

# Improved Thermodynamic Equation of State for Hydrogen Fluoride

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We modify the Lencka and Anderko fit of the chemical part of the compressibility factor of the AEOS model used to describe hydrogen fluoride. This modification results in improved agreement with experiment in the calculation of the heat capacity with little negative effect on the prediction of other properties. We report new parameters for this model and provide the equations for the fugacity coefficient.

The recent rise in production of hydrofluorocarbons (HFC's), used as alternative refrigerants, has resulted in a renewed interest in the modeling of its fluorine source, hydrogen fluoride (HF). Since HF affects the properties of its mixtures disproportionate to its amount present, a very accurate thermodynamic description of HF is needed to correctly size separation and heat-exchange equipment used in the processing of HFC's. Popular models, such as conventional cubic equations of state (EOS), have been shown to be unsuccessful in modeling HF, since extensive hydrogen bonding occurs at all but the most ideal-gas states.<sup>1</sup> Also, HF is notoriously dangerous to work with, so experimental data used in parameter fitting for any proposed model are scarce.

The way to improve current models for HF has been to explicitly include the association interactions which describe the hydrogen bonding in the system. Two distinct paths have been attempted. The first type are molecular-based models which describe each molecular interaction separately, including association. The second type explicitly includes a chemical reaction model in a conventional cubic equation of state.

There have been two attempts to model HF using molecular-based models. The first was by Economou and Peters via the association perturbed anisotropic chain theory (APACT)<sup>2</sup> in 1995, which, while providing fairly accurate results for the VLE, is not presented in a "closed-form", making it less desirable for use in process simulators. The second approach was based on the statistical associating fluid theory (SAFT) using a hard-sphere reference.<sup>3</sup> This model, too, does fairly well in its VLE prediction and is closed, but it does not predict the heat effects of HF with any accuracy. Subsequent improvements to the SAFT to remedy this problem for HF have met with only modest success.<sup>4,5</sup>

The addition of a chemical reaction which describes cluster formation in associating fluids to a cubic equation of state is not new.<sup>6</sup> Application of this idea to HF has been attempted by various researchers.<sup>7–10</sup> At the crux of this procedure is the association scheme, which one sets *a priori* to describe what oligomers will exist in the system. Several of these types of schemes have been proposed.<sup>11</sup>

Recently, we selected a thermodynamic model of the latter type for further study, namely the association + equation of state (AEOS) model of Lencka and Anderko.<sup>8</sup>

We selected this model over the others because of its computational simplicity and effectiveness at predicting phase coexistence. Our study<sup>12,13</sup> looked at the thermal properties of HF predicted by this model. We found only qualitative agreement between the AEOS and experimental data for the heat effects. We have since observed that a simple modification of the AEOS model for HF can be made to bring the heat effects into much better agreement with experiment, without compromising the fit of the other properties. This modification is the subject of this Note.

## AEOS Model

In this section, we review the AEOS model for HF, as formulated by Lencka and Anderko.<sup>8</sup> The AEOS is best expressed in terms of the compressibility factor  $Z$ , which is divided into a chemical part  $Z^{\text{ch}}$  and a physical part  $Z^{\text{ph}}$ , such that  $Z = Z^{\text{ch}} + Z^{\text{ph}} - 1$ . The chemical part treats the formation of clusters, described via self-association chemical reactions which occur between a chain of  $i$  HF monomers and a single HF monomer unit. Once these clusters form, the physical part describes the nonspecific interactions between the clusters.

In the AEOS, the equilibrium constant for a self-association reaction is given as the product of a weighting function and the dimerization constant  $K$ . If this weighting function is unity, the equilibrium constant for subsequent chain additions is uniform with chain length. However, to account for the propensity of a system to form specific oligomers at the expense of others, a Poisson-like distribution function  $f$ , which is a function of chain length, has been used. Thus,

$$K_{j,j+1} = f(j)K \quad (1)$$

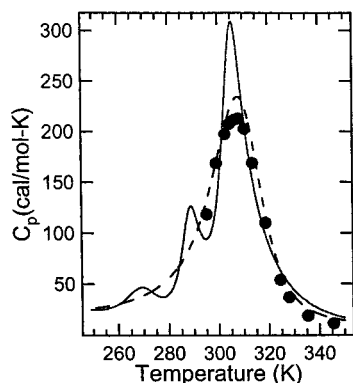
$$f(j) = \frac{\kappa^{j-1}}{(j-1)!} \quad (2)$$

where  $\kappa$  is a rough indication of the peak in this distribution. The  $i$ -merization reaction constants are then given as

$$K_i = [\prod_{j=1}^{i-1} f(j)] K^{i-1} \quad (3)$$

The chemical part of the compressibility factor is the ratio of the number of actual moles of oligomers in the system to the number of HF monomer units, which is

