Self-Association of Gases. 2. The Association of Hydrogen Fluoride[†]

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A reinvestigation of the classic HF gas $P-V-T$ data by Stohmeier and Brlegleb and by Fredenhagen using methods developed in this laboratory has shown that both data sets can be described by a monomer–trimer–hexamer association. There have been many conflicting reports about the self-association of HF gas at moderate temperatures (26–56 °C), and this prompted us to reexamine the problem of HF gas self-association. Extensive tests were made for various possible self-association models; various monomer–n-mer, monomer–n-mer–j-mer $(1,n,j)$, and indefinite self-associations were examined. The monomer–trimer–hexamer $(1,3,6)$ model described both sets of data best at all temperatures. Values of the nonideal terms, the equilibrium constants, and the thermodynamic functions $(\Delta H^\circ, \Delta U^\circ, \Delta S^\circ, \text{and} \Delta G^\circ)$ are reported for both data sets.

Introduction

At temperatures above its normal boiling point (19.7 °C) and below 80 °C, HF gas is reported to undergo a self-association; hydrogen bonds are involved in the association $(1-5)$. While the association has been studied extensively by $P-V-T$ measurements and by other techniques, the reported results seem to be at variance with each other. Hildebrand and his associates $(1, 2)$ believed that HF underwent an ideal monomer–hexamer association. Other studies have indicated that a more complex association is present $(3-5)$. Maclean, Rossotti, and Rossotti (5) applied their methods to Strohmeier and Brlegleb's (4) $P-V-T$ data; they concluded that definite evidence was obtained for the existence of HF, $(HF)_2$, and $(HF)_6$ in the gas phase. But they also stated that intermediate and higher oligomers may also be formed; they did report association constants for the monomer–dimer–hexamer association, as well as for extended series models. Using infrared spectroscopy Hollenberg (6) claimed that the absorption band at 389.5 ± 0.5 cm^{-1} was due to the HF trimer. Smith (7) also did infrared spectroscopy on HF gas in the region 320–420 cm^{-1} at various pressures; he concluded that monomer, dimer, and higher polymers may contribute to the absorption of infrared radiation, but attributed the previously reported trimer absorption band to an impurity.

Since the status of the HF gas self-association seemed ambiguous, it seemed appropriate to try methods that were developed in a previous paper for analyzing gas-phase self-associations under ideal or nonideal conditions (8). This method is formally identical with methods that have been used for analyzing self-associations in solution by membrane or vapor pressure osmometry $(9-11)$. From $P-V-T$ data one can obtain the number average molecular weights (M_{nc}), or their apparent values (M_{na}) under nonideal conditions (8). From a series of experiments at constant T one can use the M_1/M_{na} vs. c (concentration of gas in g L^{-1}) to obtain the weight av-

erage molecular weight (M_{wc}) and the weight fraction (f_1) of monomer, or their apparent values $(M_{wa}$ and $f_a)$ under nonideal conditions. Here M_1 is the molecular weight of the monomer. How these quantities $(M_{na}, M_{wa},$ and $f_a)$ are derived and how they and c can be used in the analysis of self-associations are described extensively in the previous publication and in other publications $(8, 11)$. With these quantities we can test for the presence or absence of many more types of self-associations than Maclean, Rossotti, and Rossotti (5) and others have been able to do. In addition, if an extended series of polymers of HF were present, then they might be analyzed as one of the indefinite self-association models $(12, 13)$. We will show with our methods that one can find a self-assoication model that will satisfactorily describe the observed self-association of HF gas at several temperatures. The data of Strohmeier and Brlegleb (4) will be used. In addition we will show that the same type of self-association will also describe Fredenhagen's HF data (3).

Evaluation of M_{na}, M_{wa} and ln f_a $(8-11)$

The principal data used here were collected by Strohmeier and Brlegleb (4); these are the same data that were analyzed by Maclean, Rossotti, and Rossotti (5). We will make the same assumptions that we did in the preceding paper (8); thus, we can obtain values of the apparent number average molecular weight M_{na} from measurement of the total pressure P as a function of the concentration c (in g L^{-1}) of the gas at various temperatures since

$$P = cRT/M_{na} \tag{1}$$

$$M_1/M_{na} = M_1/M_{nc} + BM_1c/2 \tag{2}$$

Here, BM_1 is the nonideal term. Values of M_{na} as a function of c were smoothed as described previously; these were used to make plots of M_1/M_{na} vs. c as shown in Figures 1 and 2. Here $M_1 = 20.01$ g mol^{-1} is the molecular weight of the monomer. The decrease in the values of M_1/M_{na} with increasing c is characteristic of a self-association. From plots of M_1/M_{na} vs. c one can obtain M_1/M_{wa} vs. c, since (8)

$$\frac{M_1}{M_{wa}} = \frac{d}{dc}\left(\frac{cM_1}{M_{na}}\right) = \frac{M_1}{M_{na}} + c\frac{d}{dc}\left(\frac{M_1}{M_{na}}\right) \tag{3}$$

$$\frac{M_1}{M_{wa}} = \frac{M_1}{M_{wc}} + BM_1c \tag{4}$$

Here M_{wa} is the apparent weight average molecular weight and M_{wc} is the weight average molecular weight. It is also possible to calculate f_a, the apparent weight fraction of monomer, since (8)

$$\ln f_a = \int_0^c \left(\frac{M_1}{M_{na}} - 1\right)\frac{dc}{c} + \left(\frac{M_1}{M_{na}} - 1\right)$$

