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On the Relationship Between the Equilibrium Constants of Consecutive Association Reactions

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On the Relationship Between the Equilibrium Constants of Consecutive Association Reactions

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ON THE RELATIONSHIP BETWEEN THE EQUILIBRIUM CONSTANTS OF CONSECUTIVE ASSOCIATION REACTIONS

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ABSTRACT

Generalized association models for fluids require a large number of adjustable parameters (equilibrium constants) unless some effort is made to interrelate the different association constants. An association model has been developed by considering the probability of consecutive association reactions and the effect of that probability on the entropy of association. The relationship between the equilibrium constants of these reactions has been expressed by a function related to the Poisson distribution. When combined with an equation of state, the model accurately represents the properties of hydrogen fluoride and its mixtures with halogenated hydrocarbons. The Poisson-distribution model is compared with the classical continuous linear association model. While the Poisson-distribution model is superior for molecules that preferentially form associates of moderate size, the continuous linear model is more appropriate for molecules that can form polymers with a high degree of polymerization.

INTRODUCTION

Association models are frequently used in conjunction with equations of state or activity-coefficient expressions to reproduce the properties of strongly nonideal mixtures. Among the numerous association models proposed in

the literature, the monomer - dimer model is most popular for carboxylic acids and the continuous linear model is often used for hydrogen-bonding fluids such as alcohols, amines or phenols. These models represent the appropriate balance between physical reality and computational simplicity. Recently, Lencka and Anderko (1993) proposed a simple accurate model for hydrogen fluoride. This model agrees with simulation data for the multimers of HF and predicts the preferential formation of multimers of intermediate size while allowing for the formation of any multimers.

In this study, we formulate an alternate association model by deriving the relationship between the equilibrium constants of consecutive association reactions on the basis of probabilistic considerations. Subsequently, the model is applied to pure HF and to mixtures containing HF and refrigerants. Finally, it is compared with other association models to determine relative advantages and disadvantages.

ASSOCIATION MODEL

We focus on the relationship between the equilibrium constants of consecutive association reactions:

$$A_j + A_1 = A_{j+1} \qquad j = 1,2,\ldots\infty \tag{1}$$

The equilibrium constants of reactions (1) depend, in general, on j and can be expressed as

$$K_{j,j+1} = f(j)\ K \tag{2}$$

where f(j) is a distribution function that depends on the nature of the associating compound. Since all values of the function f(j) are multiplied by a common factor (i.e., K), it is convenient to normalize f(j) so that f(1)=1. In that event, K is the dimerization constant (i.e., $K_{1,2}$=K). If this distribution function is known, the ratio of the total number of moles of all species in an associated system (n_T) to the number of moles that would exist in the absence of association (n_0) can be evaluated in the form (Anderko, 1991):

$$\frac{n_T}{n_0} = Z^{(ch)} = x_A\ F\left(\frac{R\ T\ K\ x_A}{v}\right) + \sum_{k=1}^{r} x_{B_k} \tag{3}$$

where (ch) stands for chemical, x is the analytical (apparent) mole fraction,

and indices A and B_k denote the associating component and the k-th nonassociating component, respectively. F denotes an algebraic function that depends on the functional form of f(j) (eq. 2). The ratio n_T/n_0 is an important quantity that enters the equation of state

$$\frac{PV}{n_0RT} = Z = Z^{(ph)} + n_T/n_0 - 1 \tag{4}$$

where P is the total pressure and V is the total volume; $Z^{(ph)}$ is equivalent to an equation of state for nonreacting monomeric species and can be expressed by a simple (e.g., cubic) equation of state. Here, (ph) stands for physical.

To postulate a probabilistic expression for f(j) for pure fluids, let us imagine a central molecule surrounded by n molecules. We assume that the probability that another molecule will join the central one and form an associate is p. Further, we assume that this probability is the same for all molecules surrounding the central molecule and the probability of the central molecule being joined by the k-th molecule is independent of the probability of the central molecule being joined by the l-th molecule (k, l = 1,...,n). Therefore, $\Pi(j)$, the probability that j molecules will join the central molecule, is given by the binomial distribution:

$$\Pi(j) = \left[\begin{matrix} n \\ j \end{matrix} \right] p^j (1 - p)^{n-j} \tag{5}$$

This is a two-parameter (n and p) distribution. Neither n nor p are known a priori. Therefore, it is necessary to simplify the distribution.

