



Prediction of isoenthalps, Joule–Thomson Coefficients and Joule–Thomson inversion curves of refrigerants by molecular simulation



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ABSTRACT

We describe molecular simulation methodology based on the recently proposed NPH MC algorithm to calculate isoenthalps (HC), Joule–Thomson coefficients, μ , (JTC) and Joule–Thomson inversion curves (JTIC), and apply it to the representative ethane-based alternative refrigerants R125, R134a and R152a over a wide range of thermodynamic conditions. Although JTIC have been calculated previously by molecular simulation, HC and JTC have rarely been studied by this approach, due to the requirement to incorporate ideal gas specific heat data, $c_p^{IG}(T)$. Traditionally, calculations of HC, JTC and JTIC have been implemented using multi-parameter empirical equations fitted to experimental data. In contrast, molecular simulation methodology requires a force field (FF) describing the molecular interactions, which contains a relatively small number of adjustable parameters. Our study uses FFs from the literature, and $c_p^{IG}(T)$ from a comprehensive compilation based solely on quantum and statistical mechanical calculations. Our simulation results are compared with pseudo-experimental results obtained from the REFPROP software package. We generated results in both single- and two-phase regions, and for thermodynamic conditions outside the range of REFPROP's capabilities. Where both sets of results are available, the simulation results are in good agreement with those of REFPROP. Our studies also suggest that more accurate quantum and statistical mechanical calculations of the refrigerant $c_p^{IG}(T)$, which are feasible with current computer technology, would improve the reliability of both empirically based and molecular simulation calculations of HC and JTC for existing refrigerants, and would also reduce the experimental data requirement for newly proposed candidate refrigerants. Finally, we also compare our results with those from new calculations using two representative cubic equations of state (EOS); they provide reasonable but not quantitatively accurate results, particularly for μ and the JTIC.

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1. Introduction

An important element of the traditional approach to designing refrigeration systems incorporating proposed new refrigerants is the development of empirical equations based on macroscopic

thermodynamic principles for the properties of the working fluid. For sufficient accuracy, these equations typically entail multiple parameters, determined by fitting to a large experimental data set (e.g., [1–4]). Such data is typically costly to obtain, particularly in the case of mixtures; in the latter case, the accuracy of the equations also tends to deteriorate. Molecular simulation is an alternative approach to predicting the thermodynamic and transport properties of fluid systems of industrial interest, and is becoming increasingly used in many fields (e.g., [5–9]). This approach can either be employed directly to simulate processes of interest when empirical equations are unavailable or of insufficient

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Nomenclature

2CLJ	2-centre LJ homogeneous diatomic model
2CLJD	2-centre LJ homogeneous diatomic dipolar model
$B_i(T)$	i th virial coefficient, function of T
c_p	molar isobaric heat capacity
D	dipole moment
\mathbf{D}_i	dipole vector of molecule i
EOS	equation of state
h	molar enthalpy
h^r	molar residual enthalpy
H	total system enthalpy
H^*	specified value of H in NPH MC algorithm
HC	curve of constant enthalpy (isoenthalp)
$\Delta H_f(298.15)$	standard enthalpy of formation at 298.15 K
IG	ideal gas
JT	Joule–Thomson
JTCC	Joule–Thomson coefficient curve
JTIC	Joule–Thomson inversion curve
k	Boltzmann's constant
L	distance between LJ centres
LJ	Lennard–Jones
MC	Monte Carlo
N	number of particles
NPH MC	Monte Carlo algorithm for fixed N , specified P and H
P	pressure
$P_{k\ell}^\beta$	transition probability for change $\Delta\beta$ from state k to state ℓ
PRMC	Peng–Robinson–Mathias–Copeman equation of state
\mathbf{r}_{12}	centre-to-centre vector of distance between molecules 1 and 2
r_{ab}	distance between LJ sites a and b on molecules 1 and 2
R	universal gas constant
RKMC	Redlich–Kwong–Mathias–Copeman equation of state
T	absolute temperature
T_{ref}	reference temperature
u	intermolecular potential
\mathcal{U}	configurational energy
v	molar volume
V	total volume
VLE	vapour–liquid equilibrium
x	quality of a vapour–liquid mixture
<i>Greek letters</i>	
β	$1/kT$
ϵ	LJ energy parameter
ϵ_0	permittivity of free space
ρ	molar density
μ	Joule–Thomson coefficient
σ	LJ size parameter
ω_i	orientation vector of molecule i

accuracy, or it can provide pseudo-experimental data which may then be fitted to such equations for subsequent use.

