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ON THE THEORY OF THE EQUATION OF STATE OF REAL GASES. II

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A comparison is made between the equation of state derived earlier and experiment.

4. INITIAL THEORETICAL FORMULAS

It was shown in the previous paper that the computation of triple, quadruple, etc. collisions is equivalent to the introduction of correlations between statistical criteria into the statistics, for which the thermal velocity components were taken. If we go from the correlation coefficient r over to the complex $n = r/(1+r)$, then the equation of state we obtained has the form

$$\frac{pv}{RT} = \Psi(n) - B\rho, \quad (29)$$

where

$$\left. \begin{aligned} \Psi(n) &= \frac{1-n}{(1+n)(1-2n)} \\ n &= \sqrt{\rho}(A_1 + A_2\rho) \end{aligned} \right\}, \quad (30)$$

$$\left. \begin{aligned} A_1 &= 0.8096 \cdot 10^{-2} + 0.4481 \cdot 10^{-2} \frac{T_h}{\rho_h} \\ A_2 &= 0.9924 \cdot 10^{-5} - 0.5481 \cdot 10^{-5} \frac{T_h}{\rho_h} \end{aligned} \right\}. \quad (31)$$

Comparing (29) with experimental results can clarify the constant B , and a clarification of the nature of the interaction forces between the molecules can thereby be made. The peculiarity of the viewpoint elucidated is the separation of the virial of the internal forces from the factors due to triple, quadruple, etc. collisions. If we turn to the usual description of the equation of state in terms of the virial coefficients, then the latter, found by using experimental data, contain not only what results from the interaction force, but also what is due to multiple collisions. And this means execution of a logical error and obtaining distorted information about the nature of the molecular interaction forces.

5. ON THE EQUATION OF STATE OF ARGON

We used the Michels measurements [1] for argon in which the pressure varied between 1 and 2900 atm and the temperature between 50 and 100°C. In order to conserve a high degree of measurement accuracy, the density in the Michels tests was expressed in Amag units (one Amag unit of the density equals $4.4636 \cdot 10^5$ mole/cm³).

The density is also defined in these units in our computations. For argon $T_k/P_k = 3.125$; then we have according to (31): $A_1 = 0.2210 \cdot 10^{-1}$, $A_2 = -0.7204 \cdot 10^{-5}$, which in turn determines the dependence of n on the density:

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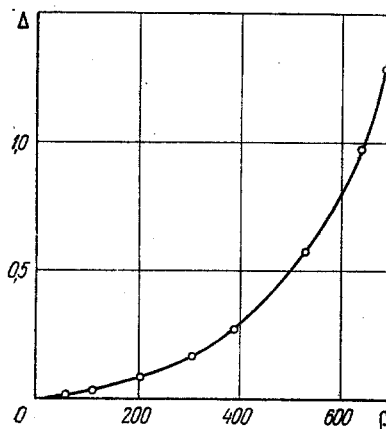


Fig. 1. Virial of the intramolecular forces for hydrogen.

TABLE 1. Compressibility Factor as a Function of the Density

ρ	Argon		Nitrogen		Carbon monoxide	
	$\frac{pv}{RT}$ theory	$\frac{pv}{RT}$ experiment	$\frac{pv}{RT}$ theory	$\frac{pv}{RT}$ experiment	$\frac{pv}{RT}$ theory	$\frac{pv}{RT}$ experiment
80	0,9410	0,9390	0,9773	0,9827	0,9590	0,9710
160	0,9162	0,9098	1,0102	1,0092	0,9784	0,9900
200	0,9176	0,9081	—	—	—	—
240	0,9301	0,9117	1,1112	1,0933	1,0747	1,0700
320	1,0054	0,9307	1,3051	1,2608	1,2735	1,2410
360	1,0496	1,0191	—	—	—	—
400	1,1233	1,0867	1,6112	1,5547	1,6074	1,5490
480	1,3328	1,2954	2,0595	2,0386	2,0991	2,0670
520	1,4725	1,4471	—	—	—	—
560	1,6458	1,6389	2,6037	2,8016	—	—
600	1,8445	1,8784	—	—	2,9865	3,4570
640	2,0806	2,1741	3,1886	3,9672	—	—

$$n = \sqrt{\rho} (0.2210 \cdot 10^{-1} - 0.7204 \cdot 10^{-5} \rho).$$

Now, just one unknown quantity $B(T)$ remains in (29). To determine it, it is necessary to form the difference, at a fixed temperature, between $\Psi(n)$ and the experimental values of the compressibility factor, i.e., to determine

$$\Delta = \Psi(n) - \left(\frac{pv}{RT} \right)_{\text{exp}}$$

The functional dependence of Δ on ρ is approximated well by a straight line, whose slope indeed determines the quantity B . For the mentioned scheme of superposing theory on experiment, the quantity $B(T)$ turned out to equal

T, °C	-50	-25	0	25	50	75
$B \cdot 10^8$	2,61	2,28	2	1,78	1,61	1,47

This dependence is approximated well by the formula

$$B(T) = \frac{0,710}{T} - 0,58 \cdot 10^{-3},$$

where the temperature T is measured in degrees Kelvin.

