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Heat Effects of Hydrogen Fluoride from Two Thermodynamic Models[1]

D. P. Visco, Jr.,[2] E. Juwono,[2] and D. A. Kofke[2, 3]

We examine two published thermodynamic models for their ability to describe the excess enthalpy and heat capacity of hydrogen fluoride (HF) over a range of temperatures. Emphasis is placed on the behavior away from the saturation curve and, thus, away from the conditions used to fit the models. The first model is the association + equation of state (AEOS) treatment of Anderko, which utilizes a biased yet unconstrained association scheme. The second model is due to Kao and co-workers and treats HF as a mixture of only monomers and hexamers. Both models are found to be effective in capturing important qualitative features of the HF heat effects. The AEOS describes well the location but not the magnitude of associated-induced maxima in the vapor-phase heat capacities, while the Kao model describes the magnitude well but is slightly off in characterizing the locations of these maxima.

KEY WORDS: associating fluids; equations of state; heat capacity; hydrogen fluoride.

1. INTRODUCTION

Hydrogen fluoride (HF) is an important precursor in the production of hydrofluorocarbons (HFCs), which have been identified as the most likely candidates for the new generation of environmentally benign refrigerants. Efficient design of separation and heat transfer equipment involving HF–HFC mixtures requires a good thermodynamic model. In particular, the model must incorporate the effects of hydrogen bonding, which occurs extensively in both liquid and vapor phases containing HF. HF is very

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[2] Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260, U.S.A.

[3] To whom correspondence should be addressed.

caustic and highly toxic and, thus, very difficult to study by experiment. Consequently, the problems of developing a good thermodynamic model are compounded by the scarcity of experimental data on HF and its mixtures, particularly away from saturation. Parameters for existing thermodynamic models are based mainly on saturated liquid and vapor densities and the vapor pressure. In this report, we examine the ability of two such models to describe the heat effects of pure HF away from the saturation line.

Existing models for HF vary significantly in their assumptions regarding the nature of HF association. The association is monovalent so, unlike, e.g., water, HF clusters form chains and rings but not networks. Within this constraint a proposed model must make assertions about the types of chains that form and their relative abundance. The most effective and popular approach treats the association as a chemical reaction, and the pure HF phase is modeled as a mixture of oligomers. It remains then to specify the "equilibrium constants" for the association reactions, and to solve for the species distribution within the context of a simple model (often a cubic equation of state) for the oligomer interactions. Models differ in their treatment of the oligomer interactions, as well as in the specification of the association equilibrium constants. Several studies have focused on HF association schemes [1–4]; some are quite sophisticated. Most models, however, are minimal and include, for example, only the monomer and hexamer in accord with some spectroscopic evidence [4]. Contradictory information exists as to the importance of the other oligomers. For example, it is normal to exclude the pentamer from proposed HF association schemes, yet recent work [5] suggest that this cluster may be more important than previously expected.

2. THERMODYNAMIC MODELS

Any of a number of thermodynamic models could have been used for this study. The AEOS [6] was chosen because of its computational simplicity combined with its use of an unconstrained association scheme; in principle, the model permits all oligomer chain lengths. Complementing this is the model of Kao et al. [7], which is computationally more demanding because it requires explicit solution of the chemical equilibrium problem, yet it uses only a simple monomer–hexamer association scheme. Relative to experimental data used in the parameter fitting of this model, the AEOS predicts vapor pressures within 0.7% and saturated liquid volumes within 2.0%. The Kao model can correlate these quantities to within 0.4 and 0.25%, respectively. It is of interest to determine the robustness of these models by extending them to predict the heat effects in HF away from saturation. Heat effects are interesting because not only are they important in practice, but also because they provide a bit of insight on the association phenomena that occur on the molecular scale. Improved understanding here can guide the development of molecular models for HF, which in turn can lead to advancements in thermodynamic models.

2.1. AEOS Model

The so-called association + equation of state (AEOS) model of HF has its origins in many papers [8–15]. We only briefly describe the theory here. The compressibility factor, Z, is divided into a chemical part, Z^{ch}, and a physical part, Z^{ph}, in a way similar to the decomposition of the second virial coefficient into chemical and physical parts [16]. The chemical part arises from the consecutive self-association reactions which occur between a chain of i HF monomers, called an i-mer, and an HF monomer; the physical part reflects contributions due to nonspecific interactions and is given by the Peng–Robinson equation of state [17].

