



Experimental and Theoretical Study of Dielectric Permeability of Nonpolar Gases

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Abstract

In the present paper we consider application of equation of state for model gases to the description of experimental dependencies of dielectric permeability on pressure and temperature for nonpolar gases. The case of argon is regarded as an example. It is demonstrated that the generalized Van-der-Waals-Berthelot equation describes the dependence of dielectric permeability on pressure and temperature with good accuracy. It is shown that the measurement of dielectric permeability using the isotherms with small temperature increments provides a means to obtain the exact tabulated equation of state. This result can be used in other areas of investigation.

Keywords: Dielectric Permeability; Van-der-Waals Equation; Berthelot Equation; Generalized Van-der-Waals-Berthelot Equation.

Introduction

The proposed work is of interest to researchers of the dielectric permittivity of gases. Having carried out a small number of measurements, and having selected a suitable equation of state, for example the Van der Waals equation, Berthelot, or as the author has shown, the generalized Van- der -Waals-Berthelot equation to calculate the permittivity of gases over a wide range of temperatures and pressures. Researchers of

the equation of state of gases, carrying out measurements of the dielectric constant in a wide range of pressures and temperatures, can calculate numerically the equations of state of gases.

Experimental Results

Measurement results on the dependence of dielectric permeability of argon on pressure and density for two isotherms $T_1=273.15$ K and $T_2=373.15$ K were presented in [1]. Unfortunately, in [1] the

measurement results were simply given as plots. Therefore, in the present paper we had to digitize these plots and corresponding values are given in Tables (1, 2).

Table (1): Dependence of dielectric permeability on pressure for T=273.15 K and T=373.15 K.

T, K	P, MPa	ϵ	T, K	P, MPa	ϵ
273.15	5.625	1.0375	373.15	5	1.0167
273.15	10.625	1.0665	373.15	9.375	1.0375
273.15	15	1.0917	373.15	15.63	1.0625
273.15	20	1.1208	373.15	23.13	1.0917
273.15	28.125	1.1667	373.15	29.38	1.1167
273.15	33.75	1.1958	373.15	33.25	1.1292
273.15	38.75	1.2167	373.15	41.88	1.1583
273.15	43.125	1.2333	373.15	48.13	1.1792
273.15	51.25	1.2583	373.15	55	1.2
273.15	55	1.2708	373.15	61.25	1.2167
273.15	60	1.2833			

Table (2): Dependence of dielectric permeability on density for T=273.15 K

T, K	$\rho \cdot 10^{-3}$, kg/m ³	ϵ	T, K	$\rho \cdot 10^{-3}$, kg/m ³	ϵ
273.15	0,1583	10,250	373.15	0,1500	10,167
273.15	0,2167	10,458	373.15	0,2083	10,417
273.15	0,2833	10,700	373.15	0,3050	10,750
273.15	0,3583	10,980	373.15	0,3500	10,917
273.15	0,4333	11,250	373.15	0,4167	11,167
273.15	0,5750	11,708	373.15	0,4667	11,333
273.15	0,6250	11,880	373.15	0,5167	1500
273.15	0,7083	12,192	373.15	0,5417	11,608
273.15	0,7667	12,400	373.15	0,5833	11,792
273.15	0,8167	12,583	373.15	0,6417	11,983
273.15	0,8417	12,683	373.15	0,6917	12,167
273.15	0,8750	12,792			

Using the experimental results given in Tables 1 and 2 we have plotted the $\varepsilon=f(P)$ and $\varepsilon=f(\rho)$ dependencies (see Figures. 1 and 2).

Figure (1): $\varepsilon=f(P)$ dependence for T=273.15 K, T=373.15 K.

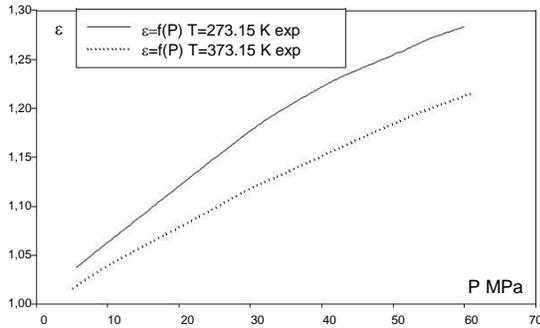
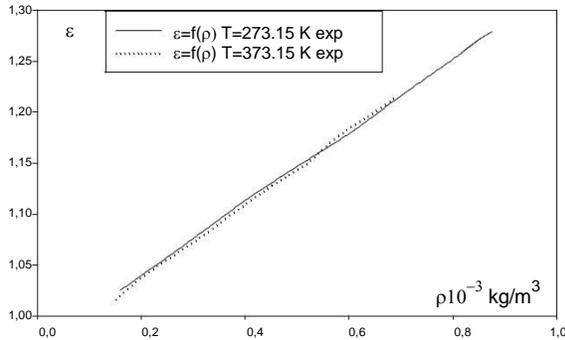