The nature of the agreement between theory and experiment at 0°C is shown in Table 1.

6. ON THE EQUATION OF STATE OF CARBON MONOXIDE

There are quite reliable measurements of the compressibility factor for carbon monoxide in the 0-150°C temperature and up to $3 \cdot 10^8$ N/m² pressure ranges, which are due to Michels and his colleagues [2]. Since $T_k/p_k = 3.873$ for carbon monoxide, then according to (31), we have $A_1 = 0.2545 \cdot 10^{-1}$, $A_2 = -0.1130 \cdot 10^{-4}$. This yields the following formula for n :

TABLE 2. Compressibility Factor

ρ , Amag units	Carbon dioxide		ρ , Amag units	Methane	
	$\frac{p\rho}{RT}$ theory	$\frac{p\rho}{RT}$ experiment		$\frac{p\rho}{RT}$ theory	$\frac{p\rho}{RT}$ experiment
50	0,7923	0,7920	28,735	0,9349	0,9335
100	0,6126	0,6290	45,347	0,9017	0,9023
200	0,3557	0,4170	67,056	0,8633	0,9180
300	0,2955	0,3320	99,056	0,8163	0,8146
400	0,5353	0,4230	120,992	0,7908	0,7890
500	1,1111	0,9580	150,324	0,7671	0,7618
600	1,7348	2,2840	183,018	0,7589	0,7433
—	—	—	224,875	0,7752	0,7394

$$n = \sqrt{\rho}(0.2545 \cdot 10^{-1} - 0.1130 \cdot 10^{-4}\rho).$$

Therefore, we know the function $\Psi(n)$ and the quantity $B(T)$ is calculated as before, by the superposition of theory on experiment. We afterwards have

T , °C	0	50	100	150
$B \cdot 10^3$	2,2750	1,8656	1,5875	1,3934
$B \cdot 10^3$ from (32)	2,2614	1,8665	1,4775	1,3568

This empirical dependence of the parameter B on the temperature is approximated well by the formula

$$B(T) = \frac{0.6964}{T} - 0.2895 \cdot 10^{-3}. \quad (32)$$

An example illustrating the agreement between theory and experiment at 0°C is presented in Table 1.

7. ON THE EQUATION OF STATE OF NITROGEN

The experimental results for the compressibility factor, obtained by Michels, refer to the 0–150°C temperature range and pressures from 1 to 5500 atm [3].

For nitrogen $T_k/p_k = 3.761$; then we have, according to (31): $A_1 = 0.2495 \cdot 10^{-1}$, $A_2 = -0.1069 \cdot 10^{-4}$, which yields in turn

$$n = \sqrt{\rho}(0.2495 \cdot 10^{-1} - 0.1069 \cdot 10^{-4}\rho).$$

The function $\psi(n)$ is now calculated as a function of the density and it is independent of the temperature. The unknown quantity $B(T)$ is calculated by the method elucidated above:

T , °C	0	25	50	75	100	125	150
$B \cdot 10^3$	1,9625	1,7752	1,5888	1,4212	1,3481	1,2393	1,1555

This dependence is approximated fairly well by the formula

$$B(T) = \frac{0.6591}{T} - 0.4517 \cdot 10^{-3}.$$

The agreement between theory and experiment is shown in Table 1.

