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EXTRAPOLATION OF HYDROGEN MOLAR VOLUMES
BY THE VIRIAL EQUATION ON WIDE PRESSURE AND
TEMPERATURE INTERVALS

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Экстраполяция молярных oбъемoв вoдopoдa нa ширoкий интервал по температуре и давлению с использованием вириального уравнения

Вириальное уравнение было использовано для аппроксимации экспериментальных молярных oбъемoв вoдopoдa при высоких и низких давлениях для экспериментального интервала температур. Показано, что вириальное уравнение в отличие от уравнений Тейта, лoгарифмического уравнения и других может применяться для широкого интервала температур и давлений. Полученные при фитировании экспериментальных данных вириальные параметры были использованы для последующей экстраполяции их на широкий диапазон температур. Прямое решение линейного уравнения третьего порядка относительно молярных oбъемoв с использованием формулы Кардано или метода Ньютона было использовано для экстраполяции экспериментальных зависимостей от высоких давлений к низким и от низких давлений — к высоким и сверхвысоким. Достаточно хорошее согласие между экспериментальными значениями молярных oбъемoв в зависимости от давления и экстраполированными значениями позволяет сделать вывод о том, что для определенного интервала температур с высокой вероятностью и доказательностью можно проводить экстраполяции на сверхвысокие давления.

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Extrapolation of Hydrogen Molar Volumes by the Virial Equation on Wide Pressure and Temperature Intervals

A virial equation was used for approximation of experimental molar volumes at high and low pressures for experimental temperatures. It was shown that the virial equation can be used for wide pressure and temperature intervals in distinction of the Tait, logarithm and other equations. The obtained under fitting of experimental data virial parameters were used for their following extrapolations on wide temperature intervals. The direct solution of the third order linear virial equations relative to molar volumes using the Kardano or Neuton methods was employed for extrapolation of experimental dependences from high pressure to low pressure and from low pressure to high and superhigh pressures. A quite good agreement between experimental values of molar volumes versus pressures and extrapolating ones allows one to conclude that for a definite temperature interval with high probability and proof it is possible to make extrapolations on superhigh pressures.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

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INTRODUCTION

The behavior of gaseous hydrogen and its heavier isotopes (deuterium and tritium) is very important for some industrial and technical applications [1–6]. Over a long period of time systematic investigations on the low and high temperature properties of hydrogen isotopes H_2 , HD and D_2 were carried out (see, as an example, [6]). The main purpose was to get a better understanding of the intermolecular interactions and influence of mass differences on the properties of gases, particularly, in wave mechanics.

The results of fitting, interpolations and extrapolations of some existing experimental dependences of molar volumes versus high pressure [8, 9] for a wide temperature interval using practically all theoretical and phenomenological formulae such as logarithmic series expansions, the van der Waals, logarithm, Tait and virial equations were presented in the previous articles [10, 11]. All dependences were compared with each other in wide temperature and pressure intervals. It was shown that all these dependences, excluding the virial equation, can be used only for pressures beginning with $P \geq 3$ kbar [10, 11] and the Tait, logarithm and virial equations give very close values up to superhigh pressures of about 20–30 kbar. Also, a method for extrapolation of all dependences for a wide temperature interval is developed [10, 11]. This method is based on extrapolation of equation coefficients using a simple temperature expansion over all temperatures where gas exists as a gas, not as a liquid. It is necessary to note that the behavior of hydrogen and its heavier isotopes such as deuterium and tritium is very important for some applications not only in the gas phase but also for creation of the so-called metal hydrides [1–5, 12–14].

As is well known, the virial equation is most proved for approximation or fitting of molar volume experimental data versus pressure and temperature.

The purpose of this article is to present a theoretical approach to the virial equation and then detailed studies of the applications of virial expansions or better virial equations for fitting of experimental dependences at high pressures [8, 9] and low pressures [6, 8, 15] and their extrapolation on very low and superhigh pressures in a wide temperature interval, correspondingly.

1. THEORETICAL FOUNDATION OF VIRIAL EXPANSIONS [8, 15–19]. STATE VIRIAL EQUATION AND STATISTICAL MECHANICS

The statistical mechanical description of the behavior of liquids and highly compressed gases is connected with grand mathematical difficulties of many-body problems. Such difficulties did not allow using the expansion with a small number of parameters, the way it was done in the theory of low-density gases, or using the symmetric properties of regular structures of particles, which can be found in solids.

Nevertheless, creation of powerful computers and advanced mathematical methods helped to achieve significant progress and success in the study of condensed matter, which makes it possible to obtain not only qualitative but also quantitative correspondence of statistical–mechanical calculations to experimental data.

First serious success in statistical calculations of the thermal state equation was connected with expansion and correct foundation of the virial equation, which is generally widely used in the theory of not very dense gases.

The dependence of the Helmholtz energy F versus volume V is determined by the configuration integral Q_N of a system of particles [8, 15–18]:

$$F(V, T) = -k_B \cdot T \cdot \ln Q_N + f(T), \quad (1)$$

$$Q_N = \int_V \dots \int_V \exp [-U_N/(k_B \cdot T)] \cdot d\mathbf{q}_1 \dots \cdot d\mathbf{q}_N, \quad (2)$$

where T and k are the temperature and Boltzmann constant, correspondingly; $f(T)$ is the well-known temperature function; $d\mathbf{q}_i, i = 1, \dots, N$ are the vectors which determine the position of particles in the system. The potential energy of the U_N system can be represented as a sum of central pair interactions between all particles:

$$U_N = \sum_{i < j}^N \Phi(|\mathbf{q}_i - \mathbf{q}_j|) \equiv \sum_{i < j}^N \Phi_{ij}. \quad (3)$$

Thus, the thermal equation of state can be determined by equality:

$$P(V, T) = -\left(\frac{\partial F}{\partial V}\right)_T = k \cdot T \cdot \frac{1}{Q_N} \cdot \left(\frac{\partial Q_N}{\partial V}\right)_T. \quad (4)$$

Let us introduce the auxiliary functions following the results from book [8]:

$$f_{ij} = \exp [-\Phi_{ij}/(k \cdot T)] - 1. \quad (5)$$

Using functions (5), the configuration integral can be presented in the following form:

$$\begin{aligned}
Q_N &= \int_V \dots \int_V \prod_{i<j}^N (1 + f_{ij}) \cdot d\mathbf{q}_1 \dots \cdot d\mathbf{q}_N = \\
&= \int_V \dots \int_V [1 + \sum_{i<j}^N f_{ij} + \sum_{i<j}^N \sum_{k<l}^N f_{ij} \cdot f_{kl} + \dots] \cdot d\mathbf{q}_1 \dots \cdot d\mathbf{q}_N = \\
&= V^N \cdot [1 + \frac{N \cdot (N-1)}{2 \cdot V} \cdot \beta_1 + \dots], \quad (6)
\end{aligned}$$

where $\beta_1 = \int_V f(r) dr$.

The next members of the expansion can be determined by more difficult groups of integrals. Using expansion (6), Eq. (4) can be written correctly in the final virial state equation form:

$$\frac{P \cdot V_M}{k_B \cdot T} = 1 + \sum_{k=1}^K \frac{b_k}{V_M^k}. \quad (7)$$

Here, $b_1 = \beta_1/2$ is the first virial coefficient, $V_M = V/N$ is the molar volume of gas, K is the number of members in a series expansion.

It is customary to take into account that the virial equation with a small number of members in expansion (7) gives a very poor approximation of experimental data of molar volume versus pressure. According to this confirmation, a lot of members of expansion (7) are important to be taken into consideration.

One of the purposes of this article is to show that expansion (7), in distinction from previous conclusions [8], can be used not only for a fairly good experimental data fit but also can be very effectively used for extrapolations of experimental dependences on wider intervals of temperatures and pressures.

2. APPROXIMATION OF HIGH PRESSURE EXPERIMENTAL MOLAR VOLUME DATA [8, 9]

Let us write the virial series expansion in two forms [20]:

$$\frac{P \cdot V}{R \cdot T} = 1 + \sum_{k=1}^K \frac{A_k}{V^k}, \quad (8.1)$$

$$\frac{P \cdot V}{R \cdot T} = \sum_{k=1}^{K'} \frac{A_k}{V^{k-1}}. \quad (8.2)$$

Table 1. The virial parameters of molar volume experimental data approximations using virial equations (8.1) and (8.2) and corresponding values of χ_i^2

T, K	χ_i^2	A_1	A_2	A_3
Virial equation (8.1)				
293.15	110.8	7.234	867.9	—
323.15	73.41	7.695	800.8	—
373.15	57.76	9.868	708.3	—
423.15	46.42	11.26	628.2	—
293.15	3.967	18.35	115.1	$1.062 \cdot 10^4$
323.15	1.916	15.92	221.0	$8.408 \cdot 10^3$
373.15	1.520	16.34	224.3	$7.365 \cdot 10^3$
423.15	23.05	16.45	240.1	$6.152 \cdot 10^3$
Virial equation (8.2)				
298.15	7.932	1.318	-17.739	$1.226 \cdot 10^3$
323.15	3.993	1.244	-11.272	$1.094 \cdot 10^3$
373.15	3.249	1.177	-4.923	$9.50 \cdot 10^2$
423.15	12.82	1.126	0.291	$8.21 \cdot 10^2$

Here, A_k , $k = 1, 2, \dots$ are the virial expansion equation coefficients, V is the molar volume, K and K' are the number of parameters, R is the universal gas constant. We wrote the second equation in such a form because the virial equation is sometimes written in the form [8]:

$$\frac{P \cdot V}{k_B \cdot T} = \left(\frac{P \cdot V}{k_B \cdot T} \right)_{\text{Solid.Sphere}} - 4 \cdot \eta - 10 \cdot \eta^2 + \frac{A_2}{V} + \frac{A_3}{V^2}, \quad (9)$$

where $(P \cdot V / k_B \cdot T)_{\text{Solid.Sphere}}$ is a state equation of a solid sphere with a diameter a , which can be determined using expressions obtained in [18, 19]. The parameter η has the form: $\eta = \pi \cdot N_A \cdot a^3 / 6 \cdot V$. Thus, using such a presentation in Eq. (8.2), the parameter A_1 should be equal to $A_1 = (P \cdot V / k_B \cdot T)_{\text{Solid.Sphere}} - 4 \cdot \eta - 10 \cdot \eta^2$.

