Thermal Properties of Hydrogen Fluoride from EOS+Association Model

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Hydrogen fluoride (HF) has found a wide variety of uses in the chemical process industry. It is used as an alkylation catalyst in the making of high-octane fuel, it provides a fluoride ion source in the electrolytic production of aluminum, and it is also the fluorine source in fluorocarbon manufacture. Intrinsic to the successful design of separation and heat-transfer equipment utilizing HF is its accurate thermodynamic description. Extensive hydrogen bonding in HF makes popular equations of state such as Peng-Robinson ill-equipped to provide a useful model. Additionally, and more debilitating, is the scarcity of HF experimental data due to its extreme caustic nature.

Recently, Lencka and Anderko (1993) proposed a thermodynamic model for HF which treats the chemical effects of the association reactions separately from the physical effects of the associated cluster interactions. This relatively simple model was used to study the heat of vaporization of HF from 233.15 K to its predicted critical point. Additionally, constant pressure and constant volume molar heat capacities are derived from the theory and compared to literature data.

Other models for HF similar to the one studied in this article have appeared recently (Chai Kao et al., 1995; Twu et al., 1993; Economou and Peters, 1995). These models, while effective in their prediction of heat of vaporization, are much more demanding computationally than that proposed by Lencka and Anderko (1993). Its simplicity and effectiveness makes the latter model appealing as a focus for this present study.

Anderko Model

Background and theory

The so-called association + equation of state (AEOS) model of HF has its origins in many articles (Heidemann and Prausnitz, 1976; Anderko, 1989a,b,c, 1990, 1991; Anderko and Malanowski, 1989; Anderko and Prausnitz, 1994). We will 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 (Lambert, 1953). 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. Thus, Z is written as

$$Z = Z^{ph} + Z^{ch} - 1 \tag{1}$$

This separation of Z has a simplicity that belies the sophistication of the ideas that justify it. The chemical contribution is expressed in terms of the ratio of the total number of associated clusters (considering all i-mers) to the apparent number of monomers (that is, the number that would be present if there were no association). In principle, this ratio depends on the detailed chemical equilibria of the association reactions, which in turn are influenced by the physical contribution to the equation of state (reflected in Z^{ph}). An important simplifying feature of the AEOS is that the physical contribution to Z is completely decoupled from the chemical equilibria. Originally (Anderko, 1989a,b,c; Anderko and Malanowski, 1989), this simplification was justified by reference to a corresponding separation of coefficients of the virial series, and to earlier findings (Ikonomou and Donohue, 1986) that the decoupling could be achieved rigorously for specific equations-of-state using specific combining rules for the multimer-multimer interactions. Later, Anderko (1990) showed more generally how cancellation of the fugacity coefficients in the i-merization equilibria could be obtained for a general cubic equation of state by proper selection of combining rules.

A critical input to the treatment is the association model, which describes how the association equilibrium constant K_i depends on i. Anderko (1991) presented another important result when he demonstrated that in the AEOS framework, Z^{ch} depends only on the dimensionless density $q \equiv RTK/v$, where R is the gas constant, T is the absolute temperature, $K(T)$ is the equilibrium constant for the dimerization reaction, and v is the apparent molar volume; this result assumes that the higher-order association equilibrium constants are given in terms of K, that is, a one-constant model is invoked.

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Table 1. Parameters for Z^{ch} (Eq. 2)

D_1	7.8291499	D_5	55.955726
D_2	−27.582139	D_6	−2.9442697
D_3	113.57927	D_7	1.6500385
D_4	−88.229013	D_8	0.10927261

Table 2. Parameters for Dimerization Constant K (Eq. 3)

Δh^o	−35.069	kJ/mol
Δc_p^o	52.68	J/mol·K
Δs^o	−133.67	J/mol·K
T^o	273.15	K

This result greatly simplifies the application of the AEOS treatment.

Lencka and Anderko's (1993) model of HF used a Poisson-like distribution to relate the higher-order association constants to the dimerization constant K. For this choice, the ideal-gas chemical equilibrium problem needed to determine $Z^{ch}(q)$ cannot be solved in a simple closed form. Instead, Lencka and Anderko characterized the dependence numerically and fit the result to a simple form

$$Z^{ch}(q) = \left(1 + \sum_{n=1}^{8} D_n q^n\right)(1+q)^{-8} \tag{2}$$

where the parameters D_n are listed in Table 1. Subsequently, they applied the model over a range of temperatures to arrive at a temperature dependence for the dimerization constant K

$$\ln K = \frac{-\Delta h^o + \Delta c_p^o T^o}{RT} + \frac{1}{R}(\Delta s^o - \Delta c_p^o(1 + \ln T^o)) + \frac{\Delta c_p^o \ln T}{R} \tag{3}$$

with parameters (Lencka and Anderko, 1993) given in Table 2. [Δh^o is the standard enthalpy of association (kJ/mol), Δc_p^o is the standard heat capacity of association (J/mol·K), Δs^o is the standard entropy of association (J/mol·K), and T^o is the reference temperature (K).]