$$= \ln f_1 + BM_1c \tag{5}$$

Here $f_1 = c_1/c$ is the weight fraction of monomer. For ideal self-associations $BM_1 = 0$, $M_{na} = M_{nc}$, $M_{wa} = M_{wc}$, and $f_a =$
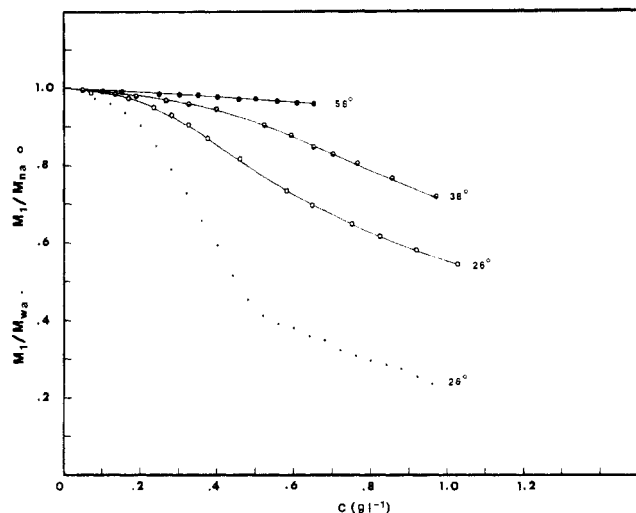
Figure 1. M_1/M_{na} vs. c plots shown were prepared from values calculated from Strohmeier and Briegleb's raw pressure data. The large circles correspond to the experimental M_1/M_{na} values. Only three temperatures are shown here for clarity. The solid line shows the regenerated fit from the eqilibrium constants and nonideal term obtained for a (1,3,6) association at each temperature. Also shown are M_1/M_{wa} values (small circles) at 26 °C which were obtained through differentiation of smoothed M_1/M_{na} data. Note the M_1/M_{wa} values drop below 0.5 ruling out the likelihood of a monomer–dimer association.
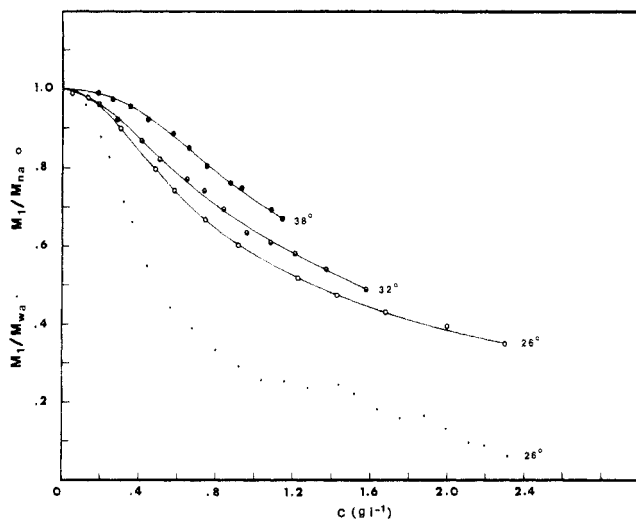
Figure 2. M_1/M_{na} vs. c plots were made for each of the three temperatures studied by Fredenhagen. Note the good fit of the regenerated data for a (1,3,6) association (solid line) to the raw data (large circles) at each of the temperatures. A plot of the M_1/M_{wa} vs. c values (small circles) also needed for the model analysis is shown for illustrative purposes.

f_1. One can combine M_{na}, M_{wa}, and in f_a in such a way that the nonideal term BM_1 is eliminated. Two such combinations that are quite useful for the analysis of self-associations are (8, 14)

$$\xi = 2M_1/M_{na} - M_1/M_{wa} = 2M_1/M_{nc} - M_1/M_{wc} \quad (6)$$

$$\eta = M_1/M_{wa} - \ln f_a = M_1/M_{wc} - \ln f_1 \quad (7)$$

One does not need to know the self-association model in advance in order to calculate ξ and η. These quantities are quite useful in testing for the presence or absence of various types of self-associations, and, once a model has been found to describe the self-association, these quantities can be used in evaluating the equilibrium constant or constants (K_i) and the nonideal term (BM_1). How these quantities are used is shown in the next section.

Tests for the Type of Self-Association

Figure 1 shows the changes in M_1/M_{na} vs. c at various temperatures for the Strohmeier and Briegleb (4) HF data, and Figure 2 shows the corresponding plots for the Fredenhagen (3) HF data. It is evident from these plots that the self-association is strongest at the lowest temperature and weakest at the highest temperature. In Figures 1 and 2 we have shown the plots of M_1/M_{wa} vs. c at the lowest temperature (26 °C) only. It is evident from both figures that the lowest value of M_1/M_{wa} is below 0.3, and the trend of the data suggests that lower values of M_1/M_{wa} might be encountered at higher concentrations.

Usually one starts to analyze a self-association using values from the strongest association (26 °C for both cases). We try to find the simplest model—the one with the fewest parameters (K_i and BM_1)—that gives a good description of the experimental data, as judged by diagnositc plots and by the variance between experimental and calculated results. The variance is defined by

$$\text{variance} = \{1/(N - p)\} \sum_{i=1}^{N} \delta_i^2 \quad (8)$$

where N is the number of data points, p is the number of parameters determined, and δ_i is defined by

$$\delta_i = [(M_1/M_{na})_{obsd} - (M_1/M_{na})_{calcd}]_i \quad (9)$$

The best fit is the model that gives the lowest variance. Unless other experiments have indicated a favored model, we usually start the analysis with the simplest case, which is the monomer–n-mer association. If no solution is found in this case, then we proceed to examine other discrete self-associations, such as a monomer–n-mer–j-mer (1,n,j) association or some indefinite self-associations, until we find a model that seems to describe the observed self-association.