The fit of molar volume experimental values presented in [8, 9] with the use of both expansions (8.1) and (8.2) was carried out by the least square method (LSM). The parameters A_i with the corresponding χ_K^2 are presented in Table 1 (see also [10, 11]). In distinction from the application of the logarithmic series expansion, Tait and logarithm equations for fitting at these approximations, all experimental data were used within the pressure range from $P = 0.5$ up to 7.0 kbar (see [10, 11]). The relative accuracy of experimental data was taken as $\delta \equiv \Delta V / V = \pm 0.01$. In Table 1, the number of experimental points is $N = 14$ [8, 9] and the number of parameters is $K = 2, 3$ for Eq. (8.1) and $K = 3$ for Eq. (8.2), correspondingly. As is seen from Table 1, the use of expression (8.2)

Table 2. Experimental (V_{exp}) and approximated (V_{approx}) values of hydrogen molar volumes using virial equation (8.1) and relative deviations $\Delta \equiv (V_{\text{exp}} - V_{\text{approx}})/V_{\text{exp}}$

P , kbar	T , K							
	298.15		323.15		373.15		423.15	
	$\chi_i^2 = 110.8$	Δ	$\chi_i^2 = 73.41$	Δ	$\chi_i^2 = 57.76$	Δ	$\chi_i^2 = 46.42$	Δ
0.5	65.57/63.884	0.026	69.80/68.690	0.016	78.27/76.816	0.019	86.68/85.709	0.011
1.0	40.79/41.340	-0.014	42.90/43.548	-0.015	47.08/47.242	-0.003	51.26/51.594	-0.007
1.5	32.31/33.334	-0.033	33.71/34.773	-0.032	36.50/37.097	-0.016	39.27/39.972	-0.018
2.0	27.91/28.868	-0.034	28.96/29.965	-0.035	31.05/31.683	-0.020	33.13/33.850	-0.022
2.5	25.16/25.869	-0.028	25.99/26.793	-0.031	27.68/28.165	-0.018	29.33/29.945	-0.021
3.0	23.22/23.687	-0.020	23.91/24.496	-0.025	25.33/25.657	-0.013	26.70/27.184	-0.018
3.5	21.77/21.987	-0.010	22.37/22.707	-0.015	23.59/23.734	-0.006	24.76/25.087	-0.013
4.0	20.63/20.615	-0.001	21.14/21.297	-0.007	22.23/22.203	0.0012	23.24/23.440	-0.009
4.5	19.59/19.627	-0.002	20.14/20.133	0.0004	21.13/20.946	0.009	22.02/22.089	-0.003
5.0	18.91/18.534	0.020	19.31/19.144	0.009	20.21/19.895	0.016	21.01/20.957	0.003
5.5	18.24/17.715	0.029	18.60/18.298	0.016	19.43/18.994	0.023	20.15/19.997	0.008
6.0	17.65/17.011	0.036	17.98/17.568	0.023	18.75/18.219	0.028	19.70/18.828	0.044
6.5	17.13/16.392	0.043	17.43/16.931	0.029	18.15/17.544	0.033	18.75/18.452	0.016
7.0	16.66/15.851	0.049	16.94/16.368	0.034	17.62/16.942	0.039	18.17/17.817	0.019

with $K = 3$ gives a better fit of experimental data than expression (8.1) with only two virial coefficients ($K = 2$). The use of expression (8.1) with three virial parameters gives a good fit, too! Unfortunately, the use of the procedure developed in [10, 11] is more difficult, i.e., for extrapolation of molar volumes it is necessary to solve an equation of the fourth order like (10) relative to molar volume V .

In Table 2, the experimental (left column) and calculated (right column) values of hydrogen molar volumes using virial equation (8.1) with two virial coefficients ($K = 2$) for the number of experimental points $N = 14$ are presented for four temperatures for illustrative comparison.

As was shown in [10] and is visible from Table 1, for fitting the experimental molar volumes versus pressure and temperature two parameters (the first case) are enough for expression (8.1) and three parameters (the second case) for expansion (8.2). But in the second case the fit of experimental data is better than in the first case. Everywhere in this article the relative mistake for experimental molar volumes was taken equal to $\delta \equiv \Delta V_{\text{exp}}/V_{\text{exp}} = \pm 0.01$.

Below in this and in the next paragraphs we will try and use both expansions (8.1) and (8.2) for extrapolation of molar volumes for low pressures (i.e., $P < 3$ kbar and much lower pressures) and compare them with existing experimental data [6, 15]. For that we will use the procedure developed in [10, 11]. Let us introduce and rewrite expression (8) in the following forms, as an equation of

Table 3. Extrapolation of two virial parameters of Eq. (10.1) and three virial parameters of Eq. (10.2) versus temperature. Top values of the parameters obtained by fitting of experimental data [8, 9] for the temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K

T, K	Equation (10.1)		Equation (10.2)		
	$A_1,$ cm^3/mol	$A_2,$ $(\text{cm}^3/\text{mol})^2$	A_1	$A_2,$ cm^3/mol	$A_3,$ $(\text{cm}^3/\text{mol})^2$
77.15	3.115	1639.564	2.261	-65.243	2686.927
123.15	3.543	1440.533	1.998	-52.698	2297.939
173.15	4.254	1246.639	1.752	-40.394	1924.025
223.15	5.220	1076.125	1.546	-29.478	1601.046
273.15	6.442	928.991	1.381	-19.949	1329.003
298.15	7.234	867.9	1.318	-17.739	1.226·10³
	7.149	864.192	1.314	-15.705	1212.083
323.15	7.695	800.8	1.244	-11.272	1.094·10³
	7.919	805.237	1.257	-11.809	1107.896
373.15	9.868	708.3	1.177	-4.923	9.50·10²
	9.652	704.863	1.173	-5.056	937.725
423.15	11.26	628.2	1.126	0.291	8.21·10²
	11.641	627.869	1.130	0.309	818.490
473.15	13.885	574.255	1.28	4.286	750.190
573.15	19.139	537.166	1.46	8.078	766.399
673.15	25.416	593.596	1.26	6.317	986.351
773.15	32.715	743.547	1.69	-0.994	1410.047
873.15	41.037	987.017	2.575	-13.856	2037.486
973.15	50.380	1324.007	3.343	-32.270	2868.668
1073.15	60.746	1754.516	4.274	-56.235	3903.594
1173.17	72.134	2278.545	5.368	-85.751	5142.264
1273.15	84.545	2896.094	6.625	-120.818	6584.677
1373.15	97.977	3607.162	8.044	-161.436	8230.833
1473.15	112.432	4411.750	9.626	-207.606	10080.733

the third order relative to variable V , respectively [10, 11]:

$$\frac{P}{R \cdot T} \cdot V^3 - V^2 - \sum_{i=1}^2 A_i \cdot V^{2-i} = 0, \quad (10.1)$$

$$\frac{P}{R \cdot T} \cdot V^3 - \sum_{i=1}^3 A_i \cdot V^{3-i} = 0. \quad (10.2)$$

One can see that for extrapolation of Eqs.(8) on a wide pressure interval it is necessary to solve this equation relatively to the molar volume V , i.e., to obtain an exact solution to Eqs. (10.1) and (10.2). In the beginning, one can

Table 4. Experimental [8,9] and directly calculated values of hydrogen molar volumes using virial equation (8.1) and the Kardano method for the pressure interval 0.5–7.0 kbar and extrapolated values in the wide pressure interval 8.0–30.0 kbar

P , kbar	T , K				
	298.15(10.1)	323.15(10.1)	373.15(10.1)	423.15(10.1)	423.15 (10.2)
0.5	65.57/65.124	69.80/68.994	78.27/77.160	86.68/85.891	86.68/87.316
1.0	40.79/41.499	42.90/43.313	47.08/47.191	51.26/51.476	51.26/51.029
1.5	32.31/33.117	33.71/34.304	36.50/36.843	39.27/39.686	39.27/39.189
2.0	27.91/28.594	28.96/29.485	31.05/31.385	33.13/33.526	33.13/33.147
2.5	25.16/25.676	25.99/26.394	27.68/27.921	29.33/29.650	29.33/29.388
3.0	23.22/23.594	23.91/24.201	25.33/25.484	26.70/26.941	26.70/26.776
3.5	21.77/22.014	22.37/22.540	23.59/23.652	24.76/24.916	24.76/24.830
4.0	20.63/20.759	21.14/21.227	22.23/22.210	23.24/23.330	23.24/23.308
4.5	19.59/19.732	20.14/20.154	21.13/21.038	22.02/22.046	22.02/22.076
5.0	18.91/18.870	19.31/19.255	20.21/20.060	21.01/20.979	21.01/21.051
5.5	18.24/18.132	18.60/18.487	19.43/19.228	20.15/20.074	20.15/20.181
6.0	17.65/17.491	17.98/17.821	18.75/18.508	19.70/19.293	19.70/19.431
6.5	17.13/16.927	17.43/17.236	18.15/17.877	18.75/18.611	18.75/18.774
7.0	16.66/16.426	16.94/16.717	17.62/17.318	18.17/18.007	18.17/18.193
	$\uparrow \chi_i^2 = 29.29$	$\uparrow \chi_i^2 = 17.50$	$\uparrow \chi_i^2 = 13.99$	$\uparrow \chi_i^2 = 11.90$	$\uparrow \chi_i^2 = 3.092$
8.0	15.569	15.830	16.368	16.984	17.207
10.0	14.259	14.478	14.926	15.439	15.711
12.0	13.288	13.479	13.865	14.309	14.614
14.0	12.529	12.699	13.041	13.434	13.760
16.0	11.913	12.067	12.376	12.730	13.070
18.0	11.400	11.541	11.823	12.146	12.499
20.0	10.962	11.093	11.353	11.652	12.010
22.0	10.583	10.706	10.948	11.226	11.587
24.0	10.250	10.365	10.592	10.853	11.216
26.0	9.954	10.063	10.277	10.523	10.902
28.0	9.689	9.793	9.995	10.228	10.592
30.0	9.449	9.548	9.741	9.962	10.338

solve both third order equations (10.1) and (10.2) versus variable V with the found virial parameters (see Table 1). The calculated exact solutions of molar volumes obtained using the Kardano method (see Appendix in [11]) are presented in Table 4 together with experimental data [8,9] (left column), and the square deviations $\chi_i^2 = \sum_{j=1}^N [(V_{\text{exp}} - V_{\text{calc}}^{\text{Kardano}})/\delta \cdot V_{\text{exp}}]^2$ are given, too.