Figure (2): $\varepsilon=f(\rho)$ dependence for T=273.15 K, T=373.15 K.



Model Selection

The gases composed of monatomic and symmetric molecules such as He, Ne, Ar, H₂, N₂, CH₄, CCl₄ do exhibit strong dipole moment. However, dielectric permeability of these gases is different from unity. The explanation of this fact given in [2] concerns electron clouds distorted by an electric field. Hence, the polarization factor is proportional to the field:

$$\mu = \alpha E,$$

Where μ is a dipole moment induced along the field direction, and the coefficient of proportionality α is referred to as the molecular polarizability. The Debye formula [2]:

$$\varepsilon - 1 = 4\pi n \left(\alpha + \frac{1}{3} \beta \mu_0^2 \right)$$

Takes the form of $\varepsilon - 1 = 4\pi n\alpha$ or $\varepsilon = 1 + 4\pi n\alpha$,

where $n = \frac{N}{V}$ is the molecular concentration connected to the density ρ by the relation

$$\rho = mn,$$

where m is the molecular mass.

As can be seen from the plot in Figure (2), the dielectric permeability is actually linearly dependent on the density. To obtain the expressions describing the dependence of dielectric permeability of gases on temperature and pressure it is necessary to introduce an appropriate model to establish the relation between the gas concentration, temperature and pressure. The basic model is the ideal gas model:

$$PV = NkT$$

Or

$$P = \frac{N}{V} kT = nkT$$

$$n = \frac{P}{kT},$$

Consequently:

$$\varepsilon = 1 + 4\pi\alpha \frac{P}{kT} \quad (1)$$

The relation (1) gives a relevant qualitative description to the behaviour of the dielectric permeability, i.e. it grows with increasing the pressure and falls with increasing the temperature. However, it follows from the expression (1) that the

dielectric permeability grows linearly with pressure and, as can be seen from the plots in Fig 1, this is not the case. Consequently, to describe the $n = f(P, T)$ dependence one should choose a more realistic model rather than the ideal gas model. For example, Van-der-Waals model could be considered.

Van-der-Waals model

The expression for the Van-der-Waals equation of state is written as [2]:

$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = NkT$$

Or

$$\left(P + \frac{N^2 a}{V^2} \right) \left(V - \frac{Nb}{V} \right) = \frac{N}{V} kT.$$

By changing the variables

$$\frac{N}{V} = n,$$

we obtain the expression that can be used to find $n(P, T)$:

$$(P + n^2 a) (1 - nb) = nkT,$$

$$abn^3 - an^2 + (bP + kT)n - P = 0. \quad (2)$$

Detailed methods for solving cubic equations are given in [3]. Let us reduce the state variables before solving the equation (2):

$$\hat{P} = \frac{P}{P_c}, \hat{T} = \frac{T}{T_c}, \hat{n} = \frac{n}{n_c}, n_c = \frac{N}{V_c}$$

Thus, the equation (2) is written as:

$$\hat{n}^3 - 3\hat{n}^2 + \frac{8\hat{T} + \hat{P}}{3} \hat{n} - \hat{P} = 0. \quad \text{By}$$

making a substitution $\hat{n} = x + 1$ we obtain:

$$\left(\frac{x+1}{3} \right)^3 - 3 \left(\frac{x+1}{3} \right)^2 + \frac{8\hat{T} + \hat{P}}{3} \left(\frac{x+1}{3} \right) - \hat{P} = 0.$$

