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Thermophysical and Thermodynamic Properties of Substances in Gaseous Phase Used in Heat-Power Engineering Taking into Account Cluster Structure

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Abstract

The research is devoted to calculated-theoretical and applied analysis of thermo physical and thermodynamic properties of substances in gaseous phase used in heat-power engineering basing on cluster model. It is impossible to make measurements under all conditions that can be in heat-power engineering practice, so the theory is required that is based on reliable model. Such a model is considered to be a molecular-cluster model and computation schemes have been developed within its frameworks. These are schemes for computation of thermodynamic properties of substances in gaseous phase. The research of gases cluster model properties is due to necessity to develop and apply it with the use of experimental data in certain heat and power processes. Cluster model application is developed for thermodynamic potentials and for calculation of gas heat capacity. The areas of new research aims based on cluster model of a substance are connected with analysing structural compounds – equilibrium and "quasi-reactive".
The provided results have been achieved by analytic method of equation system calculation for clusters of any structure. Besides, it is required to test calculation methods where parameters of cluster model of a substance in gaseous state are considered. In this connection, modern computational program is used that is based on calculation of small, medium, and large clusters under certain state parameters.

Keywords: molecule, cluster, gas, heat capacity, heat-power engineering.

1. Introduction

At present the successful development and improvement of technological process in heat and power engineering, like in any other sphere, depends on an adequate calculations and a forecasting based on the appropriate model of the process and the environment. In thermal physics, which is the basis of heat and power engineering processes related with the thermodynamic properties of processes, systems and working substances, the cluster model can be accepted like an appropriate model [1-6]. It is important in the model, that not only molecules but also multi-molecular formations not-altering chemical properties – clusters – are considered as astructural substance units. Clusters are characterized by the number of included molecules: one molecule – monomer, two molecules – dimer, three molecules – trimer etc. [7-12]. At the same time, it is necessary to take into account that intermolecular interaction forces are not so strong to keep molecules for infinitely long time in the cluster, therefore clusters are structural particles of variable composition. Clusters can generate and disintegrate depending on macro parameters such as pressure, temperature, volume.

This has an influence on the general number of structural particles in the system and so, in the cluster model we deal with thermodynamic systems of variable composition and constant configuration. This allows the application of statistical approach to describe such system consisting of molecules, even though the molecules are of the same kind, like a molecular-cluster mixture. Thereby the variability of the molar mass and dependence of all the thermal physics and thermodynamic properties on concentrations of various clusters in the molecular-cluster mixture act as an essential conduct part of such systems. This enables to take into account the demonstration of attractive and repulsive forces in non-perfect gases and to describe adequately real thermal physics and thermodynamic properties of gaseous substances.

2. Material and method

2.1 The set of equations for calculating cluster composition

The set of equations for calculating cluster composition can be represented in the form [1; 7-10]:

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$$C_1^{(c)}\left(1+\sum_{g=2}^{r}\exp\left[-\beta(g-1)\right]\right)-1=0 \quad (1)$$

$$C_1^{(c)}\sum_{g=1}^{r}\left\{g\exp\left[-\beta(g-1)\right]\right\}-\frac{\rho RT}{p\mathrm{M}_1(1-b)}=0 \quad (2)$$

$$C_1^{(c)}\exp\left[-\beta(g-1)\right]-C_g^{(c)}=0 \quad (3)$$

$$g=1\div r,$$

where: $C_g^{(c)}$ is the numerical fraction of g–dimensional clusters (clusters which consist of g molecules), dimensionless,
$C_1^{(c)}$ is the numerical fraction of monomers (clusters with size 1), dimensionless,
β is the normalization factor, dimensionless,
g is the size of cluster (number of molecules in cluster), number
R is the universal gas constant, J/(mole·K),
ρ is gas density, kg/m^3 ,
T is absolute temperature, K,
p is gas pressure, Pa,
M_1 is molar mass of monomers, kg/mole.