Following the method developed in [10] we found the virial parameters $A_i, i = 1, 2$, for expression (8.1) and $A_i, i = 1, 2, 3$, for expression (8.2) versus

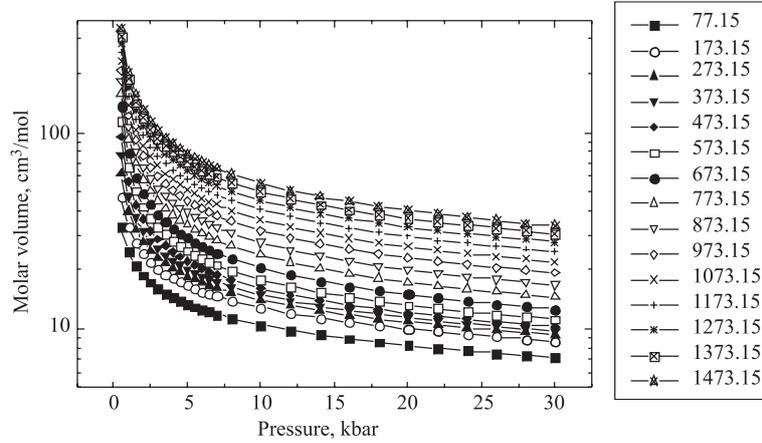


Fig. 1. Molar volumes versus pressure dependences for different temperatures. Here two virial parameters for Eq. (10.1) from Table 3 were used

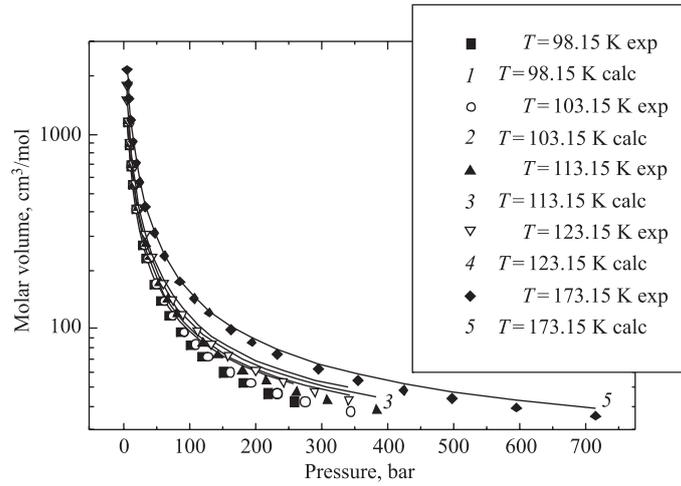


Fig. 2. Experimental (from [15]) and calculated on the base of virial parameters (see Table 3) and direct solution of Eq. (10.1) molar volumes. Here the values of χ_i^2 , numbers of experimental points and parameters N and K , and values of parameters are the following: at $T = 98.15$ K, $\chi_i^2 = 2.43 \cdot 10^3$; $N = 17$; $K = 2$; $A_1 = 3.2116$; $A_2 = 1556.7896$; at $T = 103.15$ K, $\chi_i^2 = 2.88 \cdot 10^3$; $N = 18$; $K = 2$; $A_1 = 3.2795$; $A_2 = 1534.8057$; at $T = 113.15$ K, $\chi_i^2 = 2.10 \cdot 10^3$; $N = 17$; $K = 2$; $A_1 = 3.3829$; $A_2 = 1491.5599$; at $T = 123.15$ K, $\chi_i^2 = 1.31 \cdot 10^3$; $N = 19$; $K = 2$; $A_1 = 3.4965$; $A_2 = 1449.2770$; at $T = 173.15$ K, $\chi_i^2 = 0.50 \cdot 10^3$; $N = 22$; $K = 2$; $A_1 = 4.2157$; $A_2 = 1252.3040$

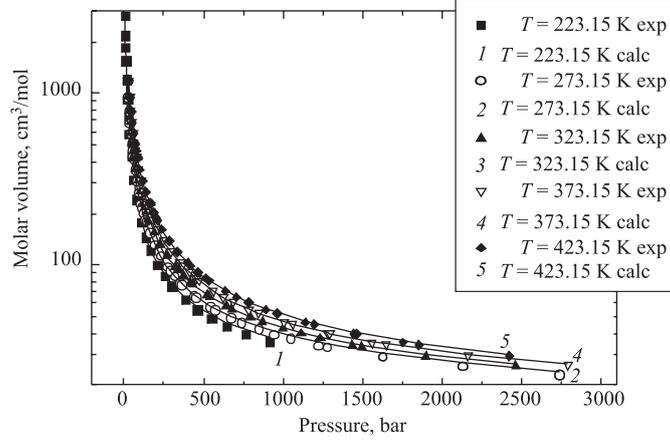


Fig. 3. Same as in Fig. 2, but here the values of χ_i^2 , numbers of experimental points and parameters N and K , and values of parameters are the following: at $T = 223.15$ K, $\chi_i^2 = 152.6$; $N = 23$; $K = 2$; $A_1 = 5.1874$; $A_2 = 1079.4004$; at $T = 273.15$ K, $\chi_i^2 = 132.0 \cdot 10^3$; $N = 40$; $K = 2$; $A_1 = 6.4117$; $A_2 = 930.5663$; at $T = 323.15$ K, $\chi_i^2 = 50.59$; $N = 39$; $K = 2$; $A_1 = 7.8885$; $A_2 = 805.8017$; at $T = 373.15$ K, $\chi_i^2 = 26.82$; $N = 39$; $K = 2$; $A_1 = 9.6179$; $A_2 = 705.1067$; at $T = 423.15$ K, $\chi_i^2 = 32.07$; $N = 38$; $K = 2$; $A_1 = 11.5998$; $A_2 = 628.4811$

temperature using the LSM. These parameters are also presented in [10, 11] and in Table 3.

Then we found exact solutions (roots of equations) to linear equations of the third order (10.1) and (10.2) relatively to the molar volumes $V(T, P)$ for each pressure P using the Kardano method (see [11], Appendix 2) and the numerical Neuton method for comparison [11]. The obtained (exact solutions) and experimental values of molar volumes versus pressure for four experimental temperatures [8, 9] and square deviations are presented in Table 4 with the use of Eq. (10.1). As one can see, this approach gives better agreement with the experimental data in the pressure interval 0.5–7.0 kbar.

Extrapolation of molar volumes on a wide temperature interval and for super high pressures using Eq. (10.2) with the extrapolated virial parameters presented in Table 3 gives very poor approximations of experimental data [7, 8] with the least square parameters equal to $\chi_i^2 = 1.323 \cdot 10^5$, $\chi_i^2 = 4.166 \cdot 10^4$, $\chi_i^2 = 5.236 \cdot 10^3$ for three temperatures $T = 298.15$, 323.15 and 373.15 K, respectively, and there is good coincidence only for $T = 423.15$ K ($\chi_i^2 = 3.09$).

We presented values of molar volumes for temperature $T = 423.15$ K in Table 4 in the fifth column. It is necessary to note that the use of extrapolated virial parameters for Eq. (10.2) for calculations of molar volumes using the Kar-

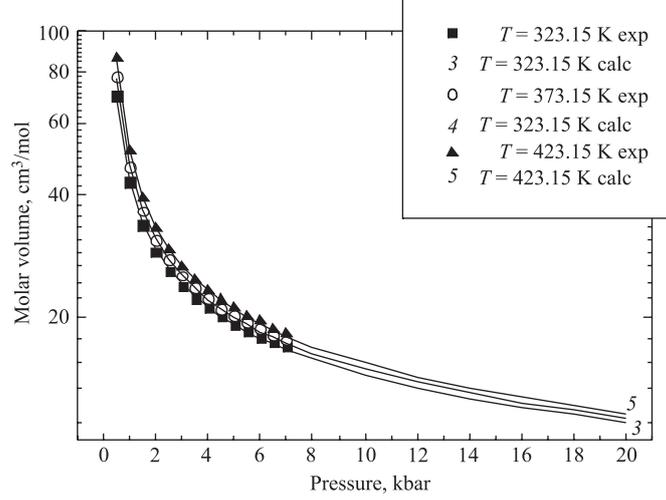


Fig. 4. Experimental (from [15], experimental values of pressure change from $P = 3.0$ kbar to $P = 7.0$ kbar) and calculated on the base of virial parameters (see Table 3) and direct solution of Eq. (10.1) molar volumes. Here the values of χ_i^2 , number of experimental points and parameters N and K , and values of parameters are the following: at $T = 323.15$ K, $\chi_i^2 = 17.39$; $N = 14$; $K = 2$; $A_1 = 7.8885$; $A_2 = 805.8017$; at $T = 373.15$ K, $\chi_i^2 = 14.08$; $N = 14$; $K = 2$; $A_1 = 9.6179$; $A_2 = 705.1067$; at $T = 423.15$ K, $\chi_i^2 = 11.79$; $N = 14$; $K = 2$; $A_1 = 11.5998$; $A_2 = 628.4811$

dano formulae (see Appendix in [11]) gives unphysical behaviour at temperatures lower than $T \leq 373.15$ K and a very strong growth at $T \geq 573.15$ K, particularly, at the low pressure $P < 2.0$ kbar.

Let us present the dependences of molar volumes from low pressure $P = 0.5$ kbar up to $P = 30.0$ kbar using the virial parameter for Eq. (10.1) from Table 3 for more interesting temperatures from our point of view. Such dependences for the wide temperature interval $77.15 \leq T \leq 1473.15$ K are presented in Fig.1. Below, we will show extrapolation of molar volume dependences at low pressure and compare them with existing original and handbook experimental data [6, 15].

2.1. Extrapolation of Molar Volume Dependences with Virial Parameters Obtained for the High Pressure Region in the Low Pressure Interval. In the beginning, virial parameters for all experimental temperatures used in the experimental measurements in [6, 15] were calculated. Most of these parameters are presented in Table 3. Then, direct solving of third order equations (10.1) and (10.2) was performed by the Kardano method (see Appendix in [11]). In Figs.2 and 3 the following calculated values and experimental data of molar volumes with the least square parameters χ_i^2 are presented.

