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THE CALCULATION OF THE COMPRESSIBILITY, THERMAL EXPANSION COEFFICIENT AND THE DETERMINATION THE EVAPORATION CURVE FOR SOME IMPORTANT REFRIGERANTS

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ABSTRACT:

The paper presents the mathematical model of computing the compressibility, thermal expansion coefficient, evaporation curve, velocity of sound and other thermophysical properties by means of statistical thermodynamics for some important refrigerants. The paper features all important forms of motion of molecules and atoms [translation, rotation, internal rotation, vibration], the influence of excitation of electrons and nuclei into higher energy levels as well as the effect of the intermolecular potential energy. Utilized as the intermolecular potential was the Lennard-Jones potential. To compute the thermodynamic values of the state in the realm of real fluids we used grand canonical distribution. For the realm of real fluids Johnson-Zollweg-Gubbins model based on the modified BWR and great number of Monte Carlo simulations was applied. For the calculation in two-phase region we applied the method of equilibrium conditions between two phases. The mathematical model enables the calculation in both sub- and supercritical region. By means of the mathematical model described above we were able to compute thermodynamical properties in one and two-phase region and to draw phase diagrams for some technically significant substances. The results of the analysis are compared with data on experiments showing a relatively good agreement.

INTRODUCTION

In refrigeration processes in liquid-gas region are of vital importance. In order to design devices for this field of activity, it is necessary to be familiar with the thermodynamic properties of state in a one-phase and two-phase environment. In most cases the thermodynamic tables and diagrams and different empirical functions obtained from measurements are used.

Calculation of thermodynamic properties of state is possible by the classical or statistical thermodynamics. Classical thermodynamics has no insight into the microstructure, but it allows the calculation of thermodynamic function of state with assistance of macroscopic observation of phenomenon. Unlike the classical thermodynamics, however, the statistical thermodynamics does enable the computation of the thermodynamic functions of the state by studying molecular structure of the matter.

COMPUTATION OF THERMODYNAMIC PROPERTIES OF STATE

To calculate thermodynamic functions of state we applied the canonical partition (Lucas, 1992). Utilizing the semi-classical formulation for the purpose of the canonical ensemble for the N indistinguishable molecules can be expressed as follows (Lucas, 1992):

$$Z = \frac{1}{N! h^{Nf}} \int \dots \int \exp\left(-\frac{H}{kT}\right) \cdot d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N d\vec{p}_1 d\vec{p}_2 \dots d\vec{p}_N \quad (1)$$

where f stands for the number of degrees of freedom of individual molecule, H designates the Hamiltonian molecule system. By means of the canonical ensemble for the system of N molecules can be like this:

$$Z = Z_0 Z_{\text{trans}} Z_{\text{vib}} Z_{\text{rot}} Z_{\text{ir}} Z_{\text{el}} Z_{\text{nuc}} Z_{\text{conf}} \quad (2)$$

Thus the partition function Z is a product of terms of the ground state (0), the translation (trans), the vibration (vib), the rotation (rot), the internal rotation (ir), the influence of electrons excitation (el), the influence of nuclei excitation (nuc) and the influence of the potential intermolecular energy (conf). Utilizing the canonical theory for computing the thermodynamic functions of the state can be put as follows (Smirnova, 1983; Gray and Gubbins, 1984)

$$\begin{aligned}
 \text{Pressure: } p &= kT \left(\frac{\partial \ln Z}{\partial V} \right)_V & \text{Internal energy: } U &= kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \\
 \text{Free energy: } A &= -kT \cdot \ln Z & \text{Entropy: } S &= k \left[\ln Z + T \left(\frac{\partial \ln Z}{\partial T} \right)_V \right] \\
 \text{Free enthalpy: } G &= -kT \left[\ln Z - V \left(\frac{\partial \ln Z}{\partial T} \right)_V \right], & \text{Enthalpy: } H &= kT \left[T \left(\frac{\partial \ln Z}{\partial T} \right)_V + V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right].
 \end{aligned} \tag{3}$$

The computation of the individual terms of the partition function and their derivatives with the exception of the configuration integral is dealt with in the works of Lucas, 1992; Gray and Gubbins, 1984.