8. ON THE EQUATION OF STATE OF CARBON DIOXIDE

Test results for carbon dioxide obtained by Michels [4] within the temperature limits 0–150°C and at pressures up to $3 \cdot 10^8$ N/m² were processed by the method described above. The function $\Psi(n)$ can be calculated by means of the critical data according to the established rule. The quantities therein equal, for carbon dioxide,

$$\frac{T_k}{p_k} = 4.175; A_1 = 0.2680 \cdot 10^{-1}, A_2 = -0.1296 \cdot 10^{-4},$$

$$n = \sqrt{\rho}(0.2680 \cdot 10^{-1} - 0.1296 \cdot 10^{-4}\rho).$$

TABLE 3. Compressibility Factor for Hydrogen

ρ , Amag units	0°C		25°C		50°C	
	$\frac{pv}{RT}$ experiment	$\Psi(n)$	$\frac{pv}{RT}$ experiment	$\Psi(n)$	$\frac{pv}{RT}$ experiment	$\Psi(n)$
58,80	1,0387	1,0368	1,0398	1,0373	1,0409	1,0393
110,01	1,0769	1,0739	1,0791	1,0748	1,0810	1,0793
205,07	1,1602	1,1544	1,1638	1,1562	1,1669	1,1610
305,39	1,2676	1,2565	1,2721	1,2590	1,2756	1,2727
391,18	1,3786	1,3636	1,3832	1,3648	1,3865	1,3827
531,68	1,6063	1,5843	1,6081	1,5822	1,6086	1,6049
638,04	1,8238	1,7989	1,8210	1,7909	1,8170	1,8111
690,28	1,9473	1,9356	1,9408	1,9101	1,9335	0,9257
845,66	2,3871	2,3962	2,3633	2,3639	2,3426	2,3451
939,05	2,7086	2,7817	2,6711	2,7167	2,6411	2,6358

Therefore, the function $\Psi(n)$ becomes known and the function $B(T)$ is found easily from the experimental results. It turned out to equal

T , °C	49,71	99,767	150,14
$B \cdot 10^8$	5,9889	4,9457	4,1878

or according to the approximating formula

$$B(T) = \frac{2,5065}{T} - 1,7780 \cdot 10^{-3}$$

A comparison between theory and experiment at 49.71°C is shown in Table 2.

9. ON THE EQUATION OF STATE OF METHANE

Michels [5] measured the compressibility factor of methane in the 0-150°C temperature range and for densities from 19 to 230 Amag units. In conformity with the methodology used, let us evaluate the function $\Psi(n)$ according to the critical data. We have

$$\frac{T_k}{\rho_k} = 4,178, n = \sqrt{\rho} (0,2682 \cdot 10^{-1} - 0,1298 \cdot 10^{-4} \rho)$$

Having calculated $\Psi(n)$, we find from the experiment results

T , °C	0	50	100	150
$B \cdot 10^8$	3,9728	3,1570	2,6234	2,2129

This dependence is approximated well by the formula

$$B(T) = \frac{1,4174}{T} - 0,1176 \cdot 10^{-2}$$

The nature of the agreement between theory and experiment at 0°C is shown in Table 2.

10. ON THE EQUATION OF STATE OF HYDROGEN

Michels and his students investigated hydrogen with special care. Their final measurements of the compressibility factor in the 30-2540 atm pressure range and for different temperatures (between 0 and 150°C) are given in [6].

To verify the universality of (31), an attempt was first made to describe the experimental results on hydrogen from the aspect of the method elucidated above. For hydrogen it turned out that

$$\frac{T_k}{\rho_k} = 2,593, n = \sqrt{\rho} (0,1971 \cdot 10^{-1} - 0,4288 \cdot 10^{-5} \rho)$$

Later the difference between $\Psi(n)$ and the experimental values of the compressibility factor at 0°C was formed; i.e.,

$$\Delta = \Psi(n) - \left(\frac{pv}{RT} \right)_{\text{exp}}$$

The quantity Δ is represented in Fig. 1 as a function of the density at 0°C. It is seen from the figure that this function is not approximated by a straight line, but it must be assumed for a reliable approximation that

$$\Delta = \rho^2(b_0 - b_1\rho).$$

The virial of the intramolecular forces is thereby made complicated as compared to the virial of these forces for the substances considered above.

This fact indicates that the hypothesis about the independence of the correlation coefficient from the temperature and the scheme to compute the function $\Psi(n)$ can be conserved for all substances, but it is hence possible to arrive at quite complex representations relative to the theory of intramolecular forces. The role of the correlation distribution function as a factor simplifying the computation of the virial coefficients is thereby smoothed out.

Therefore, the following alternative occurs: Is the mentioned scheme to compute the function $\Psi(n)$ conserved or should it be altered for the sake of simplicity of the representations of the intramolecular forces? Facts from the history of science indicate that researchers did not proceed identically in taking such alternative solutions. Thus, in studying the preceding theories from the area of electricity and magnetism, Maxwell wrote [7], "In order to master already existing theories, it is necessary to become familiar with a significant store of such complex mathematical formulas that the difficulty of keeping them in the memory is already itself a substantial obstacle to the development of science."

