



## A model for evaluating physico-chemical substance properties required by consequence analysis models

Juha Nikmo\*, Jaakko Kukkonen, Kari Riikonen

*Finnish Meteorological Institute, Air Quality Research, Sahaajankatu 20 E, FIN 00810 Helsinki, Finland*

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### Abstract

Modeling systems for analyzing the consequences of chemical emergencies require as input values a number of physico-chemical substance properties, commonly as a function of temperature at atmospheric pressure. This paper presents a mathematical model “CHEMIC”, which can be used for evaluating such substance properties, assuming that six basic constant quantities are available (molecular weight, freezing or melting point, normal boiling point, critical temperature, critical pressure and critical volume). The model has been designed to yield reasonably accurate numerical predictions, while at the same time keeping the amount of input data to a minimum. The model is based on molecular theory or thermodynamics, together with empirical corrections. Mostly, model equations are based on the so-called law of corresponding states. The model evaluates substance properties as a function of temperature at atmospheric pressure. These include seven properties commonly required by consequence analysis and heavy gas dispersion modeling systems: vapor pressure, vapor and liquid densities, heat of vaporization, vapor and liquid viscosities and binary diffusion coefficient. The model predictions for vapor pressure, vapor and liquid densities and heat of vaporization have been evaluated by using the Clausius–Clapeyron equation. We have also compared the predictions of the CHEMIC model with those of the DATABANK database (developed by the AEA Technology, UK), which includes detailed semi-empirical correlations. The computer program CHEMIC could be easily introduced into consequence analysis modeling systems in order to extend their performance to address a wider selection of substances. © 2002 Elsevier Science B.V. All rights reserved.

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\* Corresponding author. Tel.: +358-9-1929-5454; fax: +358-9-1929-5403.  
*E-mail address:* juha.nikmo@fmi.fi (J. Nikmo).

**Nomenclature**

$C$	concentration ( $\text{kg m}^{-3}$ )
$D$	binary diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$H_v$	heat of vaporization ( $\text{J kg}^{-1}$ )
$k$	$1.3805 \times 10^{-23} \text{ J K}^{-1}$ , Boltzmann's constant
$m_w$	molecular weight ( $\text{kg kmol}^{-1}$ )
$P$	pressure (Pa)
$Q$	mass flux ( $\text{kg s}^{-1}$ )
$R$	$8314.51 \text{ J (kmol K)}^{-1}$ , universal gas constant
$T$	temperature (K)
$V$	molar volume ( $\text{cm}^3 \text{ mol}^{-1}$ )

*Greek symbols*

$\delta$	polarity
$\varepsilon$	characteristic energy parameter (J)
$\eta$	dynamic viscosity ( $\text{kg (m s)}^{-1}$ )
$\mu$	dipole moment (debyes)
$\rho$	density ( $\text{kg m}^{-3}$ )
$\sigma$	characteristic length parameter ( $\text{\AA}$ )
$\omega$	acentric factor
$\Omega_D$	diffusion collision integral

*Subscripts*

a	air
b	boiling point
c	critical point
f	freezing point
l	liquid
p	pool
r	reduced
v	vapor

**1. Introduction**

Modeling systems for analyzing the consequences of chemical emergencies, as well as dispersion models of heavier-than-air gas clouds, require as input values a number of physico-chemical substance properties, commonly as a function of temperature at atmospheric pressure. The selection of physico-chemical substance properties required by the models varies widely depending on the model used, particularly in terms of the complexity of their thermodynamic treatment (see recent reviews by Bricard and Friedel [1] and Britter [2]).

The determination of these substance properties for thousands of industrially-applied chemicals can be very time-consuming and in some cases even impossible, due to the

lack of experimental data. The required properties include constant values (e.g. molecular weight and normal boiling point) and a varying number of other properties as a function of temperature or pressure (e.g. saturation vapor pressure, heat of vaporization, and vapor and liquid heat capacities and densities). Atmospheric dispersion models commonly require these properties as a function of temperature at atmospheric pressure. Source term models contained in integrated consequence analysis systems may also require properties of substances in the saturated state, as a function of temperature or pressure.

Heavier-than-air cloud dispersion models may also include a treatment for chemical transformation processes, e.g. the vapor-phase polymerization and depolymerization of HF and formation of a solution with water (e.g. Webber and Wren [3], Muralidhar et al. [4], Vesala and Kukkonen [5]). Clearly, such models require additional substance property information concerning chemical reactivity and solution activity. Some attempts have also been made in order to treat the behavior of mixtures of pure substances (e.g. Mikesell et al. [6]). Models allowing for detailed non-equilibrium (aerosol) thermodynamical processes also require very detailed substance property data (e.g. Kukkonen et al. [7]).

Lyman et al. [8] have compiled a comprehensive bibliography of standard chemical property data sources. Extensive compilations of experimental data on substance properties have been written by Lide and Frederikse [9] and Kaye and Laby [10]. Reid et al. [11] also provide a property DATABANK of experimental values for more than 600 commonly-used substances. Computerized databases containing experimental data have also been compiled: these include DIPPR—Design Institute for Physical Property Data of the American Institute of Chemical Engineers (<http://dippr.byu.edu/>), MSDS—Material Safety Data Sheets (<http://www.env-sol.com/Solutions/MSDS-W.html>) and DATABANK [12]. However, the DIPPR and MSDS databases are available only commercially. Despite these compilations, in many particular cases a complete set of reliable property data is not available. Computational estimation methods are, therefore, a necessity, these have been reviewed and evaluated by, e.g. Lyman et al. [8], Reid et al. [11] and Yaws [13].

The objective of this study was to develop a user-friendly validated analysis tool, which could be applied in order to estimate the relevant physico-chemical properties of substances. We have designed a model which yields reasonably accurate numerical predictions, while at the same time keeping the amount of input data to a minimum. The model is intended to be used in combination with consequence analysis or heavier-than-air cloud dispersion models. The scope of the model is limited to evaluating the physico-chemical properties of pure substances, as a function of temperature at atmospheric pressure. Evaluation of substance properties for mixtures, and treatment of chemical transformation in the atmosphere is outside the scope of this model.

## 2. The model for evaluating substance properties

Various semi-empirical methods have been developed for computationally evaluating the physico-chemical properties of substances (Lyman et al. [8], Reid et al. [11] and Yaws [13]). Some of these are based on molecular theory or thermodynamics, possibly also including empirical corrections. One of the basic principles in developing such methods is the law of corresponding states, which expresses the generalization of equilibrium properties, which

depend on intermolecular forces, are related to the critical properties in a universal way (Reid et al. [11]).