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**Figure 1.** Heat capacity of the super-heated vapor at 721 mmHg. The solid line is as calculated from  $Z_{LA}^{ch}$  while the dashed line is calculated from  $Z_{num}^{ch}$ . The experimental points are given as filled circles.<sup>16</sup>

written as

$$Z^{ch} = \frac{\sum_{i=1}^{\infty} N_i}{\sum_{i=1}^{\infty} i N_i} \quad (4)$$

This can be written also as

$$Z^{ch} = \frac{\sum_{i=1}^{\infty} K_i (Z^{ch} x_1 RT/v)^i}{\sum_{i=1}^{\infty} i K_i (Z^{ch} x_1 RT/v)^i} \quad (5)$$

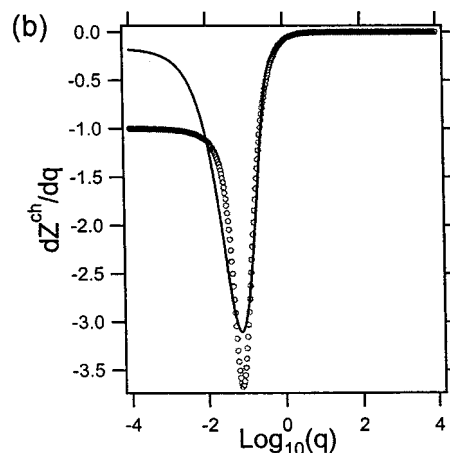
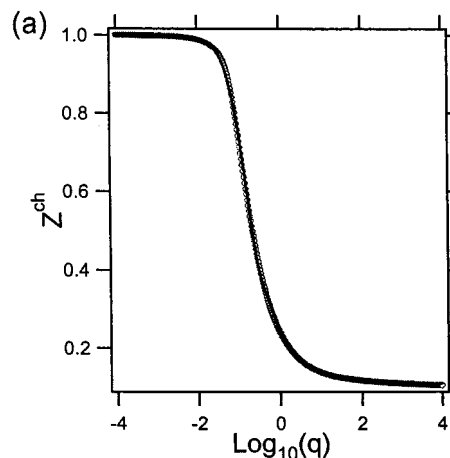
where  $x_1$  is the monomer mole fraction,  $R$  is the gas constant,  $T$  is the temperature, and  $v$  is the molar volume. The denominator of eq 5 is equal to  $RT/v$ , and so the value of  $Z^{ch}$  at a given state is found by solving for  $Z^{ch} x_1 RT/v$  and then inserting this value into eq 5 to find  $Z^{ch}$ . Anderko has shown<sup>14</sup> that  $Z^{ch}$  can be written as a function of the group  $RTK/v \equiv q$ , and so a properly chosen function of  $q$  which mimics well the behavior of  $Z^{ch}$  will result in a computationally convenient equation of state. The functional form Lencka and Anderko chose is a ratio of polynomials given as the following<sup>8</sup>

$$Z_{LA}^{ch}(q) = \frac{1 + \sum_{m=1}^8 D_m q^m}{(1 + q)^8} \quad (6)$$

where  $D_m$  are the fitted parameters for this function. (Note that  $D_m$  are fit not to experimental data but to the numerical solution of eq 5, after regression to experiment has been completed.)

Additionally, the dimerization constant is made temperature dependent and is parameterized through three parameters as follows

$$\ln K = \frac{-\Delta h^\circ + \Delta c_p^\circ T^\circ}{RT} + \frac{1}{R} (\Delta s^\circ - \Delta c_p^\circ (1 + \ln T^\circ)) + \frac{\Delta c_p^\circ \ln T}{R} \quad (7)$$



**Figure 2.** Comparison of (a)  $Z_{LA}^{ch}$  (solid line) with  $Z_{num}^{ch}$  (empty circles) and their (b) corresponding derivatives as a function of  $q$ . Note the poor agreement in the depth of the well and in the small  $q$  limit in (b).