Monomer–n-mer Self-Associations. It was originally believed by Hildebrand and his colleagues (1, 2) that HF gas underwent a monomer–hexamer association. Maclean, Rossotti, and Rossotti (5) believed that the self-association of HF gas at the various temperatures (26–56 °C) could be described as an ideal monomer–dimer self-association over portions of the pressure range, the upper limit being dependent on the temperature. Thus, it behooved us to test for monomer–n-mer self-associations; these models are described by

$$nP_1 \rightleftarrows P_n \quad (n = 2, 3, \ldots) \quad (10)$$
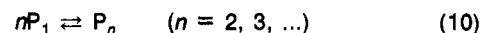
where P represents the self-associating molecule. They are the simplest models which we can analyze. We considered both the ideal case (only at 44 and 56 °C) as well as the more general nonideal case for the whole temperature range.

If one wishes to ignore nonideal effects and consider the self-association to be ideal as Maclean, Rossotti, and Rossotti (5) did, then, for the monomer–n-mer association only, one can obtain the weight fraction of monomer, f_1, from

$$f_1 = (nM_1/M_{nc} - 1)/(n - 1) \quad (11)$$

For an ideal monomer–n-mer self-association eq 11 also defines α, the fraction of n-mer that is dissociated, i.e., $\alpha = f_1$ (15). With different choices of n ($n = 2, 3, \ldots$) one can obtain values of f_1 for each value of M_1/M_{nc}. For each choice of n, these values of f_1 can be used to obtain the association constant, k_n, since (8, 10, 11)

$$(1 - f_1)/f_1^n = k_n c^{n-1} \quad (12)$$

A plot of $(1 - f_1)/f_1^n$ vs. c^{n-1} will give a straight line going through or close to the origin, if a monomer–n-mer association is present; the slope of this line is k_n. If the plot is curved, if imaginary values of f_1 are encountered, or if the slope of the

Table I. Results of Modeling Tests on Strohmeier's HF Data at 26 °C

model	k_A [a]	k_B [b]	$BM_1/(\text{L g}^{-1})$	variance
(1,2)	(k_2) 0.8 ± 0.1	N/A	−0.48 ± 0.03	2.36×10^{-3}
(1,3)	(k_3) 2.2 ± 0.8	N/A	−0.28 ± 0.02	8.84×10^{-4}
(1,4)	(k_4) 10 ± 20	N/A	−0.01 ± 0.02	8.23×10^{-4}
(1,5)	(k_5) 100 ± 600	N/A	0.45 ± 0.04	2.12×10^{-3}
(1,6)	(k_6) 3000 ± 13000	N/A	1.34 ± 0.08	1.12×10^{-3}
(1,2,3)		no solutions		
(1,2,4)		no solutions		
(1,2,6)	(k_2) 0.29 ± 0.08	(k_6) 800 ± 3600	0.74 ± 0.04	1.03×10^{-4}
(1,3,6)	(k_3) 0.93 ± 0.05	(k_6) 27 ± 1	−0.086 ± 0.002	1.44×10^{-5}
(1,3,6...)	(k_3) 0.61 ± 0.03	(k_6) 20 ± 60	0.0 ± 0.1	2.58×10^{-2}
I AK	N/A	(k) 0.81 ± 0.09	−0.41 ± 0.03	2.18×10^{-3}
II AK	N/A	(k) 0.41 ± 0.04	−0.36 ± 0.03	2.08×10^{-3}
III AK	(k_{12}) 0.043 ± 0.001	(k) 10.4 ± 0.07	−0.041 ± 0.003	1.69×10^{-5}
IV AK	(k_{12}) 0.12 ± 0.01	(k) 218 ± 8	1.8 ± 0.2	1.43×10^{-1}
I SEK	N/A	(k) 0.41 ± 0.04	−0.36 ± 0.03	2.08×10^{-3}
II SEK	N/A	(k) 0.33 ± 0.03	−0.48 ± 0.03	2.49×10^{-3}
III SEK	(k_{12}) 0.120 ± 0.005	(k) 1.87 ± 0.03	−0.064 ± 0.003	2.18×10^{-5}
IV SEK	(k_{12}) 0.20 ± 0.02	(k) 21.7 ± 0.05	−3.14 ± 0.04	2.11

[a] The units for k_n are $(\text{L g}^{-1})^{n-1}$ and for k_{12} are L g^{-1}. [b] The units for k_6 are L^5 g^{-5} and for k are L g^{-1}.

plot is negative, then the choice of models is an incorrect one. At 44 and 56 °C values of f_1 were calculated for $n = 2$ and $n = 3$. In each case the values of f_1 were used in plots based on eq 12. For both cases, upward curvature was encountered instead of the straight lines required by eq 12, if the model were correct. The curvature is more pronounced at 44 °C; Figure 3 shows plots based on eq 11 and 12 at 44 °C.

For nonideal monomer–n-mer self-associations, the quantity ξ is usually used, and f_1 is obtained from (8, 10–12)

$$f_1 = \frac{1}{4(n-1)}\left\{\left(\xi + 2 - \frac{2}{n}\right) + \left[\left(\xi + 2 - \frac{2}{n}\right)^2 - (8/n) \times (\xi - 1)\right]^{1/2}\right\} \quad (13)$$

Our analysis showed that none of the monomer–n-mer models from $n = 2$ to $n = 6$ describes the self-association of HF gas between 26 and 56 °C (see Table I). Even though the values of M_1/M_{na} vs. c for the Strohmeier and Briegleb (4) data did not go below 0.5, the values of M_1/M_{wa} vs. c did go below 0.5 at 44, 38, and 26 °C (see Figure 1) and the trend of the data suggested that even lower values of M_1/M_{wa} might be encountered. This suggested that one can rule out the likelihood of a monomer–dimer association for the Strohmeier and Briegleb (4) data at these temperatures. Furthermore, Fredenhagen's (3) experiments were carried out to a much higher concentration (see Figure 2), and at 26 °C the values of M_1/M_{na} vs. c (and also the values of M_1/M_{wa} vs. c) were below 0.4, which suggested that a monomer–dimer association could not be present.

