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COMPARISON OF VARIOUS STATE EQUATIONS FOR APPROXIMATION AND EXTRAPOLATION OF EXPERIMENTAL HYDROGEN MOLAR VOLUMES IN WIDE TEMPERATURE AND PRESSURE INTERVALS

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Сравнение различных уравнений состояния для аппроксимации и экстраполяции
молярных объемов водорода в широких интервалах температур и давлений

Выполнен численный анализ практически всех существующих зависимостей, таких как разложение по логарифмам от давления, уравнения Тейта, логарифмическое, Ван дер Ваальса и вириальное уравнения для интерполяции экспериментальных молярных объемов в зависимости от высоких давлений. Можно сделать вывод о возможности и применимости экстраполирующих выражений для экстраполяции молярных объемов в зависимости от давления и температуры. Показано, что вириальное уравнение может быть также использовано для фитирования экспериментальных данных при относительно низких давлениях $P < 3$ кбар в отличие от других выражений. Прямое решение линейного уравнения третьего порядка относительно объема с использованием экстраполированных вириальных коэффициентов позволило получить хорошее согласие между экспериментальными данными для высоких давлений и рассчитанными значениями.

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Comparison of Various State Equations for Approximation and Extrapolation
of Experimental Hydrogen Molar Volumes in Wide Temperature and Pressure Intervals

The numerical analysis of practically all existing formulae such as expansion series, Tait, logarithm, Van der Waals and virial equations for interpolation of experimental molar volumes versus high pressure was carried out. One can conclude that extrapolating dependences of molar volumes versus pressure and temperature can be valid. It was shown that virial equations can be used for fit experimental data at relatively low pressures $P < 3$ kbar too in distinction of other equations. Direct solving of linear equation of the third order relatively to volume using extrapolated virial coefficients allows us to obtain good agreement between existing experimental data for high pressure and calculated values.

INTRODUCTION

As it is well known, the creation of new universal energy bearers (carriers) like hydrogen is not an individual problem of any single branch of technique. Problems of production, keeping, transportation and applications of this new hydrogen fuel engines are common purpose of modern technique [1–5]. The remittance on hydrogen technology does not change the water balance of the whole Earth as well as the water balance of individual climate regions, where it is possible to create big systems for dissipation of water by thermochemical or by electrolyte methods. The use of heavy hydrogen isotopes of helium-third ($_2^3$He) is a way for development of thermonuclear reactors as well as power station in future [5]. So the description of hydrogen behavior at low and super high pressures at various temperatures is very important for almost all of the purposes listed above.

During long periods of time, systematic investigations on the low and high temperature properties of hydrogen isotopes H_2, HD and D_2 were carried out [5–10]. The main purpose was to achieve a better understanding of the intermolecular interactions and the influence of mass differences on the properties of gases, especially in wave mechanics.

Attempts by 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 [4,6] and references therein) failed to allow them to carry out such estimations. It was the reason for recalculation of interpolation dependences of existing experimental molar volume and compressibility data [6–9] and for carrying out its extrapolation on wider intervals of pressures and temperatures. It was carried out in article [10]. The main conclusion in this publication was the following: new correct values of parameters of experimental data interpolation using expansion (1) and Tait equation (2) (see [8]) were found, and extrapolation of molar volumes was carried out in high pressures interval from $P = 7.0$ kbar to $P = 20$ kbar and more bigger for four experimental temperatures [6–9] and in wide temperature interval from $T = 77.15$ K to approximately 1273.15 K.

The purpose of that report was firstly: to continue the calculations for interpolation of some experimental data [5–9], secondly: to carry out the comparison of another existing numerical and semitheoretical expressions and formulae for

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approximation of experimental data, thirdly: to carry out extrapolation of experimental data on wider intervals of temperature and pressure changes. The fourth one was to compare the behavior of all extrapolated dependences under such extrapolations.

1. EXPRESSIONS FOR APPROXIMATION OF EXPERIMENTAL DATA

1.1. Expansions of Compressibility on Logarithmic Dependences and Tait Equation [6, 10]. The smoothing molar volumes and compressibility of hydrogen versus pressure in pressure interval from $P_{\min} = 0.5$ kbar to $P_{\max} = 7.0$ kbar at four temperatures $T = 298.15$, 323.15, 373.15 and 423.15 K are presented in [6–10]. Let us repeat interpolation dependences of experimental data (expansion [10]):

$$\frac{P \cdot V}{R \cdot T} = Z = \sum_{i=1}^{K=3} \alpha_i \cdot (\ln P)^{i-1}, \tag{1.1}$$

$$\frac{P \cdot V}{R \cdot T} = Z = \sum_{i=1}^{K=3} \alpha_i \cdot (\ln P)^{i}, \tag{1.2}$$

where P, V, T, R, Z, α_i are pressure, molar volume, temperature, universal gas constant, compressibility and parameters of expansion, respectively.

Also we rewrite Tait equation:

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

Here $C(T)$ and $B(T)$ are parameters of Tait equation, P_0 and V_0 are initial pressure and corresponding molar volume.

It was proven using the least square method χ_i^2 (Dubna computer code «FUMILI») and the inversion mistake matrix method (own computer code «LINEAR») that it is possible to interpolate experimental values [6–9] by expressions (1) with only three parameters ($K = 3$) of expansion (1) and new parameters were obtained for Tait equation interpolation (2) [10]. It was shown that both dependences allow for approximation of experimental data beginning at pressure $P \geqslant 3.0$ kbar up to 7.0 kbar with quite good values of parameters χ_i^2. All sets of parameters are presented in [10].

1.2. Logarithm Expression [6]. The linear dependence of molar volumes in coordinates $\log P, V$ is observed for many solids, liquids and gases. It means that experimental data can be approximated by a direct line, i.e., for strongly pressed gases in interval of pressures from 2 to 10 kbar and for all temperatures of studies

$$V(P) = \frac{A}{\log (P/P_0) + A/V_0}, \tag{3}$$

where A is the tangent of inclination of direct line, P_0 is the pressure, taken as account zero, V_0 is a gas volume at this pressure. It is accepted to account that such a logarithm equation has less accuracy than Tait equation (2). However, the authors of article [6] remarked (see [6], p. 50) that after the approximation of experimental data on a narrow interval of pressure (from 300 bar to 3 kbar and temperature $T = 320$ K) with the mean accuracy of interpolation about 0.2% and finding the corresponding parameter A, this equation was used for extrapolation on pressure interval up to 10 kbar. The comparison of calculated values of molar volumes with found experimental data of other authors for a wide interval of pressures allowed concluding the deviation that occurred to be only 2% [6, 7].

Consequently, one can conclude that this logarithmic equation is possible to be used for extrapolations on wide temperature and pressure areas.

1.2.1. Approximation (Fitting) with Logarithm Equation (3). Experimental data for molar volumes and compressibility versus pressure for four temperatures are presented in [6–9] (see also detail calculations and fit in [8]). Here we will try to fit all of these data using logarithm equation (3). In the beginning we carried out interpolation of experimental values for molar volumes of hydrogen gas, presented in Table 1 using the least squares approximation. The three parameters of fitting $A(T)$, $P_0(T)$ and $V_0(T)$ of logarithm equation (3) were found by means of the least square method (computer code «FUMILI-Dubna») and presented in Table 1.

Table 1. Parameters of logarithm equation (3) and χ_i^2 for various temperatures and for different initial values P_0 and V_0

P_{initial}, kbar	$T = 298.15$ K		$T = 323.15$ K		$T = 373.15$ K		$T = 423.15$ K	
	$V_0 = 17.96$, cm^3/mol		$V_0 = 18.82$, cm^3/mol		$V_0 = 20.22$, cm^3/mol		$V_0 = 21.67$, cm^3/mol	
	χ_i^2	Parameters	χ_i^2	Parameters	χ_i^2	Parameters	χ_i^2	Parameters
1.0	22.06	$A = 24.210$ $P_0 = 1.0305$	29.71	$A = 24.132$ $P_0 = 1.0331$	41.84	$A = 24.331$ $P_0 = 1.0359$	60.94	$A = 24.534$ $P_0 = 1.0388$
2.0	3.039	$A = 22.666$ $P_0 = 2.0332$	3.982	$A = 22.412$ $P_0 = 2.0356$	4.749	$A = 22.374$ $P_0 = 2.0368$	7.568	$A = 22.291$ $P_0 = 2.0374$
3.0	0.784	$A = 21.833$ $P_0 = 3.0237$	0.860	$A = 21.488$ $P_0 = 3.0299$	0.9495	$A = 21.418$ $P_0 = 3.0289$	3.095	$A = 21.312$ $P_0 = 3.0266$

It is necessary to note that the fit was carried out with three parameters $A(T)$, $P_0(T)$ and $V_0(T)$ for the initial pressure $P_{\text{initial}} = 1$ kbar ($N = 13$, $K = 3$, $N - K = 10$), $P_{\text{initial}} = 2$ kbar ($N = 11$, $K = 3$, $N - K = 8$) and $P_{\text{initial}} = 3$ kbar ($N = 9$, $K = 3$, $N - K = 6$). The following $\chi_i^2(N - K)$ were calculated too and presented in Table 1. Here N, K and $N - K$ are the number of experimental points, number of parameters and number of degrees of freedom, correspondingly. As one can see, the best approximation (minimal value of χ_i^2) corresponds to the higher initial pressures, i.e., maybe the use of

logarithm equation for pressure less than $P < 1$ kbar is not good and for pressures more than $P > 3$ kbar it is sufficient (see also the remark in Subsec. 1.2 and Appendix 1).

In Fig. 2 the dependencies of molar volumes versus pressure in interval from $P = 3$ kbar to $P = 20$ kbar for various temperatures are presented. All curves are calculated with the use of extrapolated values of parameters (see Fig. 1).

1.3. Van der Waals Equation. As it is well known, van der Waals equation is an equation of state for fluids composed that they have nonzero size and pair wise attractive inter-particles force (such as the van der Waals force). It was based on a modification of the ideal gas law. The equation approximates the behavior of real fluids, taking into account nonzero size of molecules and the attraction between them.

