Asian Journal of Chemistry Vol. 22, No. 2 (2010), 1158-1162

Simple Determination of Enthalpy and Entropy of Refrigerant Fluids

ROZITA NEJABAT
Islamic Azad University, Neyriz Center, Neyriz, 2319 Neyriz, Iran
E-mail: nejabat_ro@yahoo.com

The present work employs a simplified procedure for calculation of parameters in Tao-Mason (TM) equation of state to calculate thermodynamic properties of refrigerant fluids. The calculations cover the ranges from the dilute vapour or gas to highly compressed liquid and supercritical region. The thermodynamic properties are the vapour and liquid densities, the enthalpy, the entropy, *etc*. The theoretical equation of state (EOS) is that of Tao-Mason which is based on statistical mechanical perturbation theory. The first parameter which plays an important role in the EOS is the second virial coefficient. In the present work this parameter is calculated from a two-parameter corresponding states correlation along with two constants *i.e.*, enthalpy of vaporization and molar density both at the normal boiling temperature. Two remained parameters in Tao-Mason EOS (*i.e.* α, λ and b) are obtained from simple equation. The novelty of the present work is that we use two scaling constants including enthalpy of vaporization and molar density both at the normal boiling temperature instead of using five scaling constants including critical temperature and pressure, Boyle temperature and pressure and acentric factor in calculating three parameters temperature dependent second virial coefficient, α and b. This EOS is applied to 12 ozone-friendly refrigerants. In general, the results are in very good agreement with experimental data.

Key Words: Enthalpy, Equation of state, Entropy, Determination.

INTRODUCTION

Equations of state (EOS) are important tool in chemical engineering designs and assumed an expanding role in the study of the phase equilibria of fluids and fluid mixtures. However, most of them suffer from the fact that they fail to represent properties accurately in a vast range of temperatures and pressures.

The most suitable equation of state for practical purposes is semi-theoretical equation of state in which theoretically based functional forms of the equation of state is used and treat some of its parameters as quantities adjustable to experiment (Table-1). This procedure reduces considerably the amount of needed experimental data, removes the direct dependence of the equation of state on the chosen intermolecular potential model and guarantees accuracy while maintaining simultaneously a relative simplicity and generality. The present work is concerned with evaluating statistical mechanical based equations of state Tao-Mason (TM) containing some adjustable parameters.

TABLE-1
INPUT PARAMETERS FOR THE 12 TEST SYSTEMS

Fluid	T_c (K)	T_{nb} (K)	ΔH_{Vap} (KJ/mol)	ρ_{nb} (mol/L)
R14: Tetrafluoro methane	227.510	145.100	1853.7	12.3374
R23: Trifluoro methane	299.293	191.132	1924.2	13.2978
R32: Difluoro methane	351.255	221.499	2070.3	23.3454
R41: Fluoro methane	317.280	195.027	2001.5	13.4922
R125: Pentafluoro ethane	339.173	225.060	1982.0	12.3562
R134a: 1,1,1,2-Tetrafluoro ethane	374.210	247.076	2276.3	13.5299
R143: 1,1,1-Trifluoro ethane	345.857	225.909	1937.0	19.4635
R152: 1,1-Difluoro ethane	386.411	249.127	2284.1	15.3220
R218: Octafluoro propane	345.020	236.360	2396.5	13.1731
R227ea: 1,1,1,2,3,3,3-Heptafluoro propane	375.950	256.730	2252.3	12.6906
R236ea: 1,1,1,2,3,3-Hexafluoro propane	412.440	279.340	2551.6	13.8357
R245ca: 1,1,2,2,3-Pentafluoro propane	447.570	298.280	2432.9	13.1557

Tao-Mason (TM) equation of state

The final form of the TM EOS is given in eqn. 1:

$$\frac{P}{\rho kT}=1+(B_2(T)-\overline{\alpha}(T))\rho+\frac{\overline{\alpha}(T)\rho}{1-\rho b(T)\lambda}+A_1(\overline{\alpha}(T)-B_2(T))b(T)\rho^2\frac{(e^{kTc/T}-A_2)}{1+1.8[\rho b(T)]^4}$$

where $A_1=0.143$; $A_2=1.64+2.65[e^{(\kappa-1.093)}-1]$ (1)

$$\kappa=1.093+0.26[(\omega+0.002)^{1/2}+4.50(\omega+0.002)] \quad (2)$$

In eqns. 1 and 2 ω is the Pitzer acentric factor.

The present study is concerned with calculating all thermodynamic properties including those not reported by Tao and Mason using TM EOS along the saturation curve and single-phase region. The comparison is made with experiment for 12 selected fluids having a variety of molecular structure and polarity including R14, R23, R32, R41, R125, R134a, R143a, R152, R218 R227ea, R236ea, R245ca.

Parameters estimation

The second virial coefficient has a main role in three equations of state considered here[1-5]. In the present study, we have used correlation equations for second virial coefficient[6]:

$$B(T)\rho_{nb}=0.1-0.054\left(\frac{\Delta H_{vap}}{RT}\right)^2-0.00028\left(\frac{\Delta H_{vap}}{RT}\right)^4$$

$$\text{where } \Delta H_{nb}=1.093RT_b\frac{\ln P_c-1.013}{0.93-T_b/T_c}$$

Other parameters in Tao-Mason equations of state (α (T) and b (T)) can be formulated in terms of enthalpy of vaporization and density in normal boiling and can be calculated with sufficient accuracy from the following formulas based on a (12, 6) potential:

$$\alpha\rho_{nb} = \frac{1}{a_1 + b_1\left(\frac{T}{\left(\Delta H_{vap}/R\right)}\right)^{c_1-1}} \qquad b\rho_{nb} = \frac{1}{a_2 + b_2\left(\frac{T}{\left(\Delta H_{vap}/R\right)}\right)^{c_2-1}}$$

$$a_1 = 0.2925 \qquad a_2 = 0.2792$$

$$b_1 = 0.2875 \qquad b_2 = 0.4155$$

$$c_1 = 1.3385 \qquad c_2 = 1.3295$$

In addition, for simplicity; κ. The parameter λ is calculated in high density from simple equation:

$$\lambda = 1/\left(a + bT^{c}\right)$$

a,b,c for every fluids were shown in Table-2.