**Table 1. Parameters from the AEOS as per the  $Z_{VK}^{ch}$  Fit<sup>a</sup>**

|                    |           |                  |            |
|--------------------|-----------|------------------|------------|
| $p_1$              | 0.586957  | $p_7$            | -0.240883  |
| $p_2$              | 0.726587  | $p_8$            | 0.726588   |
| $p_3$              | 0.874699  | $p_9$            | 0.186551   |
| $p_4$              | 0.172164  | $p_{10}$         | -0.004537  |
| $p_5$              | -1.147891 | $p_{11}$         | 0.072004   |
| $p_6$              | -2.421866 |                  |            |
| $\kappa$           | 4.274     | $\Delta h^\circ$ | -34188.112 |
| $\Delta c_p^\circ$ | 41.406    | $\Delta s^\circ$ | -129.696   |
| $b$                | 9.8044    | $f_1$            | 0.74280    |
| $f_2$              | 0.26267   | $f_3$            | -0.60385   |

<sup>a</sup> The units are as follows:  $\Delta h^\circ$ , J/mol;  $\Delta s^\circ$  and  $\Delta c_p^\circ$ , J/mol·K;  $b$ , cm<sup>3</sup>/mol;  $A(T)$ , bar·cm<sup>6</sup>/mol<sup>2</sup>.

Here, the superscript  $^\circ$  is the reference state, which was chosen to be 273 K.

To complete the EOS, a physical part must be used to account for interactions between the clusters that form. The Peng–Robinson equation of state<sup>15</sup> was chosen, with a constant value for the excluded volume parameter  $b$  and a temperature dependent energy parameter  $A(T)$  given by

$$A(T) = 10^6 \left( f_1 + f_2 \exp \left( f_3 \left( \frac{T}{100} - 4.02 \right)^2 \right) \right) \quad (8)$$

where  $f_i$  are fitted parameters.

Lencka and Anderko fit the parameters of this model, given elsewhere,<sup>8</sup> to one- and two-phase densities as well as the vapor pressure. The model does predict the

saturated liquid and vapor densities and vapor pressure well from 200 to 400 K but fails in the near-critical region. The heat of vaporization predicted by the model is only semiquantitative to qualitative. The heat capacity predicted by the model, shown in Figure 1, gets the temperature at which the peak occurs correct but overestimates the value of  $C_p$  at the peak by nearly 50%. Additionally, the model predicts shoulders in the heat capacity which are not present in the experimental data.<sup>12,13</sup>

### Observations from the $Z^{\text{ch}}$ Fit

A key component in the AEOS is the functional form chosen for the fit of the chemical contribution to the compressibility factor  $Z^{\text{ch}}$ . To calculate heat effects, one needs to take derivatives of  $Z^{\text{ch}}$ ; thus, a deficiency in the fitting of  $Z^{\text{ch}}$  will be magnified when calculating heat effects. To see the effect of using the fitted functional form chosen by Lencka and Anderko,<sup>8</sup>  $Z_{\text{LA}}^{\text{ch}}$ , versus using the solution of eq 5, hereafter, called  $Z_{\text{num}}^{\text{ch}}$ , we once again examined the heat capacity, shown in Figure 1. As can be seen, the use of  $Z_{\text{num}}^{\text{ch}}$ , although time-consuming to calculate, actually yields very good agreement with experiment and contrasts sharply with the curve given by the use of  $Z_{\text{LA}}^{\text{ch}}$ ; the anomalous shoulders vanish, and the height of the peak is better described. To explore this more, we looked at  $Z_{\text{LA}}^{\text{ch}}$  and its derivative with respect to  $q$  relative to  $Z_{\text{num}}^{\text{ch}}$  which we show in Figure 2. As can be seen, though the form chosen by Lencka and Anderko for  $Z^{\text{ch}}$  seems reasonable, the derivative is poorly described, which gives rise to the poor agreement in the heat capacity.