The form of the van der Waals equation is

$$\left(P + \frac{a}{V^2}\right) \cdot (V - b) = R \cdot T, \tag{4}$$

where a is a measure of attraction between the particles, b is the volume excluded by a mole of particles, R is the universal gas constant ($R = 8.3143$ J/(mol $\cdot$ K)). Above the critical temperature (see Table 2) van der Waals equation is an improvement of the ideal gas law, and for low temperatures the equation is also qualitatively reasonable for the liquid state and the low-pressure gaseous state. However, van der Waals model cannot be taken seriously in a quantitative sense; it is only useful for qualitative purposes [11].

Table 2. Critical parameters and parameters of van der Waals equation for hydrogen and deuterium gases (see [12], p. 318)

Substance	Formula	T_{cr}, K	P_{cr}, MPa	ρ_{cr}, g /cm^3	V_{cr}, cm^3/mol	a, $N \times$ m^4/mol^2	b, cm^3/mol
Hydrogen	n–H$_2$	33.24	1.297	0.0310	65.5	0.02484	26.635
Deuterium	n–D$_2$	38.350	1.6650	0.0623	60.3	0.02576	23.940

Equation of van der Waals can be rewritten in the form:

$$P \cdot V^3 - [P \cdot b + R_g \cdot T] \cdot V^2 + a \cdot V - a \cdot b = 0. \tag{4.1}$$

This equation can be solved with the use of Kardano roots of the third order linear equation (see Appendix 2) if parameters $b(T)$ and $a(T)$ are known.

Also parameters of van der Waals equation are possible to present in the form:

$$a = \frac{27}{24} \times R \times T_{cr} \times V_{cr}, \quad b = \frac{1}{3} \times V_{cr}.$$

We tried to carry out the approximation of high pressure experimental data [6, 7] and low temperature liquid hydrogen experimental data [5] using van

der Waals equation with the parameters presented in Table 1. Unfortunately, it was impossible. Our attempts to interpolate experimental data with two parameters $a(T)$ and $b(T)$ and equation in the van der Waals form (4) using the least square method (i.e., computer code «FUMILI») were unsatisfactory too.

So even though such an equation has deep physical sense, it cannot be used for qualitative interpolation and approximation of experimental data.

1.4. Virial Equation (Expansion Series). The classical virial expansion expresses the pressure of a many-particle system in equilibrium as a power series in the density. The virial expansion was introduced in 1901 by Heike Kamerlingh Onnes as a generalization of the ideal gas law. He wrote for a gas containing N atoms or molecules,

$$\frac{P}{k_B \cdot T} = \rho + B_2 \cdot \rho^2 + B_3 \cdot \rho^3 + \ldots \qquad (5)$$

where P is the pressure, $k_B = 1.38054 \cdot 10^{-23}$ J/K is the Boltzmann constant, T is the absolute temperature, and $\rho = N_A/V$ (molecules/cm^3) is the molecular or atomic density of the gas. Note that for the gas containing $N_A = 6.022 \cdot 10^{23}$ (Avogadro's number) molecules truncation of the virial expansion after the first term leads to $P \cdot V = N_A \cdot k_B \cdot T \equiv R \cdot T$, which is the ideal gas law. Writing $\beta = (k_B \cdot T)^{-1}$, the virial expansion can be written in the closed form as follows:

$$\frac{\beta \cdot P}{\rho} \equiv \frac{P \cdot V}{R \cdot T} = 1 + \sum_{i=1}^{\infty} B_{i+1}(T) \cdot \rho^i = 1 + \sum_{i=1}^{\infty} \frac{C_{i+1}(T)}{V^i}, \qquad (6)$$

where $C_{i+1}(T) \equiv B_{i+1}(T) \cdot (N_A)^i$ and V (cm^3/mol) is a molar volume of gas. The virial coefficients $B_i(T)$ are characteristic of the interactions between the particles in the system and in general depend on temperature T. By the way, C_2 (cm^3/mol), C_3 (cm^6/mol^2) and other terms are the second, the third and so on virial coefficients. Practically only virial forms of the gas state equation have been theoretically proven. At low density ($V \to \infty$) Eq. (6) transformed to equation of ideal state of gas. Virial coefficients depend on temperature but do not depend on pressure and mass density and describe the additional term on nonideality of gas, which is connected with twice, thrice and more complicated interactions of gas atoms. For following approximations of experimental data we will use Eq. (6) in two forms:

$$\frac{P \cdot V}{R \cdot T} = 1 + \sum_{i=1}^{M} \cdot \frac{a_i(T)}{V^i}, \quad \text{or} \qquad (7.1)$$

$$\frac{P \cdot V}{R \cdot T} = \sum_{i=1}^{M} \frac{a_i(T)}{V^{i-1}}. \qquad (7.2)$$

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Here M is the limited number of parameters $a_i(T)$ — in virial expansion depending on temperature. Sometimes Eq. (7.2) can be written as [7, 8]:

$$\frac{P \cdot V}{R \cdot T} = \left(\frac{P \cdot V}{R \cdot T}\right)_{\text{Solid,Sphere}} - 4 \times \eta - 10 \times \eta^2 + \frac{C_2}{V} + \frac{C_3}{V^2}, \qquad (8)$$

here $(P \cdot V / R \cdot T)_{\text{Solid,Sphere}}$ is the state equation of solid spheres with diameter a, which can be determined using the expression obtained in [15, 16]. Parameter η has the form: $\eta = \pi \cdot N_A \cdot a^3 / 6V$. We will discuss the virial equation in more detail in the next report and partially below.

The expansion in Amagat unit of density practically analogous to virial expression (5) was introduced in a relatively old article [17] for approximation of experimental values of densities and the product $P \cdot V$ for hydrogen and deuterium gases in wide temperature interval (from $t = -175\,^{\circ}\text{C}$ to $t = +150\,^{\circ}\text{C}$ with a temperature step $\Delta t = 10-25\,^{\circ}\text{C}$) and pressure interval of a few international atmospheres (so-called bar) to about 3 kbar:

$$P \cdot V = \sum_{k=0}^{K} A_k \cdot \rho^k. \qquad (9)$$

Here the parameter $A = R \cdot T$ [17]. In the following article (third part of series of articles) we will use all of above-presented dependences excluding (8) and (9) for approximation of experimental data and extrapolation on wider intervals of pressure and temperatures.

Experimental data was approximated using equations (7.1) and (7.2) with various numbers of parameters. Firstly, it is necessary to emphasize (to mark) that at such approximations we used all experimental values of molar volumes (from 0.5 to 7.0 kbar) without cutting off molar values at pressure less than 3.0 kbar and results of such approximations are presented in Table 3. Number of experimental points was 14 and numbers of parameters varied from $M = 2$ to $M = 4$.

The use of virial equations (7.1) and (7.2) for extrapolation of molar volumes versus the pressure and temperatures was more accurate (correct) because the interpolation of experimental molar volumes is possible to be carried out for low pressures too (in pressure interval $0.5 \leqslant P \leqslant 3.0$ kbar) in distinction of all other equations, such as expansion series ((1.1)) and ((1.2)), Tait equation (2) and logarithm equation (3).

One can conclude that the use of only two parameters within equation (7.1) and three parameters within equation (7.2) approximates experimental data presented in [6–9] quite well.

It is possible to mark, taking into account the conclusions within Appendix 1, that it is not necessary to increase the number of parameters for a more correct

Table 3. Parameters of approximations of experimental values of molar volumes using virial equations (7.1) and (7.2) and the corresponding values of χ_i^2. Relative accuracy of experimental data was taken to be better than $\pm 1.0\%$

T, K	χ_i^2	A_1	A_2	A_3	A_4
Virial equation (7.1)					
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	$6.152 \cdot 10^3$	—
293.15	1.572	17.366	49.534	$1.361 \cdot 10^4$	$-3.442 \cdot 10^4$
323.15	0.196	17.618	35.278	$1.426 \cdot 10^4$	$-5.543 \cdot 10^4$
373.15	0.131	17.623	72.771	$1.244 \cdot 10^4$	$-5.048 \cdot 10^4$
423.15	10.67	17.594	97.073	$1.118 \cdot 10^4$	$-5.236 \cdot 10^4$
Virial equation (7.2)					
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	$8.21 \cdot 10^2$	—
298.15	1.677	1.044	11.380	$3.227 \cdot 10^2$	$8.444 \cdot 10^3$
323.15	0.404	1.063	8.780	$4.542 \cdot 10^2$	$6.149 \cdot 10^3$
373.15	0.254	1.044	10.950	$4.119 \cdot 10^2$	$5.432 \cdot 10^3$
423.15	10.96	1.0385	11.387	$4.241 \cdot 10^2$	$4.185 \cdot 10^3$

experimental data fit. And we will show and argue that in this article and the following (third) article of our cycle of works.

In Table 4 the experimental and calculated values of molar volumes of hydrogen using virial equation (7.1) with two coefficients (i.e., $M = 2$) are presented for four temperatures for direct (vivid) comparison.

In Table 4 one can see that approximations of experimental values at low pressure are a little bit better than at higher pressure. From our point of view such an approximation is possible to be used for extrapolation of Eq. (7.1) for

Table 4. Experimental ($V_{\exp}$) and calculated (V_{calc}) values of molar volumes of hydrogen [5] values (V_{calc}) using virial equation (7.1) and their relative deviations δ. Here number of parameters is $M = 2$

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	0.0257	69.80/68.690	0.0159	78.27/76.816	0.0186	86.68/85.709	0.0112
1.0	40.79/41.340	-0.0135	42.90/43.548	-0.015	47.08/47.242	-0.003	51.26/51.594	-0.007
1.5	32.31/33.334	-0.0327	33.71/34.773	-0.032	36.50/37.097	-0.016	39.27/39.972	-0.018
2.0	27.91/28.868	-0.0343	28.96/29.965	-0.035	31.05/31.683	-0.020	33.13/33.850	-0.022
2.5	25.16/25.869	-0.0282	25.99/26.793	-0.031	27.68/28.165	-0.018	29.33/29.945	-0.021
3.0	23.22/23.687	-0.0201	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	-0.0007	21.14/21.297	-0.007	22.23/22.203	0.0012	23.24/23.440	-0.009
4.5	19.59/19.627	-0.0019	20.14/20.133	0.0004	21.13/20.946	0.0087	22.02/22.089	-0.003
5.0	18.91/18.534	0.0199	19.31/19.144	0.0086	20.21/19.895	0.0156	21.01/20.957	0.0025
5.5	18.24/17.715	0.0288	18.60/18.298	0.0162	19.43/18.994	0.0225	20.15/19.997	0.0076
6.0	17.65/17.011	0.0362	17.98/17.568	0.0229	18.75/18.219	0.0283	19.70/18.828	0.0443
6.5	17.13/16.392	0.0431	17.43/16.931	0.0286	18.15/17.544	0.0334	18.75/18.452	0.0159
7.0	16.66/15.851	0.0486	16.94/16.368	0.0338	17.62/16.942	0.0385	18.17/17.817	0.0194

small pressures as well ($P < 1$ kbar). We carried out such an interpolation for comparison with experimental values presented below in the next section and in more detail in the following article too.