For this model, Z^{ch} is equal to the number of moles of substances which exist, be they monomers, dimers, etc., to the number of apparent (without knowledge of association) moles of HF. The association scheme is continuous, and the equilibrium constants which define the relative amounts of each i-mer are given by a Poisson-like distribution relative to the dimerization constant. A continuous association scheme prevents Z^{ch} from being solved in closed form. However, Lencka and Anderko [6] fit Z^{ch} to an analytic function in a dimensional group q, defined as RTK/v, where R is the gas constant, T is the temperature, K is the dimerization constant, and v is the molar volume. With this step, the AEOS is put into a closed form.

The AEOS contains nine parameters (beyond those used to characterize Z^{ch} in terms of q): the standard enthalpy, entropy, and heat capacity of the the dimerization reaction; a Peng–Robinson (PR) size parameter; four terms characterizing the temperature dependence of a PR energy parameter; and a parameter describing how the association equilibrium changes with oligomer chain length. These parameters were fit by Lencka and Anderko [6] using one- and two-phase vapor densities [18–23], saturated liquid densities [23–25], and vapor pressures [23, 24, 26] ranging from 200 to 500 K. Using these parameters and standard thermodynamic manipulations, we can obtain from this model expressions for any thermodynamic quantity of interest [27].

2.2. Kao Model

The Kao model [7] treats HF as a mixture of two distinct components, HF monomers and HF hexamers. The physical interactions between these "mixture components" are described by the Peng–Robinson equation of state [17]. The association is incorporated as a chemical reaction between the monomers and hexamers with the relative amounts of each at a specific temperature given by an equilibrium constant. Unlike the AEOS, the Kao model is not closed and requires solution of both phase equilibria and chemical equilibria equations. In its final form the model contains three parameters: the equilibrium constant and two PR EOS parameters. However, no temperature dependence is specified, so the parameters must be refit to different values at each temperature. Kao et al. performed such a fit to saturated liquid [23, 25] and vapor densities [23, 28, 29] and the vapor pressure [23, 28, 29] for about 30 temperatures from 253 to 461 K.

2.3. Heat Effects from the Kao Model

Heat effects in the Kao model are conveniently separated into two contributions. First is the enthalpy associated with the formation of the monomer–hexamer mixture in the ideal-gas state. Second is the enthalpy associated with the "compression" of this ideal-gas mixture to the density of interest. The first contribution requires knowledge of the enthalpy of formation of the hexamer from the monomer. This is obtained from the temperature dependence of the association constant:

$$\frac{d \ln K}{dT} = \frac{\Delta h_a^*}{RT^2} \tag{1}$$

where Δh_a^* is the ideal gas enthalpy of association. This term contributes greatly to the overall enthalpy of the mixture, so it is important that it is accurately described. Kao et al. have reported Δh_a^* among their tabulated results, but it is not clear how they performed the numerical differentiation of their tabled K data. We have found that the following functional form for $\ln K$ adequately describes its temperature dependence while not overfitting the curve:

$$\ln K = \frac{A}{RT^2} + \frac{B}{RT} + \frac{C}{R} \tag{2}$$

where R is in $\mathrm{cal \cdot mol^{-1} \cdot K^{-1}}$. The availability of experimental data limits our interest to the temperature range 218 to 353 K, so we have fit this form to Kao et al.'s association-constant data over only this range. The resulting values for the A, B, and C parameters are presented in Table I. Values of Δh_a^* yielded by this form are in reasonable accord with the values of Kao et al.

Table I. Fitting Parameters for ln K [Eq. (2)]

Use	Temp. range (K)	$A \times 10^{-5\,a}$	$B \times 10^{-4\,a}$	$C \times 10^{-2\,a}$
C_p vap				
15.5 kPa	253–353	−13.5539	4.7736	−1.4126
56.0 kPa	273–353	−13.6386	4.7759	−1.4125
96.1 kPa	293–353	−17.7653	5.0314	−1.4519
C_p liq (98.8 kPa)	218–293	−0.1763	3.4138	−1.0940

[a] The units for these parameters are as follows: A in $\text{cal} \cdot \text{K} \cdot \text{mol}^{-1} \cdot \text{atm}^{-5}$, B in $\text{cal} \cdot \text{mol}^{-1} \cdot \text{atm}^{-5}$, and C in $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \cdot \text{atm}^{-5}$.

The second contribution to the enthalpy, that associated with the transformation from the ideal-gas mixture to the real mixture, requires knowledge of the derivatives of the EOS parameters with respect to temperature. These values, a_1, a_6, b_1, and b_6, are tabulated by Kao et al. as functions of temperature, but their derivatives are not provided. Unfortunately the temperature dependence of their tabled values is not very smooth. We found that a sixth-degree polynomial in the absolute temperature was appropriate to describe the temperature dependence. Regardless, the adequacy of this description is not critical to the characterization of the heat effects as the EOS contribution to the enthalpy for many states of interest is much less than the association contribution. Values for the fitting constants are listed in Table II. Note that separate parameters for b_1 need not be found, as one of the assumptions of the Kao model is that b_1 is one-sixth of b_6 at all temperatures.