Some estimation methods are based on consideration of molecular structure, these suggest that a macroscopic property can be computed from the so-called group contributions. This technique uses molecular structural information in order to compute thermodynamic quantities. The molecule is divided into appropriate groups and the related values of group contributions can be obtained from tabulations (Lyman et al. [8], Reid et al. [11]). Once the group contributions are known, they can be entered into equation-oriented techniques for further property estimation. However, these methods require detailed knowledge of the structure of the molecule and the related group contributions.

The volumetric behavior of pure gases and liquids as functions of temperature and pressure (the pressure-volume-temperature relation) can be estimated applying the Benedict–Webb–Rubin (BWR) equation of state or a cubic equation of state, e.g. Peng–Robinson (Reid et al. [11]). The cubic equations cannot be used to predict, with confidence, the volumetric behavior of polar molecules.

We have on the one hand selected methodologies, which are based on molecular theory or thermodynamics, together with empirical corrections to allow for the inadequacies of the theory. On the other hand, we have attempted to keep the number of model input values at a minimum. Due to the latter requirement, it was not possible to apply group contribution methods in this model. We have applied the law of corresponding states for all the substance properties modeled, except for the vapor density, for which we simply applied the ideal gas law.

Methods are presented in the following for computing the vapor pressure, vapor and liquid densities, heat of vaporization, vapor and liquid viscosities and binary diffusion coefficient, all of these as a function of temperature at atmospheric pressure. The limits of validity and estimates of accuracy are also reported for each property evaluation method, as far as these are known from the available literature.

Some consequence analysis systems also require other substance properties, e.g. the specific heat capacities of vapor and liquid. However, it is not possible to evaluate these properties with reasonable accuracy, using only the limited set of input values that have been selected here.

### 2.1. Vapor density

The density of vapor is given by the ideal gas law

$$\rho_v = \frac{Pm_w}{RT}, \quad (1)$$

where  $P$  is the pressure,  $m_w$  the molecular weight,  $R$  the universal gas constant and  $T$  the temperature.

Reid et al. [11] have presented equations to account for the non-ideal behavior of gases at high temperatures and pressures. However, for the purposes of environmental analysis, where temperatures commonly range from  $-20$  to  $+50$  °C and the pressure does not deviate substantially from atmospheric pressure, the ideal gas law provides a simple, accurate estimation method for most compounds, Lyman et al. [8]. Lyman et al. [8] have compared

estimates of the vapor density of 15 gases at 0 °C, using the ideal gas law against experimental values, the absolute average deviation was 1%. However, the accuracy of the ideal gas law deteriorates as the critical point is approached.

## 2.2. Vapor pressure

Applying a modified BWR equation of state for the simple (Ar, Kr and methane) and reference (*n*-octane) fluids, Lee and Kesler [14] have derived a three-parameter (critical temperature, critical pressure and acentric factor) corresponding state form to estimate the vapor pressure as a function of temperature (Reid et al. [11], p. 207)

$$P_v = P_c \exp(f_0 + \omega f_1), \quad (2)$$

where  $P_c$  is the critical pressure,  $\omega$  is the acentric factor and

$$\begin{aligned} f_0 &= 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln(T_r) + 0.169347 T_r^6 \\ f_1 &= 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.43577 T_r^6, \end{aligned} \quad (3)$$

where the reduced temperature  $T_r = T/T_c$  and  $T_c$  is the critical temperature. The acentric factor is given by

$$\omega = \frac{\alpha}{\beta}, \quad (4)$$

where

$$\begin{aligned} \alpha &= -\ln\left(\frac{P_c}{101325}\right) - 5.97214 + 6.09648 T_{br}^{-1} + 1.28862 \ln(T_{br}) - 0.169347 T_{br}^6 \\ \beta &= 15.2518 - 15.6875 T_{br}^{-1} - 13.4721 \ln(T_{br}) + 0.43577 T_{br}^6, \end{aligned} \quad (5)$$

where  $T_{br} = T_b/T_c$  and  $T_b$  is the normal boiling point. According to Reid et al. [11], Eq. (2) generally predicts vapor pressures within an accuracy of from 1 to 2% between  $T_b$  and  $T_c$ . Below  $T_b$ , Eq. (2) may underpredict  $P_v$  by several percent. The method is not recommended to be used for polar compounds (Reid et al. [11]).

## 2.3. Heat of vaporization

A two-parameter (critical temperature and acentric factor) corresponding states method is applied to estimate the heat of vaporization. Pitzer et al. [15], Pitzer and Curl [16] and Curl and Pitzer [17], have shown that the compressibility factor and other derived thermodynamic functions can be adequately represented, at constant reduced temperature and pressure, by a linear function of the acentric factor. In particular, the heat of vaporization is given by

$$H_v = T(S^{(0)} + \omega S^{(1)}), \quad (6)$$

where  $S^{(0)}$  is for a simple (spherical molecule) fluid and the term  $S^{(1)}$  represents the deviation of the real fluid from  $S^{(0)}$ . These are functions of  $T_r$  only. From the tabulated  $S^{(0)}$  and  $S^{(1)}$

functions given by Pitzer et al. [15] and extended to low reduced temperatures by Carruth and Kobayashi [18], an analytical representation for the heat of vaporization of a pure liquid can be constructed (Reid et al. [11], p. 220)

$$H_v = \frac{RT_c}{m_w} (7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456}). \quad (7)$$

According to Reid et al. [11], Eq. (7) is one of the most accurate and convenient. The method is recommended for use between  $0.6 < T_r \leq 1.0$ , we have also applied the method below  $T_r = 0.6$ .