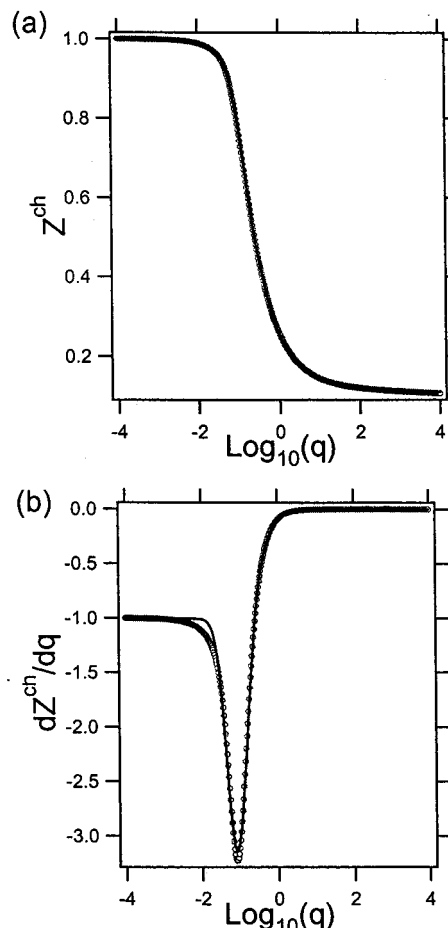
At this point we can take two paths. The first path is to change the parameters of the original  $Z^{\text{ch}}$  fit to allow for better agreement with  $dZ_{\text{num}}^{\text{ch}}/dq$ . The second path is to investigate other functional forms for  $Z^{\text{ch}}$  which better agree with  $Z_{\text{num}}^{\text{ch}}$ .

If we differentiate  $Z_{\text{LA}}^{\text{ch}}$  and notice that  $\lim_{q \rightarrow 0} dZ_{\text{num}}^{\text{ch}}/dq = -1$ , it is seen by inspection that  $D_1$  must be equal to 7.0. If we add this constraint to the fit and incorporate knowledge of  $dZ_{\text{num}}^{\text{ch}}/dq$  into determining  $D_n$ , only marginal improvement is made in the prediction of the heat capacity. This led us to try different functional forms for  $Z^{\text{ch}}$ , described below.

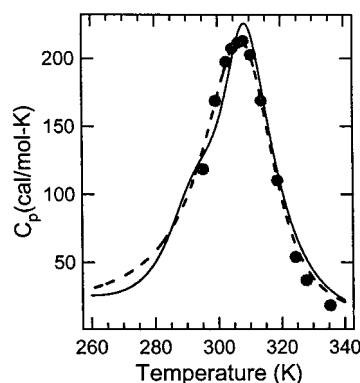
### Modifications to AEOS

We explored several functional forms for  $Z^{\text{ch}}$  as well as the introduction of rings to the model and report the best combination.<sup>1</sup> We find that a model which includes only chains and is fit to only two-phase data (saturated liquid and vapor densities and vapor pressure) gave the best agreement with experiment. The next step is to find a functional form which best mimics  $Z_{\text{num}}^{\text{ch}}$  and  $dZ_{\text{num}}^{\text{ch}}/dq$ . This was accomplished as described below.

By inspection of Figure 2, it is seen that a combination of a highly peaked, symmetric function added to a step function could potentially describe the form of  $dZ_{\text{num}}^{\text{ch}}/dq$ . Therefore, a Gaussian function was added to an error function as the form for this new function. This



**Figure 3.** Comparison of (a)  $Z_{\text{VK}}^{\text{ch}}$  (solid line) with  $Z_{\text{num}}^{\text{ch}}$  (empty circles) and their (b) corresponding derivatives as a function of  $q$ . Note that the values for  $Z_{\text{num}}^{\text{ch}}$  (and its derivative) are different here than in Figure 2, as a different value of  $\kappa$  is used.