The set of equation takes into consideration a proper volume fraction of particles that is expressed in terms of effective collision diameter in the following general rule [8, 10]:

$$b=\frac{2}{3}n^{(n)}\pi\sigma^3 \quad (4)$$

where:
σ is the effective molecules collision diameter, m,
$n^{(n)}$ is concentration, 1/m^3

The compressibility factor (z, dimensionless) of cluster mixture is expressed through the concentration of cluster subcomponents:

$$z=\frac{1}{(1-b)\sum_{g=1}^{r}gC_g^{(c)}} \quad (5)$$

Molar mass of such mixture is determined taking into account concentrations of respective clusters [7; 10]:

$$\langle\mathrm{M}\rangle=\sum_{g=1}^{r}C_g^{(c)}\mathrm{M}_g \quad (6)$$

where $\langle\mathrm{M}\rangle$ is average molar mass of cluster mixture, kg/mole
$\mathrm{M}_g = g\mathrm{M}_1$ – molar mass of g-dimensional clusters, kg/mole.

The equation of state in the cluster model is the equation, which uses a compressibility factor z [7; 10] by way of the deviation from the idealness factor:

$$p=znkT=zp_{id} \quad (7)$$

where: n is concentration, 1/m^3 ,
k is Boltzmann Constant, 1.38×10^{-23} J/K,
p_{id} is perfect gas pressure, Pa

Specific internal energy (u, J/kg) and enthalpy (h, J/kg) can be count in the following way:

$$u=c_vT \quad (8)$$

and enthalpy:

$$h=c_pT \quad (9)$$

where c_v, c_p are specific heats at constant volume and pressure respectively (J/(kg·K)).

From these formulas the conclusion can be drawn that in order to determine values of u and h, first of all, it is a necessary to find heat capacity of gas using the cluster model.

Specific heat c_v at constant volume with regard for the cluster composition is calculated by formula:

$$c_v=\frac{R}{2}\frac{\sum_{g=1}^{r}C_g^{(c)}i_g}{\sum_{g=1}^{r}C_g^{(c)}\mathrm{M}_g} \quad (10)$$

where i_g is number of degrees of freedom of a g - dimensional cluster.

Specific heat c_p at constant pressure with regard for gas clusters:

$$c_p=c_v+\frac{R}{\left(\sum_{g=1}^{r}C_g^{(c)}\mathrm{M}_g\right)} \quad (11)$$

2.2 Calculation work and prognostication

Another characteristic of this cluster model in respect to calculations and forecasting, is the necessity to use effective numerical methods, high-performance computational resources and the development of special algorithms based on formulas of the cluster model. The following methods are used in such cases: the bisection method, the secant method, the iteration method, Newton's method, Ridders' method [10-13]. After comparison of the results, Newton's method was chosen for the realization. On the basis of Newton's method the algorithm for finding concentrations of large-size (up to 100) clusters was developed. The results for the water vapour are shown in the tables below.

Table 1. The concentration of cluster subcomponents of water vapour at T=800K

Pressure, MPa	C_1	C_2	C_3	C_4	C_5
P=4,0	0,96233	0,03625	0,00137	0,00005	-
P=10,0	0,87417	0,11000	0,01384	0,00174	0,00022
P=16,0	0,79993	0,16004	0,03202	0,00641	0,00128

Table 2. The molar mass of water vapour taking into account the cluster composition

Pressure, MPa	Temperature, K	Molar mass of cluster water vapour $\langle M \rangle$, kg/mole	Molar mass of water vapour M_1, kg/mole	$\langle M \rangle / M_1$
4,0	800	0,0189	0,018	1,0536
10,0	800	0,0205	0,018	1,1439
16,0	800	0,0225	0,018	1,2501

Table 3. The values of the compressibility factor for water vapor

Pressure, MPa	Temperature, K	z_{calc}	z_{refer} [14]
4,0	800	0,9722	0,9728
10,0	800	0,9294	0,9300
16,0	800	0,8841	0,8844

Table 4. The value of specific heat of water vapor taking into account the molecular-cluster composition