The various derivatives and expressions of the fundamental equations (3) have an important physical significance. These paper presents expressions which are very important for planning the refrigeration processes.

$$\begin{aligned}
 \text{The coefficient of thermal expansion:} & \quad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \\
 \text{The isothermal compressibility:} & \quad \chi = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \\
 \text{The heat capacity at constant volume per mole:} & \quad C_v = \left(\frac{\partial U}{\partial T} \right)_V \\
 \text{The heat capacity at constant pressure per mole:} & \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p
 \end{aligned} \tag{4}$$

The velocity of the mechanical longitudinal waves propagation between 16 s^{-1} and 20000 s^{-1} we call the velocity of sound (Gommon 1976). The calculation the speed of sound is very important in measurement (acoustic resonance level gauge).

In real fluids we can calculate the isentropic speed of sound c_0 (Bird 1954, Younglove 1993):

$$c_0 = \sqrt{-v^2 \left(\frac{\partial p}{\partial v} \right)_s} = \sqrt{-v^2 \frac{\frac{c_p}{T} \left(\frac{\partial T}{\partial v} \right)_p}{\left(\frac{\partial v}{\partial T} \right)_p - \frac{c_p}{T} \left(\frac{\partial T}{\partial p} \right)_v}} \tag{5}$$

In equation (5) is v specific volume and c_p specific heat capacity.

CONFIGURATIONAL INTEGRAL

In the realm of real fluid Johnson-Zollweg-Gubbins (1993) model based on molecular dynamic and Monte Carlo simulations with help of Lennard-Jones intermolecular potential and modified Benedict-Web-Rubin equation of state (MBWR) was used. On these basis we can express configurational free energy A_{conf} :

$$A_{\text{conf}}^* = \sum_{i=1}^8 \frac{a_i \rho^{*i}}{i} + \sum_{i=1}^6 b_i G_i, \quad (5)$$

$$\rho^* = \frac{N\sigma^3}{V}, \quad T^* = \frac{kT}{\varepsilon}, \quad A_{\text{conf}}^* = \frac{A_{\text{conf}}}{NE} \quad (6)$$

$$F = \exp(-\gamma \rho^{*2}), \quad \gamma=3$$

Table 1: Coefficients for MBWR equation of state

i	a_i	b_i	G_i
1	$x_1 T^* + x_2 \sqrt{T^*} + x_3 + x_4 / T^* + x_5 / T^{*2}$	$x_{20} / T^{*2} + x_{21} / T^{*3}$	$(1 - F)/(2\gamma)$
2	$x_6 T^* + x_7 + x_8 / T^* + x_9 / T^{*2}$	$x_{22} / T^{*2} + x_{23} / T^{*4}$	$-(F\rho^{*2} - 2G_1)/(2\gamma)$
3	$x_{10} T^* + x_{11} + x_{12} / T^*$	$x_{24} / T^{*2} + x_{25} / T^{*3}$	$-(F\rho^{*4} - 4G_2)/(2\gamma)$
4	x_{13}	$x_{26} / T^{*2} + x_{27} / T^{*4}$	$-(F\rho^{*6} - 6G_3)/(2\gamma)$
5	$x_{14} T^* + x_{15} / T^{*2}$	$x_{28} / T^{*2} + x_{29} / T^{*3}$	$-(F\rho^{*8} - 8G_4)/(2\gamma)$
6	x_{16} / T^*	$x_{30} / T^{*2} + x_{31} / T^{*3} + x_{32} / T^{*4}$	$-(F\rho^{*10} - 10G_5)/(2\gamma)$
7	$x_{17} / T^* + x_{18} / T^{*2}$		
8	x_{19} / T^{*2}		

The equation (5) accurately correlates thermophysical properties from $0.7 \leq T^* \leq 6$. In equation (5) are x_j 's the adjustable parameters in the equation of state. The equation (5) is especially accurate for vapour-liquid equilibrium conditions.