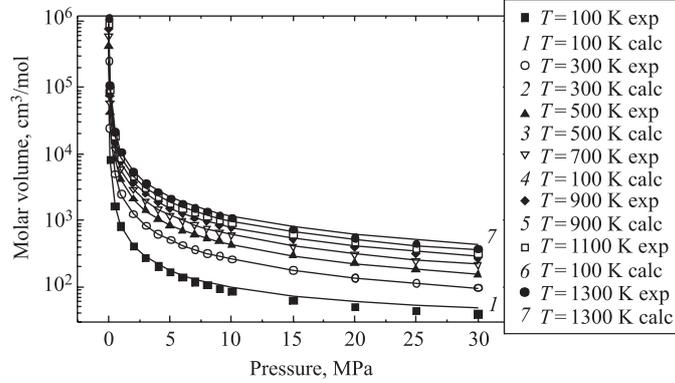


Fig. 5. Experimental [6] and calculated dependences of molar volumes versus pressure for different temperatures. Here two virial parameters for Eq. (10.1) from Table 3 were used. Here the values of χ_i^2 , numbers of experimental points and parameters N and K , and values of parameters are the following: at $T = 100$ K, $\chi_i^2 = 2.194 \cdot 10^3$; $N = 17$; $K = 2$; $A_1 = 3.249$; $A_2 = 1548.6$; at $T = 300$ K, $\chi_i^2 = 32.51$; $N = 17$; $K = 2$; $A_1 = 7.17$; $A_2 = 860.57$; at $T = 500$ K, $\chi_i^2 = 0.26$; $N = 17$; $K = 2$; $A_1 = 15.14$; $A_2 = 557.63$; at $T = 700$ K, $\chi_i^2 = 64.21$; $N = 17$; $K = 2$; $A_1 = 27.14$; $A_2 = 639.81$; at $T = 900$ K, $\chi_i^2 = 243.4$; $N = 17$; $K = 2$; $A_1 = 43.19$; $A_2 = 1107.09$; at $T = 1100$ K, $\chi_i^2 = 543.1$; $N = 17$; $K = 2$; $A_1 = 63.28$; $A_2 = 1485.49$; at $T = 1300$ K, $\chi_i^2 = 2.19 \cdot 10^3$; $N = 14$; $K = 2$; $A_1 = 87.41$; $A_2 = 3194.00$

All experimental data in [15] were given in the so-called AMAGAT values, so we recalculated these data to provide them in commonly measured units. In Table 6, the number of parameters is equal to $K = 2$, the number of experimental points varies from $N = 17$ to $N = 40$, the units of measurement of virial parameters are $[A_1] = \text{cm}^3/\text{mol}$, $[A_2] = (\text{cm}^3/\text{mol})^2$.

Experimental values (from [8, 9] of pressure change from $P = 3.0$ kbar to $P = 7.0$ kbar) and calculated on the base of virial parameters (see Table 3) and direct solution of Eq. (10.1) molar volumes are presented in Fig. 4.

One can conclude from Fig. 2–4 that extrapolation of molar volume versus pressure using virial parameters obtained by approximating high pressure experimental data [8, 9] on low pressure dependences [15] gives not so bad extrapolation. It is necessary to note that in the cases of the temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K the obtained virial parameters give a very good approximation in high ($0.5 \leq P \leq 7.0$ kbar) and low ($20.0 < P \leq 3000.0$ bar) pressure intervals.

Let us repeat the procedure for extrapolation of experimental data in the low pressure [6] ($0.01 \leq P \leq 30.0$ MPa, as is well known $1 \text{ MPa} = 10 \text{ bar}$) interval just for a very wide temperature interval ($50 \leq T \leq 1500$ K). For that

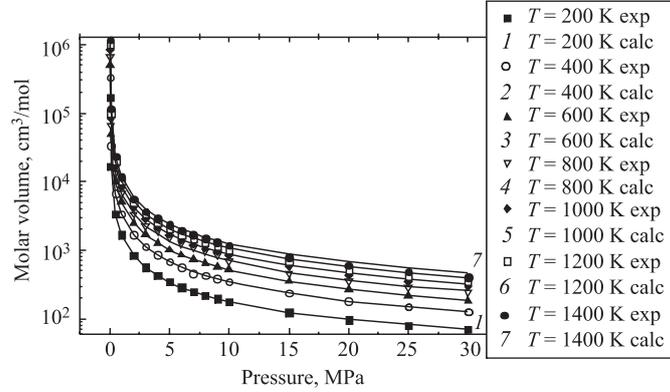


Fig. 6. Same as in Fig. 5. Here two virial parameters for Eq. (10.1) from Table 3 were used. Here the values of χ_i^2 , number of experimental points and parameters N and K , and values of parameters are the following: at $T = 200$ K, $\chi_i^2 = 20.13$; $N = 17$; $K = 2$; $A_1 = 4.71$; $A_2 = 1156.46$; at $T = 400$ K, $\chi_i^2 = 66.13$; $N = 17$; $K = 2$; $A_1 = 10.65$; $A_2 = 660.97$; at $T = 600$ K, $\chi_i^2 = 18.32$; $N = 17$; $K = 2$; $A_1 = 20.64$; $A_2 = 550.58$; at $T = 800$ K, $\chi_i^2 = 664.9$; $N = 17$; $K = 2$; $A_1 = 34.66$; $A_2 = 825.31$; at $T = 1000$ K, $\chi_i^2 = 363.1$; $N = 17$; $K = 2$; $A_1 = 52.73$; $A_2 = 1485.15$; at $T = 1200$ K, $\chi_i^2 = 650.5$; $N = 17$; $K = 2$; $A_1 = 74.84$; $A_2 = 2530.10$; at $T = 1400$ K, $\chi_i^2 = 3.960 \cdot 10^3$; $N = 14$; $K = 2$; $A_1 = 100.98$; $A_2 = 3960.17$

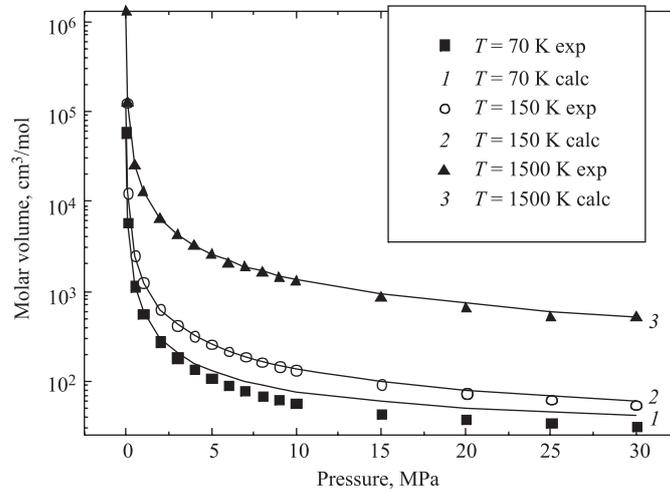


Fig. 7. Dependences of molar volumes versus pressure for various temperatures. Here two virial parameters for Eqs. (8.1) and (10.1) from Table 3 were used: at $T = 70$ K, $\chi_i^2 = 1.005 \cdot 10^4$; $N = 14$; $K = 2$; $A_1 = 3.01$; $A_2 = 1685.0$; at $T = 150$ K, $\chi_i^2 = 250.2$; $N = 14$; $K = 2$; $A_1 = 3.85$; $A_2 = 1341.0$; at $T = 1500$ K, $\chi_i^2 = 1.22 \cdot 10^3$; $N = 14$; $K = 2$; $A_1 = 115.57$; $A_2 = 4820.0$

we will use again the extrapolated virial coefficients obtained for high pressures ($0.5 \leq P \leq 7.0$ kbar) and for four experimental temperatures [8, 9]. Results from this extrapolation are given in Figs. 5, 6 and 7.

As one can see, extrapolation from high pressures ($0.5 \leq P \leq 7.0$ kbar) to low pressures ($0.01 \leq P \leq 30.0$ MPa) in the wide temperature interval from 70 to 1500 K is possible and in the temperature range $150 \leq T \leq 1200$ K such an extrapolation can be considered very good because the χ_i^2 parameter is suitable and small. It is necessary to note that the use of Eqs. (8.2) and (10.2) with three parameters extrapolated on a wide temperature interval brings very poor agreement of experimental [6] and calculated values of molar volumes.

As an example, the parameter is $\chi_i^2 = 4.131 \cdot 10^3, 9.551 \cdot 10^3, 2.336 \cdot 10^3, 2.491 \cdot 10^3, 2.495 \cdot 10^4$ for $T = 200, 300, 400, 500, 600$ K, respectively.

3. APPROXIMATION OF LOW PRESSURE EXPERIMENTAL MOLAR VOLUME DATA [6, 16] AND EXTRAPOLATION OF MOLAR VOLUME DEPENDENCES IN THE HIGH PRESSURE REGION

Let us fit the experimental data presented in [6, 16] with the help of virial expansions (8.1) and (8.2). In the beginning, we approximated the experimental data presented in [6]. In it both presentations of virial expansions were used. The experimental molar volumes and calculated values obtained using the least square method (LSM) (see Appendix 1 in [11]), three virial parameters and χ_i^2 for each temperature are presented in Figs. 8 and 9.

It is necessary to note that there is poor extrapolation at $T = 50, 70$ and 400 K. Here, the number of points $N = 17$ and the number of parameters $K = 3!$

Let us make the next step in extrapolating virial parameters on a wide temperature interval including the experimental temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K. The extrapolated and smoothed out parameters are presented in Fig. 10 for the calculated virial parameters using the LSM and extrapolation expression (11) (see [11]) given in Figs. 8 and 9.

The experimental [6] and calculated with the Kardano method (see Appendix in [11]) hydrogen molar volumes with virial parameters from Fig. 10. are presented in Fig. 11. The square deviations of these values are also given.

The experimental [8, 9] and calculated with the Kardano method (see Appendix in [11]) hydrogen molar volumes for temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K with the virial parameters from Fig. 10 are presented in Table 5. The square deviations of these values are given, too. The parameters χ^2 are calculated for all temperatures at $\delta = \Delta V/V = \pm 0.01$.