Monomer–n-mer–j-mer (1,n,j) Self-Associations. Since infrared spectroscopy (6, 7, 16–18) of HF gas indicated that dimer, trimer, tetramer, and hexamer might be present, and since the analysis of Maclean, Rossotti, and Rossotti (5) gave evidence for a monomer–dimer–hexamer (1, 2, 6) association, as well as other models for the HF gas self-association, we tested for the presence of a monomer–n-mer–j-mer (1,n,j) association. These self-associations can be described by the general relation

$$mP_1 \rightleftarrows qP_n + rP_j \quad (14)$$

$$j > n; n = 2, 3, \dots \text{ and } j = 3, 4, \dots$$

Four possible self-associations were considered here: monomer–dimer–trimer (1,2,3), monomer–dimer–tetramer (1,2,4), monomer–dimer–hexamer (1,2,6), and monomer–trimer–hexamer (1,3,6). For the analysis of these self-associations
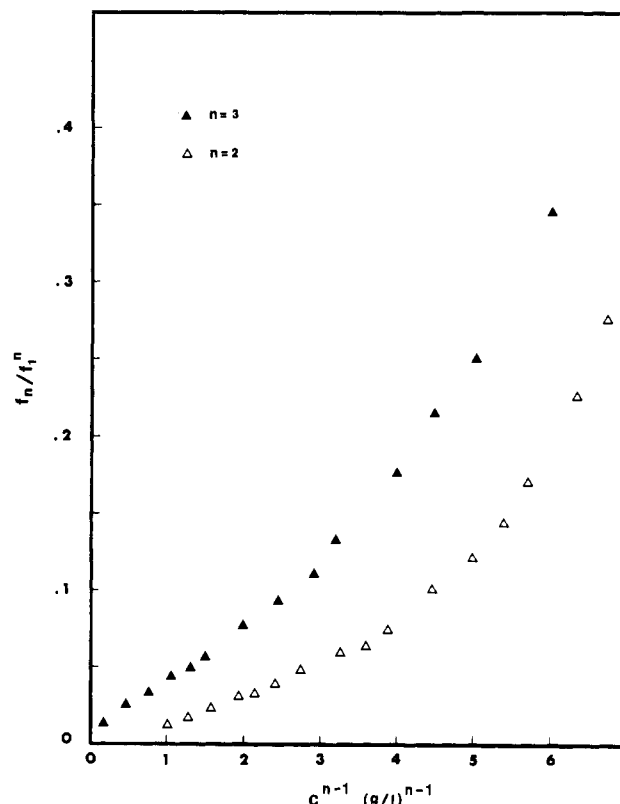

Figure 3. Tests for ideal monomer–dimer and monomer–trimer associations for the 44 °C data of Strohmeier and Briegleb. The obvious curvature in both cases rules out either of these possibilities.

methods based on the quantities η and ξ were used. Here it is noted that

$$\eta = M_1/M_{wa} - \ln f_a = 1/[j - (j - 1)f_1 - (j - n)f_n] - \ln f_1 \quad (15)$$

$$\xi = (2M_1/M_{na}) - (M_1/M_{wa}) = 2(n + nf_1[j - 1] + f_n[j - n])/jn$$
$$- [\eta + \ln f_1] \quad (16)$$

From eq 15 one obtains

$$f_n = [j - (j - 1)f_1 - 1/(\eta + \ln f_1)]/(j - n) = g(f_1) \quad (17)$$

Now substitute eq 17 into eq 16 to convert it to one equation in one unknown, f_1; this can be solved by successive approximations of f_1, since $0 \le f_1 \le 1$. Knowing f_1 values at each
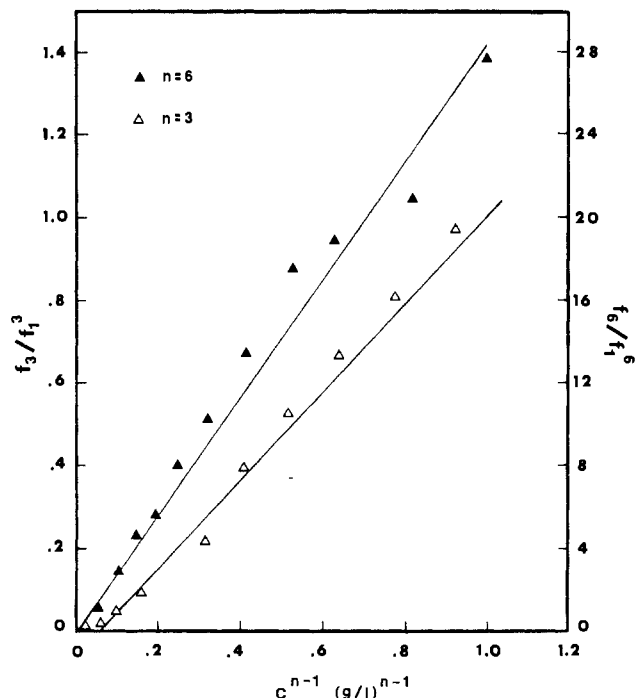
Figure 4. Diagnostic plot for the (1,3,6) association model. A requirement for the success of this model is that plots of $f_n/f_1{}^n$ vs. c^{n-1} for $n = 3$ and 6 give points which lie on a straight line going through or near the origin.

value of c, η, and ξ, one can also obtain values of f_n from eq 17. Then one can obtain values of f_j, since

$$f_j = 1 - f_1 - f_n \qquad (18)$$

The equilibrium constants, k_n and k_j, are obtained from plots based on

$$f_q/f_1{}^q = k_q c^{q-1} \qquad (q = n \text{ or } j) \qquad (19)$$

The results obtained from these plots are shown in Figure 4 for the (1,3,6) model at 26 °C. The nonideal term BM_1 is obtained from

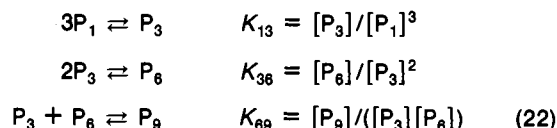$$(M_1/M_{na}) - (M_1/M_{nc}) = BM_1 c/2 \qquad (20)$$

Here

$$M_1/M_{nc} = [n + f_1(nj - n) + f_n(j - n)]/(nj) \qquad (21)$$

This procedure was tried with the four $(1, n, j)$ models described earlier. The results are displayed in Table I, and it is evident that the (1,3,6) model has the lowest variance and hence the best fit.