DETERMINING THE EQUILIBRIUM STATES BETWEEN VAPOUR AND LIQUID

Determining the equilibrium states between the liquid and the gaseous phases conditions for equilibrium are applied:

$$T' = T'', \quad p' = p'', \quad \mu' = \mu'', \quad (7)$$

where ' in equation (7) means the liquid phase, '' means the gaseous phase, μ constitutes the chemical potential.

Due to complexity of the equations in the presented mathematical model the states on the coexistence curve are obtained on the numerical basis.

By applying these states, thermodynamic properties in the two phase environment can be calculated.

RESULTS AND COMPARISSON WITH EXPERIMENTAL DATA

1-T=166 K	2-T=188 K	3-T=210 K
4-T=222 K	5-T=255 K	6-T=282 K

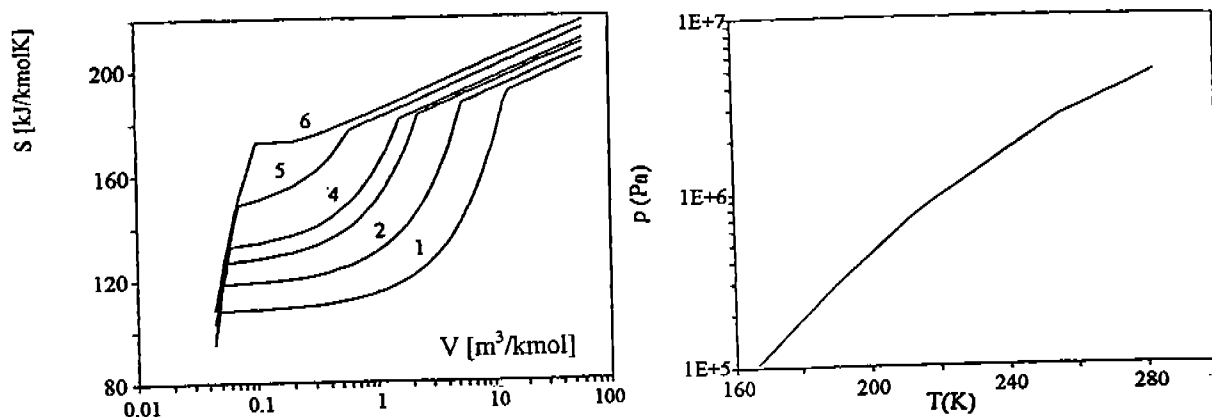


Figure 1: Entropy and vapour pressure in one- and two- phase region for C_2H_4 (R-1150)

Table 2: The comparisson between the analytical calculation (Simul) and the experimental data (Exp) for argon (R-740) in the region of compressed liquid

T K	V m ³ / kmol	P MPa		C _v kJ/kmolK		C _p kJ/kmolK		χ Gpa ⁻¹		C ₀ m/s	
		Simul.	Exp.	Simul.	Exp.	Simul.	Exp.	Simul.	Exp.	Simul.	Exp.
110	.0317	4.65	4.5	17.7	18.9	43.3	45.6	4.09	3.42	678	701
200	.0329	110	100	17.1	17.8	32.1	34.5	2.39		804	851
300	.1187	22	20	13.3	13.8	28.0	30.5	40.40	42.96	386	371
300	.0521	63	60	14.3	14.9	29.1	32.4	7.99		574	570
300	.0412	110	100	15.1	15.7	29.4	31.0	3.8	3.72	716	731
400	.0507	106	100	14.1	14.6	26.3	26.8	4.9		685	689
500	.0602	105	100	13.6	14.1	24.9	26.4	5.9		685	683
600	.0702	110	100	13.3	13.7	23.4	25.0	5.4		755	731

Table 3: The comparisson between the analytical calculation (Simul) and the experimental data (Exp) for carbon dioxide (R-744) in the region of boiling liquid

T K	V m ³ / kmol	p bar		C _p kJ/kmolK		β 1/K	
		Simul.	Exp.	Simul.	Exp.	Simul.	Exp.
253	.04253	1.62	1.96	90.2	94.7	0.0037	
263	.04465	2.82	2.64	94.4	98.8	0.0052	
273	.04753	3.33	3.48	105.6	106.0	0.0072	0.0080
283	.05102	4.26	4.49	118.2	126.8	0.0114	
293	.05683	5.41	5.72	213.2	216.2	0.0159	0.0014
298	.06186	6.52	6.43	407.5	445.8		0.0017