We assume that n is large and finite. Also, the quantity p is necessarily between zero and unity. Thus, the conditions that are necessary to apply the Poisson distribution are satisfied and eq. (5) can be simplified to

$$\Pi(j) = \frac{(np)^j}{j!} e^{-np} = \frac{\kappa^j}{j!} e^{-\kappa} \tag{6}$$

where the product (np) is denoted by κ.

For the elementary association reaction (1), the entropy change has a component that results from the probability that j molecules form an aggregate with the central molecule:

$$\Delta s_{j,j+1} = \Delta s^{(\dagger)} + R\ln P(j) = \Delta s^{(\dagger)} + R\ln\left[\frac{\kappa^j}{j!} e^{-\kappa} \right] = \Delta s^{\dagger} + R\ln\left[\frac{\kappa^j}{j!} \right] \tag{7}$$

where $\Delta s^{(\dagger)}$ is the component of the association entropy that is not related to

the size of the multimer and $\Delta s^{\dagger}=\Delta s^{(\dagger)}+R\ln(e^{-\kappa})$. Therefore, the Gibbs energy change for reaction (1) is:

$$\Delta g_{j,j+1} = \Delta h_{j,j+1} - T\Delta s_{j,j+1} = \Delta h^{\dagger} - T\Delta s^{\dagger} - RT\ln\left[\frac{\kappa^{j}}{j!}\right] =$$

$$= \Delta g^{\dagger} - RT\ln\left[\frac{\kappa^{j}}{j!}\right] \qquad (8)$$

The consecutive association constant $K_{j,j+1}$ then becomes

$$K_{j,j+1} = \exp\left(-\frac{\Delta g^{\dagger}}{RT}\right)\left[\frac{\kappa^{j}}{j!}\right] \qquad (9)$$

For normalization, it is convenient to introduce the dimerization constant $K_{1,2}=K$.

$$K_{1,2} = K = \exp\left(-\frac{\Delta g^{\dagger}}{RT}\right)\kappa \qquad (10)$$

The distribution function defined by eq. (2) becomes then:

$$f(j) = \frac{\kappa^{j-1}}{j!} \qquad (11)$$

Eq. (11) is similar, although not identical, to the equation proposed by Lencka and Anderko (1993) for HF on the basis of simulation data:

$$f(j) = \frac{\kappa^{j-1}}{(j-1)!} \qquad (12)$$

RESULTS

For the physical contribution to the compressibility factor $Z^{(ph)}$ (eq. 4), the Peng-Robinson (1976) equation of state has been adopted because of its popularity in practical calculations:

$$Z^{(ph)} = \frac{v}{v-b} - \frac{a(T)\,v}{RT\,[v(v+b) + b(v-b)]} \qquad (13)$$

The ratio n_T/n_0 is calculated from the f(j) distribution function according to a procedure described by Anderko (1991). Thus, the complete equation of state is defined by eq. (4) and characterized by four parameters:

a(T), b, κ, and K(T).

The parameters of the equation of state have been determined for pure HF by fitting the equation to PVT data in the one- and two-phase regions as well as vapor-pressure data. The algorithm has been described in detail by Łencka and Anderko (1993) and will not be repeated here.

For the distribution function (11), the parameter κ has been found to be 6.0. The distribution function f(j) (eq. 11) with κ=6.0 is plotted in Fig. 1 for the initial 20 multimers and compared with the distribution function proposed earlier by Łencka and Anderko (1993). Although both distribution functions are qualitatively similar, the probabilistic distribution (eq. 11) shows a less pronounced maximum.