When we open the brackets, we have:

$$x^3 + \left(\frac{8\hat{T} + \hat{P}}{3} - 3 \right) x + \frac{2(4\hat{T} - \hat{P})}{3} - 2 = 0,$$

$$p = \left(\frac{8\hat{T} + \hat{P}}{3} - 3 \right), \quad q = \frac{2(4\hat{T} - \hat{P})}{3} - 2, \quad (3)$$

$$D = \left(\frac{q}{2} \right)^2 + \left(\frac{p}{3} \right)^3 = \left(\frac{4\hat{T} - \hat{P}}{3} - 1 \right)^2 + \left(\frac{8\hat{T} + \hat{P}}{9} - 1 \right)^3,$$

$$\left(\frac{4\hat{T} - \hat{P}}{3} - 1 \right)^2 \geq 0.$$

The values of the gas parameters do not approach the critical point by far and, consequently:

$$\hat{T} = \frac{T}{T_c} > 1, \quad \hat{P} = \frac{P}{P_c} > 1, \quad \frac{8\hat{T} + \hat{P}}{9} > 1,$$

$$\left(\frac{8\hat{T} + \hat{P}}{9} - 1 \right) > 0, \quad D > 0.$$

Expectedly, the equation (3) has a single real solution as

$$p = \left| \frac{\hat{n}^3 - 1}{9} \right| > 0, \quad \text{and then}$$

$$x = -2 \sqrt{\frac{p}{3}} \operatorname{ctg}(2\varphi), \quad \operatorname{tg}(\varphi) = \sqrt[3]{\operatorname{tg}\left(\frac{\omega}{2}\right)},$$

$$\operatorname{tg}(\omega) = \frac{2}{q} \sqrt{\left(\frac{p}{3}\right)^3}, \quad \hat{n} = x + 1.$$

Computer calculations can be readily applied to the set of expressions (3). As a result, we obtain tabulated functions $\hat{n} = \hat{n}(\hat{P}, \hat{T}) = f(P, T)$. For argon $T_c = 150.86$ K, $P_c = 4.898$ MPa, $V_c = 7.49 \cdot 10^{-5}$ m³/mol. If we turn to the original parameters we obtain:

For argon $T_c = 150.86$ K, $P_c = 4.898$ MPa, $V_c = 7.49 \cdot 10^{-5}$ m³/mol. If we turn to the original parameters we obtain:

$$n \cdot 10^5 \text{ mol} / \text{m}^3 = f(P, T = 273.15),$$

$$n \cdot 10^5 \text{ mol} / \text{m}^3 = f(P, T = 373.15)$$

; by multiplying n by the Avogadro constant $N_A = 6.02 \cdot 10^{23}$, we finally have:

$$n \cdot 10^{28} \text{ 1} / \text{m}^3 = f(P, T = 273.15),$$

$$n \cdot 10^{28} \text{ 1} / \text{m}^3 = f(P, T = 373.15)$$

It was proposed in [4] to use the expression $\alpha = r^3$ to determine the polarization factor of hydrogen or a more strict quantum-mechanical expression

$$\alpha = \frac{9}{2} r^3,$$

where r is the radius of the electron orbit. Polarization factors for noble gases were given in [4] as well; corresponding values are presented in Table 3.

Table (3): Polarization factors for noble gases.

Gas	Ne	Ar	Kr	Xe
$\alpha \cdot 10^{10} \text{ m}^2$	0.394	1.65	2.51	4.10

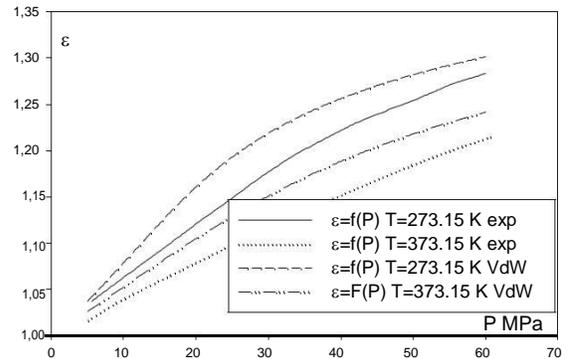
Using the expression

$$\varepsilon = 1 + 4\pi n\alpha$$

we obtain $\varepsilon(P)$ dependencies for $T = 273.15 \text{ K}$ and $T = 373.15 \text{ K}$. The calculation results are shown in Figure (3). As

can be seen from the plots presented in Figure (3), implementation of the Van-der-Waals model provides a fairly good qualitative description for the dependence of dielectric permeability on pressure. However, quantitative agreement between the experimental and calculated results is not achieved within the regarded model.