Pressure, MPa	Temperature, K	$c_{v\ calc}$, kJ/(kg·K)	c_v, kJ/(kg·K) [14]	$c_{p\ calc}$, kJ/(kg·K)	c_p, kJ/(kg·K) [14]
4,0	800	1,314	1,742	1,752	2,283
10,0	800	1,210	1,835	1,614	2,528
16,0	800	1,107	1,940	1,477	2,843

Table 5. The value of the internal energy of water vapor taking into account the molecular-cluster composition

Pressure, MPa	Temperature, K	u_{calc}, kJ/kg
4,0	800	1051,5
10,0	800	968,5
16,0	800	886,3

Table 6. The value of the enthalpy of water vapor taking into account the molecular-cluster composition

Pressure, MPa	Temperature, K	h_{calc}, kJ/kg	h, kJ/kg [14]
4,0	800	1402,1	3506,7
10,0	800	1291,4	3443,2
16,0	800	1181,7	3374,2

3. Results and discussion

As it can be seen from Table 1, when pressure rises, higher order clusters concentration increases – there are more trimers, quadrometres, etc. The data from Table 2 illustrates decline of cluster mixture molar mass compared to the mass of monomers at definite pressure and temperature. Besides as pressure grows, the inclination increases – molar mass of cluster mixture becomes heavier than molar mass of pure material. This indicates the intensification of cluster formation processes in high pressure interval for gases.

The data from Tables 1 and 2 points to difference of real gas characteristics from ideal ones and the cluster model provided above explains this by presence of different size clusters in gas that consists of one substance molecules.

The data from Table 3 demonstrates satisfactory conformance of computations based on the cluster model for compressibility factor in comparison with recognized reference data. This provides grounds for applying cluster model approaches for description and computation of thermophysical and thermodynamical properties of a substance in gaseous phase.

The data from tables 4, 5 and 6 indicate the necessity to research and to describe mechanisms of generation and disintegration of clusters, i.e. the necessity to research evolution of cluster composition when macro-parameters are changed.

Comparing the calculated values of specific heats (Table 4), the internal energy (Table 5) and the enthalpy (Table 6) with reference data from [14] it is evident they differ, which is caused by the following reasons: heat capacity in the formulas (8), (9) determining by the formulas (10), (11) taking into account the cluster composition is so-called „equilibrium" heat capacity, which calculated internal energy and enthalpy (they can be also called „equilibrium" components) conform to (8), (9). The difference between heat values, internal energy values and enthalpy values calculated by formulas of gas cluster model and values from reference data may enable to reveal the contribution of the quasi-reactive component of these thermodynamic characteristics. It is related to generation and disintegration of clusters' energy that is the evolution of the cluster composition. This is a development perspective for further researches and it can be concluded that the large difference in comparing values between tables 4-6 indicates a more intensive process of the cluster generation and the disintegration of large-size clusters [15]. In the presence of small-size clusters the difference remains approximately the same becomes insignificant. Methods of determining and measuring the values presented in reference books [14] and in works of modern researchers [16-20] are also important.

4. Conclusions

The foregoing gives rise to the following conclusions. The processes of clusters generation and disintegration go on without change in chemical properties of a substance. This requires search for optimal and adequate method for computation of real gas properties that are used in technologies and heat power engineering. Cluster model of a substance enables the development of valid methods, schemes and algorithms for computation of thermophysical and thermodynamical properties of real gases (formulas (1) – (9)), specific heat c_v at constant volume and specific heat c_p at constant pressure with regard for gas clusters are presented (formulas (10) – (11)).

The cluster model is productive in respect of non-perfect gas properties description: it enables to define such parameters and properties of gas as molar mass, pressure, the compressibility factor, internal energy, enthalpy, heat capacity etc. (that is possible with the up-to-date computational power and software) and allows to research and predict various effects in gas systems on the basis of macro parameter gradients, including at nano-level, and also research the issues of the phase transformation.

Cluster model of a substance is an adequate in the aspect of studying mechanisms of intermolecular interaction and behavior of gases in any intervals of macro-parameters.

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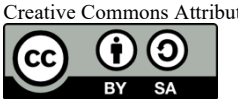

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