To simplify the numerical calculations, an analytic function was found to reproduce the $Z^{(ch)}$ values that were obtained from the proposed distribution function:

$$F(q) = Z^{(ch)}_{pure} = \frac{1 + \sum_{k=1}^{8} a_k q^k}{(1 + q)^8} \qquad (14)$$

Parameters a_i (i = 1,...,8) are listed in Table 1. Figure 2 shows function F(q), which is equal to the chemical contribution to the compressibility factor of a pure fluid. For comparison, Fig. 2 also shows the function F(q) obtained by Łencka and Anderko (1993).

The temperature dependence of the dimerization constant K is given by:

$$\ln K = \frac{-\Delta g^o}{R\,T} = \frac{-\Delta h^o + \Delta c^o_p\, T_o}{R\,T} + \frac{1}{R}\,(\Delta s^o - \Delta c^o_p - \Delta c^o_p \ln T_o) + \frac{\Delta c^o_p}{R} \ln T. \qquad (15)$$

The standard Gibbs energy of dimerization Δg^o (eq. 15) is related to the quantity $\Delta g^\dagger$ (eqs. 8 - 10) by $\Delta g^o = \Delta g^\dagger - RT\ln\kappa$. For HF, when T_0 is chosen to be 273.15 K, Δh^0=-35.938 kJ/mol, Δs^0=-136.51 J/molK, and Δc^o_p=58.44 J/molK. For the $Z^{(ph)}$ contribution, eq. (13) has been used with

$$b/(cm^3\ mol^{-1}) = 9.88 \qquad (16)$$

$$a/(bar\ cm^6\ mol^{-2}) = 10^6\ [0.5530 + 0.2133 \exp(-0.7003\ (T/100 - 4.02)^2)]. \qquad (17)$$

Equation (4), coupled with eq. (11), accurately reproduces the properties of pure HF as illustrated in Fig. 3 which compares calculated and experimental gas-phase compressibility factors. Fig. 4 shows the two-phase vapor + liquid region for pure HF.

The equation of state has been applied to mixtures using the classical

quadratic mixing rules for the $Z^{(ph)}$ contribution:

$$a = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i x_j (a_i a_j)^{1/2}(1 - \theta_{ij}) \tag{18}$$

$$b = \sum_{i=1}^{\infty} x_i b_i \tag{19}$$

where θ_{ij} is the only required binary parameter. Vapor-liquid equilibria have been calculated for three binary systems related to the separation of refrigerants. Binary parameters are listed in Table 2 and the quality of reproducing the VLE data is illustrated in Figs. 5 and 6. As shown in Figs. 5 and 6, the equation of state outlined here, coupled with Eq. (11), accurately represents vapor-liquid and vapor-liquid-liquid equilibria in binary systems containing HF.

COMPARISON WITH THE CONTINUOUS LINEAR MODEL

The properties of associating fluids such as aliphatic alcohols, phenols or amines can be represented using the classical continuous linear model. Therefore, it is instructive to examine the differences between the continuous model and that based on the Poisson distribution.

Unlike the Poisson model, the continuous linear association model assumes that the probability of reaction (1) is independent of j. Subsequently, all the consecutive association constants $K_{j,j+1}$ (eq. 2) are equal to each other. For association reactions where j is not limited and may be very large (i.e., polymerization), the continuous linear model is physically more appropriate. Therefore, we expect that the continuous model provides a good approximation for fluids that form primarily linear associated structures.

The model based on the Poisson distribution is more appropriate when j is limited. This is usually the case when ring structures predominate in the system. Hydrogen fluoride is an example of a compound for which the Poisson model leads to satisfactory results whereas the linear model does not. A model based on the binomial distribution is particularly useful for ion solvation where the maximum number of solvating molecules is small (typically 6 for monovalent and 12 for bivalent ions), as shown by Schönert (1990).

Figure 7 presents a quantitative comparison of the two models. In this figure, the consecutive association constants $K_{j,j+1}$ are shown for HF and two hydroxyl derivatives, which can be represented by the continuous linear model. Similar values of $K_{j,j+1}$ are observed for small values of j (j = 1, 2) which correspond to dimerization and trimerization. However, significant deviations

appear for higher j's. The association constants for the continuous linear model remain constant for all values of j ranging from one to infinity. Since the Poisson model favors the formation of associates of moderate size (such as pentamers, hexamers or heptamers), the Poisson $K_{j,j+1}$ constants show a maximum at j = 5 and 6. For these values of j, the Poisson association constants are much higher than those for the continuous model. However, for the Poisson model, the $K_{j,j+1}$ constants drop rapidly and become insignificant at higher values of j ($j \geq 10 - 12$) because continuous polymerization is essentially prohibited by the Poisson model.