Let us perform the fitting of the experimental data presented in [6] using virial expansion (8.1) to compare it with the data fitted using expansion (8.2). The experimental molar volumes and calculated values obtained with the least

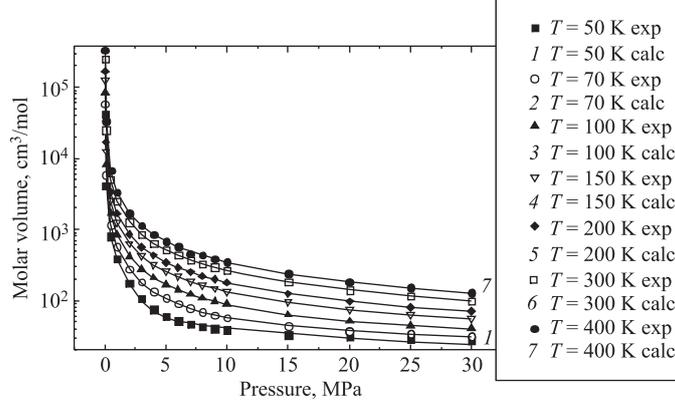


Fig. 8. Dependence of the molar volume experimental (V_{exp}) and calculated (V_{LSM}) values versus pressure obtained using the least square method (LSM) (see Appendix 1 in [11]) and Eq. (8.2) with three virial parameters and χ_i^2 for each temperature. Here the parameters T , χ_i^2 , N , K and A_1 , A_2 , A_3 have the following values: at $T = 50$ K, $\chi_i^2 = 508.6$; $N = 17$; $K = 3$; $A_1 = 1.0494$; $A_2 = -54.58$; $A_3 = 1992.7$; at $T = 70$ K, $\chi_i^2 = 48.50$; $N = 17$; $K = 3$; $A_1 = 1.0159$; $A_2 = -24.00$; $A_3 = 1315.5$; at $T = 100$ K, $\chi_i^2 = 4.35$; $N = 17$; $K = 3$; $A_1 = 1.0050$; $A_2 = -5.88$; $A_3 = 899.02$; at $T = 150$ K, $\chi_i^2 = 1.97$; $N = 17$; $K = 3$; $A_1 = 0.9969$; $A_2 = 4.68$; $A_3 = 686.82$; at $T = 200$ K, $\chi_i^2 = 0.032$; $N = 17$; $K = 3$; $A_1 = 1.0009$; $A_2 = 10.05$; $A_3 = 543.75$; at $T = 300$ K, $\chi_i^2 = 0.0036$; $N = 17$; $K = 3$; $A_1 = 1.0003$; $A_2 = 14.13$; $A_3 = 420.15$; at $T = 400$ K, $\chi_i^2 = 61.83$; $N = 17$; $K = 3$; $A_1 = 1.0008$; $A_2 = 8.34$; $A_3 = 1396.36$

square method (LSM) (see Appendix 1 in [11]), two virial parameters and χ_i^2 for each temperature are presented in Fig. 12.

Then we extrapolated virial parameters with smoothing on a wide temperature interval including the experimental temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K. The experimental [6] and calculated values of molar volumes obtained using the Kardano method (see Appendix 2 in [11]) and derived virial parameters are presented in Fig. 13. It is necessary to note that extrapolation of molar volumes at temperatures $T = 50, 70, 100$ and 150 K yields poor results because parameters χ^2 are large.

Let us extrapolate virial parameters with smoothing on the experimental temperature interval including temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K. The derived data are presented in Table 6.

As one can see, the behavior of molar volumes versus pressure at $T = 423.15$ K is unphysical because beginning with the pressure $P = 4.0$ kbar molar volumes are smaller than at the corresponding pressure at a lower temperature $T = 373.15$ K.

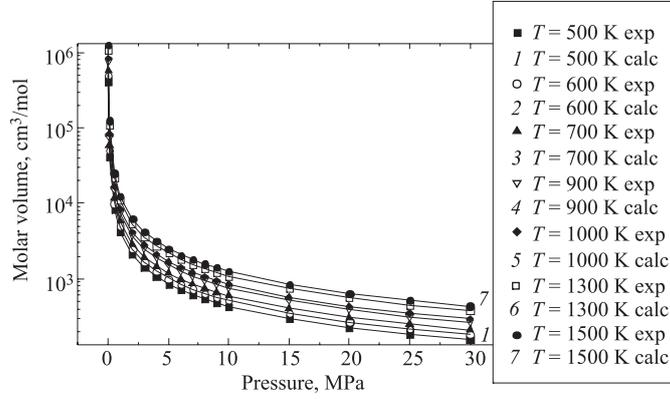


Fig. 9. Same as in Fig.8, but here parameters T , χ_i^2 , N , K and A_1 , A_2 , A_3 have the following values: at $T = 500$ K, $\chi_i^2 = 0.034$; $N = 17$; $K = 3$; $A_1 = 1.0005$; $A_2 = 16.20$; $A_3 = 333.0$; at $T = 600$ K, $\chi_i^2 = 1.62$; $N = 17$; $K = 3$; $A_1 = 0.9996$; $A_2 = 16.18$; $A_3 = 424.52$; at $T = 700$ K, $\chi_i^2 = 0.01$; $N = 17$; $K = 3$; $A_1 = 1.0006$; $A_2 = 16.5335$; $A_3 = 315.85$; at $T = 900$ K, $\chi_i^2 = 0.078$; $N = 17$; $K = 3$; $A_1 = 1.0005$; $A_2 = 16.46$; $A_3 = 338.37$; at $T = 1000$ K, $\chi_i^2 = 0.45$; $N = 17$; $K = 3$; $A_1 = 1.0017$; $A_2 = 15.36$; $A_3 = 535.69$; at $T = 1300$ K, $\chi_i^2 = 0.087$; $N = 17$; $K = 3$; $A_1 = 1.0012$; $A_2 = 14.79$; $A_3 = 781.62$; at $T = 1500$ K, $\chi_i^2 = 9.32$; $N = 17$; $K = 3$; $A_1 = 1.0008$; $A_2 = 7.86$; $A_3 = 4265.44$

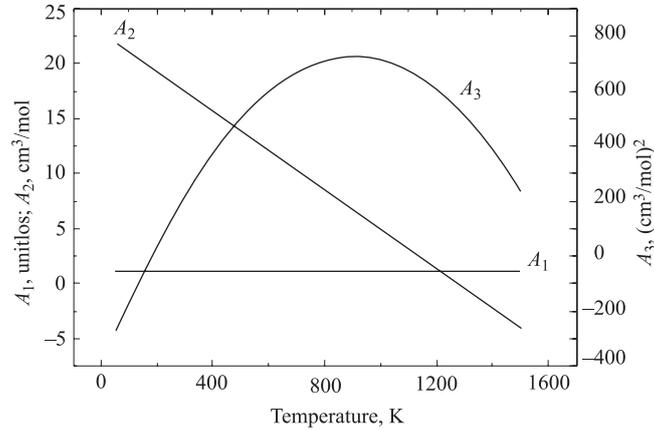


Fig. 10. Dependences of extrapolated and smoothed out virial parameters versus temperature for Eqs. (8.2) and (10.2)

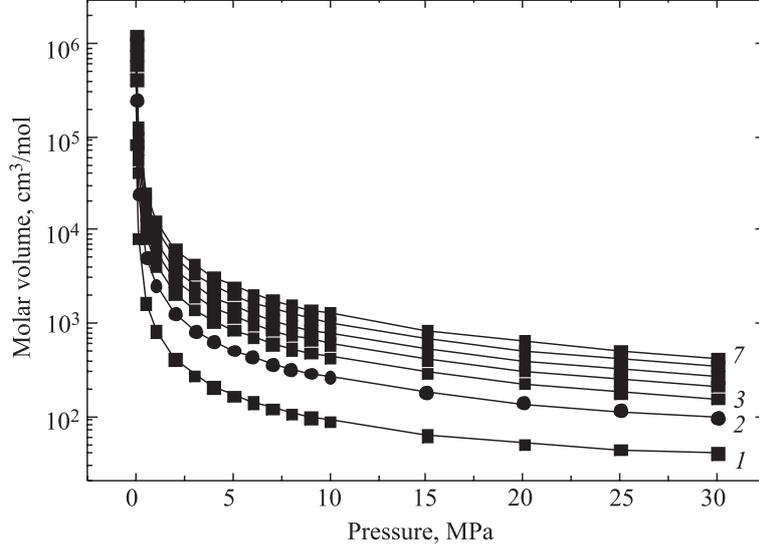


Fig. 11. Dependences of experimental [6] and calculated hydrogen molar volumes versus pressure with Eq. (10.2) and the Kardano method (see Appendix in [11]) and smoothed virial parameters from Fig. 10. Here parameters T , χ_i^2 , N , K and A_1 , A_2 , A_3 have the following values: Curve 1 at $T = 100$ K, $\chi_i^2 = 74.92$; $N = 17$; $K = 3$; $A_1 = 1.013$; $A_2 = -1.448$; $A_3 = 714.593$; Curve 2 at $T = 300$ K, $\chi_i^2 = 25.09$; $N = 17$; $K = 3$; $A_1 = 1.0076$; $A_2 = 8.218$; $A_3 = 587.103$; Curve 3 at $T = 500$ K, $\chi_i^2 = 0.52$; $N = 17$; $K = 3$; $A_1 = 1.003$; $A_2 = 15.126$; $A_3 = 455.697$; Curve 4 at $T = 700$ K, $\chi_i^2 = 3.318$; $N = 17$; $K = 3$; $A_1 = 1.000$; $A_2 = 19.274$; $A_3 = 320.376$; Curve 5 at $T = 900$ K, $\chi_i^2 = 2.757$; $N = 17$; $K = 3$; $A_1 = 0.998$; $A_2 = 20.663$; $A_3 = 181.139$; Curve 6 at $T = 1200$ K, $\chi_i^2 = 1.956$; $N = 17$; $K = 3$; $A_1 = 0.997$; $A_2 = 17.574$; $A_3 = -35.059$; Curve 7 at $T = 1500$ K, $\chi_i^2 = 19.63$; $N = 17$; $K = 3$; $A_1 = 1.000$; $A_2 = 8.277$; $A_3 = -260.067$

Very accurate and correct results for dependences of molar volumes versus pressure in a very wide temperature interval 98.15–423.15 K with the step about 15–25° were obtained in a relatively old article [15]. All the measured parameters such as ρ , $P \cdot V$ were presented in the so-called AMAGAT units of measurements, and pressure — in the international atmosphere. Fitting of experimental data was performed using a practically virial expansion but with six parameters of expansion [15]:

$$P \cdot V = \sum_{k=0}^K A_k \cdot \rho^k. \quad (11)$$

This expression is practically an analogy to virial expansion (8.1), where ρ is the density of hydrogen and the parameter $A_0 = R_g \cdot T$, R_g is the universal gas