Equations (7.1) and (7.2) can be presented in the following forms, consequently:

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

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

We found parameters (A_i, $i = 1, 2$ for expression (7.1) and A_i, $i = 1, 2, 3$ for expression (7.2)) of virial expansions using «LINEAR» computer code. And these are presented in Table 3. Then we found exact solutions (roots of equations) for linear equations of the third order (10.1) relative molar volumes $V(T, P)$ for each pressure P with the use of the Kardano method (see Appendix 2) and numerical Newton's method for comparison. The obtained (exact solution) and experimental values of molar volumes versus pressure for four experimental temperatures [6–9] and relative deviations ($\delta = (V_{\text{exp}} - V_{\text{calc}})/V_{\text{exp}}$) are presented in Table 5.

If anybody will try to carry out extrapolation of the dependences obtained by fit of experimental data on wide temperature and pressure intervals (at low pressures and high or super high pressures), it is clear that it is necessary to solve Eqs. (10.1) or (10.2) and to obtain exact solutions (find the roots of equations) for each pressure and to find the molar volume. It is impossible to use just Eq. (10.2) and parameters A_i, $i = 1, 2, 3$ for extrapolation at temperatures lower than 423.15 K! We will discuss it in more detail in the next section of this article.

It is very easy to see that here the values of $\chi_i^2 \equiv \sum_{i=1}^{N} \left\{ \frac{V_i^{\text{exp}} - V_i^{\text{Kardano}}}{\{0.01 \cdot V_i^{\text{exp}}\}} \right\}^2$, where $N = 14$, $M = 2$, are lower than in the case of most direct fit of experimental values (see Table 3). So the use of exact solutions of Eq. (11.1) at $M = 2$ gives better approximation of experimental data if parameters $A_1(T)$ and $A_2(T)$ are known. We will use this conclusion for the following extrapolation of experimental values for the wide temperature and pressure intervals.

In distinction of these results, the use of parameters obtained after fit of experimental data [5–7] by virial expansion (7.2) (see Table 3 at $M = 3$) and the following direct solution of linear third order equation (10.2), the least square χ_i^2 have the values: $\chi_i^2(298.15 \text{ K}) = 1.323 \cdot 10^5$, $\chi_i^2(323.15 \text{ K}) = 4.166 \cdot 10^4$, $\chi_i^2(373.15 \text{ K}) = 5.236 \cdot 10^3$, $\chi_i^2(423.15 \text{ K}) = 3.09$ [13, 14].

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Table 5. Experimental (left value) and calculated (right value) molar volumes obtained from Eq. (10.1) at $M = 2$ using Kardano formulae (see Appendix 2)

P, kbar	T, K						
	298.15		323.15		373.15		423.15
	$\chi_i^2 = 23.82$		$\chi_i^2 = 16.44$		$\chi_i^2 = 13.03$		$\chi_i^2 = 11.68$
	$V_{\exp}/V_{\text{calc}}$	Δ	$V_{\exp}/V_{\text{calc}}$	δ	$V_{\exp}/V_{\text{calc}}$	δ	$V_{\exp}/V_{\text{calc}}$	δ
0.5	65.57/64.358	0.019	69.80/68.828	0.014	78.27/77.322	0.012	86.68/85.821	0.010
1.0	40.79/41.110	-0.008	42.90/43.190	-0.007	47.08/47.313	-0.005	51.26/51.428	-0.003
1.5	32.31/32.843	-0.016	33.71/34.203	-0.015	36.50/36.943	-0.012	39.27/39.649	-0.010
2.0	27.91/28.376	-0.017	28.96/29.398	-0.015	31.05/31.471	-0.014	33.13/33.496	-0.011
2.5	25.16/25.490	-0.013	25.99/26.317	-0.013	27.68/27.998	-0.011	29.33/29.624	-0.010
3.0	23.22/23.431	-0.009	23.91/24.130	-0.009	25.33/25.554	-0.009	26.70/26.918	-0.008
3.5	21.77/21.866	-0.004	22.37/22.475	-0.005	23.59/23.716	-0.005	24.76/24.896	-0.006
4.0	20.63/20.624	0.0003	21.14/21.166	-0.001	22.23/22.270	-0.002	23.24/23.313	-0.003
4.5	19.59/19.606	-0.001	20.14/20.096	0.002	21.13/21.094	0.002	22.02/22.030	-0.001
5.0	18.91/18.751	0.008	19.31/19.200	0.006	20.21/20.964	0.005	21.01/20.964	0.002
5.5	18.24/18.020	0.012	18.60/18.435	0.009	19.43/19.279	0.008	20.15/20.060	0.004
6.0	17.65/17.385	0.015	17.98/17.771	0.012	18.75/18.557	0.010	19.70/19.280	0.021
6.5	17.13/16.826	0.018	17.43/17.188	0.014	18.15/17.924	0.012	18.75/18.598	0.008
7.0	16.66/16.328	0.020	16.94/16.670	0.016	17.62/17.364	0.015	18.17/17.996	0.010

So our attempts to use the developed scheme for extrapolation of experimental data [6–9] on wider intervals in temperature and pressure are very important:

1. Use of «LINEAR» computer code for determination of expansion virial parameters depending on temperature.

2. Extrapolation of these parameters on wide temperature interval.

3. Direct solving of the third order equation by Kardano method (Appendix 2). Developed scheme was used for extrapolation of molar volumes using Eq. (7.1) and gave good results.

2. APPROXIMATION OF EXPERIMENTAL PARAMETERS WITHIN WIDE TEMPERATURE INTERVAL DATA AND COMPARISON OF EXTRAPOLATION MOLAR DEPENDENCES USING EXPRESSIONS (1)–(3), (7.1), (7.2), (8) and (9)

In the beginning all parameters which are obtained at fit of experimental data [5–7] by expressions (1.1) and (1.2) (three parameters were used in both expansion series) and by Tait equation (2) (two parameters), by logarithm equation (3) (three parameters) and then by virial expansions (7.1) and (7.2) were extrapolated using our computer code «LINEAR» for the wide temperature interval following simplest expansion [10], where $K_\alpha = 3$:

$$\alpha_i = \sum_{k=1}^{K_\alpha=3} \beta_{i,k} \cdot T^{k-1}, \tag{11}$$

where α_i $(i = 1, \ldots, M_\alpha)$ are the parameters of equations, $\beta_{i,k}$ $(k = 1, \ldots, K_\alpha)$ are the coefficients of temperature expansion parameters, T is temperature in Kelvin degree. In principle it is necessary to increase the number of expansion coefficients K_α up to good value of χ_i^2 or exchange the form of expansion (11) or take another formulae. In complete Tables 6.1 and 6.2 the values of all parameters α_i and following values of coefficients $\beta_{i,k}$ and their corresponding χ_i^2 are presented for all equations which were used for fit of experimental values.

Temperature dependences of Tait equation parameters together with the extrapolating molar volumes in temperature interval were presented in article [10] (see Figs. 1–5). It was shown that at the use of Tait extrapolation parameters for extrapolation of molar volumes over temperatures higher than $T > 1273.15$ K the behavior of dependences became unphysical. Besides that the decreasing of dependences at high temperature seems to decrease very slowly. So the conclusion was made that Tait equation is impossible to be used for pressures less than $P < 3$ kbar and for extrapolation at high temperatures too. In this article we will present all parameters and extrapolation dependences for all presented equations and expansions in detail for comparison again.

Table 6.1. Parameters α_i, $i = 1, 2, 3$ and following values of coefficients $\beta_{i,k}$, $i = 1, 2, 3$ and $k = 1, 2, 3$ and their χ_i^2

Equation (1.1),
$$\frac{PV}{RT} = \alpha_1 + \alpha_2 \ln P + \alpha_3 \ln^2 P$$

T, K	α_1	α_2	α_3
298.15	4.1058	−2.1296	0.65061
323.15	3.9055	−2.0105	0.60227
373.15	3.6530	−1.92026	0.56330
423.15	3.4389	−1.8226	0.52509
χ_i^2	$\beta_{1.1}$	$\beta_{1.2}$	$\beta_{1.3}$
0.3925	7.6690	−0.0169	0.00002
χ_i^2	$\beta_{2.1}$	$\beta_{2.2}$	$\beta_{2.3}$
1.213	−4.9975	0.0151	−0.00002
χ_i^2	$\beta_{3.1}$	$\beta_{3.2}$	$\beta_{3.3}$
3.794	1.45666	−0.0040	0.0

Equation (1.2),
$$\frac{PV}{RT} = \alpha_1 \ln P + \alpha_2 \ln^2 P + \alpha_3 \ln^3 P$$

T, K	α_1	α_2	α_3
298.15	2.2107	−0.2743	0.8233
323.15	1.9647	−0.1514	0.7236
373.15	1.8413	−0.1464	0.6381
423.15	1.7404	−0.1355	0.5675
χ_i^2	$\beta_{1.1}$	$\beta_{1.2}$	$\beta_{1.3}$
3.100	5.0637	−0.0149	0.00002
χ_i^2	$\beta_{2.1}$	$\beta_{2.2}$	$\beta_{2.3}$
783.8	−1.9566	0.0094	−0.00001
χ_i^2	$\beta_{3.1}$	$\beta_{3.2}$	$\beta_{3.3}$
8.223	2.6289	−0.0090	0.00001