Indefinite Self-Associations. The analysis of Strohmeier and Briegleb's (4) HF gas association data by Maclean, Rossotti, and Rossotti (5) indicated that, even though there was definite evidence for a monomer–dimer–hexamer (1,2,6) self-association, intermediate and higher oligomers might be present. Briegleb and Strohmeier (19) themselves concluded that a large number of HF species were present. Pressure dependence of the infrared spectrum suggested to Smith (7) that several species might be present. Heat capacity measurements by Franck (20, 21) and his co-workers have been interpreted in terms of several oligomers of HF. Tobolsky and Thach (12) have shown that a self-association originally described by eight equilibrium constants could be described within the same precision by an ideal, two-equilibrium-constant, indefinite self-association. Because of these reasons, we have examined the HF gas self-association data to see if it could be described by an indefinite model. More models (nine) are available to us at present than were available previously.

Self-associations that appear to continue without limit are known as indefinite self-associations. They can be divided into two classes: SEK (sequential, equal equilibrium constant) and AK (attenuated equilibrium constant) indefinite self-associations. For the SEK model there are four basic types to test for (13, 14). The SEK model requires that the term kc_1, which is encountered in the infinite series describing c, M_1/M_{nc}, and M_1/M_{wc}, be less than 1 ($0 \le kc_1 \le 1$) so that the series can be summed. Here c_1 is the concentration (in g L⁻¹) of monomer and k is the intrinsic equilibrium constant (in L g⁻¹). Note that $k = K/M_1$, where K is the molar association constant and M_1 is the monomer molecular weight. The AK model (14, 22, 23) is less restrictive since $0 \le kc_1 \le \infty$. We considered four types of AK associations; these are the analogues of the four types of SEK self-associations. Since the indefinite associations are discussed in detail elsewhere, the reader is referred to previous works dealing with the development and use of these models. None of these eight models fit the data as well as did the (1,3,6) model (see Table I). The additional SEK model was also tested to see if an improvement over the (1,3,6) model fit could be obtained by considering an indefinite association represented by simultaneous associations of the types

$$3P_1 \rightleftharpoons P_3 \qquad K_{13} = [P_3]/[P_1]^3$$

$$2P_3 \rightleftharpoons P_6 \qquad K_{36} = [P_6]/[P_3]^2$$

$$P_3 + P_6 \rightleftharpoons P_9 \qquad K_{69} = [P_9]/([P_3][P_6]) \qquad (22)$$

etc. The molar concentrations of the associating species can be represented by

$$[P_3] = K_{13}[P_1]^3$$

$$[P_6] = K_{36}[P_3]^2 = K_{13}{}^2 K_{36}[P_1]^6$$

$$[P_9] = K_{69}[P_3][P_6] = K_{13}{}^3 K_{36}K_{69}[P_1]^9 \qquad (23)$$

etc., for an ideal self-association or for a nonideal self-association if it be assumed that the activity coefficients of the associating species c can be described by $\ln y_i = lBM_1c$ ($i = 1, 2, \ldots$) for c in g L⁻¹. Now assume that $K_{13} \ne K_{36}$, K_{69}, etc., and that $K_{36} = K_{69} = \ldots = K$. If one converts to concentrations in g L⁻¹, the total solute concentration becomes

$$c = c_1 + 3k_3c_1{}^3 + 6k_3{}^2kc_1{}^6 + 9k_3{}^3k^2c_1{}^9 + \ldots$$

$$= c_1[1 + 3k_3c_1{}^2/(1 - k_3kc_1{}^3)^2]$$

$$= c_1[1 + 3x/(1 - y)^2] \qquad \text{if } k_3kc_1{}^3 < 1 \qquad (24)$$

$$x = k_3c_1{}^2 \qquad y = k_3kc_1{}^3$$

$$k_3 = k_{13}/M_1{}^2 \qquad k = K/M_1$$

Similarly, the expressions for M_1/M_{na} and M_1/M_{wa} become

$$M_1/M_{na} =$$
$$[1 + x/(1 - y)]/[1 + 3x/(1 - y)^2] + BM_1 c/2 \qquad (25)$$

$$M_1/M_{wa} =$$
$$[1 + 3x/(1 - y)^2]/[1 + 9x(1 + y)/(1 - y)^3] + BM_1 c \qquad (26)$$

These quantities can be combined to yield ξ and η, which can then be used in the analysis. In all cases the fit with this model was not as good as that obtained with the (1,3,6) model (see Table I).