#### 2.4. Liquid density

A three-parameter (critical temperature, critical pressure and acentric factor) corresponding states method is used to estimate the liquid density. Applying the assumption that thermodynamic functions can be represented by a linear function of the acentric factor, Bhirud [19] has shown that the molar volume of a saturated liquid  $V_1$  can be expressed as

$$\ln \left( \frac{P_c V_1}{RT} \right) = a + \omega b, \quad (8)$$

where  $a$  and  $b$  are functions of  $T_r$ . Bhirud [19] used experimental data for seven compounds to evaluate the generalized functions  $a$  and  $b$ . Eq. (8) yields (Lyman et al. [8], p. 19–12)

$$\rho_l = \frac{m_w P_c}{RT \exp(a + \omega b)}, \quad (9)$$

where

$$\begin{aligned} a &= 1.39644 - 24.076T_r + 102.615T_r^2 - 255.719T_r^3 + 355.805T_r^4 \\ &\quad - 256.671T_r^5 + 75.1088T_r^6 \\ b &= 13.4412 - 135.7437T_r + 533.380T_r^2 - 1091.453T_r^3 + 1231.43T_r^4 \\ &\quad - 728.227T_r^5 + 176.737T_r^6 \end{aligned} \quad (10)$$

The acentric factor is estimated by (Lyman et al. [8], p. 19–12)

$$\omega = \frac{3}{7} \left( \frac{T_{br}}{1 - T_{br}} \right) \log \left( \frac{P_c}{101325} \right) - 1. \quad (11)$$

The evaluation of the acentric factor  $\omega$  in Eq. (11) is different, compared with the corresponding method in Eq. (4) used in evaluating the vapor pressure.

Bhirud [19] compared the predictions obtained using this correlation with the experimental values for 24 organic compounds, in the temperature range from  $T_r = 0.28$  to 1.0. The average deviation was found to be 0.76%. Bhirud [19] concluded that the correlation is accurate over an extensive temperature range, and is applicable to normal (i.e. for all non-polar and a few slightly polar) fluids.

### 2.5. Vapor viscosity

The dynamic viscosity of a pure vapor is estimated by the law of corresponding states method as suggested by Lucas (Reid et al. [11], p. 397)

$$\eta_v = \frac{10^{-7}}{\xi} [0.807T_r^{0.618} - 0.357 \exp(-0.449T_r) + 0.340 \exp(-4.058T_r) + 0.018] F_P^0 F_Q^0 \quad (12)$$

where  $F_P^0$  and  $F_Q^0$  are correction factors to account for polarity and quantum effects, respectively, and

$$\xi = 0.176 \left( \frac{T_c}{m_w^3 (10^{-5} P_c)^4} \right)^{1/6} \quad (13)$$

For nonpolar gases,  $F_P^0 = 1$ . To obtain  $F_P^0$  for polar gases, the dipole moment of the substance is required. However, the evaluation of the dipole moment is not possible using only the simple input values assumed here, therefore, we have simply set  $F_P^0 = 1$ .

Eq. (12) may be used with an expectation of errors from 0.5 to 1.5% for nonpolar compounds [11]. The method is not suitable for highly associated gases like acetic acid. The viscosity of a vapor is strongly dependent on pressure near the critical point and at high pressures, corresponding to reduced temperatures from about 1 to 2 [11]. Since, the method is applied typically near the normal boiling point and at atmospheric temperatures, we can here neglect the effect of pressure on vapor viscosity.

For all substances except for He, H<sub>2</sub> and D<sub>2</sub>,  $F_Q^0 = 1$ . We have used this numerical value as a default, and the model is, therefore, not valid for the above mentioned three substances.

### 2.6. Liquid viscosity

Hildebrand [20] showed that the fluidity of non-associating liquids is proportional to the fractional excess of its molar volume  $V$  over the molar volume  $V_0$ , at which the molecules are so close that viscous flow ceases:

$$\frac{1}{\eta_l} = E \frac{V - V_0}{V_0}, \quad (14)$$

where  $\eta_l$  is the dynamic viscosity of liquid and the parameter  $E$  denotes the capacity of molecules to absorb momentum due to molecular mass, flexibility, or rotation. Przedzicki and Sridhar [21] have obtained the values of parameters  $E$  and  $V_0$  by linear regression from the viscosity data of 27 compounds. The parameters  $E$  and  $V_0$  can be correlated by the following equations:

$$E = -1.12 + \frac{V_c}{12.94 + 0.1m_w - 0.23 \times 10^{-5} P_c + 0.0424T_f - 11.58(T_f/T_c)} \quad (15)$$

and

$$V_0 = 0.0085\omega T_c - 2.02 + \frac{V_f}{0.342(T_f/T_c) + 0.894}, \quad (16)$$

where  $V_f$  is the molar volume of the liquid at the freezing temperature  $T_f$ . The molar volumes of a liquid ( $V$  and  $V_f$ ) are computed from Eq. (9).

A comparison of calculated and experimental viscosities showed that the errors varied widely and, except for a few materials, the above-mentioned technique underestimated the liquid viscosity [11]. According to [11], Eq. (14) should not be used for alcohols, or below  $T_f$  values of about 0.55.

### 2.7. Binary diffusion coefficient

The theory describing diffusion in binary gas mixtures at low to moderate pressure has been extensively developed [11]. The theory results from solving the Boltzmann equation, for which the so called Chapman–Enskog solution is

$$D_{AB} = \frac{3}{16} \frac{(4\pi kT/M_{AB})^{1/2}}{n\pi\sigma_{AB}^2\Omega_D} f_D \times 10^{-4}, \quad (17)$$

where  $k$  is Boltzmann's constant,  $\sigma_{AB}$  is a characteristic length,  $\Omega_D$  is the diffusion collision integral,  $f_D$  is a correction term which is of the order of unity and

$$M_{AB} = 2 \left( \frac{1}{m_w} + \frac{1}{m_a} \right)^{-1}, \quad (18)$$

where  $m_a$  is the molecular weight of air. Several proposed methods for estimating  $D_{AB}$  in low-pressure binary gas systems retain the general form of Eq. (17), with empirical constants based on experimental data [11].

The diffusion coefficient for binary gases is estimated by the method of Wilke and Lee (Reid et al. [11], p. 587)

$$D_{AB} = \frac{(3.03 - 0.98/(M_{AB})^{1/2}) \times 10^{-3} T^{3/2}}{10^{-5} P (M_{AB})^{1/2} \sigma_{AB}^2 \Omega_D} \times 10^{-4}, \quad (19)$$

where

$$\sigma_{AB} = \frac{\sigma_w + \sigma_a}{2} \quad (20)$$

and

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}. \quad (21)$$

Here  $\sigma_w$  and  $\sigma_a$  are characteristic length parameters (the Lennard–Jones lengths) of the substance and air, respectively and

$$T^* = \frac{kT}{\varepsilon_{AB}} \quad (22)$$



and

$$\varepsilon_{AB} = (\varepsilon_w \varepsilon_a)^{1/2}, \quad (23)$$

where  $\varepsilon_w$  and  $\varepsilon_a$  are the characteristic energy parameters (the Lennard–Jones energies) of the substance and air, respectively. The constants  $A$  to  $H$  have the following values

$$\begin{aligned} A &= 1.06036, & B &= 0.15610, & C &= 0.19300, & D &= 0.47635, & E &= 1.03587, \\ F &= 1.52996, & G &= 1.76474, & H &= 3.89411. \end{aligned}$$

The characteristic energy parameter is given by (Reid et al. [11], p. 587)

$$\varepsilon = 1.15kT_b. \quad (24)$$

The characteristic length parameter is given by (Reid et al. [11], p. 587)

$$\sigma = 0.118 \left( \frac{m_w}{\rho_{lb}} \right)^{1/3}, \quad (25)$$

where  $\rho_{lb}$  is the density of the liquid at the normal boiling point. For air  $\sigma_a = 3.62 \text{ \AA}$  and  $\varepsilon_a/k = 97 \text{ K}$ .