Tait equation (2),
$$V = \alpha_1 \left\{ 1 - \alpha_2 \ln \frac{\alpha_3 + P}{\alpha_3 + P_0} \right\}$$

T, K	α_1	α_2	α_3
298.15	23.231	0.2076	−1.625
323.15	23.955	0.2097	−1.685
373.15	25.388	0.2118	−1.766
423.15	26.769	0.2132	−1.843
χ_i^2	$\beta_{1.1}$	$\beta_{1.2}$	$\beta_{1.3}$
0.02046	13.686	0.03457	−0.00001
χ_i^2	$\beta_{2.1}$	$\beta_{2.2}$	$\beta_{2.3}$
0.02465	0.16333	0.00022	0.0
χ_i^2	$\beta_{3.1}$	$\beta_{3.2}$	$\beta_{3.3}$
0.18	−0.65026	−0.00438	0.0

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Table 6.2. Parameters α_i, $i = 1, 2, 3$ and following values of coefficients $\beta_{i,k}$, $i = 1, 2, 3$, $k = 1, 2, 3$ and their χ_i^2

Logarithm equation (3),

$$V(P) = \frac{\alpha_1}{\lg(P/\alpha_2) + \alpha_1/\alpha_3}$$

T, K	α_1, cm³/mol	α_2, kbar	α_3, cm³/mol
298.15	21.833	3.0237	23.22
323.15	21.488	3.0299	23.91
373.15	21.418	3.02289	25.33
423.15	21.312	3.0266	26.70
χ_i^2	$\beta_{1.1}$	$\beta_{1.2}$	$\beta_{1.3}$
0.2928	27.575	−0.03091	0.00004
χ_i^2	$\beta_{2.1}$	$\beta_{2.2}$	$\beta_{2.3}$
0.0194	2.87675	0.00083	0.0
χ_i^2	$\beta_{3.1}$	$\beta_{3.2}$	$\beta_{3.3}$
0.0746	17.4662	0.01437	0.00002

Equation (7.1),

$$\frac{PV}{RT} = 1 + \frac{\alpha_1}{V} + \frac{\alpha_2}{V^2}$$

T, K	α_1, cm³/mol	α_2, (cm³/mol)²	—
298.15	7.234	867.9	—
323.15	7.695	800.8	—
373.15	9.866	708.3	—
423.15	11.530	628.9	—
χ_i^2	$\beta_{1.1}$	$\beta_{1.2}$	$\beta_{1.3}$
15.6	2.88	−0.00093	0.00005
χ_i^2	$\beta_{2.1}$	$\beta_{2.2}$	$\beta_{2.3}$
0.73	2017.8	−5.263	0.00468

There are only two parameters in expansion series (7.1)

Equation (7.2),

$$\frac{PV}{RT} = \alpha_1 + \frac{\alpha_2}{V} + \frac{\alpha_3}{V^2}$$

T, K	α_1	α_2, cm³/mol	α_3, (cm³/mol)²
298.15	4.1058	−2.1296	0.65061
323.15	3.9055	−2.0105	0.60227
373.15	3.6530	−1.92026	0.56330
423.15	3.4389	−1.8226	0.52509
χ_i^2	$\beta_{1.1}$	$\beta_{1.2}$	$\beta_{1.3}$
0.3925	7.66902	−0.01692	0.0000
χ_i^2	$\beta_{2.1}$	$\beta_{2.2}$	$\beta_{2.3}$
1.213	−4.99747	0.01513	−0.00002
χ_i^2	$\beta_{3.1}$	$\beta_{3.2}$	$\beta_{3.3}$
3.794	1.45658	−0.00396	0.0

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The example of temperature dependences of parameters $V_0(T)$, $A(T)$ and $P_0(T)$ for logarithm equation (3) is presented in Fig. 1. Also the pressure dependences of molar volumes for various temperatures are presented in Fig. 2.

One can see that behavior of all curves has physical character and below we will compare logarithm extrapolated curves with other extrapolations with
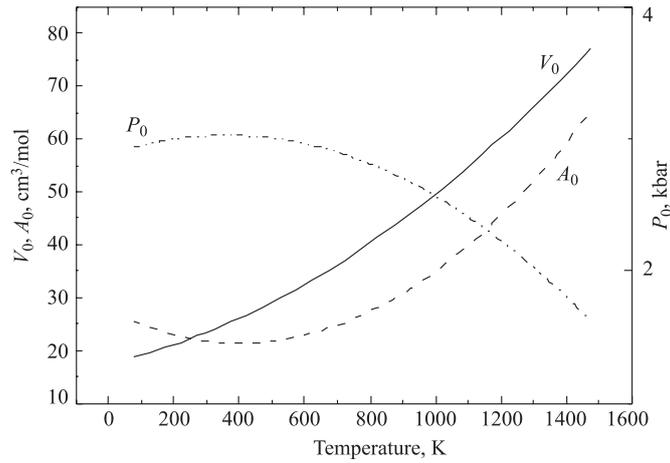

Fig. 1. Parameters $V_0(T)$, $A(T)$ and $P_0(T)$ for logarithm equation (3) versus temperature
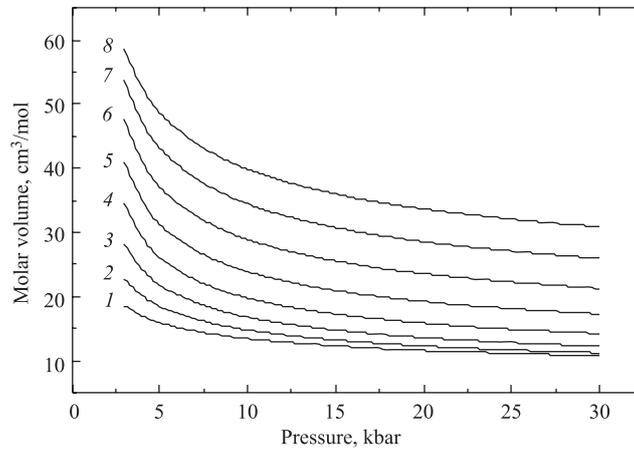

Fig. 2. Dependences of extrapolated molar volumes using logarithm equation (3) versus pressure. The curves 1–8 correspond to temperatures: $T = 77$, 273, 473, 673, 873, 1073, 1273 and 1473 K, respectively

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the use of (1.1), (1.2), (2) and (7.1) and (7.2) equations. Such wide areas of extrapolations are necessary for estimations of validity.

In Tables 7–9 the corresponding parameters for all Eqs. (1.1), (1.2), (2), (3), (7.1) and (7.2) in temperature wide areas from 77.15 to 723.15 K are presented.

As one can see only approximation of second parameter (α_2) in expansion series (1.2) does not have good value ($\chi_i^2 = 783.8$).

We carried out calculations of parameters values for experimental temperatures $T = 298.15, 323.15, 373.15$ and 423.15 K with the corresponding χ_i^2 (i.e., approximation) and its extrapolation for low and high temperatures too. All these extrapolating parameters versus temperature are presented in Figs. 1–4 and in Tables 7, 8 and 9.

Table 7. Parameters of series expansions (1.1) and (1.2) versus temperature [10]

T, K	Parameters of expansion series (1.1)				Parameters of expansion series (1.2)			
	χ_i^2	α_0	α_1	α_2	χ_i^2	α_1	α_2	α_3
77.15	Extrap.	3.76763	–1.28273	1.83811	Extrap.	6.07933	–3.23807	1.10637
123.15	Extrap.	3.30489	–0.96613	1.55653	Extrap.	5.56668	–2.93272	0.98182
173.15	Extrap.	2.86931	–0.67930	1.28971	Extrap.	5.06583	–2.64185	0.86297
223.15	Extrap.	2.50394	–0.45216	1.06377	Extrap.	4.62373	–2.39373	0.76133
273.15	Extrap.	2.20878	–0.28470	0.87873	Extrap.	4.24037	–2.18836	0.67690
298.15	0.248	2.1207	–0.2743	0.8233	0.643	4.10348	–2.11819	0.64795
323.15	0.035	1.98382	–0.1769	0.73456	0.367	3.91575	–2.02575	0.60969
373.15	0.023	1.82908	–0.12885	0.63128	0.4408	3.64988	–1.90588	0.55970
423.15	1.759	1.74454	–0.14046	0.56889	2.932	3.44275	–1.82876	0.52693
473.15	Extrap.	1.73021	–0.21175	0.54738	Extrap.	3.29436	–1.79440	0.51137
523.15	Extrap.	1.78609	–0.34274	0.56676	Extrap.	3.20471	–1.80278	0.51302
575.15	Extrap.	1.91218	–0.53341	0.62702	Extrap.	3.17381	–1.85392	0.53190
623.15	Extrap.	2.10847	–0.78377	0.72817	Extrap.	3.20165	–1.94781	0.56798
673.15	Extrap.	2.37498	–1.09381	0.87020	Extrap.	3.28823	–2.08444	0.62129
723.15	Extrap.	2.71169	–1.46355	1.05312	Extrap.	3.43356	–2.26383	0.69181

All temperature-dependent parameters here were obtained by fitting of experimental parameters using expansion (12) for temperatures $298.15 \leqslant T \leqslant 423.15$ K and extrapolation for low $T < 298.15$ K and for higher $T > 423.15$ K.