**Figure 4.** Heat capacity of the super-heated vapor at 721 mmHg. The solid line is as calculated from  $Z_{\text{VK}}^{\text{ch}}$  while the dashed line is calculated from  $Z_{\text{num}}^{\text{ch}}$ . The experimental points are as per Figure 1.

was given as

$$\frac{dZ_{\text{VK}}^{\text{ch}}}{dq} = -1 + w_1 \exp\left(-\frac{(x - w_2)^2}{w_3}\right) + \frac{1}{2}[\text{erf}(w_4 x + w_5) + 1] \quad (9)$$

where  $x = \ln q$  and  $w_j$  are fitting parameters. Upon integration to obtain  $Z^{\text{ch}}$  it was observed that the region of large  $q$  was not modeled correctly. Thus, a decay

function,  $w_6 \exp(x)/(1 + w_7 \exp(x))$ , was added to allow the flexibility to capture this tail. Integration of this formula leads to the final function we report

$$Z_{\text{VK}}^{\text{ch}} = p_1 + \frac{1}{2} \exp(x) [\text{erf}(p_2 x + p_3) - 1] + p_4 \text{erf}(p_5 x + p_6) + p_7 \text{erf}(p_8 x + p_9) + \frac{p_{10} \exp(x)}{1 + p_{11} \exp(x)} \quad (10)$$

where  $p_1$  is a fitted constant of integration and  $p_{2-11}$  are constants given in terms of  $w_{1-7}$ . Following Lencka and Anderko,<sup>8</sup> once the parameters for  $Z_{\text{VK}}^{\text{ch}}$  have been fixed, we once again modify the other model parameters (excluding  $\kappa$ ) in order to best reproduce the experimental saturated liquid and vapor densities and vapor pressure. All of our model parameters are contained in Table 1.

Since the value for the parameter  $\kappa$  is different from the value reported by Lencka and Anderko,<sup>8</sup> the distribution function of equilibrium constants and the value of  $Z_{\text{num}}^{\text{ch}}$  as a function of  $q$  are changed. To demonstrate how this new functional form,  $Z_{\text{VK}}^{\text{ch}}$ , compares with  $Z_{\text{num}}^{\text{ch}}$ , we plot this relationship and that for the derivatives in Figure 3. As can be seen, the  $Z_{\text{VK}}^{\text{ch}}$  fit is very reasonable and the comparison between the derivatives is in better agreement relative to that shown in Figure 2. In Figure 4 we present the heat capacity from the new parameter set as calculated via  $Z_{\text{num}}^{\text{ch}}$  and  $Z_{\text{VK}}^{\text{ch}}$ . Good agreement is seen between the two, and the comparison with experiment is much improved relative to that obtained from  $Z_{\text{LA}}^{\text{ch}}$ , although a very slight shouldering remains as a result of including the  $q/(1 + q)$  term for  $Z_{\text{VK}}^{\text{ch}}$  to account for the tail in  $Z_{\text{num}}^{\text{ch}}$ .

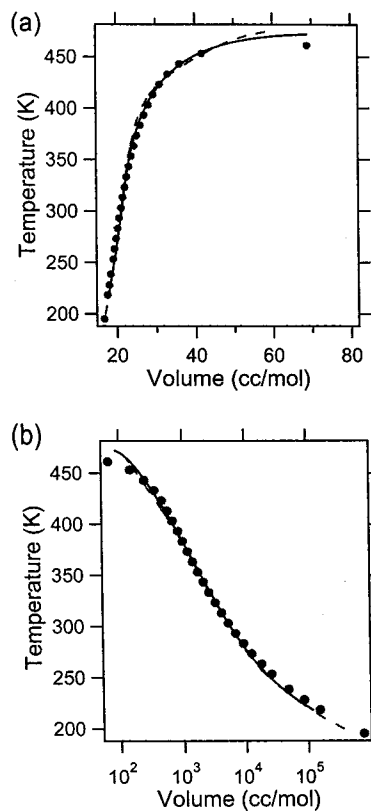
Now that a new functional form,  $Z_{\text{VK}}^{\text{ch}}$ , has been developed which improves the accuracy of the heat capacity fit and removes the unphysical shoulders, care must be taken to examine that agreement with other important quantities is satisfactory.

In Figure 5 we present the saturated liquid and vapor volumes as predicted by the original AEOS and with the modified form for the fit of the chemical compressibility factor, while Figure 6 shows the vapor pressure and Figure 7 gives the heat of vaporization. The most noticeable difference between the two is found in the heat of vaporization. Although the original AEOS gives a more reasonable result relative to experiment at lower temperatures, the modified form does better at higher temperatures.