Results and Discussion

Because of the ambiguities in print concerning the nature of the self-association of HF gas at moderate temperatures (25–56 °C), we investigated rather thoroughly the various possibilities for the observed self-association. Tests for ideal monomer–

Table II. Results of Modeling Tests at All Temperatures

$T/°C$	best model	$k_3/(L^2 g^{-2})$	$k_6/(L^5 g^{-5})$	$BM_1/(L g^{-1})$	variance
26^a	(1,3,6)	0.93 ± 0.05	27 ± 1	− 0.086 ± 0.002	1.44 × 10⁻⁵
32^a	(1,3,6)	0.56 ± 0.04	8.3 ± 0.5	− 0.013 ± 0.002	1.47 × 10⁻⁵
38^a	(1,3,6)	0.23 ± 0.03	1.70 ± 0.08	− 0.1233 ± 0.0008	1.39 × 10⁻⁶
44^a	(1,3,6)	0.046 ± 0.004	0.52 ± 0.01	− 0.1430 ± 0.0001	5.12 × 10⁻⁸
56^a	(1,3,6)	0.0285 ± 0.0008	0.05 ± 0.01	− 0.0859 ± 0.0001	2.62 × 10⁻⁸
26^b	(1,3,6)	1.68 ± 0.07	22 ± 2	− 0.060 ± 0.001	2.59 × 10⁻⁵
32^b	(1,3,6)	1.45 ± 0.03	5.7 ± 0.6	− 0.074 ± 0.001	8.60 × 10⁻⁶
38^b	(1,3,6)	0.31 ± 0.03	2.5 ± 0.5	− 0.045 ± 0.001	7.08 × 10⁻⁶

[a] From Strohmeier and Briegleb's data. [b] From Fredenhagen's data.
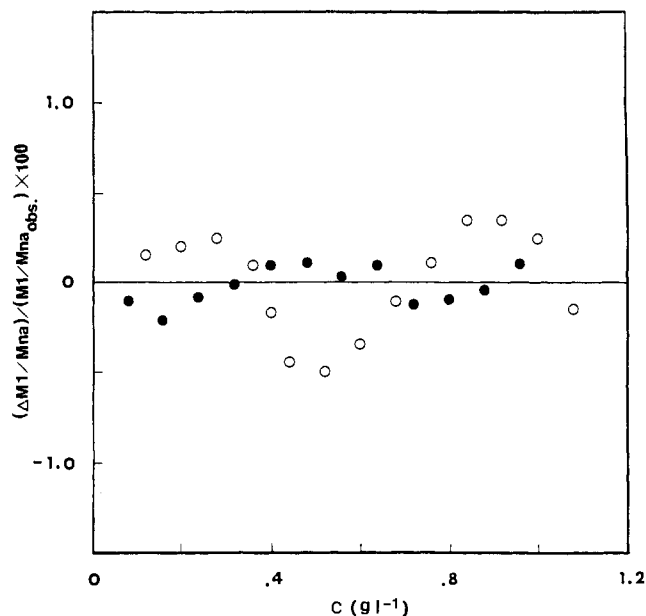

Figure 5. Deviation plot for the monomer–trimer–hexamer association model. This plot shows the relative percent difference between the observed and regenerated values of M_1/M_{na} at 38 °C. Open circles denote the fit to Fredenhagen's data and filled circles show the fit to the data of Strohmeier and Briegleb. Note that the maximum difference observed over the entire concentration range for either data set is about 0.5.

Figure 6. van't Hoff plot of ln K_{iP} vs. $1/T$ (i = 3 or 6) for the trimerization (A) and the hexamerization (B) of HF gas. These data are taken from the (1,3,6) association model test results on Strohmeier and Briegleb's data (O) and Fredenhagen's data (●). The K_{iP} are the pressure association constants. The lines through the data represent the least-squares fits.

dimer–hexamer and ideal monomer–trimer–hexamer self-associations failed. Of the 18 nonideal models tested the best model that we have been able to find to describe Fredenhagen's (3) or Strohmeier and Briegleb's (4) P–V–T data for HF gas is a nonideal monomer–trimer–hexamer (1,3,6) model. Remarkably, both sets of data gave the same model for the self-association at all temperatures! (See Table II.) Figure 5 shows a deviation plot based on eq 20, 21, and 2 for the data of Strohmeier and Briegleb, and of Fredenhagen at 38 °C. That we were able to distinguish between the various models is a tribute to the care with which Fredenhagen, Strohmeier, and Briegleb carried out their experiments.

The thermodynamic data for the two sets of experiments are given in Table III. Here we have listed the values of the nonideal term (BM_1), the molar (K_{iM}; i = 3 or 6) and pressure (K_{iP}; i = 3 or 6) association constants, and the values of the thermodynamic state functions $\Delta G°$, $\Delta H°$, and $\Delta S°$. A monomer–trimer–hexamer association can be considered to be made up of two simultaneous self-associations: a monomer–trimer and a monomer–hexamer association. The values of $\Delta U°$ and $\Delta H°$ were obtained from the appropriate van't Hoff plots in ln K_{iM} or ln K_{iP} vs. $1/T$ (i = 3 or 6). These plots are shown in Figure 6, A and B, for the two data sets. For the trimerization, the values of $\Delta H°$ were quite similar in both cases. On the other hand, there were some differences in the $\Delta H°$ values in both data sets for the hexamerization. It should be noted that the Fredenhagen (3) experiments were carried out over three temperatures; small errors in the Fredenhagen
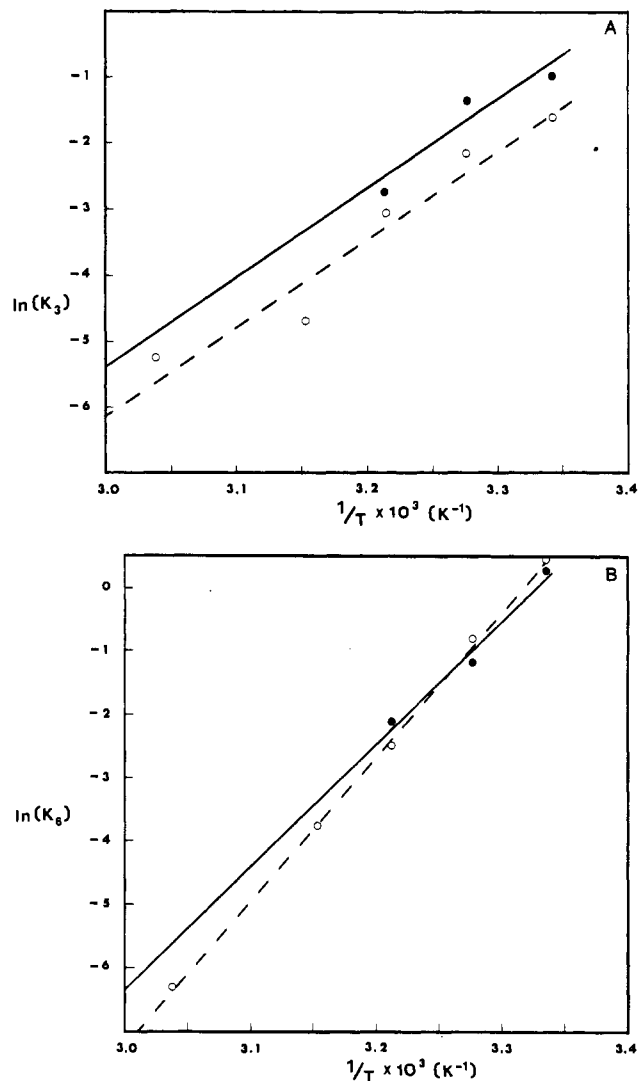
data could affect the slope of the van't Hoff plots more. It is evident from the van't Hoff plots that the trimerization and hexamerization associations are exothermic. The negative values of $\Delta S°$ reflect the increase in order of the system on self-association. It is also evident from Table III that the association equilibria are enthalpic instead of entropic.