Finally, Lencka and Anderko (1993) described the physical part of the compressibility factor by the Peng-Robinson equation of state

$$Z^{ph} = \frac{v-b}{v} - \frac{av}{RT(v^2 + 2bv - b^2)} \tag{4}$$

with $b = 9.69$ cm^3/mol and a given by

$$a(T) = 10^6\left\{0.7187 + 0.2734 \exp\left[-0.6232\left(\frac{T}{100} - 4.02\right)^2\right]\right\} \tag{5}$$

in units of cm^6·bar/mol^2.

Heat effects

The enthalpy of any fluid is conveniently written in terms of the ideal gas (IG) and residual (r) contributions

$$h(T,P) = h^{IG}(T) + h^r(T,P) \tag{6}$$

In the ideal gas state only monomer exist ($Z^{ch} = 1$), thus, we apply the rigid rotor/harmonic oscillator approximations for the heteronuclear diatomic HF to compute the ideal gas contribution from statistical mechanics (McQuarrie, 1976) as

$$h^{IG}(T) = \frac{7}{2}R(T - T^o) + R\theta\left(\frac{1}{e^{\theta/T} - 1} - \frac{1}{e^{\theta/T^o} - 1}\right) \tag{7}$$

where θ is characteristic temperature of vibration and $\theta =$ 5,955.16 K for HF (Atkins, 1982); ^{o} is the arbitrary reference state at which $h^{IG} \equiv 0$.

The residual part of the enthalpy is handled more easily when separated into a chemical and physical contribution, corresponding to the separation of Z. Standard thermodynamic manipulations (Prausnitz et al., 1986) then yield for the chemical contribution

$$h^{r^{(ch)}} = [\Delta c_p^o(T^o - T) - \Delta h^o - RT](Z^{ch} - 1) \tag{8}$$

and for the physical contribution, solely from the Peng-Robinson equation of state (Melhem et al., 1989)

$$h^{r^{(ph)}} = \frac{1}{2\sqrt{2}b}\left[a - T\left(\frac{da}{dT}\right)\right] \ln \frac{[v + b(1-\sqrt{2})]}{[v + b(1+\sqrt{2})]} \tag{9}$$

with da/dT derived from Eq. 5.

Then, the complete residual enthalpy is given by

$$h^r = h^{r^{(ch)}} + h^{r^{(ph)}} + RT(Z-1) \tag{10}$$

Corresponding formulas for the components of the heat capacity are presented in the Appendix.

Results

In Figure 1 we plot the heat of vaporization predicted by the AEOS, along with published experimental data. Note that we have excluded the data below 333 K from Jarry and Davis (1953) as these have been previously concluded to be unreliable (Yabroff et al., 1964). The heat of vaporization of HF is unusual in that it rises to a pronounced maximum at about 405 K before falling off sharply to zero at the critical point, 461.1 K. We see that the AEOS compares favorably to data at lower temperatures and is qualitatively correct up to the critical point. This is not too surprising as the model uses experimental liquid and vapor volumes and vapor pressures in determining the parameters used for the AEOS.

A more stringent test of the model is how it predicts second-derivative properties such as the heat capacity. In Figure 2 we show the constant volume molar heat capacity c_v predicted from the model, compared to experimental data from Franck and Spalthoff (1957) for the liquid and the vapor. The predictions of the theory are in the vicinity of the experimental data. Rather than follow the data exactly however, the model predicts values of c_v that are at times either greater or less than the experimental data over the ranges shown. Particularly bad is the constant-pressure molar heat capacity c_p of the compressed liquid; this quantity is presented on the same figure, and one can see that the prediction of the the-