In addition to the ability to calculate nonideal volumetric properties, in order to calculate total fluid thermal properties, molecular simulation methodology requires the availability of the coupled ideal gas property for the fluid. Although technology for the first-principles prediction of ideal gas thermal properties is now at an advanced stage of development, methods for the calculation of the

nonideal property contributions is still evolving. For these, molecular simulations require as basic input a mathematical model of the intermolecular forces of the constituent molecules, referred to as a “force field”. Such models incorporate a relatively small number of parameters, and they can be systematically refined by incorporating increasingly accurate molecular-level understanding. Once developed, the force field may be used by means of appropriate molecular simulation algorithms to predict a wide range of both thermodynamic and transport properties (e.g., [10]), and to gain molecular-level insight into phenomena involving these properties. These are significant advantages in principle over the empirical equation approach, which typically requires different multi-parameter equations for different properties, requiring different sets of experimental data to determine the relevant parameters. In addition, molecular simulation methodology is intrinsically capable of making predictions outside the range of thermodynamic conditions over which the empirical equation parameters have been determined. This technology can thus in principle provide a cost-efficient screening method for the development of new compounds for specific purposes.

The main impediments to the widespread use of molecular simulation methodology in the refrigeration industry are the lack of first-principles methods to calculate force fields and of efficient algorithms to accurately calculate certain refrigerant properties. Progress in first-principles force field development for complex nonideal fluids such as those that arise in refrigeration is still in its infancy, and most available refrigerant force fields in the literature have been determined by fitting calculated results to experimental vapour–liquid equilibrium (VLE) data; this is still a significant reduction in the amount of experimental data needed in comparison with traditional multi-parameter empirical equation approaches. However, it has recently been shown that it is possible to develop refrigerant force fields by employing extensions of existing force fields of similar molecules, with no requirement for additional experimental data [10].

In addition to force fields, the employment of molecular simulation methodology requires the availability of algorithms to accurately calculate properties and to simulate relevant processes. Among the most important refrigerant properties are isoenthalpic curves (HC), Joule–Thomson coefficient curves (JTCC), and Joule–Thomson inversion curves (JTIC). Molecular simulation algorithms for volumetric property prediction are readily available, and these have been used primarily to study the JTIC, which depends only on such properties [11–19]. However, methods for calculating HC and JTCC are much less well-developed, particularly for realistic nonideal fluid systems. Escobedo and Chen [20] proposed calculating HC in single-phase fluid regions by integration of the Joule–Thomson coefficient. These workers, in addition to Lagache et al. [21] and Lustig [22], also proposed identical methods for the calculation of the Joule–Thomson coefficient in such regions by means of statistical mechanical fluctuation formulae.

The purpose of this paper is to demonstrate the use of molecular simulation methodology to accurately calculate HC, JTCC, and JTIC for three representative ethane-based alternative refrigerants over a range of thermodynamic conditions. We employ the NPH MC molecular simulation algorithm [23,24], which is a Monte Carlo (MC) method for the direct calculation of system properties for a fixed number of molecules, N , and specified values of total enthalpy, H , and pressure, P . It can thus directly calculate HC, from which JTCC and JTIC may be obtained numerically. The method is more computationally efficient and accurate than other approaches, and can additionally treat multiphase regions. The algorithm also permits the direct calculation of the final temperature of a fluid resulting from a finite pressure change for a specified enthalpy change, a problem of general interest (e.g., [25]), and of a pure-fluid vapour–liquid fluid equilibrium temperature for

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