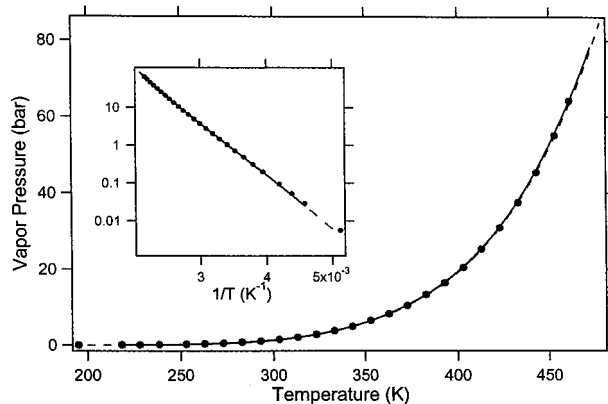
In Figure 8 we compare with experiment the heat capacity as predicted by the  $Z_{\text{VK}}^{\text{ch}}$ -based and the  $Z_{\text{LA}}^{\text{ch}}$ -based models. The new functional form chosen for  $Z_{\text{num}}^{\text{ch}}$  now provides near quantitative values for the heat capacity.

## Conclusions

A successful, closed-form thermodynamic model was recently reported for hydrogen fluoride.<sup>8</sup> When tested on its prediction of heat effects,<sup>12,13</sup> the model exhibited shortcomings based on the functional form used to describe the chemical contribution to the compressibility factor  $Z^{\text{ch}}$ . In this work we have modified the fit of  $Z^{\text{ch}}$  to better reproduce the heat capacity without compromising the accurate prediction of other properties. The



**Figure 5.** (a) Saturated liquid and (b) vapor volumes. The results from  $Z_{\text{LA}}^{\text{ch}}$  are given as a dashed line while the results from  $Z_{\text{VK}}^{\text{ch}}$  are given as a solid line. The experimental data are given as filled circles.<sup>9</sup>



**Figure 6.** Vapor pressure. The inset shows the lower temperatures. The lines and symbols are as per Figure 5.

fugacity coefficient based on the new fit to  $Z_{\text{num}}^{\text{ch}}$  is given in the Appendix.

## Acknowledgment

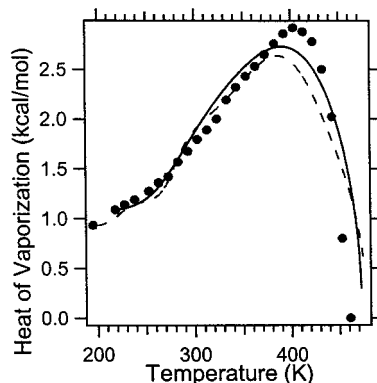
Acknowledgment is made to the National Science Foundation for support of this research. (Award CTS-9720705).

## Appendix

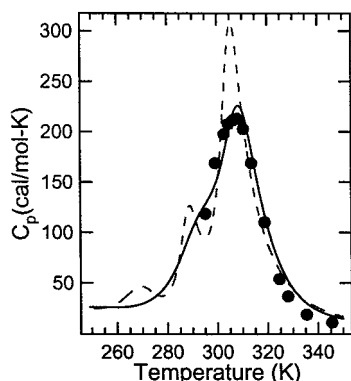
The fugacity coefficient is defined as

$$\ln \Phi = \int_0^{\rho} \frac{Z - 1}{\rho} d\rho - \ln(Z) + Z - 1 \quad (11)$$

Since  $Z = Z^{\text{ch}} + Z^{\text{ph}} - 1$ , we can write the fugacity



**Figure 7.** Heat of vaporization. The lines are as per Figure 5. The experimental data are given as filled circles.<sup>17</sup>



**Figure 8.** Heat capacity of the superheated vapor at 721 mmHg. The lines are as per Figure 5. The experimental data are given as filled circles.<sup>16</sup>

coefficient as

$$\ln \Phi = \int_0^\rho \frac{Z^{\text{ch}} - 1 + Z^{\text{ph}} - 1}{\rho} d\rho - \ln(Z) + Z - 1 \quad (12)$$

$$\ln \Phi = \int_0^\rho \frac{Z^{\text{ch}} - 1}{\rho} d\rho + \int_0^\rho \frac{Z^{\text{ph}} - 1}{\rho} d\rho - \ln(Z) + Z - 1 \quad (13)$$

$$\ln \Phi = \Lambda^{\text{ch}} + \Lambda^{\text{ph}} - \ln(Z) + Z - 1 \quad (14)$$