Table 5. The experimental [8, 9] and calculated with the Kardano method (see Appendix in [11]) hydrogen molar volumes for the experimental temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K with the virial parameters from Fig. 10

$P,$ kbar	T, K							
	298.15		323.15		373.15		423.15	
A_1	$A_1 = 1.00768;$		$A_1 = 1.00705;$		$A_1 = 1.00586;$		$A_1 = 1.00475;$	
A_2	$A_2 = 8.14156;$		$A_2 = 9.15904;$		$A_2 = 11.06468;$		$A_2 = 12.79788;$	
A_3	$A_3 = 588.30017$		$A_3 = 572.09308$		$A_3 = 539.49542$		$A_3 = 506.65305$	
χ^2	$\chi^2 = 798.5$ $N = 14, K = 2$		$\chi^2 = 573.2$ $N = 14, K = 2$		$\chi^2 = 309.1$ $N = 14, K = 2$		$\chi^2 = 141.5$ $N = 14, K = 2$	
	$V_{\text{exp}},$ cm^3/mol	$V_{\text{Kardano}},$ cm^3/mol	$V_{\text{exp}},$ cm^3/mol	$V_{\text{Kardano}},$ cm^3/mol	$V_{\text{exp}},$ cm^3/mol	$V_{\text{Kardano}},$ cm^3/mol	$V_{\text{exp}},$ cm^3/mol	$V_{\text{Kardano}},$ cm^3/mol
0.5	65.57	63.538	69.80	68.001	78.27	76.982	86.68	85.993
1.0	40.79	39.460	42.90	41.763	47.08	46.387	51.26	51.022
1.5	32.31	31.062	33.71	32.665	36.50	35.863	39.27	39.048
2.0	27.91	26.594	28.96	27.853	31.05	30.347	33.13	32.814
2.5	25.16	23.742	25.99	24.794	27.68	26.868	29.33	28.905
3.0	23.22	21.724	23.91	22.639	25.33	24.432	26.70	26.183
3.5	21.77	20.202	22.37	21.018	23.59	22.610	24.76	24.155
4.0	20.63	19.000	21.14	19.741	22.23	21.181	23.24	22.572
4.5	19.59	18.020	20.14	18.702	21.13	20.023	22.02	21.292
5.0	18.91	17.201	19.31	17.835	20.21	19.059	21.01	20.231
5.5	18.24	16.502	18.60	17.097	19.43	18.242	20.15	19.333
6.0	17.65	15.897	17.98	16.459	18.75	17.536	19.70	18.560
6.5	17.13	15.366	17.43	15.899	18.15	16.919	18.75	17.885
7.0	16.660	14.473	16.94	15.403	17.62	16.373	18.17	17.289
8.0	—	14.092	—	14.559	—	15.447	—	16.281
10.0	—	12.870	—	13.278	—	14.047	—	14.763
12.0	—	11.970	—	12.335	—	13.022	—	13.657
14.0	—	11.268	—	11.603	—	12.229	—	12.804
16.0	—	10.701	—	11.011	—	11.590	—	12.118
18.0	—	10.228	—	10.409	—	11.060	—	11.551
20.0	—	9.827	—	10.102	—	10.611	—	11.072

constant. Below, a slightly another type of dependences was used for approximation of experimental data and extrapolation on wider intervals of pressure and temperature

$$\frac{P \cdot V}{R_g \cdot T} \equiv Z = \sum_{k=0}^K A'_k \cdot \rho^k, \quad (12)$$

where Z is the compressibility, and for approximation of recalculated experimental data customary units of measurements were used. As was shown, for good

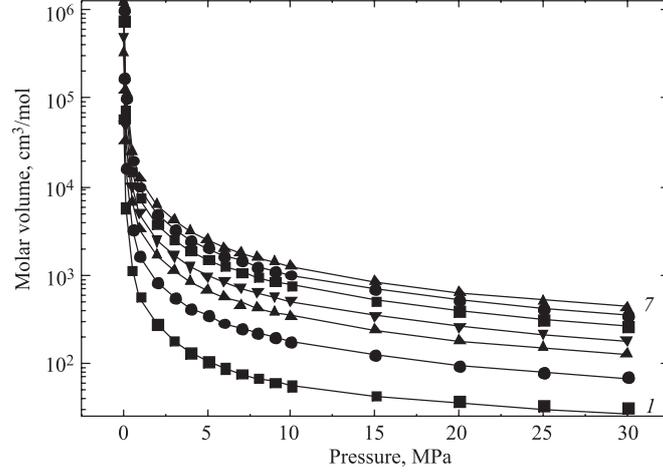


Fig. 12. Dependences of experimental molar volumes (V_{exp}) and calculated (V_{LSM}) values versus pressure obtained using the least square method (LSM) (see Appendix 1 in [11]) and Eqs. (8.1) and (10.1) with two virial parameters and χ_i^2 for each temperature. Here parameters T , χ_i^2 , N , K and A_1 , A_2 , have the following values: Curve 1 at $T = 70$ K, $\chi_i^2 = 396.1$; $N = 17$; $K = 2$; $A_1 = -17.289$; $A_2 = 934.478$; Curve 2 at $T = 200$ K, $\chi_i^2 = 1.83$; $N = 17$; $K = 2$; $A_1 = 11.343$; $A_2 = 394.495$; Curve 3 at $T = 400$ K, $\chi_i^2 = 68.11$; $N = 17$; $K = 2$; $A_1 = 14.0995$; $A_2 = 387.001$; Curve 4 at $T = 600$ K, $\chi_i^2 = 9.93$; $N = 17$; $K = 2$; $A_1 = 6.933$; $A_2 = 2114.338$; Curve 5 at $T = 900$ K, $\chi_i^2 = 0.28$; $N = 17$; $K = 2$; $A_1 = 15.290$; $A_2 = 904.421$; Curve 6 at $T = 1200$ K, $\chi_i^2 = 0.75$; $N = 17$; $K = 2$; $A_1 = 19.505$; $A_2 = -1246.765$; Curve 7 at $T = 1500$ K, $\chi_i^2 = 9.79$; $N = 17$; $K = 2$; $A_1 = 14.271$; $A_2 = 1564.433$

fitting three parameters are enough for virial equations (8.1) and (8.2) using the least square fitting and third order linear equations (10.1) and (10.2) for extrapolation of molar volumes on wide temperature and pressure intervals. In Tables 7 and 8 the number of experimental points (N), the number of parameters (K), the values of χ_i^2 are presented for Eqs. (8.1) and (8.2), respectively.

Here, a very strong growth of values χ_i^2 ($N, K = 7$) takes place for all temperatures at $K = 7$. As one can see, fitting of experimental data using expansion (8.2) is much better at the number of parameters $K = 3$ than in the case with Eq. (8.1), i.e., this case corresponds to a third order linear equation relative to the molar volume V . The three virial parameters for each temperature value are presented in Table 9 for virial equation (8.2) with parameters χ_i^2 . As was shown in Appendix 1 [11], fitting of the experimental values of functions versus their arguments is quite well if the values of $\chi_i^2 \approx N - K$. It takes place in the case of $K = 3$ for using Eq. (8.2) at the relative accuracy $\delta = \Delta V/V = \pm 0.01$.

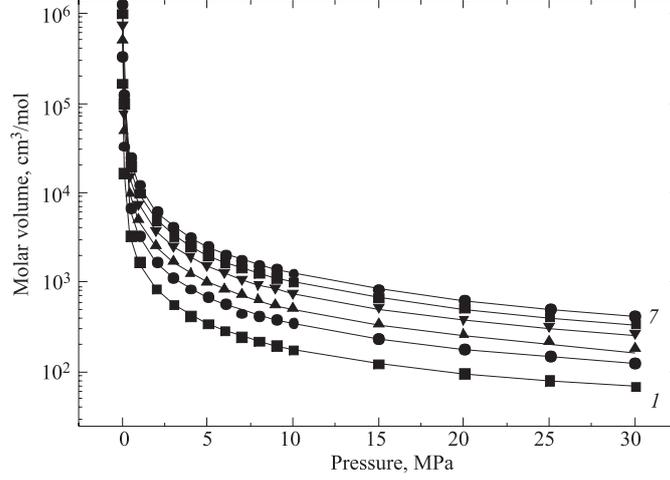


Fig. 13. Dependences of experimental [6] and calculated values of molar volumes versus pressure obtained with the Kardano method (see Appendix 2 in [11]) and derived virial parameters. Here parameters T , χ_i^2 , N , K and A_1 , A_2 , have the following values: Curve 1 at $T = 200$ K, $\chi_i^2 = 1.23$; $N = 17$; $K = 2$; $A_1 = 11.343$; $A_2 = 394.508$; Curve 2 at $T = 400$ K, $\chi_i^2 = 63.44$; $N = 17$; $K = 2$; $A_1 = 14.100$; $A_2 = 387.029$; Curve 3 at $T = 600$ K, $\chi_i^2 = 237.7$; $N = 17$; $K = 2$; $A_1 = 0.228$; $A_2 = -5.392$; Curve 4 at $T = 900$ K, $\chi_i^2 = 94.67$; $N = 17$; $K = 2$; $A_1 = 1.858$; $A_2 = -80.055$; Curve 5 at $T = 1200$ K, $\chi_i^2 = 38.77$; $N = 17$; $K = 2$; $A_1 = 4.580$; $A_2 = -203.670$; Curve 6 at $T = 1500$ K, $\chi_i^2 = 19.23$; $N = 17$; $K = 2$; $A_1 = 8.392$; $A_2 = -376.237$

For Eqs. (10.1) and (10.2), it is necessary to change the units of measurement of the parameters from A_2 [cm^3/g] and A_3 [$(\text{cm}^3/\text{g})^2$] to A'_2 [cm^3/mol] and A'_3 [$(\text{cm}^3/\text{mol})^2$] using the expressions:

$$A'_2 \equiv A_2/M_{H_2}, \quad A'_3 \equiv A_3/M_{H_2}^2, \quad (13)$$

where $M_{H_2} = 2.0144$ g/mole is the mass of one hydrogen mole. Let us use the virial parameters obtained by the least square method (LSM) for extrapolation of molar volumes versus pressure starting from low pressure (see experimental data presented in [15]), derived by a direct solving of third order linear equation (10.2) relative to the molar volume V by the Kardano method (see Appendix in [11]). The following dependences of molar volumes versus pressures for different temperatures are presented in Fig. 14. Also, the square deviations of experimental data for molar volumes and directly calculated values of molar volumes for both pressure intervals with experimental data, i.e., for low pressures at the temperatures from 98.15 to 423.15 K ($5-6 \leq P \leq 3000.0$ bar [15]) and for high pressure ($0.5 \leq P \leq 7.0$ kbar [7, 8]) are presented. As it is impossible to present all molar volume experimental dependences versus pressure for low