Reid et al. [11] compared the predictions obtained using Eq. (19) with the experimental values for 51 binary systems, in the temperature range from  $T = 195$  to  $1068 \text{ K}$ . The average absolute error was found to be 7.0%.

### 2.8. The computer model

The pure substance constants required as input by the model are the molecular weight  $m_w$ , the freezing or melting point  $T_f$ , the normal boiling point  $T_b$ , the critical temperature  $T_c$ , the critical pressure  $P_c$  and the critical volume  $V_c$ . These properties are readily available for a wide range of substances, (e.g. Lyman et al. [8], Lide and Frederikse [9], Kaye and Laby [10] and Reid et al. [11]). We have written a computer program called CHEMIC (Model for evaluating CHEMical substance properties for toxic or flammable Compounds), which computes the set of Eqs. (1), (2), (7), (9), (12), (14) and (19). The model output parameters are the vapor pressure, vapor and liquid densities, heat of vaporization, vapor and liquid viscosity's and binary diffusion coefficient, all of these are found as a function of temperature at atmospheric pressure. The model can be executed on a personal computer.

### 3. Evaluation of the model

First, the results of the numerical program were examined by comparing the computed values of substance properties with example results reported in Lyman et al. [8] and Reid et al. [11], the results were identical. This phase was simply a check of the fidelity of the computer code to the original equations.

Secondly, the predictions of the CHEMIC model for vapor pressure, vapor and liquid densities and heat of vaporization are evaluated by using the Clausius–Clapeyron equation. Thirdly, we compare the predictions of substance properties by the CHEMIC model with

those extracted from DATABANK. This phase is a direct comparison of CHEMIC predictions with correlations that are based on experimental data. In the following, we shall discuss these two latter comparisons in more detail.

It is known from theoretical considerations that the model is not valid for the so-called quantum gases (He, H<sub>2</sub> and D<sub>2</sub>). The model is most likely invalid also for associating and strongly polar compounds (for instance, HF), and alcohols. It is advised that the model should not be applied for such substances.

### 3.1. Evaluation of the CHEMIC predictions using the Clausius–Clapeyron equation

When the vapor phase of a pure fluid is in equilibrium with the liquid phase, the equality of chemical potential, temperature and pressure in both phases leads to the Clausius–Clapeyron equation (e.g. Reid et al. [11])

$$\frac{dP_v}{dT} = \frac{H_v}{T(\rho_v^{-1} - \rho_l^{-1})}. \quad (26)$$

The CHEMIC model predicts separately all substance properties in this equation ( $P_v$ ,  $H_v$ ,  $\rho_v$  and  $\rho_l$ ) as a function of the temperature. The consistency of these predictions can, therefore, be evaluated by using the Clausius–Clapeyron equation.

Differentiation of the vapor pressure as defined by Eqs. (2) and (3) yields

$$\frac{dP_v}{dT} = (f'_0 + \omega f'_1)P_v, \quad (27)$$

where

$$\begin{aligned} f'_0 &= 6.09648(T_r T)^{-1} - 1.28862T^{-1} + 1.016082T_r^5 T_c^{-1} \\ f'_1 &= 15.6875(T_r T)^{-1} - 13.4721T^{-1} + 2.61462T_r^5 T_c^{-1}. \end{aligned} \quad (28)$$

The predictions of CHEMIC for  $dP_v/dT$  are evaluated from Eqs. (27) and (28).

For presentation purposes, we denote the right-hand-side term in Eq. (26) as  $h(T)$ ,

$$h(T) = \frac{H_v}{T(\rho_v^{-1} - \rho_l^{-1})}, \quad (29)$$

and define a function  $g(T)$  as the ratio of the left- and right-hand-side terms of Eq. (26), respectively,

$$g(T) = \frac{dP_v/dT}{h(T)}. \quad (30)$$

The predictions of the CHEMIC model for the left- and right-hand sides of Eq. (26), and their ratio are presented in Fig. 1(a–c) for three example substances. The variation of the functions  $dP_v/dT$ ,  $h(T)$  and  $g(T)$  are presented in the reduced temperature ( $T_r$ ) range from approximately 0.4–0.5 to 1.0, for ammonia (NH<sub>3</sub>), chlorine (Cl<sub>2</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>). The values of the critical temperature are 406, 417 and 282 K for ammonia, chlorine and ethylene, respectively. The scales of  $dP_v/dT$  and  $h(T)$  are logarithmic, and scale of  $g(T)$  is linear.

Clearly, an ideal model would produce identical values of  $dP_v/dT$  and  $h(T)$ , and values of  $g(T)$  that are equal to unity. The variation of these functions in terms of  $T_r$  is very similar

