9057	

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CONCLUSION

Interpolations of experimental data [4–8] using expansion series (1) and (5) were carried out for three sets of parameters at $K = 3, 4, 5$ for each expansion in pressure interval from $P = 3.0$ kbar to $P = 7.0$ kbar. It was shown that unlike calculations presented in [4, 5] for good approximation of experimental values (see Tables 1 and 2) three parameters of expansions (1) or (5) are quite sufficient. Approximation produced in [4, 5] of experimental data with five parameters of expansion (1) has very high value of parameter χ_i^2 (determination of χ_i^2 is presented by Eq. (4)) and cannot be estimated as a good one, rather as much worse.

One can conclude using the method of least square approximation (computer code «FUMILI») and the method of inversion of mistake matrix (computer code «LINEAR») that the obtained parameters (see Tables 5–7) at $K = 3$ can be used not only for approximation of experimental data, but also for extrapolation of molar volumes for wide intervals of temperatures and pressures. Unfortunately, such an expansion provides very weak approximations at pressures $P < 3.0$ kbar.

We have repeated approximations of experimental data ([4–6], see Tables 1 and 2) using Tait equation (2) and such equations in form (3). Our recalculations and comparison of our results and results presented in [4, 5] allowed one to conclude that there is a mistake in Tait equation in the book [5]: mixed up natural logarithms and tenth logarithms. So, this is a reason of so high values of $\chi_i^2(T)$ for the approximation with Tait equation.

By the way, we recalculated the approximation of experimental data (see Tables 1 and 2) with the fifth parameters presented in Table 3 with exchanging in Eq. (1) natural logarithm $(\ln_e(P))$ by the tenth logarithm $(\log_{10}(P))$, however the results were practically the same as presented in Table 4.

Our extrapolations of molar volumes on high pressures interval from $P = 7.0$ kbar to $P = 20$ kbar for four experimental temperatures $T = 298.15$ K, $T = 323.15$ K, $T = 373.15$ K and $T = 423.15$ K using Tait equation (2) and expansion (1) with number of parameters $K = 3$ (parameters from Tables 6 and 9) allow us to mention that these different functions (1) and (2) produce practically the same values of extrapolating molar volumes, because the numerical parameters which were introduced by us (7.1) and (7.2) have very close values: $\Delta_1(T = 298.15$ K$) = 0.3644$ and $\Delta_1(T = 423.15$ K$) = 5.197$ (see expression (7.1)). From this fact we can conclude that our extrapolation is not so bad.

All what we wrote above about the behavior of hydrogen atoms in gas phase is possible to be very easily applied to the behavior of heavier isotopes of hydrogen, excluding mass densities and molar weights/mass. Other parameters of such isotopes should be very close.

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Our last conclusion concerns the so-called cold fusion in hydrides: in any case there is no reason to try to obtain any nuclear reactions of fusion of deuterium–deuterium or tritium–deuterium atoms in any metal hydrides! It was established in a lot of experimental studies, for example, see results presented in [14–17].

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