Figure (3): Experimental and calculated dependencies of dielectric permeability of argon on pressure at different temperatures. Calculation was conducted in the framework of Van-der-Waals model.



Berthelot model

Let us consider another gas model, namely, Berthelot model [5]

$$\left(P + \frac{N^2 a}{TV} \right) (V - Nb) = NkT$$

$$\left(P + \frac{N^2 a}{TV} \right) \left(\frac{V}{N} - \frac{Nb}{N} \right) = \frac{N}{V} kT.$$

For this case we can imitate what we did in the previous subsection and we finally have:

$$n^3 - 3n^2 + \frac{T(8T+P)}{3} - PT = 0.$$
 By making a substitution $n = x + 1$ we obtain the equation that can be solved using the algorithm discussed above:

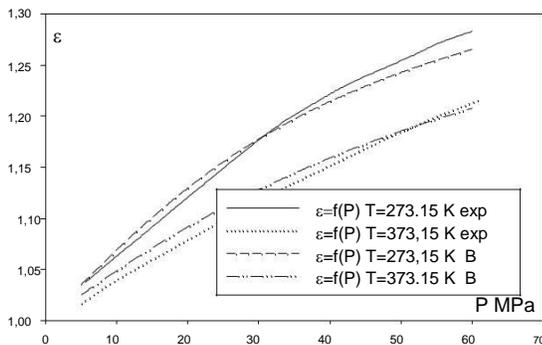
$$x^3 + \left(\frac{T(8T+P)}{3} - 3 \right) x + \frac{2(T(4T-P)-3)}{3} = 0,$$

$$p = \frac{T(8T+P)}{3} - 3, q = \frac{2(T(4T-P)-3)}{3}.$$

The calculation results obtained within the Berthelot model are presented in Figure (4).

As can be seen from the plots presented in Figure (4), implementation of the Berthelot model provides the description for the dependence of dielectric permeability of argon on pressure with relative accuracy up to several percent.

Figure (4): Experimental and calculated dependencies of dielectric permeability of argon on pressure at 273.15 K and 373.15 K. Calculation was conducted in the framework of Berthelot model.



Van-der-Waals-Berthelot model

A generalized Van-der-Waals-Berthelot equation:

$$\left(P + \frac{N^2 a}{T V} \right) (V - Nb) = NkT$$

was proposed in a number of works [6,7]. For different values of the β parameter this equation describes the evaporation line of liquid gases and metals with high accuracy. Experimental evaporation line for argon and the line calculated by the generalized Van-der-Waals-Berthelot equation are given in Figure (5).

As can be seen from the plots in Figure (5), the experimental evaporation line for argon and the one calculated by the

generalized Van-der-Waals-Berthelot equation agree within tenth and hundredth of one percent. Below we provide the results on the calculation of the dependence of dielectric permeability of argon on the density calculated by the generalized Van-der-Waals-Berthelot equation:

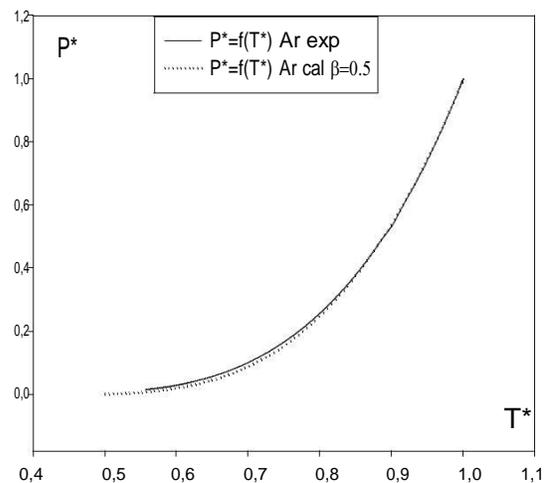
$$\hat{n}^3 - 3\hat{n}^2 + \frac{T}{3} \frac{(8T + P)}{\hat{n} - PT} = 0. \quad \hat{n} = x + 1$$

By making a standard substitution we can rewrite the above equation as:

$$x^3 + \left[\frac{\hat{T}^\beta (8\hat{T} + \hat{P})}{3} - 3 \right] + \frac{2}{3} \left[\hat{T}^\beta (4\hat{T} - \hat{P}) - 3 \right] = 0,$$

$$p = \left[\frac{\hat{T}^\beta (8T + \hat{P})}{3} - 3 \right], \quad q = \frac{2}{3} \left[\hat{T}^\beta (4\hat{T} - \hat{P}) - 3 \right].$$