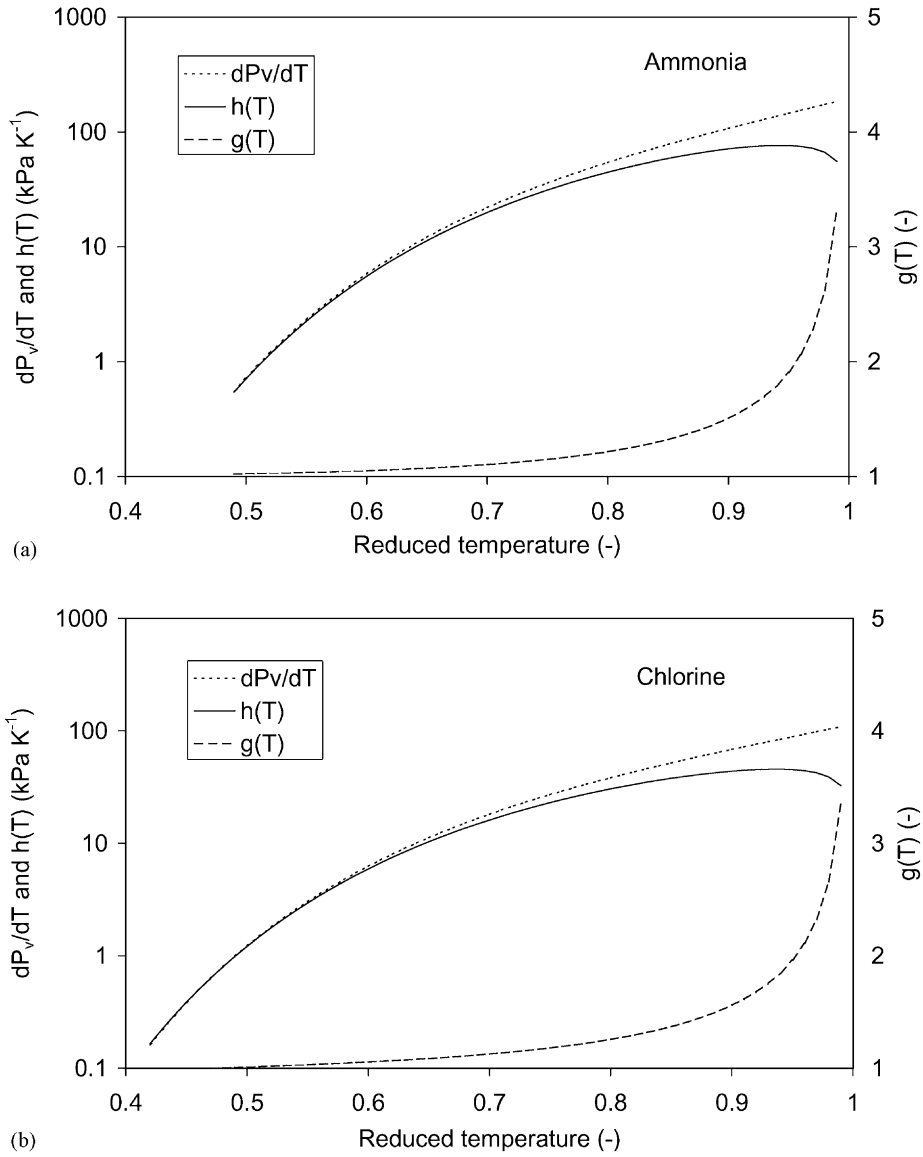


Fig. 1. (a–c) The predictions of the CHEMIC model for the left- and right-hand sides of the Clausius–Clapeyron (Eq. (26)), and their ratio for ammonia, chlorine and ethylene. Notation:  $h(T) = H_v(T(\rho_v^{-1} - \rho_l^{-1}))^{-1}$  and  $g(T) = (dP_v/dT)(h(T))^{-1}$ .

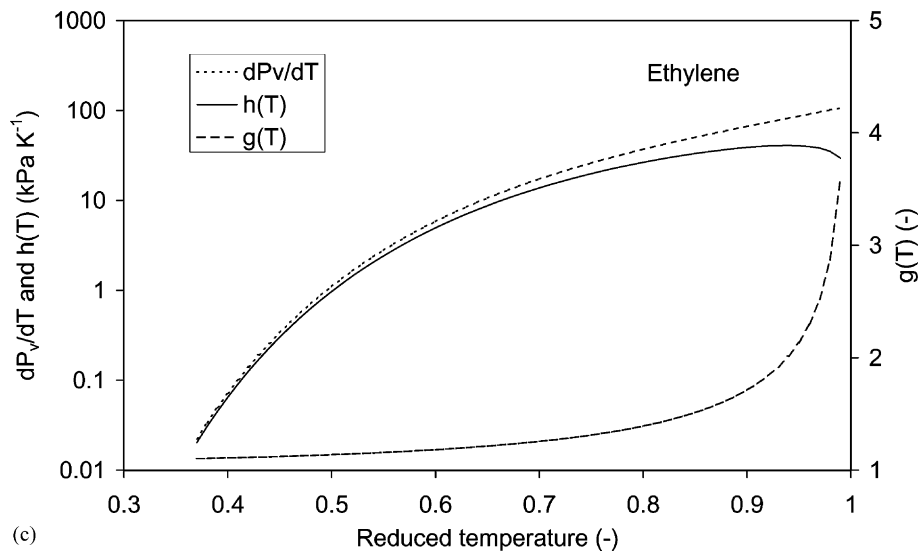


Fig. 1. (Continued).

for all the substances considered, despite their widely varying critical temperatures. The Clausius–Clapeyron equation is well approximated by the model for small and moderate values of  $T_r$ , however, the model predictions deteriorate as the temperature approaches the critical temperature. For instance, the values of  $g(T)$  are smaller than 1.2, when the reduced temperature is below 0.79, 0.77 and 0.63 for ammonia, chlorine and ethylene, respectively.

One obvious reason for the deterioration of model predictions near the critical temperature is that the ideal gas law (Eq. (1)) tends not to be accurate in that regime. The ideal gas law has been applied here, as in environmental analysis, the temperatures considered are substantially lower than the critical temperature for most compounds of interest. Clearly, this is the case for ammonia and chlorine. However, the model presented here should not be applied for substances that have a very low critical temperature, such as ethylene for which  $T_c = 9^\circ\text{C}$ .

### 3.2. Comparison of the CHEMIC predictions and the DATABANK values

We have compared the predicted results of the CHEMIC model with the DATABANK values for three widely used toxic (ammonia,  $\text{NH}_3$ , chlorine,  $\text{Cl}_2$  and sulfur dioxide,  $\text{SO}_2$ ) and six flammable compounds (ethylene oxide,  $\text{C}_2\text{H}_4\text{O}$ , vinyl chloride,  $\text{C}_2\text{H}_3\text{Cl}$ , propane,  $\text{C}_3\text{H}_8$ , butadiene,  $\text{C}_4\text{H}_6$ , butane,  $\text{C}_4\text{H}_{10}$  and toluene,  $\text{C}_7\text{H}_8$ ), and for one chemical warfare agent (phosgene,  $\text{COCl}_2$ ). The average and maximum deviations between the CHEMIC predictions and the DATABANK values are shown in Table 1, for the temperature interval from 240 to 300 K.