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Table 8. Parameters of Tait (2) and logarithm (3) equations versus temperature

T, K	Tait equation (2) parameters				Logarithm equation (3) parameters			
	χ_i^2	V_0, cm³/mol	C	B, kbar	χ_i^2	A, cm³/mol	P_0, kbar	V_0, cm³/mol
77.15	Extrap.	18.29087	0.18374	−1.1005	Extrap.	25.41838	2.93416	18.68026
123.15	Extrap.	19.23079	0.19044	−1.2296	Extrap.	24.34912	2.96193	19.50454
173.15	Extrap.	20.31749	0.19676	−1.3593	Extrap.	23.37055	2.98663	20.48559
223.15	Extrap.	21.47196	0.20207	−1.4780	Extrap.	22.58329	3.00561	21.55528
273.15	Extrap.	22.69419	0.20638	−1.5855	Extrap.	21.98734	3.01890	22.71362
298.15	0.2434	23.231	0.2076	−1.6280	0.6784	21.833	3.0237	23.20177
323.15	0.0776	23.955	0.2097	−1.6801	0.8460	21.488	3.0299	23.96059
373.15	0.1058	25.388	0.2118	−1.7705	0.9495	21.418	3.0289	25.29621
423.15	1.850	26.769	0.2132	−1.8423	3.095	21.312	3.0266	26.72047
473.15	Extrap.	28.084	0.2131	−1.8957	Extrap.	21.51672	3.01493	28.23338
523.15	Extrap.	29.377	0.2119	−1.9306	Extrap.	21.87736	2.99966	29.83492
573.15	Extrap.	30.626	0.2094	−1.9469	Extrap.	22.42930	2.97869	31.52511
623.15	Extrap.	31.831	0.2056	−1.9448	Extrap.	23.17257	2.95201	33.30394
673.15	Extrap.	32.993	0.2006	−1.9242	Extrap.	24.10714	2.91962	35.17141
723.15	Extrap.	34.111	0.1944	−1.8851	Extrap.	25.23303	2.88152	37.12751

Calculated values of molar volumes and mean distances between hydrogen molecules ($L_{H_2-H_2}(P,T) \cong [V/N_A]^{1/3}$) versus the pressure up to $P = 20$ kbar for several temperatures ($T = 123.15, 223.15, 298.15, 423.15, 473.15, 523.15, 573.15, 673.15, 723.15$ K) using expressions (1.1) and (1.2), Tait equation (2), logarithm equation (3) and virial expansion (7.1) are presented in Tables 10.1–10.9 for comparison.

For description and estimations of close proximities and divergences of extrapolating molar volume dependences for various equations let us introduce special parameters. Firstly, one can introduce the mean curve:

$$\overline{V}(P,T) = \frac{1}{L} \sum_{k=1}^{L} V^{(k)}(P,T), \qquad (12)$$

Table 9. Two parameters of virial equation (7.1) and three parameters of virial equation (7.2) versus temperature. For temperatures $T = 298.15$, 323.15, 373.15 and 423.15 K top values are the parameters obtained by fit of experimental data (computer code «LINEAR») and bottom values using expansion (11) and coefficients $\beta_{i,k}$, which are presented in Table 6.2

T, K	Virial equation (7.1) parameters			Virial equation (7.2) parameters			
	χ_i^2	A_1, cm³/mol	A_2, (cm³/mol)²	χ_i^2	A_1	A_2, cm³/mol	A_3, (cm³/mol)²
77.15	Extrap.	5.860	1502.0	Extrap.	2.261	−65.243	2686.927
123.15	Extrap.	5.481	1342.0	Extrap.	1.998	−52.698	2297.939
173.15	Extrap.	5.468	1183.0	Extrap.	1.752	−40.394	1924.025
223.15	Extrap.	5.872	1040.0	Extrap.	1.546	−29.478	1601.046
273.15	Extrap.	6.692	913.3	Extrap.	1.381	−19.949	1329.003
298.15	110.8	7.234	867.9	7.932	1.318	−17.739	$1.226 \cdot 10^3$
323.15	73.41	7.695	800.8	3.993	1.244	−11.272	$1.094 \cdot 10^3$
373.15	57.76	9.868	708.3	3.249	1.177	−4.923	$9.50 \cdot 10^2$
423.15	46.42	11.26	628.2	12.82	1.126	0.291	$8.21 \cdot 10^2$
473.15	Extrap.	14.13	565.5	Extrap.	1.128	4.286	750.190
523.15	Extrap.	17.04	518.5	Extrap.	1.167	6.876	732.826
573.15	Extrap.	20.35	487.4	Extrap.	1.246	8.078	766.399
623.15	Extrap.	24.09	472.3	Extrap.	1.365	7.891	850.907
673.15	Extrap.	28.24	473.2	Extrap.	1.526	6.317	986.351
723.15	Extrap.	32.81	490.1	Extrap.	1.727	3.356	1172.731
773.15	Extrap.	37.79	522.9	Extrap.	1.969	−0.994	1410.047

where index k is the number of curve and corresponds to a kind of curve (1.1), (1.2), (2), (3) or (7.1), index L is the quantity of curves in average value of sum (12). Secondly, one can introduce so-called mean square deviation:

$$[\mathrm{X}i^{(k)}]^2 \equiv \sum_{n=1}^{N} \left\{ \frac{V^{(k)}(P_n, T) - \overline{V}(P_n, T)}{\Delta V^{(k)}(P_n, T) + \Delta \overline{V}(P_n, T)} \right\}^2, \tag{13}$$

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Table 10.1. Molar volumes V (cm^3/mol) and mean distance $L_{\mathrm{H_2-H_2}}$ (Å) between hydrogen molecules at $T = 123.15$ K

P, kbar	$T = 123.15$ K				
	V (cm^3/mol)/$L_{\mathrm{H_2-H_2}}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	14.069/2.859	13.235/2.801	19.231/3.173	19.418/3.183	18.474/3.130
4.0	12.689/2.762	12.023/2.713	17.591/3.080	17.659/3.084	16.558/3.018
5.0	11.840/2.699	11.173/2.647	16.462/3.012	16.499/3.015	15.235/2.936
6.0	11.214/2.651	10.592/2.601	15.601/2.959	15.659/2.963	14.246/2.901
7.0	10.706/2.610	10.183/2.567	14.904/2.914	15.013/2.921	13.466/2.817
8.0	10.273/2.574	9.884/2.541	14.318/2.876	14.494/2.887	12.831/2.772
9.0	9.894/2.542	9.656/2.522	13.814/2.841	14.066/2.859	12.299/2.733
10.0	9.556/2.513	9.476/2.506	13.370/2.811	13.704/2.834	11.844/2.699
11.0	9.251/2.486	9.329/2.493	12.975/2.783	13.392/2.812	11.449/2.669
12.0	8.973/2.461	9.206/2.482	12.618/2.757	13.119/2.793	11.101/2.642
13.0	8.717/2.437	9.099/2.472	12.293/2.733	12.878/2.776	10.790/2.617
14.0	8.481/2.415	9.004/2.464	11.994/2.711	12.662/2.760	10.513/2.594
15.0	8.262/2.394	8.919/2.456	11.718/2.690	12.468/2.746	10.260/2.573
16.0	8.058/2.374	8.841/2.449	11.461/2.670	12.292/2.733	10.029/2.554
17.0	7.867/2.355	8.769/2.442	11.221/2.651	12.131/2.721	9.818/2.536
18.0	7.689/2.337	8.702/2.436	10.996/2.633	11.982/2.710	9.625/2.519
19.0	7.520/2.320	8.638/2.430	10.784/2.616	11.845/2.699	9.444/2.503
20.0	7.362/2.304	8.577/2.424	10.584/2.600	11.718/2.690	9.278/2.488

here $\Delta V = 0.01 \times V$, i.e., deviation is less than 1%. Furthermore, let us calculate such a new curves (12) and values (13) for all Tables 10.1–10.9, i.e., for temperatures: $T = 123.15, 223.15, 298.15, 423.15, 473.15, 523.15, 573.15, 673.15$ and 723.15 K.

As one can see from this Table so-called Tait, logarithm and virial equation curves lie very closely and deviation is very small, but (1.1) and (1.2) curves are very different from the first ones.

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Table 10.2. Molar volumes V (cm³/mol) and mean distance $L_{H_2-H_2}$ (Å) between hydrogen molecules at $T = 223.15$ K

P, kbar	$T = 223.15$ K				
	V (cm³/mol)/$L_{H_2-H_2}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	20.354/3.233	19.791/3.203	21.472/3.291	21.572/3.296	21.745/3.305
4.0	18.190/3.114	17.802/3.092	19.281/3.175	19.272/3.175	19.297/3.176
5.0	16.816/3.034	16.383/3.008	17.832/3.094	17.800/3.092	17.641/3.083
6.0	15.798/2.971	15.397/2.946	16.747/3.030	16.754/3.030	16.419/3.010
7.0	14.981/2.919	14.692/2.900	15.880/2.977	15.962/2.982	15.467/2.950
8.0	14.295/2.874	14.170/2.866	15.158/2.931	15.333/2.942	14.697/2.901
9.0	13.701/2.834	13.769/2.838	14.539/2.890	14.818/2.909	14.056/2.858
10.0	13.178/2.797	13.451/2.816	13.998/2.854	14.386/2.880	13.511/2.820
11.0	12.712/2.764	13.191/2.798	13.516/2.821	14.017/2.855	13.039/2.787
12.0	12.290/2.733	12.973/2.783	13.083/2.790	13.696/2.833	12.624/2.757
13.0	11.907/2.704	12.786/2.769	12.689/2.762	13.413/2.814	12.257/2.730
14.0	11.556/2.677	12.622/2.757	12.328/2.736	13.161/2.796	11.928/2.706
15.0	11.232/2.652	12.476/2.747	11.995/2.711	12.935/2.780	11.631/2.683
16.0	10.933/2.628	12.344/2.737	11.685/2.687	12.731/2.765	11.361/2.662
17.0	10.654/2.606	12.224/2.728	11.396/2.665	12.545/2.752	11.113/2.643
18.0	10.394/2.584	12.112/2.720	11.125/2.644	12.374/2.739	10.886/2.624
19.0	10.151/2.564	12.007/2.712	10.870/2.623	12.217/2.727	10.675/2.607
20.0	9.923/2.545	11.909/2.704	10.629/2.604	12.072/2.716	10.480/2.591

Calculated values $[Xi^{(k)}]^2$ (here $k = $ (1.1), (1.1), (2), (3) and (7.1)) using all five curves are equal to: $[Xi^{(1.1)}]^2 = 62.71$; $[Xi^{(1.2)}]^2 = 218.1$; $[Xi^{(2)}]^2 = 70.53$; $[Xi^{(3)}]^2 = 56.27$; $[Xi^{(7.1)}]^2 = 62.24$. Such values — only for three curves ($k = 2$, 3, (7.1)) — have the following quantities: $[Xi^{(2)}]]^2 = 33.57$; $[Xi^{(3)}]^2 = 103.4$; $[Xi^{(7.1)}]^2 = 27.70$. One can conclude that coincidence between Tait equation (2) and virial equation (7.1) curves is really very good! The analogical values of $[Xi^{(k)}]^2$ for mean distances will be in nine times less, because relative errors