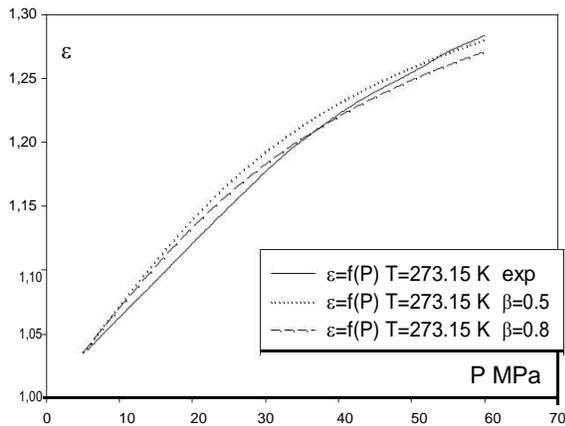
Figure (5): Experimental evaporation line for argon and the line calculated by generalized Van-der-Waals-Berthelot equation.



The results of the calculation of dielectric permeability are presented in Figures (6, 7). It is evident from the figure given above that the best possible agreement between the experimental and calculated results on the dielectric permeability can be achieved with

the use of the least square method and adjustment of the β parameter.

Figure (6): Experimental and calculated dependencies of dielectric permeability on pressure. Calculation was conducted in the framework of Van-der-Waals-Berthelot model for different values of β parameter.



However, it should be kept in mind that the Van-der-Waals and Berthelot models as well as the proposed generalized Van-der-Waals-Berthelot model are just three representative models among multiple equations of state. Particularly, the first and second Dieterici equations should be mentioned [5]:

$$P = \frac{RTe^{-\frac{a}{RTV}}}{(V-b)} \quad \text{And}$$

$$P = \frac{RT}{(V-b)} - \frac{a}{V^{5/3}}$$

Alongside with the models presented in [8].

Discussion of non-ideal agreement between experimental data and calculation results obtained within different models

As can be seen from the calculation results given above, employment of the model gases provides a means to describe the dependence of dielectric permeability on pressure with relative accuracy up to several percent. At the same time, the accuracy of description of evaporation lines of gases and metals demonstrated in [6, 7] for the generalized Van-der-Waals-Berthelot model cannot be achieved here. This is due to the fact that the model equations were derived with only Van-der-Waals molecular interaction taken into account. However, molecules become polarized when the dielectric permeability is changed and one should consider dipolar interaction which depends on the field strength E and provides changes in the dielectric permeability. Our upcoming research will be aimed at introduction of the terms associated with the dipolar interaction into the gas equations of state.

Calculation results for dependence of dielectric permeability on temperature on isobars

Below we present the calculation results for the dependence of dielectric permeability on temperature on isobars: $P = 20$ MPa, $P = 30$ MPa, $P = 40$ MPa, $P = 50$ MPa. The calculation was carried out for different values of the β parameter of the generalized Van-der-Waals-Berthelot equation.

To validate the calculation for isobars we have selected reference points ($P=20$ MPa, $T=273.15$ K), ($P=20$ MPa, $T = 373.15$ K), ($P=30$ MPa, $T = 273.15$ K), ($P=30$ MPa, $T = 373.15$ K), ($P=40$ MPa, $T = 273.15$ K), ($P=40$ MPa, $T = 373.15$ K), ($P=50$ MPa, $T = 273.15$ K), ($T = 50$

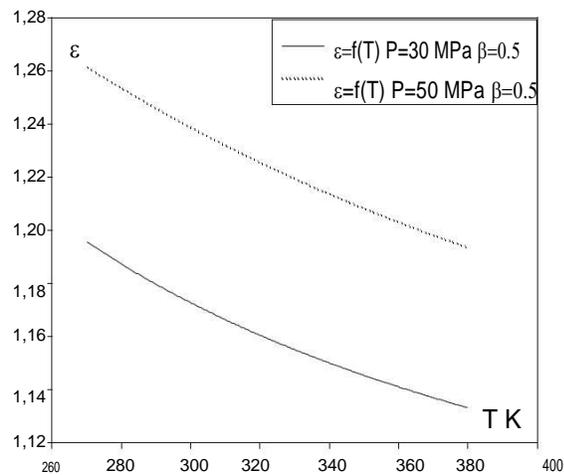
MPa, T=373.15 K) on the experimental curves and compared them with the calculation

results for isobars. The results of the comparison are presented in Table (4).