The substances are presented in terms of increasing polarity, defined by Brokaw [22].

$$\delta = \frac{10^7}{2} \times \frac{\mu^2}{\epsilon\sigma^3}, \quad (31)$$

Table 1  
Average and maximum values of the absolute deviation between the CHEMIC predictions and the DATABANK values in the temperature range from 240 to 300 K.<sup>a</sup>

Property	Substance										Range of average deviations (%)
	Non-polar					Polar					
	C <sub>4</sub> H <sub>6</sub> (%)	C <sub>4</sub> H <sub>10</sub> (%)	C <sub>3</sub> H <sub>8</sub> (%)	Cl <sub>2</sub> (%)	C <sub>7</sub> H <sub>8</sub> (%)	COCl <sub>2</sub> (%)	C <sub>2</sub> H <sub>3</sub> Cl (%)	SO <sub>2</sub> (%)	C <sub>2</sub> H <sub>4</sub> O (%)	NH <sub>3</sub> (%)	
Vapor pressure	4.3 (6.2)	5.0 (8.5)	1.6 (3.6)	2.3 (2.7)	13 (13)	6.0 (9.3)	4.2 (9.1)	3.4 (5.9)	7.4 (11)	1.9 (4.2)	1.6–13
Heat of vaporization	0.6 (0.7)	1.4 (1.5)	0.4 (0.6)	1.5 (1.8)	1.6 (1.6)	0.5 (0.5)	4.1 (4.3)	1.4 (1.5)	0.6 (0.6)	0.8 (0.8)	0.4–4.1
Density of liquid	4.5 (4.5)	0.2 (0.2)	0.7 (0.8)	4.5 (4.6)	2.1 (2.2)	3.6 (3.6)	3.9 (3.9)	2.1 (2.3)	9.5 (9.6)	14 (14)	0.2–14
Dynamic viscosity of vapor	6.9 (7.5)	2.2 (2.4)	0.8 (1.8)	1.8 (2.9)	0.9 (2.4)	1.5 (1.9)	3.3 (3.6)	0.6 (0.8)	4.6 (4.8)	12 (13)	0.6–12
Dynamic viscosity of liquid	27 (27)	2.9 (5.5)	15 (21)	60 (63)	26 (32)	46 (49)	14 (16)	53 (57)	57 (60)	21 (21)	2.9–60
Binary diffusion coefficient	7.8 (7.8)	7.9 (7.9)	7.6 (7.6)	8.0 (8.0)	8.2 (8.2)	8.3 (8.3)	7.9 (7.9)	8.0 (8.0)	7.6 (7.6)	5.8 (5.8)	5.8–8.3
Polarity	0.000	0.000	0.000	0.006	0.006	0.119	0.260	0.420	0.499	0.700	

<sup>a</sup> The average deviation is defined as  $\Delta P_{\text{ave}} = (1/n) \sum_{i=1}^n |100(P_{C,i} - P_{D,i})/P_{D,i}|$  (%), where  $n$  is the number of data points ( $n = 13$ ),  $P$  is a substance property and the subscripts  $C$  and  $D$  refer to the values computed using the CHEMIC model and property data extracted from DATABANK, respectively. The maximum absolute deviation is defined as  $\Delta P_{\text{max}} = \max\{|100(P_C - P_D)/P_D|\}$  (%). The maximum absolute deviations are shown in parenthesis.

where  $\mu$  is the dipole moment. The substances  $C_4H_6$ ,  $C_4H_{10}$ ,  $C_3H_8$ ,  $Cl_2$  and  $C_7H_8$  are classified as non-polar,  $COCl_2$ ,  $C_2H_3Cl$ ,  $SO_2$ ,  $C_2H_4O$  and  $NH_3$  are polar.

The CHEMIC predictions and the DATABANK values have been presented in Fig. 2(a–f) for three substances, in order to illustrate the dependency of these properties on the temperature.