TABLE-2
INPUT PARAMETERS FOR CALCULATION OF λ

Fluid	a	b	c
R14: Tetrafluoro methane	3.051796	- 0.035150	0.65000
R23: Trifluoro methane	3.045710	-0.067190	0.43990
R32: Difluoro methane	4.435981	-0.111590	0.55000
R41: Fluoro methane	3.561277	-0.087220	0.67000
R125: Pentafluoro ethane	2.908310	-0.047610	0.59000
R134a: 1,1,1,2-Tetrafluoro ethane	4.998500	-0.061092	0.64980
R143: 1,1,1-Trifluoro ethane	3.051796	-0.043956	0.65000
R152: 1,1-Difluoro ethane	2.901071	-0.035140	0.65000
R218: Octafluoro propane	3.043980	-0.021300	0.43220
R227ea: 1,1,1,2,3,3,3-Heptafluoro propane	3.855530	-0.312638	0.34998
R236ea: 1,1,1,2,3,3-Hexafluoro propane	4.235681	-0.131590	0.55000
R245ca: 1,1,2,2,3-Pentafluoro propane	3.051796	-0.035146	0.65030

RESULTS AND DISCUSSION

The aim of the present study is to the examine the capability of molecular-based equations of state including Tao-Mason (TM) in predicting thermodynamic surfaces of 12 selected fluids in a broad range of temperatures and pressures covering single phase (liquid or gas) and two phase (liquid-vapour) regions.

Thermodynamic properties from equation of state

P-V Isotherms: The calculation of the density or the molar volume from the given pressure and temperature is one of the most frequently performed operations in phase equilibrium calculations[8,9]. The ability of the present equations of state to predict PVT data is presented. Table-3 lists the absolute average data of the calculated densities of, respectively, the vapour (saturated and compressed), liquid (saturated and compressed) and supercritical regions for 12 chosen systems using Tao-Mason equation of state. In the temperature range 100 K up to 1100 K and pressures ranging from zero to 3200 bar the deviations of the calculated vapour, liquid and supercritical densities from the literature data[6] are at most 1, 3 and 4 %, respectively.

Enthalpy: The residual enthalpy can be calculated from:

$$H^R = -RT^2 \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} + RT(Z-1) \qquad H^{ig}(T) = H^{ig}(T_0) + \int_{T_0}^{T} C_P^{ig}\, dT$$

where C_P^{ig} stands for ideal gas heat capacity at constant pressure and subscript zero refers to reference state.

The absolute average data of the enthalpy and the internal energy of all considered systems have been given in Table-3. As it is obvious, the maximum observed deviation in the enthalpy from the literature data[6] at vapour, liquid and supercritical regions are less than 1, 3.6 and 3 %, respectively.

TABLE-3
MEAN ABSOLUTE AVERAGE DEVIATION (AAD) BETWEEN CALCULATED AND LITERATURE DATA FOR THE VAPOUR, LIQUID AND SUPERCRITICAL REGIONS USING TM EQUATION OF STATE AND THE RANGES OF TEMPERATURES AND PRESSURE COVERED

Fluid	Number of points	Range of temp. (K)	Range of pressure (bar)	Density (%)	Enthalpy (%)	Entropy (%)
R14	20	100-600	0-500	1.39	1.49	2.14
R23	10	200-500	0-500	1.79	1.66	1.19
R32	20	200-500	0-200	2.17	1.66	1.97
R41	20	200-500	0-500	1.16	1.47	1.43
R125	20	150-500	0-400	1.94	1.81	2.01
R134a	25	150-450	0-500	0.60	1.38	1.40
R143	11	170-650	0-100	1.60	1.43	1.54
R152	18	100-500	0-600	2.14	1.48	1.49
R218	17	150-450	0-200	1.56	1.65	1.60
R227ea	20	200-500	0-120	1.19	2.07	1.57
R236ea	11	100-500	0-100	1.01	0.97	0.93
R245ca	15	200-600	0-200	1.27	1.19	1.12

Entropy: The residual entropy is obtained through the following equation and an equation of state:

$$S^R = -R\int_0^{\rho}\left\{T\left(\frac{\partial Z}{\partial T}\right)_{\rho} + Z - 1\right\}\frac{d\rho}{\rho}, \quad S = S_0 + \int_{T_0}^{T} C_P^{ig} dT/T - R\ln(P/P_0) + S^R$$

where P_0 is the reference pressure.

Tables-3 represent absolute average data of the entropy for all considered fluids over the temperature range from 100 to 1100 K and pressure range from zero to 3200 bar using TM EOS. In vapour phase deviations are to within 2 %, in liquid phase to within 10 % and in supercritical region within 3 %. The exception in supercritical region is propane in which deviation in entropy lies within 12 %. In the present work, we have taken saturated liquid at normal boiling as reference state for each fluid. In this state the enthalpy and entropy are put equal to zero. In order to calculate enthalpy and entropy of fluids at any temperature and pressure one must employ a method to estimate latent heat of vaporization at normal boiling point.

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(*Received*: 19 January 2009; *Accepted*: 16 October 2009) AJC-7964