Table 10.3. Molar volumes V (cm^3/mol) and mean distance $L_{H_2-H_2}$ (Å) between hydrogen molecules at $T = 298.15$ K

P, kbar	$T = 298.15$ K				
	V (cm^3/mol)/$L_{H_2-H_2}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	23.245/3.380	23.164/3.376	23.215/3.378	23.305/3.382	23.594/3.396
4.0	20.592/3.246	20.656/3.249	20.575/3.245	20.563/3.244	20.759/3.255
5.0	18.899/3.154	18.865/3.152	18.878/3.153	18.843/3.151	18.870/3.153
6.0	17.652/3.083	17.615/3.081	17.626/3.082	17.638/3.082	17.491/3.074
7.0	16.660/3.024	16.715/3.028	16.633/3.023	16.733/3.029	16.426/3.010
8.0	15.835/2.974	16.056/2.987	15.809/2.972	16.021/2.985	15.569/2.957
9.0	15.129/2.929	15.547/2.956	15.106/2.927	15.441/2.949	14.860/2.911
10.0	14.512/2.888	15.144/2.930	14.493/2.887	14.957/2.918	14.259/2.872
11.0	13.965/2.852	14.808/2.908	13.949/2.851	14.545/2.981	13.741/2.836
12.0	13.475/2.812	14.542/2.890	13.460/2.817	14.187/2.867	13.288/2.805
13.0	13.031/2.787	14.309/2.875	13.016/2.786	13.874/2.845	12.887/2.776
14.0	12.626/2.758	14.106/2.861	12.610/2.756	13.596/2.826	12.529/2.750
15.0	12.255/2.730	13.927/2.849	12.235/2.729	13.347/2.809	12.206/2.727
16.0	11.913/2.705	13.767/2.838	11.887/2.703	13.122/2.793	11.913/2.705
17.0	11.596/2.680	13.621/2.828	11.563/2.678	12.918/2.779	11.646/2.684
18.0	11.301/2.657	13.487/2.819	11.259/2.654	12.731/2.765	11.400/2.665
19.0	11.026/2.636	13.362/2.810	10.973/2.631	12.559/2.753	11.172/2.647
20.0	10.768/2.615	13.246/2.802	10.703/2.610	12.400/2.741	10.962/2.631

between $L_{H_2-H_2}$ and V are connected with relation $\dfrac{\Delta L}{L} = \dfrac{1}{3}\dfrac{\Delta V}{V}$. So one can conclude that in spite of different view of equations the differences between curves for pressure from $P = 3$ kbar up to $P = 20$ kbar are very small.

Calculated values $[Xi^{(k)}]^2$ using all five curves are equal to: $[Xi^{(1.1)}]^2 = 307.2$; $[Xi^{(1.2)}]^2 = 59.87$; $[Xi^{(2)}]^2 = 140.9$; $[Xi^{(3)}]^2 = 48.41$; $[Xi^{(7.1)}]^2 = 53.58$ for Table 10.5. See also comments after Table 10.3. Such values — only for

Table 10.4. Molar volumes V (cm³/mol) and mean distance $L_{H_2-H_2}$ (Å) between hydrogen molecules at $T = 423.15$ K

P, kbar	$T = 423.15$ K				
	V (cm³/mol)/$L_{H_2-H_2}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	26.697/3.539	26.590/3.534	26.768/3.542	26.829/3.545	26.941/3.550
4.0	23.248/3.380	23.327/3.384	23.212/3.378	23.183/3.377	23.330/3.384
5.0	21.055/3.270	21.020/3.268	21.041/3.269	20.972/3.266	20.979/3.266
6.0	19.464/3.185	19.419/3.183	19.470/3.186	19.456/3.185	19.293/3.176
7.0	18.222/3.116	18.279/3.119	18.240/3.117	18.335/3.123	18.007/3.104
8.0	17.206/3.057	17.440/3.071	17.228/3.058	17.464/3.072	16.984/3.044
9.0	16.349/3.006	16.802/3.033	16.369/3.007	16.761/3.031	16.145/2.993
10.0	15.611/2.960	16.303/3.003	15.623/2.960	16.179/2.995	15.439/2.949
11.0	14.963/2.918	15.902/2.978	14.963/2.918	15.686/2.964	14.834/2.910
12.0	14.389/2.880	15.572/2.957	14.371/2.879	15.262/2.937	14.309/2.875
13.0	13.873/2.845	15.294/2.939	13.835/2.843	14.891/2.913	13.846/2.844
14.0	13.407/2.813	15.056/2.924	13.345/2.809	14.563/2.892	13.434/2.815
15.0	12.982/2.783	14.849/2.911	12.894/2.777	14.271/2.872	13.064/2.789
16.0	12.593/2.755	14.666/2.899	12.475/2.746	14.008/2.855	12.730/2.765
17.0	12.234/2.729	14.501/2.888	12.086/2.718	13.770/2.838	12.425/2.743
18.0	11.903/2.704	14.352/2.878	11.721/2.690	13.553/2.823	12.146/2.722
19.0	11.594/2.680	14.215/2.869	11.378/2.663	13.353/2.809	11.889/2.703
20.0	11.306/2.658	14.088/2.860	11.055/2.638	13.169/2.796	11.652/2.685

three curves ($k = 2, 3, (7.1)$) — have the following quantities: $[Xi^{(2)}]^2 = 65.67$; $[Xi^{(3)}]^2 = 115.2$; $[Xi^{(7.1)}]^2 = 13.46$.

Presented molar volumes and mean distances $L_{H_2-H_2}$ (Å) between hydrogen were obtained by *interpolation* of experimental data (see Table 1 [10]) for temperature interval $298.15 \leqslant T \leqslant 423.15$ K and pressure $3.0 \leqslant P \leqslant 7.0$ kbar and *extrapolation* for $T > 423.15$ K and $T < 298.15$ K at pressure $P > 7.0$ kbar.

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Table 10.5. Molar volumes V (cm^3/mol) and mean distance $L_{\mathrm{H_2-H_2}}$ (Å) between hydrogen molecules at $T = 473.15$ K

P, kbar	$T = 473.15$ K				
	V (cm^3/mol)/$L_{\mathrm{H_2-H_2}}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	28.302/3.609	27.952/3.594	28.084/3.599	28.096/3.600	28.646/3.623
4.0	24.476/3.438	24.399/3.435	24.225/3.426	24.160/3.423	24.660/3.447
5.0	22.088/3.323	21.920/3.314	21.897/3.313	21.792/3.308	22.082/3.322
6.0	20.379/3.235	20.217/3.226	20.226/3.226	20.177/3.224	20.243/3.227
7.0	19.057/3.163	19.017/3.161	18.921/3.155	18.987/3.159	18.847/3.151
8.0	17.982/3.102	18.143/3.112	17.850/3.095	18.064/3.107	17.740/3.088
9.0	17.081/3.050	17.484/3.074	16.942/3.041	17.321/3.064	16.834/3.035
10.0	16.306/3.003	16.974/3.043	16.154/2.993	16.707/3.027	16.075/2.989
11.0	15.628/2.961	16.568/3.019	15.457/2.950	16.187/2.996	15.426/2.948
12.0	15.028/2.922	16.236/2.999	14.833/2.910	15.740/2.968	14.863/2.912
13.0	14.490/2.887	15.959/2.981	14.269/2.872	15.351/2.943	14.368/2.879
14.0	14.004/2.854	15.724/2.967	13.752/2.837	15.007/2.921	13.929/2.849
15.0	13.562/2.824	15.520/2.954	13.277/2.804	14.700/2.901	13.535/2.822
16.0	13.157/2.796	15.340/2.942	12.837/2.773	14.424/2.883	13.179/2.797
17.0	12.784/2.769	15.180/2.932	12.427/2.743	14.174/2.866	12.855/2.774
18.0	12.438/2.744	15.035/2.923	12.043/2.714	13.946/2.850	12.559/2.753
19.0	12.118/2.720	14.902/2.914	11.683/2.687	13.738/2.836	12.287/2.733
20.0	11.818/2.697	14.779/2.906	11.343/2.661	13.545/2.823	12.035/2.714

Analysis of data presented in Tables 10.1–10.9 allowed us to conclude that:

1. There is good agreement between Tait equation (2) and virial equation extrapolations in wide temperature interval from $T = 123.15$ K to $T = 573.15$ K.

2. There is no big difference between Tait equation (2) and virial equation extrapolations and logarithm equation (3) extrapolation.

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Table 10.6. Molar volumes V (cm^3/mol) and mean distance $L_{H_2-H_2}$ (Å) between hydrogen molecules at $T = 523.15$ K

P, kbar	$T = 523.15$ K				
	V (cm^3/mol)/$L_{H_2-H_2}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	30.355/3.694	29.362/3.653	30.6258/3.705	31.389/3.735	30.648/3.706
4.0	26.100/3.513	25.499/3.486	26.3451/3.542	26.717/3.540	26.248/3.519
5.0	23.511/3.392	22.852/3.360	23.8008/3.406	23.952/3.414	23.417/3.388
6.0	21.687/3.302	21.063/3.270	21.9842/3.317	22.085/3.322	21.406/3.288
7.0	20.290/3.230	19.821/3.205	20.5702/3.245	20.719/3.252	19.884/3.208
8.0	19.161/3.169	18.930/3.156	19.4124/3.183	19.666/3.196	18.681/3.142
9.0	18.217/3.116	18.269/3.119	18.4321/3.128	18.821/3.150	17.700/3.086
10.0	17.407/3.069	17.764/3.090	17.5819/3.079	18.125/3.111	16.878/3.038
11.0	16.699/3.027	17.368/3.067	16.8314/3.035	17.539/3.077	16.178/2.995
12.0	16.072/2.988	17.048/3.048	16.1596/2.994	17.035/3.047	15.571/2.957
13.0	15.511/2.953	16.785/3.032	15.5516/2.956	16.597/3.021	15.039/2.923
14.0	15.003/2.921	16.563/3.019	14.9963/2.920	16.211/2.997	14.567/2.892
15.0	14.541/2.890	16.373/3.007	14.4852/2.887	15.867/2.976	14.144/2.864
16.0	14.117/2.862	16.206/2.997	14.0119/2.855	15.559/2.956	13.763/2.838
17.0	13.726/2.835	16.058/2.988	13.5712/2.825	15.280/2.939	13.416/2.814
18.0	13.364/2.810	15.924/2.979	13.1588/2.796	15.026/2.922	13.100/2.792
19.0	13.028/2.786	15.802/2.972	12.7713/2.768	14.793/2.907	12.809/2.771
20.0	12.714/2.764	15.690/2.965	12.4059/2.741	14.579/2.893	12.540/2.751

3. Virial expansion curves grow more quickly with temperature increasing at low pressure $P < 3$ kbar (see Tables 10.8 and 10.9). It is visible beginning from $T > 673.15$ K.