The “physical” part of the natural logarithm of the fugacity coefficient is given as

$$\Lambda^{\text{ph}} = \ln(Z^{\text{ph}}) - \ln(Z^{\text{ph}} C_b) - \frac{C_a}{2\sqrt{2}C_b} \times \ln\left(\frac{Z^{\text{ph}} + (1 + \sqrt{2})C_b}{Z^{\text{ph}} - (\sqrt{2} - 1)C_b}\right) \quad (15)$$

where  $C_a = AZ^{\text{ph}}/(RTv)$  and  $C_b = bZ^{\text{ph}}/v$ , with  $A$  given by eq 8 and  $b$  found from Table 1.

The “chemical” part of the natural logarithm of the fugacity coefficient is given as a sum of six terms in  $x = \ln q$ :

$$\Lambda^{\text{ch}} = \lambda_1 + \lambda_2 + \lambda_3 + \lambda_4 + \lambda_5 + \lambda_6 \quad (16)$$

$$\lambda_1 = -\exp(x)/2 \quad (17)$$

$$\lambda_2 = (p_4/p_5)[(p_5x + p_6) \operatorname{erf}(p_5x + p_6) + \exp(-(p_5x + p_6)^2/\sqrt{\pi})] \quad (18)$$

$$\lambda_3 = (p_7/p_8)[(p_8x + p_9) \operatorname{erf}(p_8x + p_9) + \exp(-(p_8x + p_9)^2/\sqrt{\pi})] \quad (19)$$

$$\lambda_4 = \exp(x) \operatorname{erf}(p_2x + p_3)/2 - \frac{1}{2} \exp\left(\frac{1 - 4p_2p_3}{4p_2^2}\right) \times \operatorname{erf}\left(\frac{2p_2^2x - 1 + 2p_2p_3}{2p_2}\right) - \frac{1}{2} \exp\left(\frac{1 - 4p_2p_3}{4p_2^2}\right) \quad (20)$$

$$\lambda_5 = (p_{10}/p_{11}) \ln(1 + p_{11} \exp(x)) \quad (21)$$

$$\lambda_6 = (p_1 - 1)x \quad (22)$$

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## ADDITIONS AND CORRECTIONS

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Volume 38, Number 12

**Recovery of Vanadium and Molybdenum from Spent Petroleum Catalyst of PEMEX.** Marín S. Villarreal, B. I. Kharisov,\* L. M. Torres-Martínez, and V. N. Elizondo

Page 4624. The authors' names should appear as S. Villarreal Marín and N. Elizondo Villarreal.

Page 4628. Additional acknowledgment is as follows: S.V.M. thanks CONACyT for Scholarship No. 112247.

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10.1021/ie991085j

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Volume 38, Number 9

**Selectivity and Deactivation of Diffusion-Limited Reactions in a Pore-Fractal Catalyst.** Moshe Sheintuch

Page 3269. The reference to the paper by Mougin et al. should read as follows:

Mougin, P.; Pons, M.; Villiermaux, J. Reaction and Diffusion at an Artificial Fractal Interface: Evidence of a New Diffusional Regime. *Chem. Eng. Sci.* **1996**, *51*, 2293–2302.

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Volume 38, Number 10

**Improved Thermodynamic Equation of State for Hydrogen Fluoride.** Donald P. Visco, Jr. and David A. Kofke\*

Page 4129. In the Appendix, we provide the equations needed to determine the various contributions to the fugacity coefficient. Equation 15, the "physical" part of the natural logarithm of the fugacity coefficient, should read as follows:

$$\Lambda^{\text{ph}} = \ln(Z^{\text{ph}}) - \ln(Z^{\text{ph}} - C_b) - \frac{C_a}{2\sqrt{2}C_b} \times \ln\left(\frac{Z^{\text{ph}} + (1 + \sqrt{2})C_b}{Z^{\text{ph}} - (\sqrt{2} - 1)C_b}\right) \quad (15)$$

All of the results previously reported were based on this equation.

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