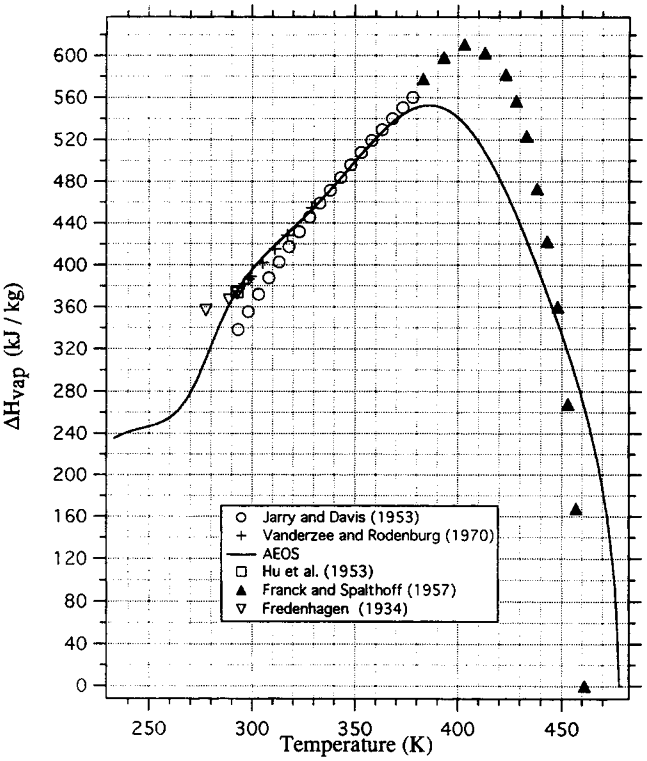

Figure 1. Heat of vaporization as function of temperature.

The AEOS model is compared to experimental data from the literature.

ory lies nowhere near the experimental data (Hu et al., 1953). Further analysis has revealed the cause is the overestimation of the chemical contribution to the molar heat capacity predicted by the model. This, in turn, indicates an overemphasis of association in the liquid at this state.

The constant-pressure heat capacity of the superheated vapor displays interesting behavior. Figure 3 presents this quantity as a function of temperature for several pressures. A prominent feature of these curves is a pronounced maximum which arises from the association effects. That the peaks have their origin in an association effect is clear from plots of mean association number $\chi = 1/Z^{ch}$, which are superimposed on the figure. At each pressure, the association number begins a marked rise at about the point of the heat capacity maximum. The phenomenon is reminiscent of a phase transition at which an order parameter undergoes a discontinuous change that yields a singularity in the heat capacity. Of course, the effect is substantially attenuated here, as the multimers are not suddenly formed from the monomers at a sharply defined temperature. Although the theory overestimates the heights of the heat capacity maxima, it does well in locating the temperatures at which they occur. Also, the theory seems to indicate the presence of additional, smaller heat capacity maxima. Such features are not observed in the experimental data, although those taken at 56 kPa seem to display a shoulder. For all the pressures shown, c_p converges to its ideal gas value at higher temperatures. At lower temperatures, the ideal gas contribution is a very small part of the total heat capacity; although not evident from the figure, the physical contribution to c_p is smaller than either the ideal gas or the chemical parts at the conditions presented in Figure 3.

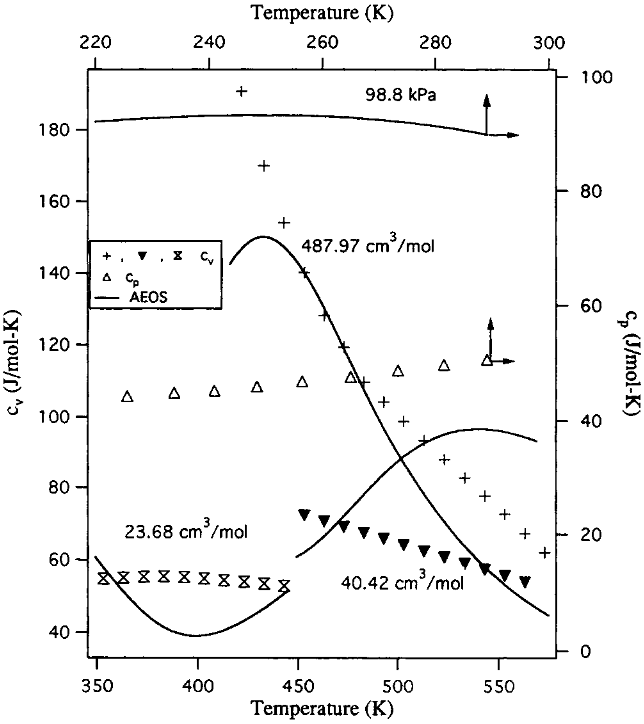

Figure 2. Molar heat capacities of liquid and vapor.