Table 6. The experimental [8,9] and calculated with the Kardano method (see Appendix 2 in [11]) hydrogen molar volumes for the experimental temperatures $T = 298.15$, 323.15 , 373.15 and 423.15 K with virial parameters from Fig. 10

P , kbar	T , K							
	298.15		323.15		373.15		423.15	
A_1	$A_1 = 13.62410$;		$A_1 = 13.91931$;		$A_1 = 14.16168$;		$A_1 = 13.93995$;	
A_2	$A_2 = 521.51453$		$A_2 = 513.61877$		$A_2 = 448.80673$		$A_2 = 318.63412$	
χ_i^2	$\chi^2 = 580.6$ $N = 14, K = 2$		$\chi^2 = 405.4$ $N = 14, K = 2$		$\chi^2 = 462.3$ $N = 14, K = 2$		$\chi^2 = 1.214 \cdot 10^3$ $N = 14, K = 2$	
	V_{exp} , cm ³ /mol	V_{Kardano} , cm ³ /mol	V_{exp} , cm ³ /mol	V_{Kardano} , cm ³ /mol	V_{exp} , cm ³ /mol	V_{Kardano} , cm ³ /mol	V_{exp} , cm ³ /mol	V_{Kardano} , cm ³ /mol
0.5	65.57	65.813	69.80	70.042	78.27	77.917	86.68	85.007
1.0	40.79	40.821	42.90	43.019	47.08	46.781	51.26	49.620
1.5	32.31	31.988	33.71	33.531	36.50	35.990	39.27	37.493
2.0	27.91	27.275	28.96	28.495	31.05	30.327	33.13	31.206
2.5	25.16	24.266	25.99	25.292	27.68	26.758	29.33	27.286
3.0	23.22	22.140	23.91	23.036	25.33	24.263	26.70	24.571
3.5	21.77	20.538	22.37	21.341	23.59	22.399	24.76	22.558
4.0	20.63	19.276	21.14	20.008	22.23	20.941	23.24	20.994
4.5	19.59	18.249	20.14	18.925	21.13	19.760	22.02	19.736
5.0	18.91	17.391	19.31	18.022	20.21	18.780	21.01	18.697
5.5	18.24	16.661	18.60	17.254	19.43	17.950	20.15	17.820
6.0	17.65	16.029	17.98	16.591	18.75	17.234	19.70	17.067
6.5	17.13	15.476	17.43	16.010	18.15	16.609	18.75	16.413
7.0	16.660	14.985	16.94	15.496	17.62	16.057	18.17	15.836
8.0	—	14.151	—	14.623	—	15.122	—	14.864
10.0	—	12.886	—	13.300	—	13.712	—	13.410
12.0	—	11.956	—	12.330	—	12.684	—	12.357
14.0	—	11.235	—	11.579	—	11.890	—	11.549
16.0	—	10.652	—	10.973	—	11.253	—	10.904
18.0	—	10.169	—	10.470	—	10.725	—	10.372
20.0	—	9.758	—	10.044	—	10.279	—	9.923

pressure (see [15]), i.e., the experimental pressure values are very different for each temperature value, we presented in Table 10 only extrapolated dependences of molar volumes versus pressures from the minimum pressures $P = 0.5$ kbar up to maximum $P = 20.0$ kbar with the square deviations of experimental and calculated values. This is a far easier way.

Here χ_i^2 , N and χ_{i1}^2 , N are the average square deviations and number of parameters between experimental values from [8,9] and [15] and calculation ones, respectively.

Table 7. The value χ^2_i obtained by fitting of experimental data [15] with a various number of parameters (K) and experimental points (N) using expression (8.1). The temperatures are varied from 98.15 to 423.15 K

$T, K \rightarrow$	98.15	103.15	113.15	123.15	138.15	153.15	173.15	223.15	273.15	323.15	373.15	423.15
$N \rightarrow$	18	22	23	21	40	22	$N = 22$	$N = 23$	$N = 40$	$N = 39$	$N = 39$	$N = 21$
$K \downarrow$	$\chi^2_i(N, K, T) \downarrow$											
2	4390.0	370	213	1370	654	329	370	213	654	329	253	131
3	103.0	443	30.78	91.34	61.37	14.04	9.80	7.19	3.26	1.68	1.69	1.98
4	85.87	440	6.70	87.46	55.32	13.12	9.33	7.01	0.266	1.59	1.67	1.70
5	60.63	326	6.64	73.75	52.00	10.11	7.73	5.19	0.272	0.937	0.986	0.95
6	50.31	262	6.59	59.81	52.80	9.30	6.22	8.69	17.21	0.77	2.53	0.96

Table 8. The value χ^2_i obtained by fitting of experimental data [15] with a various number of parameters (K) and experimental points (N) using expression (8.2). The temperatures are varied from 98.15 to 423.15 K

$T, K \rightarrow$	98.15	103.15	113.15	123.15	138.15	153.15	173.15	223.15	273.15	323.15	373.15	423.15
$N \rightarrow$	18	22	23	21	40	22	22	23	40	39	39	21
$K \downarrow$	$\chi^2_i(N, K, T) \downarrow$											
2	487.2	372.7	322.2	487.2	409.3	364.4	305.5	220.4	1296	663.5	544.3	282.1
3	7.332	6.554	5.354	9.093	6.973	5.606	4.202	2.348	26.27	9.625	7.147	2.426
4	0.129	0.101	0.069	0.120	0.075	0.053	0.033	0.011	0.0685	0.048	0.025	0.008
5	0.010	0.001	0.002	0.0049	0.0073	0.051	0.004	0.054	0.010	0.004	0.007	0.002
6	10.72	13.80	161.6	2.205	5.369	25.55	14.87	4.755	0.063	2.329	20.41	1.904

Table 9. Parameters A_1 , A_2 and A_3 for virial expression (8.2) versus temperature obtained by means of the least square method (see Appendix 1 in [11]) for compressibility (or molar volumes versus pressure or mass density measurements [15])

$T, K \downarrow$	$\chi_i^2(N, K, T) \downarrow$	A_1	$A_2, \text{cm}^3/\text{g}$	$A_3 (\text{cm}^3/\text{g})^2$
98.15	7.332	1.011 ± 0.005	-4.234 ± 0.601	244.5 ± 12.3
103.15	6.554	1.010 ± 0.005	-3.416 ± 0.608	238.5 ± 12.5
113.15	5.354	1.009 ± 0.005	-2.020 ± 0.621	227.9 ± 12.8
123.15	9.093	1.008 ± 0.004	-1.157 ± 0.523	228.6 ± 10.5
138.15	6.973	1.007 ± 0.004	0.288 ± 0.004	215.2 ± 10.7
153.15	5.606	1.006 ± 0.004	1.481 ± 0.522	202.9 ± 10.7
173.15	4.202	1.005 ± 0.004	2.659 ± 0.530	190.0 ± 10.9
223.15	2.348	1.004 ± 0.004	4.623 ± 0.527	164.7 ± 11.2
273.15	26.27	1.014 ± 0.003	3.986 ± 0.332	185.5 ± 5.2
323.15	9.625	1.009 ± 0.004	5.405 ± 0.366	156.6 ± 6.1
373.15	7.147	1.008 ± 0.004	6.000 ± 0.367	143.0 ± 6.2
423.15	2.426	1.005 ± 0.004	6.748 ± 0.411	124.5 ± 7.4

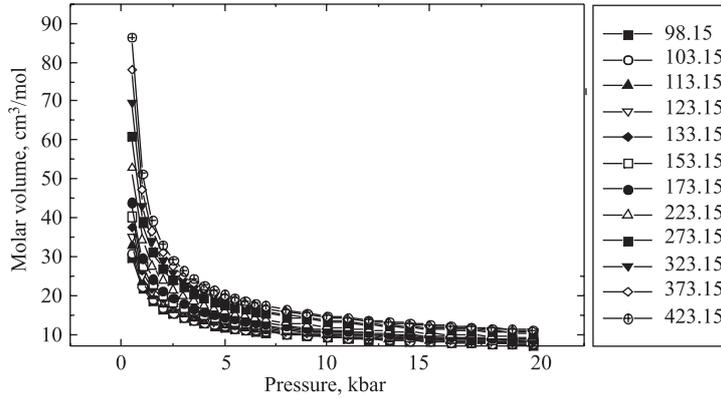


Fig. 14. The dependences of molar volumes versus pressures for different temperatures extrapolated on superhigh pressures using the virial parameters for Eq. (8.2) from Table 9 derived by direct solving of third order linear equation (10.2) with the Kardano method. Here parameters T , χ_i^2 and N have the following values ($K = 3$): Curve 1 at $T = 98.15$ K, $\chi_i^2 = 29.26$, $N = 17$; Curve 2 at $T = 103.15$ K, $\chi_i^2 = 26.96$, $N = 18$; Curve 3 at $T = 113.15$ K, $\chi_i^2 = 25.71$, $N = 18$; Curve 4 at $T = 123.15$ K, $\chi_i^2 = 30.53$, $N = 19$; Curve 5 at $T = 138.15$ K, $\chi_i^2 = 29.70$, $N = 21$; Curve 6 at $T = 153.15$ K, $\chi_i^2 = 31.97$, $N = 22$; Curve 7 at $T = 173.15$ K, $\chi_i^2 = 30.09$, $N = 22$; Curve 8 at $T = 223.15$ K, $\chi_i^2 = 33.34$, $N = 22$; Curve 9 at $T = 273.15$ K, $\chi_i^2 = 60.62$, $N = 40$; Curve 10 at $T = 323.15$ K, $\chi_i^2 = 51.48$, $N = 39$; $\chi_{i1}^2 = 150.7$, $N_1 = 14$; Curve 11 at $T = 373.15$ K, $\chi_i^2 = 51.49$, $N = 39$; $\chi_{i1}^2 = 104.1$, $N_1 = 14$; Curve 12 at $T = 423.15$ K, $\chi_i^2 = 47.40$, $N = 38$; $\chi_{i1}^2 = 103.2$, $N_1 = 14$