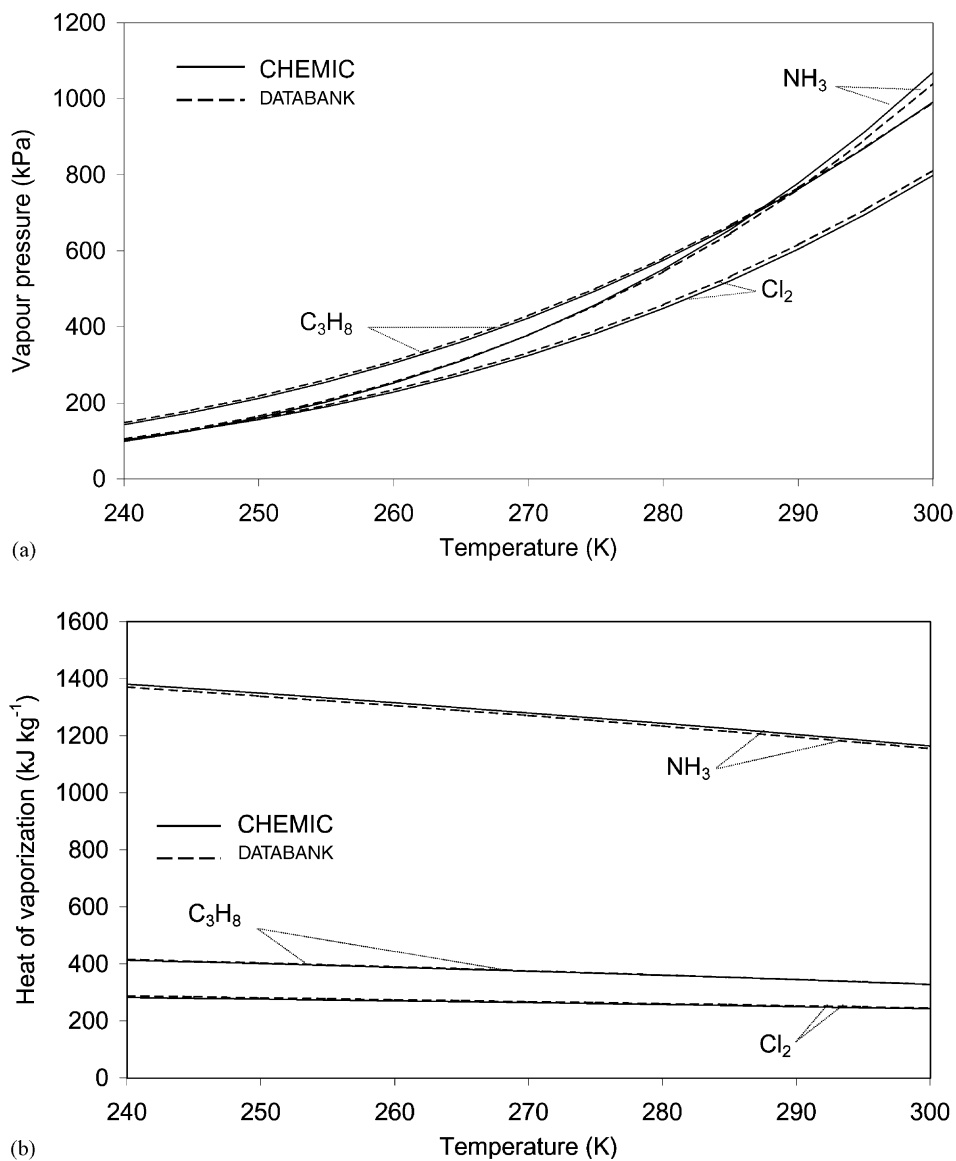


Fig. 2. (a–f) Variation of the substance properties of ammonia, chlorine and propane with temperature, computed with the CHEMIC model, and extracted from DATABANK.

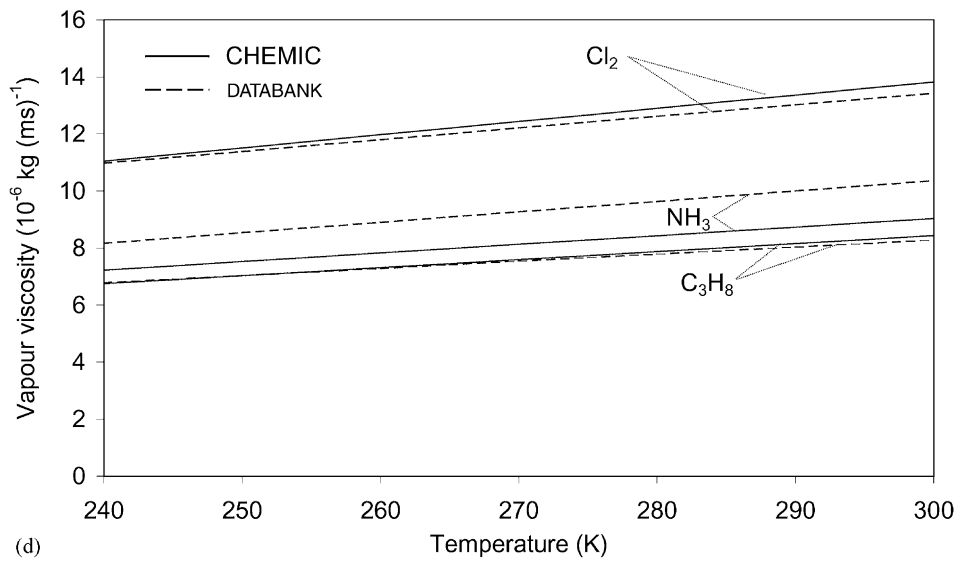
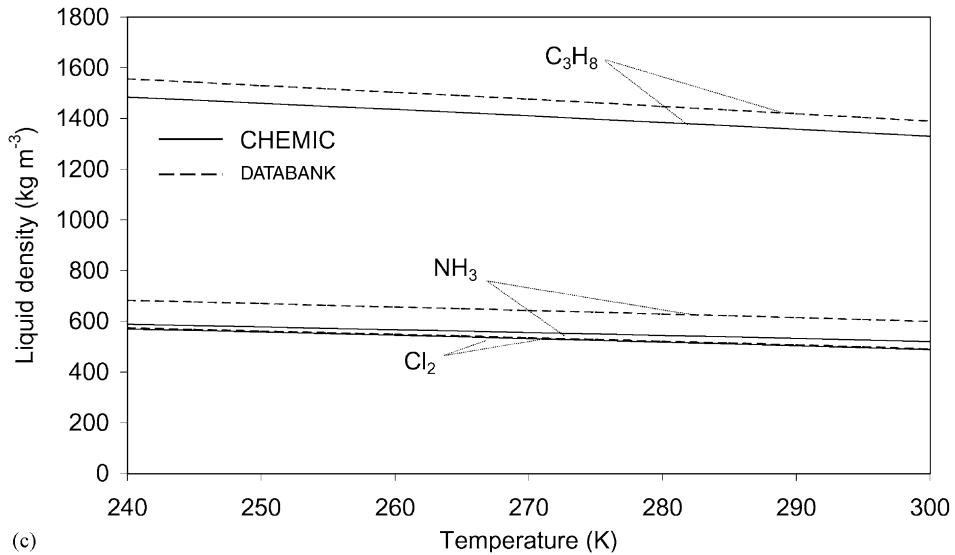


Fig. 2. (Continued).

For some of the evaluation methods, the suggested range of validity is expressed in terms of the reduced temperature  $T_r$ . The temperature in terms of  $T_r$  ranges from 0.59 to 0.74, 0.58 to 0.72, 0.65 to 0.81, 0.51 to 0.63, 0.56 to 0.71, 0.56 to 0.70, 0.41 to 0.51, 0.56 to 0.71, 0.53 to 0.66 and 0.56 to 0.70 for the substances  $\text{NH}_3$ ,  $\text{Cl}_2$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4\text{O}$ ,  $\text{C}_4\text{H}_6$ ,  $\text{SO}_2$ ,  $\text{C}_7\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{COCl}_2$  and  $\text{C}_2\text{H}_3\text{Cl}$ , respectively.