4. Expansions (1.1) and (1.2) can be used for extrapolations of molar volumes on wide temperature and pressure interval only in narrow temperature range (see Tables 10.4–10.6).

5. Expansion (1.2) more worse than expansion (1.1) practically for all temperatures, just can be used for interpolation of experimental data like in [6–9].

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Table 10.7. Molar volumes V (cm^3/mol) and mean distance $L_{\mathrm{H_2-H_2}}$ (Å) between hydrogen molecules at $T = 573.15$ K

P, kbar	$T = 573.15$ K				
	V (cm^3/mol)/$L_{\mathrm{H_2-H_2}}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	33.087/3.802	31.047/3.722	31.451/3.738	31.389/3.735	30.648/3.706
4.0	28.327/3.610	26.854/3.546	26.854/3.546	26.717/3.540	26.248/3.519
5.0	25.522/3.487	24.049/3.418	24.163/3.423	23.952/3.414	23.417/3.388
6.0	23.584/3.396	22.195/3.328	22.253/3.331	22.085/3.322	21.406/3.288
7.0	22.115/3.324	20.935/3.264	20.772/3.255	20.719/3.252	19.884/3.208
8.0	20.934/3.264	20.050/3.217	19.562/3.191	19.666/3.196	18.681/3.142
9.0	19.948/3.212	19.409/3.182	18.538/3.134	18.821/3.150	17.700/3.086
10.0	19.102/3.166	18.929/3.156	17.652/3.083	18.125/3.111	16.878/3.038
11.0	18.362/3.124	18.560/3.135	16.870/3.037	17.539/3.077	16.178/2.995
12.0	17.705/3.086	18.269/3.119	16.170/2.994	17.035/3.047	15.571/2.957
13.0	17.116/3.052	18.033/3.105	15.537/2.955	16.597/3.021	15.039/2.923
14.0	16.582/3.020	17.838/3.094	14.959/2.918	16.211/2.997	14.567/2.892
15.0	16.094/2.990	17.671/3.084	14.428/2.883	15.867/2.976	14.144/2.864
16.0	15.647/2.962	17.527/3.076	13.936/2.850	15.559/2.956	13.763/2.838
17.0	15.233/2.936	17.400/3.069	13.478/2.818	15.280/2.939	13.416/2.814
18.0	14.849/2.911	17.286/3.062	13.049/2.788	15.026/2.922	13.100/2.792
19.0	14.491/2.887	17.181/3.056	12.647/2.759	14.793/2.907	12.809/2.771
20.0	14.157/2.865	17.085/3.050	12.267/2.731	14.579/2.893	12.540/2.751

6. Only virial expansion can be used for fit and interpolation of experimental data at low pressure $P < 3$ kbar.

Concluding this article we also present the extrapolated molar volumes versus the pressure for different temperatures and relatively low pressure $P \leqslant 3$ kbar (Fig. 3) and high pressure $3 \leqslant P \leqslant 20$ kbar (Fig. 4) obtained by using virial equation (7.1). We divided whole curve into two parts, because it is difficult to present whole curve in linear scale.

Table 10.8. Molar volumes V (cm³/mol) and mean distance $L_{H_2-H_2}$ (Å) between hydrogen molecules at $T = 673.15$ K

P, kbar	$T = 673.15$ K				
	V (cm³/mol)/$L_{H_2-H_2}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	41.484/4.099	35.829/3.904	34.912/3.870	34.576/3.858	38.467/3.997
4.0	35.414/3.889	30.892/3.716	29.783/3.671	29.322/3.652	32.664/3.785
5.0	32.111/3.764	27.794/3.587	26.828/3.545	26.230/3.518	28.950/3.636
6.0	29.933/3.677	25.873/3.502	24.744/3.451	24.150/3.423	26.325/3.523
7.0	28.317/3.609	24.655/3.447	23.132/3.374	22.632/3.350	24.348/3.432
8.0	27.028/3.554	23.863/3.409	21.818/3.309	21.463/3.291	22.792/3.357
9.0	25.950/3.506	23.334/3.384	20.708/3.252	20.528/3.242	21.527/3.294
10.0	25.019/3.464	22.974/3.366	19.747/3.201	19.758/3.201	20.472/3.239
11.0	24.198/3.425	22.722/3.354	18.901/3.154	19.110/3.166	19.576/3.191
12.0	23.462/3.390	22.541/3.345	18.144/3.112	18.554/3.135	18.801/3.149
13.0	22.794/3.358	22.408/3.339	17.460/3.072	18.071/3.108	18.124/3.111
14.0	22.184/3.327	22.307/3.334	16.836/3.035	17.645/3.083	17.524/3.076
15.0	21.621/3.299	22.227/3.330	16.261/3.000	17.266/3.061	16.988/3.044
16.0	21.099/3.272	22.161/3.326	15.730/2.967	16.927/3.040	16.506/3.015
17.0	20.614/3.247	22.104/3.323	15.235/2.936	16.619/3.022	16.069/2.988
18.0	20.159/3.223	22.053/3.321	14.772/2.906	16.340/3.005	15.670/2.963
19.0	19.733/3.200	22.006/3.318	14.338/2.877	16.084/2.989	15.304/2.940
20.0	19.331/3.178	21.961/3.316	13.928/2.849	15.848/2.974	14.967/2.918

CONCLUSION

Numerical analysis of practically all existing formulae such as expansion series (1.1) and (1.2), Tait equation (2), logarithm equation (3), van der Waals equation (4), virial equations (7.1), (7.2) and (8) allowed us to make the following conclusions.

1. Van der Waals equation in spite of deep physical sense concluding in it is impossible to be used for any approximation of experimental results.

Table 10.9. Molar volumes V (cm³/mol) and mean distance $L_{H_2-H_2}$ (Å) between hydrogen molecules at $T = 723.15$ K

P, kbar	$T = 723.15$ K				
	V (cm³/mol)/$L_{H_2-H_2}$ (Å)				
	Expansion (1.1), $K = 3$	Expansion (1.2), $K = 3$	Tait equation (2)	Logarithm equation (3)	Virial equation (7.1)
3.0	47.598/4.292	39.225/4.024	36.744/3.937	36.196/3.917	41.595/4.103
4.0	40.686/4.073	33.857/3.831	31.440/3.737	30.695/3.708	35.288/3.884
5.0	37.087/3.949	30.619/3.705	28.391/3.613	27.458/3.573	31.250/3.730
6.0	34.776/3.865	28.698/3.626	26.243/3.519	25.280/3.475	28.397/3.613
7.0	33.082/3.802	27.544/3.576	24.583/3.443	23.691/3.401	26.248/3.519
8.0	31.732/3.749	26.842/3.546	23.230/3.279	22.467/3.341	24.558/3.442
9.0	30.599/3.704	26.412/3.527	22.087/3.323	21.489/3.292	23.184/3.377
10.0	29.614/3.664	26.150/3.515	21.099/3.272	20.683/3.251	22.039/3.320
11.0	28.738/3.627	25.991/3.508	20.228/3.227	20.004/3.215	21.066/3.270
12.0	27.947/3.594	25.896/3.504	19.449/3.185	19.422/3.183	20.225/3.226
13.0	27.224/3.562	25.842/3.501	18.745/3.146	18.916/3.155	19.490/3.187
14.0	26.558/3.533	25.812/3.500	18.102/3.109	18.470/3.130	18.840/3.151
15.0	25.940/3.506	25.796/3.499	17.512/3.075	18.074/3.108	18.259/3.118
16.0	25.364/3.479	25.787/3.499	16.965/3.043	17.718/3.087	17.736/3.088
17.0	24.824/3.454	25.782/3.498	16.456/3.012	17.397/3.068	17.262/3.060
18.0	24.316/3.431	25.777/3.498	15.980/2.983	17.104/3.051	16.830/3.035
19.0	23.837/3.408	25.770/3.498	15.533/2.955	16.836/3.035	16.434/3.011
20.0	23.384/3.386	25.760/3.497	15.112/2.928	16.589/3.020	16.069/2.988

2. Most of these equations can be used only for relatively high pressure $P \geqslant 3$ kbar, it was proved after our attempts to fit experimental results in pressure interval P less than 3 kbar.