Table 10. The calculated with the Kardano method (see Appendix 2 in [11]) hydrogen molar volumes versus pressure for the experimental temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K for Eqs. (8.1) and (8.2) with extrapolating virial parameters

$P,$ kbar	$V_{\text{Kardano}}, \text{cm}^3/\text{mol}$				η
	(Table 6)	(Table 5)	(Table 4)	(Fig. 14)	
$T = 298.15$ K					
14.0	11.235	11.268	12.529	—	0.103
16.0	10.652	10.701	11.913	—	0.106
18.0	10.169	10.228	11.400	—	0.108
20.0	9.758	9.827	10.962	—	0.110
$T = 323.15$ K					
14.0	11.579	11.603	12.699	12.058	0.087
16.0	10.973	11.011	12.067	11.442	0.091
18.0	10.470	10.409	11.541	10.931	0.093
20.0	10.044	10.102	11.093	10.497	0.095
$T = 373.15$ K					
14.0	11.890	12.229	13.041	12.544	0.088
16.0	11.253	11.590	12.376	11.889	0.091
18.0	10.725	11.060	11.823	11.346	0.093
20.0	10.279	10.611	11.353	10.885	0.095
$T = 423.15$ K					
14.0	11.549	12.804	13.434	12.859	0.140
16.0	10.904	12.118	12.730	12.168	0.143
18.0	10.372	11.551	12.146	11.597	0.146
20.0	9.923	11.072	11.652	11.114	0.148

As one can see, extrapolation of high pressure experimental data using expansion (8.2) gives very fine results, the relative accuracies $\delta_i \equiv (V_i^{\text{exp}} - V_i^{\text{Kardano}})/0.01 \cdot V_i^{\text{exp}}\%$ being less than $\pm 5\%$. Let us compare the molar volumes at high pressures $P \geq 16$ kbar obtained by various extrapolations. Such values for all used extrapolation dependences are presented in Table 10.

Let us also introduce the parameter $\eta \equiv [V_{\text{Kardano}}^{\text{Table 4}} - V_{\text{Kardano}}^{\text{Table 6}}]/V_{\text{Kardano}}^{\text{Table 4}}$ based on the data presented in Table 6. The calculated values of molar volumes were obtained by extrapolation of all these values from low pressures (see [6]) to high and superhigh pressures (see Tables 5, 6) and extrapolation of high pressure values [8, 9] ($0.5 \leq P \leq 7.0$ kbar) to superhigh pressures $P \geq 8.0$ kbar. The values of parameter η are less than 15%, so the deviations from the minimum values of molar volumes (Table 6) and maximum values of molar volumes (Table 4) are not large, therefore this extrapolation can be really valid and correct, too! Let us calculate the values of $\delta_i \equiv (V_i^{\text{exp}} - V_i^{\text{Kardano}})/0.01 \cdot V_i^{\text{exp}}\%$, δ_i^2 and χ_i^2 for

Table 11. Parameters characterizing accuracy of extrapolation

P , kbar	$T = 323.15$ K	$T = 373.15$ K	$T = 423.15$ K
	$V_{\text{calc}}/V_{\text{exp}}$		
0.5	69.658/69.80 $\delta = 0.20; \delta^2 = 0.04$	78.067/78.27 $\delta = 0.26; \delta^2 = 0.07$	86.519/86.68 $\delta = 0.19; \delta^2 = 0.036$
1.0	43.093/42.90 $\delta = -0.45; \delta^2 = 0.20$	47.269/47.08 $\delta = -0.40; \delta^2 = 0.16$	51.392/51.26 $\delta = -0.26; \delta^2 = 0.0676$
1.5	33.804/33.71 $\delta = -0.39; \delta^2 = 0.15$	36.626/36.50 $\delta = -0.35; \delta^2 = 0.12$	39.335/39.27 $\delta = -0.17; \delta^2 = 0.0289$
2.0	28.867/28.96 $\delta = 0.32; \delta^2 = 0.10$	31.031/31.05 $\delta = 0.06; \delta^2 = 0.004$	33.049/33.13 $\delta = -0.24; \delta^2 = 0.0576$
2.5	25.719/25.99 $\delta = 1.04; \delta^2 = 1.08$	27.495/27.68 $\delta = 0.67; \delta^2 = 0.45$	29.107/29.33 $\delta = 0.76; \delta^2 = 0.5776$
3.0	23.496/23.91 $\delta = 1.73; \delta^2 = 2.99$	25.015/25.33 $\delta = 1.24; \delta^2 = 1.54$	26.360/26.70 $\delta = 1.27; \delta^2 = 1.61$
3.5	21.821/22.37 $\delta = 2.45; \delta^2 = 6.01$	23.157/23.59 $\delta = 1.85; \delta^2 = 3.42$	24.313/24.76 $\delta = 1.80; \delta^2 = 3.24$
4.0	20.501/21.14 $\delta = 3.02; \delta^2 = 9.13$	21.700/22.23 $\delta = 2.28; \delta^2 = 5.20$	22.715/23.24 $\delta = 2.26; \delta^2 = 5.11$
4.5	19.426/20.14 $\delta = 3.55; \delta^2 = 12.60$	20.518/21.13 $\delta = 2.90; \delta^2 = 8.41$	21.423/22.02 $\delta = 2.71; \delta^2 = 7.34$
5.0	18.527/19.31 $\delta = 4.05; \delta^2 = 16.40$	19.534/20.21 $\delta = 3.34; \delta^2 = 11.16$	20.352/21.01 $\delta = 3.13; \delta^2 = 9.80$
5.5	17.762/18.60 $\delta = 4.50; \delta^2 = 20.25$	18.698/19.43 $\delta = 3.77; \delta^2 = 14.21$	19.446/20.15 $\delta = 3.49; \delta^2 = 12.18$
6.0	17.100/17.98 $\delta = 4.89; \delta^2 = 23.91$	17.977/18.75 $\delta = 4.21; \delta^2 = 17.72$	18.665/19.70 $\delta = 5.25; \delta^2 = 27.56$
6.5	16.520/17.43 $\delta = 5.22; \delta^2 = 27.25$	17.346/18.15 $\delta = 4.23; \delta^2 = 17.90$	17.984/18.75 $\delta = 4.09; \delta^2 = 16.73$
7.0	16.005/16.94 $\delta = 5.52; \delta^2 = 30.47$	16.788/17.62 $\delta = 4.72; \delta^2 = 22.28$	17.383/18.17 $\delta = 4.33; \delta^2 = 18.75$
	$\chi^2 = 150.6$	$\chi^2 = 102.6$	$\chi^2 = 103.1$

calculated and experimental values [8, 9] for the pressures $0.5 \leq P \leq 7.0$ kbar. The resulting values are presented in Table 11.

CONCLUSION

1. The virial equations (8.1) and (8.2) can be used for fit of experimental data [6, 8, 9, 16] at relatively low pressure $P < 3$ kbar too in distinction of another equations (see [10–12]). Direct solving of linear equations (10.1) and (10.2) of the third order using extrapolated virial coefficients A_1 and A_2 (8.1) and A_1, A_2

and A_3 (8.2) allows one to obtain good agreement between existing experimental data for high pressure [8, 9] and calculated values. Such a possibility to get good agreement is the evidence of validity of virial equation (7.1). Equations (7.2) or (8) do not allow one to get such a result (see Fig. 4 or Table 11).

2. Scheme of molar dependences extrapolation developed here includes four stages (see [10, 11]):

- interpolation (approximation) of experimental data with the determination (calculation) of parameters of equations (expansion series (1.1) and (1.2), Tait equation (2), logarithm equation (3), van der Waals equation (4), virial equations (8.1), (8.2) and (10)) for experimental temperatures;
- extrapolation of temperature-dependent parameters on wide temperature interval using simple expression (11) (see [11]) and determination of coefficients of series expansions $\beta_{i,j}$, $i = 1, 2, 3$ and $j = 1, 2, 3$ (see [11]);
- extrapolation of molar volumes or mean distances between hydrogen molecules on wide pressure and temperature interval;
- check of validity of such an interpolation.

3. In distinction from these results, the use of parameters obtained after fitting of experimental data [6–9] by virial expansion (7.2) (see Table 3 at $M = 3$) and subsequent direct solving of third order linear equation (10.2) the least square χ_i^2 gives the following worst possible values (excluding the value at the temperature $T = 423.15$ K): $\chi_i^2(298.15 \text{ K}) = 1.323 \cdot 10^5$, $\chi_i^2(323.15 \text{ K}) = 4.166 \cdot 10^4$, $\chi_i^2(373.15 \text{ K}) = 5.236 \cdot 10^3$, $\chi_i^2(423.15 \text{ K}) = 3.09$ (see [11]).

The extrapolation of molar volume versus pressure using virial parameters obtained by approximating high pressure experimental data [8, 9] on low pressure dependences [16] gives a not so bad extrapolation (see Figs. 2 and 4). It is necessary to note that in the cases of temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K the obtained virial parameters give a very good approximation in high ($0.5 \leq P \leq 7.0$ kbar) and low ($20.0 < P \leq 3000.0$ bar) pressure intervals.

The extrapolation from high pressures ($0.5 \leq P \leq 7.0$ kbar) to low pressures ($0.01 \leq P \leq 30.0$ MPa) in the wide temperature interval from 70 to 1500 K is possible and in the temperature range $150 \leq T \leq 1200$ K such an extrapolation can be considered very good because the χ_i^2 parameter is suitable and small. It is necessary to note that the use of Eqs. (8.2) and (10.2) with three parameters extrapolated on a wide temperature interval brings very poor agreement of experimental [6] and calculated values of molar volumes: the parameters are $\chi_i^2 = 4.131 \cdot 10^3, 9.551 \cdot 10^3, 2.336 \cdot 10^3, 2.491 \cdot 10^3, 2.495 \cdot 10^4$ for $T = 200\text{--}600$ K, respectively.

From our point of view developed scheme for approximation of existing experimental data for dense hydrogen gas and its heavier isotopes (deuterium (D_2), tritium (T_2), HD, HT and DT gases) and following extrapolation on wide temperature and pressure intervals can be used for other dense gases too.

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