Table 4: The comparison between the analytical calculation (Simul) and the experimental data (Exp.) for carbon dioxide (R-744) in the region of saturated vapour

T K	V m ³ /kmol	P bar		c ₀ m/s	
		Simul.	Exp.	Simul.	Exp.
223	2.432	7.11	6.83	226.7	223.6
233	1.667	10.58	8.9	227.5	224.2
243	1.144	15.52	14.3	226.9	222.9
253	0.843	21.10	19.7	223.5	220.8
263	0.613	27.82	26.5	219.3	217.5
273	0.448	36.37	34.8	214.4	212.7
283	0.325	47.20	44.9	209.9	206.3
293	0.228	61.7	57.3	203.7	197.9
301	0.155	76.5	73.7	194.1	189.8

Table 5: The comparison between the analytical calculation (Simul.) and the experimental data (Exp) for difluordichlormethane (R-12) in the region of superheated vapour

		10 bar			20 bar		
T K		V m ³ /kmol	H kJ/kmol	S kJ/kmolK	V m ³ /kmol	H kJ/kmol	S kJ/kmolK
373	Simul.	2.81	29120	97.1	1.25	28440	91.0
	Exp	2.79	29936	97.9	1.21	28646	89.6
423	Simul.	3.30	36900	106.1	1.55	35380	105.4
	Exp	3.29	34637	109.1	1.53	33358	101.8
473	Simul.				1.82	40840	114.1
	Exp.				1.79	38274	104.5

Figure 1 features the graphic course of thermodynamic functions of the state computed by means of the mathematical model. The values presented the liquid, gas and two-phase regions. The results presented feature ethylene (C₂H₄).

The constants necessary for the computation like the characteristic rotation-, vibration-, electronic etc. temperatures are obtained by means of experimental data (Herzberg, 1966; Herzberg, 1984; Bellamy). The inertia moments are obtained analytically applying the know-how of atomic structure of the molecule. Constants for Lennard-Jones potential are obtained from literature of Gray 1984, Bird 1954 and Lucas 1992.

Similarly as with ethylene (R-1150), the analytical calculation was also carried out for argon (R-740), difluordichlormethane (R-12), and carbon dioxide (R-744). The comparison of our analytical (Simul) with experimental results (Exp) by Maxwell 1955, Edmister 1964, Ecker & Drake 1959 and Petrak 1993, 1980, Ashrae Refrigerant Tables and Chart, 1985; Ermakova et al., Younglove 1995, are presented in the tables 2,3,4,5.

Table 2 shows the comparison between the analytical calculation and the experimental data for argon (R-740) in the region of liquid. Tables 3 and 4 show the deviation of the results for carbon dioxide between the analytical computation with help of statistical thermodynamics and experimental data. Table 5 shows the deviation of the results for difluordichlormethane (R-12) for the real gas region between the analytical computation and the experimental values.

The results show relatively good harmony. In the region of real gases (Tables 4,5) the results are an equally good match. Somewhat larger deviations can however be found in the region of real liquid (Table 2,3) due to the large influence of the attraction forces, whereas the Lennard-Jones potential is a crude simplification

NOMENCLATURE

A	free energy	S	entropy
c_0	velocity of sound	T	temperature
C_v	heat capacity at constant volume per mole	U	internal energy
c_p	specific heat capacity at constant pressure	v	specific volume
C_p	heat capacity at constant pressure per mole	V	volume
E	potential energy	Z	partition function
G	free enthalpy	β	coefficient of thermal expansion
H	enthalpy, hamiltonian	μ	chemical potential
k	Boltzmann constant	χ	isothermal compressibility
N	number of molecules in system	ρ	density
p	pressure, momentum		

Superscripts and subscripts

0	ground state	pot	potential energy
conf	configuration	rot	rotation
el	influence of electron excitation	trans	translation
ir	internal rotation	vib	vibration
nuc	influence of nuclear excitation		

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