A positive nonideal term, BM_1, could be interpreted as indicating repulsion between the gas molecules, such as that caused by excluded volume (24, 25). Negative values for BM_1 could indicate attraction between the molecules, and this could be interpreted as a self-association. The effect of a negative BM_1 would be to increase the extent of self-association (the

Table III. Thermodynamic Parameters for the Monomer-Trimer-Hexamer Association

				1 → 3						1 → 6			
$T/^\circ C$	$10^2 BM_1/$ (L g^{-1})	$K_3/$ (L^2 mol^{-2})	$10^5 K_p/$ atm^{-2}	ΔH° or $\Delta U^\circ/$ (kJ mol^{-1})	$\Delta G^\circ/$ (kJ mol^{-1})	$\Delta S^\circ/$ (J mol^{-1} K^{-1})	$10^{-6} K_6/$ (L^5 mol^{-5})	$10^3 K_p/$ atm^{-5}	ΔH° or $\Delta U^\circ/$ (kJ mol^{-1})	$\Delta G^\circ/$ (kJ mol^{-1})	$\Delta S^\circ/$ (J mol^{-1} K^{-1})
26[a]	-6 ± 1	224 ± 9	370 ± 10	(-110 ± 50)[c]	2.46 ± 0.08	-400 ± 100	12 ± 1	1300 ± 100	(-140 ± 20)[c]	-0.7 ± 0.2	-460 ± 40
32	-7.4 ± 0.1	194 ± 4	310 ± 7	(-110 ± 50)[d]	2.97 ± 0.08	-400 ± 100	3.0 ± 0.3	300 ± 30	(-140 ± 20)[d]	3.0 ± 0.2	-500 ± 40
38	-4.5 ± 0.1	41 ± 4	63 ± 6		7.1 ± 0.2	-400 ± 100	1.3 ± 0.3	120 ± 30		5.4 ± 0.4	-500 ± 40
26[b]	-8.6 ± 0.2	124 ± 7	210 ± 10	(-100 ± 20)[c]	3.9 ± 0.2	-400 ± 100	14.4 ± 0.5	1620 ± 50	(-176 ± 4)[c]	-1.21 ± 0.08	-630 ± 10
32	-7.3 ± 0.2	75 ± 5	120 ± 8	(-100 ± 20)[d]	5.4 ± 0.2	-400 ± 100	4.4 ± 0.3	450 ± 30	(-174 ± 4)[d]	2.0 ± 0.1	-630 ± 10
38	-12.33 ± 0.08	31 ± 4	48 ± 6		7.9 ± 0.4	-400 ± 100	0.91 ± 0.04	84 ± 4		6.4 ± 0.1	-630 ± 10
44	-14.30 ± 0.01	6.1 ± 0.5	9.0 ± 0.7		12.4 ± 0.2	-400 ± 100	0.278 ± 0.005	23.3 ± 0.4		9.92 ± 0.04	-630 ± 10
56	-8.59 ± 0.01	3.8 ± 0.1	5.2 ± 0.1		14.4 ± 0.04	-400 ± 100	0.027 ± 0.005	1.9 ± 0.3		17.20 ± 0.08	-630 ± 10

[a] From Fredenhagen's data. [b] From Strohmeier and Briegleb's data. [c] ΔU° calculated from molar equilibrium constants. [d] ΔH° calculated from K_p values. ΔS° quantities calculated by using this result.

values of M_{na}/M_1) with increasing c *(26)*. Since slightly negative values of BM_1 were found (see Table II) here, we did try to analyze the data by another model, which we call the trimer indefinite self-association. This model gave a poorer variance at each temperature than did the (1,3,6) model.