We tend to simplicity from psychological rather than logical motives. According to Maxwell, it stands to reason that our perception should proceed in its historical development along the path of discovering simple and beautiful laws. He wrote, "For a successful development of a theory it is first necessary to simplify the deductions of previous investigations and to reduce them to a form more accessible to perception."

Our countryman M. V. Lomonosov arrived at these same ideas long before Maxwell. He wrote [8] "Nature is very simple; what contradicts this should be rejected." For Lomonosov the simplicity criterion is accumulated experience and the easiness of perception.

The appeal to the classics of natural science is not accidental. In this case two equations of state can be proposed for hydrogen, which cleverly describe the experimental material but are distinguished from each other just by some degree of complexity.

By awarding the preference to the simpler theory we assume that the correlation coefficient for hydrogen varies with the temperature; i.e., $n = n(\rho, T)$; then the experimental results on the compressibility factor can be described only by the function $\Psi(n)$. The formula

$$\frac{p\rho}{RT} = \Psi(n), \quad (33)$$

where

$$n = \sqrt{\rho} [A_1(T) + A_2(T)\rho], \quad (34)$$

can thereby be used for the equation of state of hydrogen. According to these representations, the effect of the intramolecular forces does therefore not appear in compressed hydrogen.

The theory is superposed on experiment at two points $\rho = 110.01$ and 845.66 for all temperatures. The parameters $A_1(T)$ and $A_2(T)$ hence turned out to equal

$T, ^\circ\text{C}$	0	25	50	100
$A_1 \cdot 10^4$	0,1640	0,1651	0,1695	0,1718
$A_2 \cdot 10^5$	-0,2590	-0,2776	-0,3341	-0,3693

It is seen from Table 3 that the function $\Psi(n)$ describes the test results on the compressibility factor well.

The question arises: Why is it sufficient to take account of only the correlation in the components of the atom or molecule thermal velocities to describe the behavior of the hydrogen compressibility factor? Figure 2 can yield the answer. The Michels experimental results on the compressibility factors of hydrogen and argon at 0°C are superposed here.

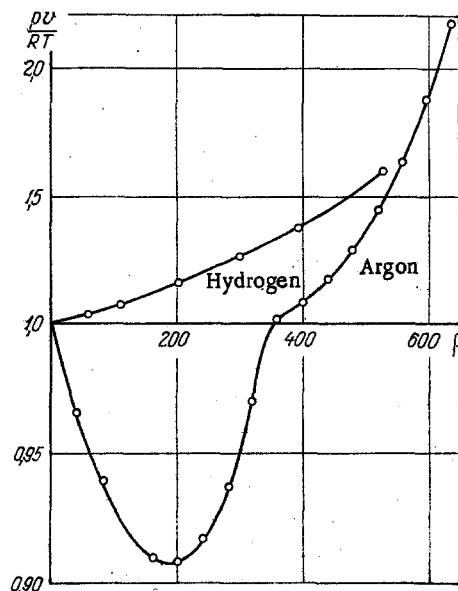


Fig. 2. Experimental behavior of the compressibility factor for hydrogen at 0°C according to Michels data.

They are analogous even for other temperatures. Attention should be turned to the fact that the compressibility factor for hydrogen is always greater than one with the increase in the density. This indicates that only the repulsive forces originating because of molecule collisions continue to act in compressed hydrogen while the role of just multiple collisions is increased with the increase in density. The compressibility factor for argon behaves somewhat differently. It is here less than one with the increase in the density from zero to 350 Amag units, and later becomes greater than one with the increase in compression, and hence grows. This can be explained by the assumption that the opposition of two forces, of repulsion and the intramolecular forces of attraction, holds here. This is namely why the virial of the intramolecular forces must be taken into account in its equation of state. The role of the function Ψ here reduces to the fact that it separates the virial of the internal forces from the factors due to multiple collisions.

At present there are experimental results on the compressibility factors for neon, helium, and deuterium. Their behavior does not in any way differ qualitatively from that of hydrogen. Hence, their equation of state is also determined just by the function Ψ , but the behavior of the parameters $A_1(T)$ and $A_2(T)$ will be distinct. It is interesting to note that the numerical values of T_k/p_k are close for these substances; i.e., empirical formulas analogous to (31) can be selected to determine $A_1(T)$ and $A_2(T)$.

However, at this stage our problem was limited to the clarification of the role of the function Ψ in the theory of the equation of state of real gases.

NOTATION

p , pressure; v , specific volume; ρ , density; T_k , p_k , critical temperature and pressure; R , universal gas constant; T , temperature.

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