Table II. Constants Used in Fitting EOS Parameters to the Following Functional Form: $D(T) = d_0 + d_1 T + d_2 T^2 + d_3 T^3 + d_4 T^4 + d_5 T^5 + d_6 T^6$

EOS parameters	a_1	a_6	b_6
d_0	-3.589×10^{7}	-1.057×10^{9}	-1.192×10^{3}
d_1	9.299×10^{5}	2.328×10^{7}	2.709×10^{1}
d_2	-8.591×10^{3}	-2.040×10^{5}	-2.384×10^{-1}
d_3	4.123×10^{1}	9.389×10^{2}	1.113×10^{-3}
d_4	-1.089×10^{-1}	-2.396×10^{0}	-2.887×10^{-6}
d_5	1.508×10^{-4}	3.219×10^{-3}	3.943×10^{-9}
d_6	-8.558×10^{-8}	-1.779×10^{-6}	-2.213×10^{-12}

3. RESULTS

Kao et al. [7] examined the heat of vaporization as part of their study. They found that the model characterizes well the anomalous shape of the curve, including its large maximum upon approach of the critical temperature. Of course, this success is not surprising, given that the model is fit point-by-point to the vapor pressure and the liquid and vapor densities. We [27] too have found that the AEOS performs admirably when applied to this task but, because it attempts an analytic description of the temperature dependence of its modeling parameters, it does not exhibit the quantitative accuracy displayed by the Kao model (except perhaps at lower temperature, where the Kao model seems to fail).

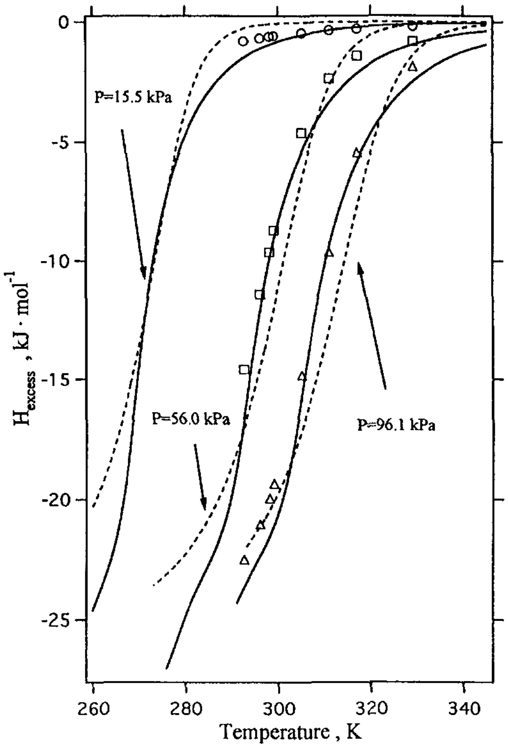

Fig. 1. Excess enthalpy of the superheated vapor at low pressure. The AEOS model (solid line) and the Kao model (dashed line) are compared to the smoothed data (open circle, open square, open triangle) of Vanderzee and Rodenburg [29]. Pressures as indictated.

Figure 1 shows the excess enthalpy, H_{excess}, of the superheated vapor at low pressures as a function of temperature. On average, the AEOS seems to overestimate the values for H_{excess} and shows sharper deviations from ideality than what experiments predict. In contrast, the Kao model predicts initially smaller deviations from ideality, but tends to fall off less sharply to nonideality than both the AEOS and the experimental data. On the whole the description provided by both models is rather good, given that they are fit primarily to volumetric data at saturation.

A more stringent test of any thermodynamic model is how it predicts second-derivative properties such as the heat capacity. In Fig. 2, we show the constant-pressure heat capacity of the superheated vapor at the same states shown in Fig. 1. Both models show the prominent feature of these