The analysis done by Maclean, Rossotti, and Rossotti *(5)* indicated that a (1,2,6) association could give a good description of the Strohmeier and Briegleb *(4)* HF data; they did not attempt to analyze Fredenhagen's *(3)* HF data. At the time that Maclean, Rossotti, and Rossotti *(5)* did their analysis, the interrelationship between M_{nc} and M_{wc} (or M_{na} and M_{wa}) was not known. Nor did they have any methods, except for statistical theories, to correct for nonideal behavior. It should be noted that a (1,2,6) association gave a poor analysis of both sets of HF data using our methods (see Table I), but the (1,3,6) association gave a much better description, based on variances, of the HF gas association. Interestingly, they *(5)* obtained ΔH° = -169 kJ mol^{-1} from the plot of ln K_p vs. $1/T$ for the hexamerization and ΔS° = 831 J mol^{-1}. The ΔH° value is of the same order as our value (see Table III) but the ΔS° is different. Briegleb and Strohmeier *(19)* analyzed their data as an extended series involving at least nine equilibria and have reported the thermodynamic functions for these steps. For the hexamerization they also got ΔH° = -167 kJ mol^{-1}. Even though they did very careful and elegant experiments, it is surprising that they could obtain so many equilibrium constants with the precision that they reported. White and Kilpatrick *(27)* used eight equilibrium constants to describe the self-association of 2-*n*-butylbenzimidazole and of benzotriazole in benzene. Tobolsky and Thach *(12)* showed that the White and Kilpatrick *(27)* data could be described by a two-equilibrium-constant, ideal indefinite self-association (an ideal type III SEK model). We were unable to find a two-equilibrium-constant, indefinite model (the types III and IV SEK or AK models) to describe the HF gas self-association data.

The thermodynamic *P-V-T* data can be used in many cases to tell which type of association is present and what are the values of the equilibrium constants (K_i) and the nonideal term (BM_1). The analysis is not complicated by the necessity of introducing parameters other than K_i and BM_1, such as heat capacities or extinction coefficients. Our methods cannot specify what type of bonding is involved, nor do they give information about the nature of the aggregate, such as whether the aggregate is linear or cyclic. On the other hand spectroscopic methods can do this, but they may not be as good as our methods for determining the type of self-association present and evaluating K_i and BM_1. Our analysis of the *P-V-T* data gives a very good description of the M_1/M_{na} vs. c data (see Figures 1 and 2), whereas Smith's *(7)* analysis of the HF gas self-association from infrared data seemed to be able to describe the M_{na}/M_1 (the association factor or the apparent number average degree of polymerization) vs. c data only over part of the concentration range.

In previous publications we have referred to BM_1 as a nonideal term or as the second virial coefficient *(8, 11, 13, 14)*. Properly speaking, it should be referred to only as a nonideal term. When dimer is present, a virial expansion of M_1/M_{na} as a function of total gas concentration c leads to *(9, 28)*

$$M_1/M_{na} = 1 - \{(k_2 - BM_1)/2\}c - (\tfrac{4}{3}k_3 - 2k_2^2)c^2 + \dots \tag{27}$$

Here $-(k_2 - BM_1)/2$ corresponds to the second virial coefficient and is not the same as BM_1. Thus, BM_1 should be referred to as the nonideal term. When dimer is absent, then $k_2 = 0$ and the second virial coefficient becomes $BM_1/2$.

We use models for the analysis of self-associations, because it is virtually impossible to analyze self-associations using virial

expansions of M_1/M_{na}, and also M_1/M_{wa}, vs. c. From eq 30 one notes that

$$\lim_{c \to 0} M_1/M_{na} = 1 \tag{28}$$

$$\lim_{c \to 0} \frac{d}{dc}(M_1/M_{na}) = \frac{-k_2 + BM_1}{2} \tag{29}$$

A virial expansion of M_1/M_{wa} vs. c leads to the following results (28, 29):

$$\lim_{c \to 0} M_1/M_{wa} = 1 \tag{30}$$

$$\lim_{c \to 0} \frac{d}{dc}(M_1/M_{wa}) = -k_2 + BM_1 \tag{31}$$

Since the limiting slopes (eq 29 and 31) of these virial expansions are multiples of each other, one cannot use a combination of these two quantities to extract k_2 and BM_1. For very strong self-associations, the plots of M_1/M_{na} vs. c (or M_1/M_{wa} vs. c) may be quite steep in the vicinity of $c = 0$, which would make the evaluation of the limiting slope or other limiting derivatives quite difficult. Although Derechin (30) has developed a multinomial theory for the analysis of self-associations, his method would require the availability of successive derivatives of M_1/M_{na} vs. c (or of M_1/M_{wa} vs. c) in the vicinity of zero concentration. This is the area where the experimental data would be the least precise. These difficulties can be overcome by using modeling with the quantities M_1/M_{wa}, M_1/M_{na}, and ln f_a. With modeling one can evaluate the equilibrium constant or constants (K_i) and the nonideal term (BM_1). For example, when one evaluates the quantity ξ, one eliminates the nonideal term, i.e.

$$\xi = 2M_1/M_{na} - M_1/M_{wa} = 2M_1/M_{nc} - M_1/M_{wc}$$

provided that the activity coefficients (y_i) of the self-associating species obey the relation ln $y_i = iBM_1 c$ ($i = 1, 2, ...$). The numerical value of ξ is independent of the model used, but in order to test for or analyze a self-association various models for M_1/M_{wa} must be used as described here (see eq 16 for the monomer-n-mer-j-mer model, for example) and elsewhere (11, 14, 23, 24). It is through modeling that we can determine the nonideal term and the equilibrium constant or constants; it cannot be done at present directly from a virial expansion of M_1/M_{na} (or of M_1/M_{wa}) vs. c

Since this was written, Redington (31, 32) has published some recent work on the nonideal self-association of HF gas using published vapor density data (including that of Strohmeier and Briegleb (4)) and infrared data. Nonideality was taken into account; the virial coefficients were calculated from some proposed intermolecular potential energy functions. Redington's (31, 32) treatment leads to a model for the nonideal association of HF gas that includes oligomers extending through dodecamer. Interestingly, his second virial coefficients (see Table IV of ref 31) are negative and seem to be of the same order of magnitude as the nonideal terms in our work.

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