Table (4): Comparison between experimental and calculated results on dependence of dielectric permeability on temperature obtained for several isobars.

T, K	P, Mpa	ϵ_e	ϵ_c	δ	T, K	P, Mpa	ϵ_e	ϵ_c	δ
273.2	20	1.1208	1.1334	0.23	373.15	20	1.0795	1.0931	1.3
273.2	30	1.1764	1.1928	1,39	373.15	30	11,187	1.1358	1.5
273.2	40	12,214	1.2202	0.1	373.15	40	1.152	1.1625	0.9
273.2	50	1.2545	1.2588	0.35	373.15	50	11,849	1.1967	1

Figure (7): Dependence of dielectric permeability of argon on temperature obtained for P=30 MPa and P=50 MPa isobars.

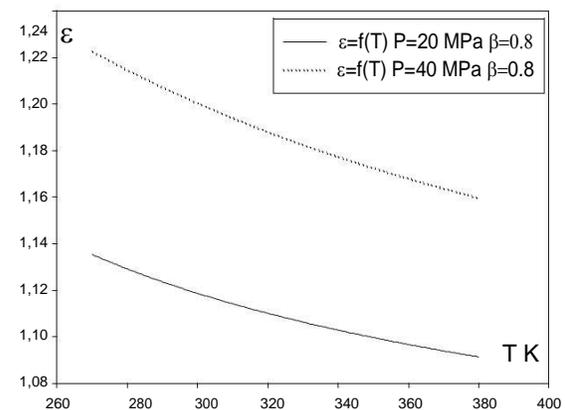


The dependencies of dielectric permeability on temperature presented in (Figures 7, 8) demonstrate that the generalized Van-der-Waals-Berthelot equation gives at least qualitative description to the dependence of dielectric permeability

on temperature. Fairly good agreement

between the experimental and calculated results (the mismatch is below 1.5%) obtained for the reference points provides the evidence for the quantitative agreement as well. The slight difference is due to the fact that one has to introduce specific terms into the equation of state to take into account the dipolar interactions within the volume of polarized gases.

Figure (8): Dependence of dielectric permeability of argon on temperature obtained for P=20 MPa and P=40 MPa isobars.



Determination of contribution from dipolar interaction to equation of state

The Debye formula for dielectric permeability of nonpolar gases is one of few expressions (if not the only expression) that establish a linear relationship between the molecular concentration and directly measurable value of the dielectric permeability:

$$\varepsilon(P, T) = 1 + 4\pi\alpha n(P, T) \quad \text{or}$$

$$n(P, T) = \frac{\varepsilon(P, T) - 1}{4\pi\alpha}.$$

If we turn to volume, we finally obtain:

$$n(P, T) = \frac{N_A}{V} = \frac{\varepsilon(P, T) - 1}{4\pi\alpha}, \quad \text{or}$$

$$V(P, T) = \frac{4\pi\alpha N_A}{(\varepsilon(P, T) - 1)} \left[\frac{\text{mol}}{\text{m}^3} \right] \quad (4)$$

We can obtain tabulated equation of state without electrostatic field by conducting experiments for different values of temperature and pressure and measuring the volume. This experiment can be carried out for piston-cylinder setup. Then, we can calculate $V(P, T, E)$ using the relation (4) after measuring the dielectric permeability for different strengths of the electrostatic field E with the same values temperature and pressure as in the previous experiment. To validate the results the volume of the system should be measured as well. Hence, we obtain tabulated equation of state $V(P, T, E)$. One can compare the equations of state with and without the electrostatic field E and evaluate the contribution from the dipole interaction

between molecules and assess the dependence of the equation of state on the electrostatic field strength E .

Conclusions

1. It was demonstrated that the model equations of state (in particular, the generalized Van-der-Waals-Berthelot equation) provide the description for the dependence of dielectric permeability of gas on pressure and temperature with relative accuracy up to several percent.

2. The slight difference between the experimental data and the dependence of dielectric permeability on temperature and pressure calculated within different models was explained.

3. A method for evaluation of the contribution from dipolar interaction to the equation of state was proposed. Alongside with that, an approach to investigation of the dependence of this contribution on the strength E of the applied electrostatic field with measuring the dielectric permeability was suggested.

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