3. All extrapolating dependences of molar volumes versus pressure are very close in relatively wide temperature interval (see Tables 10.1–10.9), in spite of significant distinctions in its forms, i.e., one can conclude that extrapolating dependences of molar volumes versus pressure and temperatures can be valid.
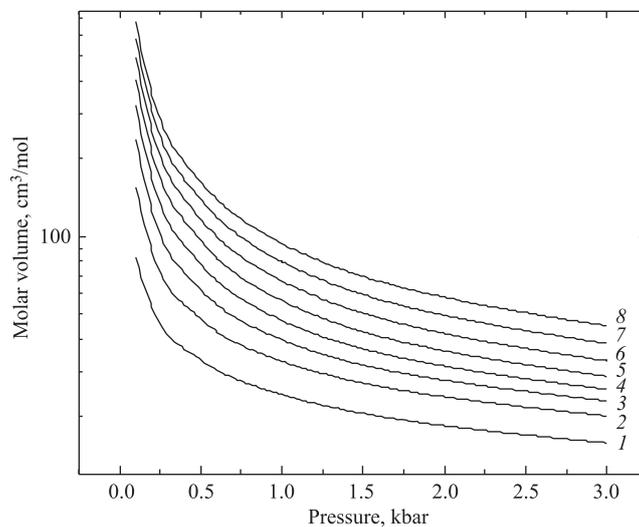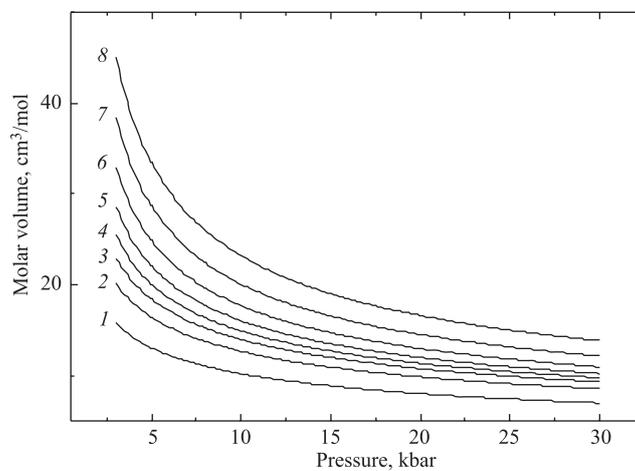
Fig. 3. Extrapolated molar volume dependences versus pressure for different temperatures obtained by using virial equation (7.1). It is the first part of whole curve at low pressure $P \leqslant 3$ kbar. Curves *1–8* correspond to temperatures: 77.15, 273.15, 473.15, 673.15, 873.15, 1073.15, 1273.15, 1473.15 K, respectively

Fig. 4. Extrapolated molar volume dependences versus pressure for different temperatures obtained by using virial equation (7.1). It is the second part of whole curve at pressure $3 \leqslant P \leqslant 20$ kbar. Curves *1–8* correspond to temperatures: 77.15, 273.15, 473.15, 673.15, 873.15, 1073.15, 1273.15, 1473.15 K, respectively

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4. The virial equations (7.1) and (7.2) can be used for fit experimental data [6–9] at relatively low pressure $P < 3$ kbar too in distinction of another equations. Direct solving of linear equation of the third order (10.1) using extrapolated virial coefficients A_1 and A_2 (7.1) allows us to obtain good agreement between existing experimental data for high pressure [6–9] and calculated values (see Table 5). Such a possibility to get good agreement is the evidence of validity of virial equation (7.1). Equation (7.2) or (8) does not allow us to get such a result (see Fig. 4 and comments before Table 5).

5. Scheme of molar dependences extrapolation developed here includes four stages:

— 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 (7.1), (7.2) and (8)) for experimental temperatures;

— extrapolation of temperature-dependent parameters on wide temperature interval using simple expression (11) and determination of coefficients of series expansions $\beta_{i,j}$, $i = 1, 2, 3$ and $j = 1, 2, 3$ (see Tables 6.1 and 6.2);

— extrapolation of molar volumes or mean distances between hydrogen molecules on wide pressure and temperature interval;

— check of validity of such an interpolation.

We will check validity of virial equation as the most developed in the next article (the third part).

Appendix 1
LEAST SQUARE METHODS OF APPROXIMATION
(χ_i^2 MINIMIZATION)

Probably the most common application of minimization in scientific research is a least square fitting, where the function to be minimized is the sum of squares of deviations between measured values and predictions of a model containing variable parameters [8, 15, 16]:

$$\Phi(\alpha_k, k = 1, K) = \sum_{n=1}^{N} f_n^2(\alpha_k, k = 1, K) =$$

$$= \sum_{n=1}^{N} \left(\frac{Y_n^{\exp} - F_n(\alpha_k, k = 1, K)}{\Delta Y_n^{\exp}} \right)^2, \quad \text{(A-1.1)}$$

where $Y_n^{\exp}$ and $\Delta Y_n^{\exp}$ are measured values and their errors, and $F_n(\alpha_k, k{=}1, K)$ are the values predicted by the theoretical or phenomenological model, depending on some parameters $\alpha_k(k = 1, K)$. Minimizing $\Phi(\alpha_k, k = 1, K)$ then yields

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best values (estimates) of K parameters, based on N measurements Y_n^{exp} with random errors ΔY_n^{exp}, where N must be greater than or equal to K, and usually the inequality $N > K$ is realized.

Let us consider the second derivative matrix for $\Phi(\alpha_k, k = 1, K)$:

$$\frac{\partial^2 \Phi}{\partial \alpha_l \cdot \partial \alpha_m} = 2 \cdot \left(\sum_{n=1}^{N} \frac{\partial f_n}{\partial \alpha_l} \cdot \frac{\partial f_n}{\partial \alpha_m} + \sum_{n=1}^{N} f_n \cdot \frac{\partial^2 f_n}{\partial \alpha_l \cdot \partial \alpha_m} \right). \qquad \text{(A-1.2)}$$

There are two important special cases. First of all linear least squares (the second sum is exactly zero), so that $\dfrac{\partial^2 \Phi}{\partial \alpha_l \cdot \partial \alpha_m}$ is quadratic, and the whole minimization problem is reduced to the inversion of the above matrix of errors $\dfrac{\partial^2 \Phi}{\partial \alpha_l \cdot \partial \alpha_m}$. The own computer code «LINEAR» was written by authors for linear least squares variant. And there is more general case of nonlinear least squares method, the linearization approximation consists in taking: $\dfrac{\partial^2 \Phi}{\partial \alpha_l \cdot \partial \alpha_m} \approx 2 \cdot \sum_{n=1}^{N} f_n \cdot \dfrac{\partial^2 f_n}{\partial \alpha_l \cdot \partial \alpha_m}$. The computer code «FUMILI-Dubna» was written for nonlinear least squares variant.

For interpolation of experimental data we used the least square method, which supposes minimization of expression (4) [16, 17], i.e., to calculate the parameters $\alpha_k (k = 1, \ldots, K)$ of approximating expression $F_n(\alpha_k, k = 1, \ldots, K)]$ by minimization of functional (10). 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 comparison of numbers of parameters and experimental points and corresponding value χ_i^2.

Necessary to note here that extrapolation signifies that the expansion of experimentally found functional dependence which exactly takes place for limited branch of argument value changes in wider area, i.e., propagation (prolongation) is carried out in this area limits. Such a way one can obtain data, which are impossible to get by immediate measurements or when such data are absent (see [17], p. 156).

It was proved that the critical value of the number of approximating parameters exists (see [16, 17]), i.e., such a critical value $K = K_{\text{critical}}$ determines optimal approximation. If anybody will spend approximation by polynomials with degree $K > K_{\text{critical}}$ it is possible to approach calculated data to experimental ones and obtain much better harmony (agreement), unfortunately it is inevitable to get worse consent with true curve, which all specialists try to estimate ([16], p. 165).

From physical point of view, extrapolation, of course, correctly speaking, is not very legitimate operation, because we suppose that functional dependence would be kept as well over the boundaries of studied interval of arguments. Sometimes for such a confirmation there are no enough foundations. Only one foundation can be suggested, the physical nature of phenomenon does not change. So in many cases extrapolation is very useful and unique method of obtaining new data [17–19].

Appendix 2
KARDANO METHOD FOR SOLVING
OF THE THIRD ORDER LINEAR EQUATIONS

For obtaining roots of equations such as

$$\frac{P \cdot V}{R \cdot T} = A_1(T) + \frac{A_2(T)}{V} + \frac{A_3(T)}{V^2}, \tag{A-2.1}$$

it is better to rewrite this expression in the form:

$$a_1 X^3 + a_2 X^2 + a_3 X + a_4 = 0. \tag{A-2.2}$$

where

$$a_1 \equiv \frac{P}{R \cdot T}, a_2 \equiv A_1(T), a_3 \equiv A_2(T), a_4 \equiv A_3(T),$$

then it is necessary to use the change of one set of parameters to another one:

$$R \equiv a_2/a_1, S \equiv a_3/a_1, T \equiv a_4/a_1,$$

and Eq. (A-2.2) becomes as

$$X^3 + R \cdot X^2 + S \cdot X + T = 0. \tag{A-2.3}$$

Then we carry out the exchange of variable X on another one $Y = X + R/3$, and Eq. (A-2.3) takes a new form:

$$Y^3 + P \cdot Y + Q = 0, \tag{A-2.4}$$

where

$$P = \frac{3 \cdot S - R^2}{3}, \quad Q = \frac{2 \cdot R^3}{27} - \frac{R \cdot S}{3} + T.$$

Discriminant of Eq. (A-2.4) has the form:

$$D = \left(\frac{P}{3}\right)^3 + \left(\frac{Q}{2}\right)^2. \tag{A-2.5}$$

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The roots of Eq. (A-2.5) can be written as

$$
\begin{cases}
Y_1 = U + V, \\
Y_2 = -\dfrac{U+V}{2} + i \cdot 3^{1/2} \cdot \dfrac{U-V}{2}, \\
Y_3 = -\dfrac{U+V}{2} - i \cdot 3^{1/2} \cdot \dfrac{U-V}{2},
\end{cases}
\qquad \text{(A-2.6)}
$$

where

$$
U = (-0.5 \cdot Q + D^{1/2})^{1/3} \qquad \text{(A-2.7)}
$$

$$
\text{and} \quad V = (-0.5 \cdot Q - D^{1/2})^{1/3}, \qquad \text{(A-2.8)}
$$

(see [17], p. 146).

If $D \geqslant 0$, Eqs. (A-2.1) and (A-2.2) have one real root, and two imaginary roots, if $D < 0$. Equation (A-2.4) has three real roots. For calculations without image numbers, one can use the following method; let us introduce $\rho = \{-P^3/27\}^{1/2}$, and $\cos \varphi = -Q/2\rho$, then roots will be

$$
\begin{aligned}
Y_1 &= 2 \cdot \rho^{1/3} \cdot \cos(\varphi/3), \\
Y_2 &= 2 \cdot \rho^{1/3} \cdot \cos(\varphi/3 + 2 \cdot \pi/3), \\
Y_3 &= 2 \cdot \rho^{1/3} \cdot \cos(\varphi/3 + 4 \cdot \pi/3).
\end{aligned}
\qquad \text{(A-2.9)}
$$

By the way, for solving of equations with more than three members it is better to use the method of Newton (see [17], p. 497) or the method of dividing of segment in half.

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