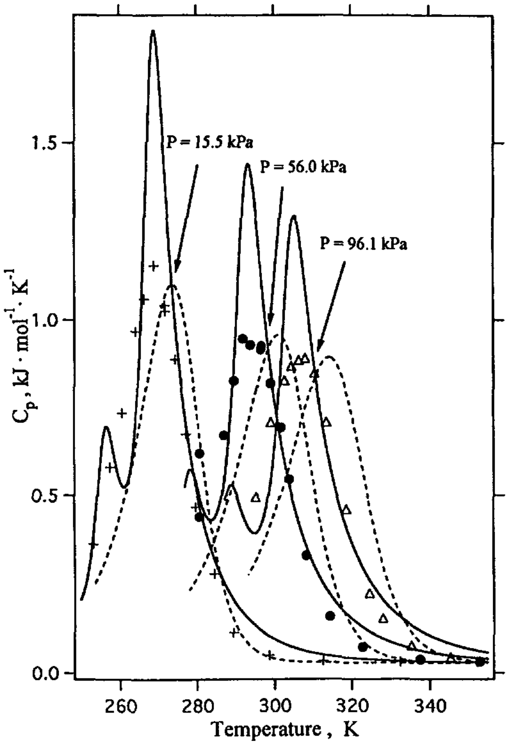

Fig. 2. Constant pressure molar heat capacity for the superheated vapor at low pressures. The AEOS model (solid line) and the Kao model (dashed line) are compared to experimental data (cross, filled circle, open triangle) from Franck and Meyer [30]. Pressures as indicated.

curves, which is a sharp maximum that arises from the association effects. It is seen, however, that while the AEOS predicts the correct temperature at which the peaks occur, it severely overestimates the maximum values of C_p. The Kao model is much closer to the predicted height of the maximum values but tends to overestimate the temperature at which they occur. The AEOS also predicts secondary maxima below the peaks in the heat capacity indicative of a change in the important clusters over that temperature region. The Kao model, constrained to only monomers and hexamers, is devoid of this effect. The experimental data do not support the existence of additional peaks, although the 56.0 kPa curve seems to exhibit a shoulder. Both models, as expected, collapse to the value of the ideal gas heat capacity at higher temperatures.

Our final test of the models compares the constant pressure liquid heat capacities C_p at 98.8 kPa to experimental values. This is shown in Fig. 3.

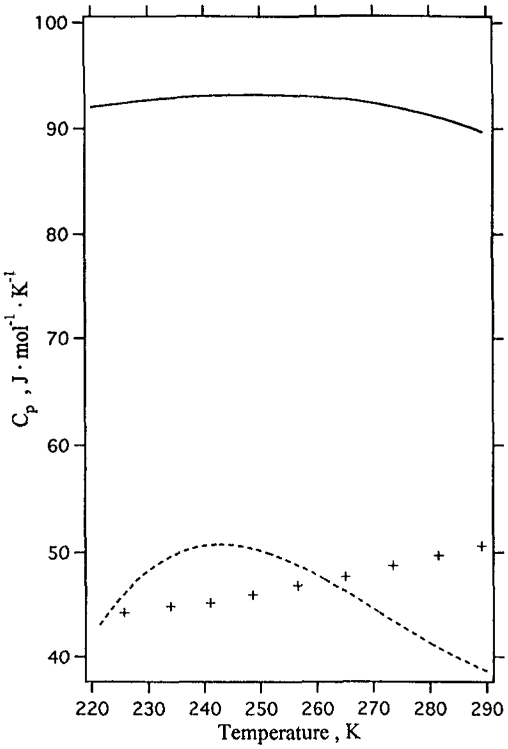

Fig. 3. Constant pressure molar heat capacity for the compressed liquid at 98.8 kPa. The AEOS model (solid line) and the Kao model (dashed line) are compared to experimental data (cross) from Hu et al. [31].

The AEOS overestimates C_p by a factor of two, while the Kao model fluctuates above and below the literature data with errors of about 10%. The overestimation for the AEOS is due in large part to the high value predicted by Z^{ch} for this state, which translates into a higher than predicted amount of association in the liquid.

4. CONCLUDING REMARKS

The issue here is whether a simple association scheme for HF can accurately predict the heat effects relative to an unconstrained, yet biased association scheme. The simple association scheme of the Kao model, using only monomers and hexamers, was able to predict the heat of vaporization, liquid heat capacity, and maximum vapor heat capacity better than the AEOS. Only in the location of the peaks in the vapor heat capacity did the AEOS outperform the Kao model.

We would be remiss if we did not emphasize the fact that the data sets used in fitting the parameters of both models are not the same. Additionally, as alluded to when describing the models, the procedure used for determining the parameters (i.e., temperature dependent parameters vs. parameters fit at each temperature) were different. Thus, any conclusions drawn directly on the validity of either association scheme without using identical data sets and parameter fitting methodologies would be premature.

An extension of the Kao model to incorporate more oligomers would add a level of complexity in parameter fitting which would seem to counteract its usefulness. Thus, a fixed association scheme using a closed form EOS like the AEOS may be an effective compromise between the two extremes studied here. On the other hand, when treating heat effects it is most important to obtain a good characterization of the temperature dependence of the association equilbria. Much of the effectiveness of the Kao model stems from its nonparametric description of the equilibrium with temperature. A model that correctly incorporates the qualitative features of association (i.e., does not neglect important oligomers) has a better likelihood of describing the heat effects while using only a simple model for the temperature dependences.

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