The AEOS model is compared to experimental data from the literature. Conditions of constant pressure or volume are indicated.

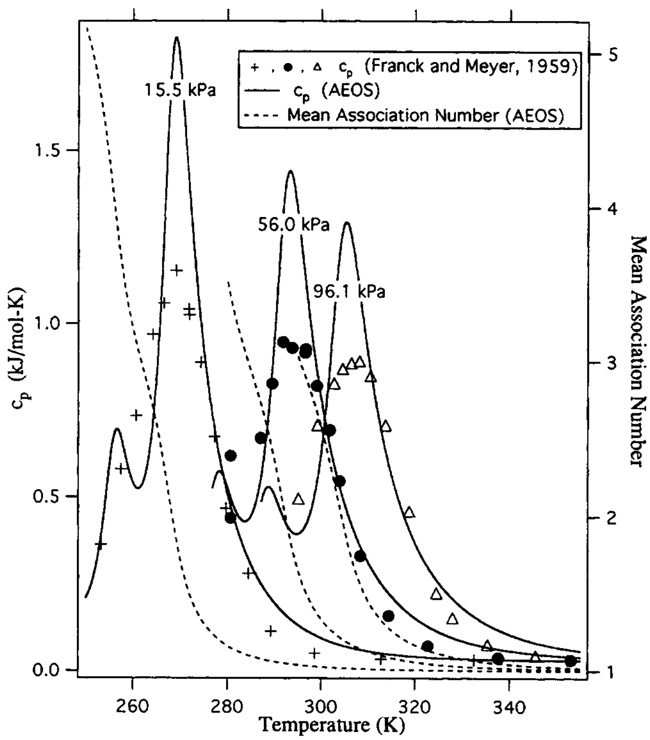

Figure 3. Constant-pressure molar heat capacity for superheated vapor at low pressures.

The AEOS model is compared to experimental data from the literature. The mean association number predicted by the AEOS model is plotted on right axis. Pressures as indicated.

Conclusions

It has been shown by Lencka and Anderko (1993) that the addition of an associating term to a cubic equation of state can effectively model the vapor-liquid equilibria of HF, most notably at temperatures below 400 K. We have shown that the heat effects obtained from this model compare well to experimental data taken from the literature, even though these data were never used to fit the parameters of the model. Although the model does well overall, we observe some quantitative differences between it and the data. The model does not capture effectively the smooth temperature dependence of the liquid heat capacities. Instead, the model heat capacities sometimes weave above and below the actual data over a range of temperature. The model does capture accurately the location but not the magnitude of association-induced maxima in the superheated vapor heat capacities.

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Appendix

The enthalpy was written as

$$h = h^{IG} + h^{r^{(ch)}} + h^{r^{(ph)}} + RT(Z-1) \qquad \text{(A1)}$$

The constant volume molar heat capacity is thus

$$c_v = \left(\frac{\partial (h - RTZ)}{\partial T}\right)_v = \left(\frac{\partial h^{IG}}{\partial T}\right)_v + \left(\frac{\partial h^{r^{(ch)}}}{\partial T}\right)_v + \left(\frac{\partial h^{r^{(ph)}}}{\partial T}\right)_v - R \qquad \text{(A2)}$$

The individual terms are as follows

$$\left(\frac{\partial h^{IG}}{\partial T}\right)_v = \frac{7}{2}R + \frac{e^{\theta/T} R \theta^2}{(e^{\theta/T} - 1)^2 T^2} \qquad \text{(A3)}$$

$$\left(\frac{\partial h^{r^{(ch)}}}{\partial T}\right)_v = (1 - Z^{ch})(\Delta c_p^o + R) + (\Delta c_p^o (T^o - T) - \Delta h^o - RT)\left(\frac{\partial Z^{ch}}{\partial T}\right)_v \qquad \text{(A4)}$$

$$\left(\frac{\partial h^{r^{(ph)}}}{\partial T}\right)_v = -\ln\left(\frac{v + (1-\sqrt{2})b}{v + (1+\sqrt{2})b}\right)\left(\frac{T\dfrac{d^2 a}{dT^2}}{2\sqrt{2}b}\right) \qquad \text{(A5)}$$

The constant pressure molar heat capacity is then written as

$$c_p = c_v - (RZT^2/v)\left[\frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)_v + \frac{1}{T}\right]^2 \Bigg/ \left[\frac{1}{Z}\left(\frac{\partial Z}{\partial v}\right)_T - \frac{1}{v}\right] \qquad \text{(A6)}$$

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