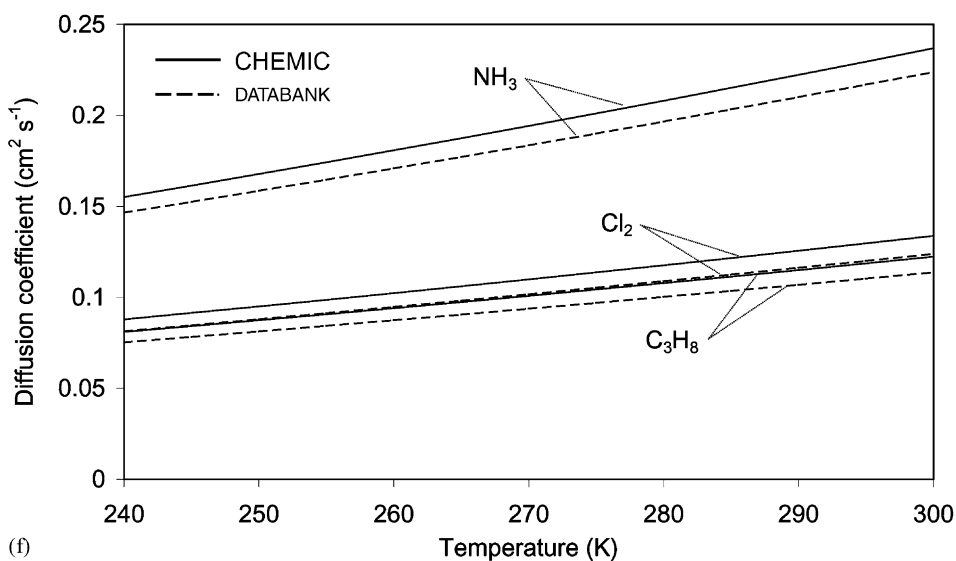
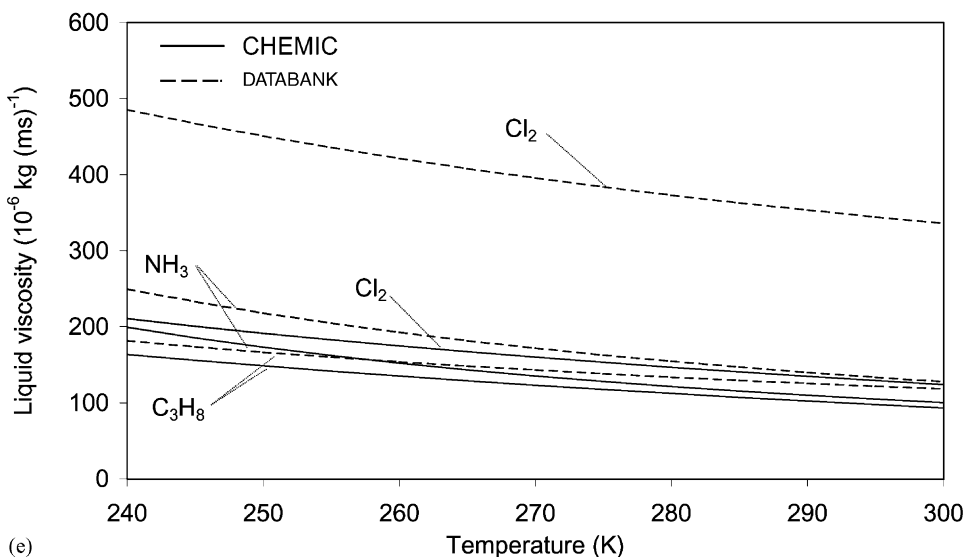


Fig. 2. (Continued).

The values of the heat of vaporization and binary diffusion coefficient, obtained from CHEMIC and DATABANK agree well (the average deviations range from 0.4 to 4.1% and 5.8 to 8.3%, respectively, for the substances considered). The agreement is fairly good also for the values of vapor pressure, density of liquid and dynamic viscosity of vapor (the average deviations range than from 1.6 to 13%, 0.2 to 14% and 0.6 to 12%, respectively). However,



the values of substance properties for the dynamic viscosity of liquid deviate substantially for some of the selected compounds (the average deviations range from 2.9 to 60%).

The thermodynamic properties of gaseous HF show large deviations from ideal gas behavior, because of the high degree of association (polymerization) in the gas phase (Vanderzee and Rodenburg [23]). It is, therefore, to be expected based on theoretical considerations that the model presented here is not valid for HF. Numerical comparisons of the CHEMIC model with the DATABANK values for this compound also show that the deviations of substance properties are not within acceptable limits.

#### 4. Conclusions

A model has been developed for evaluating the physico-chemical properties required by consequence analysis modeling systems. The model equations are mostly based on the so-called law of corresponding states. The model requires only a limited set of input data, and can easily be introduced into consequence analysis modeling systems in order to extend their performance to address a wider selection of substances. The pure substance constants required as input by the model are readily available for a wide range of substances in standard reference books.

However, due to the requirement of using such a simple set of input values, the CHEMIC model has the following inherent limitations. The model is not valid for the so-called quantum gases (He, H<sub>2</sub> and D<sub>2</sub>). The model is also invalid for associating or strongly polar compounds (for instance, HF), alcohols and substances that have a very low critical temperature (for instance, ethylene). In case of such substances, more detailed experimentally-derived data is required in order to evaluate the relevant substance properties.

The model predictions for vapor pressure, vapor and liquid densities and heat of vaporization have been evaluated by using the Clausius–Clapeyron equation for three example substances (ammonia, chlorine and ethylene). The Clausius–Clapeyron equation is well approximated by the model for small or moderate values of the reduced temperature (approximately  $T_r < 0.8$ ). In environmental analysis, this is the temperature regime considered for most compounds of interest. However, the model predictions deteriorate substantially, as the temperature approaches the critical temperature ( $T_c$ ). This is probably caused by the poor performance of the ideal gas law near  $T_c$ . The model presented is, therefore, not valid for substances that have a sufficiently low critical temperature, i.e. one that is within or only slightly higher than the temperature regime considered.

We also have compared the predictions of the CHEMIC model with the values extracted from the DATABANK database, which includes detailed semi-empirical correlations. The comparison was performed for six substance properties, for nine commonly used toxic or flammable compounds and one chemical warfare agent. The compounds selected are theoretically in the validity regime of the model, i.e. they are not associating or strongly polar, although, some of these are classified as polar molecules.

The values obtained from CHEMIC and DATABANK agree well or fairly well for the following five properties: vapor pressure, heat of vaporization, density of liquid, dynamic viscosity of vapor and binary diffusion coefficient, the average deviations range from 0.2 to 14% for these substances. However, for the dynamic viscosity of liquid of these substances,

the average deviations obtained from CHEMIC and DATABANK range from 2.9 to 60%. We conclude that the CHEMIC model can be applied for evaluating the five above-mentioned substance properties within reasonable accuracy. However, for evaluating liquid viscosity, the use of more detailed semi-empirical correlations is recommended, if the relevant data is available.

In future work, the model performance should be quantitatively evaluated more extensively. This should include both (i) direct testing against experimental substance property data (or correlations based on measured data) for a wider range of substances, and (ii) indirect testing in the context of various consequence analysis systems. It would probably be possible to extend the model applicability to higher values of the reduced temperature by replacing the ideal gas law by cubic equations of state or similar methods, although, this would also increase the numerical complexity of the model.

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