Figure 8 illustrates how the differences between the two association models manifest themselves in the chemical contribution to the compressibility factor ($z^{(ch)}$). Since infinite polymerization is allowed by the continuous model, $z^{(ch)}$ tends to zero for very large values of the dimerization constant K. On the other hand, the $z^{(ch)}$ term calculated from the Poisson distribution reaches a nearly constant value for high K constants because the Poisson distribution predicts formation of multimers of moderate size.

CONCLUSIONS

The Poisson distribution function (eq. 11) provides an appropriate basis for interrelating the equilibrium constants of consecutive association reactions when multimers of small or moderate size are preferentially formed. When combined with an equation of state, the Poisson distribution function makes it possible to represent accurately the properties of both pure hydrogen fluoride and its mixtures with nonassociating components. Vapor-liquid and vapor-liquid-liquid equilibria can be represented using only one binary physical parameter. While the Poisson model gives accurate results for hydrogen fluoride, it is not appropriate for fluids that form multimers of unlimited size. For those fluids, the classical linear continuous association model provides a better representation.

ACKNOWLEDGEMENT

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Table 1. Parameters for eq. (13).

a_1	7.4406	a_5	-52.8696
a_2	4.0483	a_6	19.3785
a_3	-12.9523	a_7	0.4612
a_4	105.2042	a_8	0.10653

Table 2. Binary parameters θ_{12} used for mixture calculations and deviations between experimental and calculated total pressures.

Mixture	Ref.	θ_{12}	δP, Percent*
HF - CHF_2Cl	Wilson et al. (1989)	- 0.01	1.1
HF - CF_3CCl_3	Knapp et al. (1991)	- 0.02	1.9
HF - HCl	Gillespie et al. (1985)	0.05	2.8

*$\delta P = \frac{100}{N} \sum \left| (P_i^{cal} - P_i^{exp})/P_i^{exp} \right|$, where N is the number of experimental points

FIGURE CAPTIONS

Figure 1. Distribution functions f(j) obtained from the Poisson distribution (eq. 11, solid circles) and proposed by Łencka and Anderko (1993) on the basis of simulation data (eq. 12, hollow circles).

Figure 2. The function $F(q) = Z^{(ch)}_{pure}$ (eq. 13) derived from the Poisson distribution (solid line) and that obtained by Łencka and Anderko (1993) on the basis of simulation data (dotted line).

Figure 3. Gas-phase compressibility factors of pure hydrogen fluoride at 273.15 K (lower curve), 299.15 K (middle curve) and 311.15 K (upper curve). Experimental data: ■ - Long et al. (1943); ♦ - Jarry and Davis (1953); ● - Fredenhagen (1934) and o - Strohmeier and Briegleb (1953). The lines show results obtained from the equation of state proposed in this work.

Figure 4. Vapor-liquid coexistence curve of pure HF calculated from the EOS (lines) and measured by Franck and Spalthoff (1957, circles).

Figure 5. Vapor-liquid equilibria in the system HF - CHF_2Cl at 258.15 K. Solid lines show results obtained from the equation of state proposed in this work by fitting one binary parameter θ_{12}.

Figure 6. Vapor-liquid-liquid equilibria in the system HF - CF_3CCl_3 at 383.15 K. Solid lines show results obtained from the equation of state by fitting one binary parameter θ_{12}.

Figure 7. Consecutive association constants $K_{j,j+1}$ (eq. 2) for hydrogen fluoride (●), ethanol (o), and phenol (□) at 300 K and 400 K. The constants for ethanol and phenol are from Anderko (1990).

Figure 8. Comparison of the function $Z^{(ch)}_{pure}(RTK/v)$ based on the Poisson distribution (solid line) with that obtained from the continuous linear association model (dashed line).

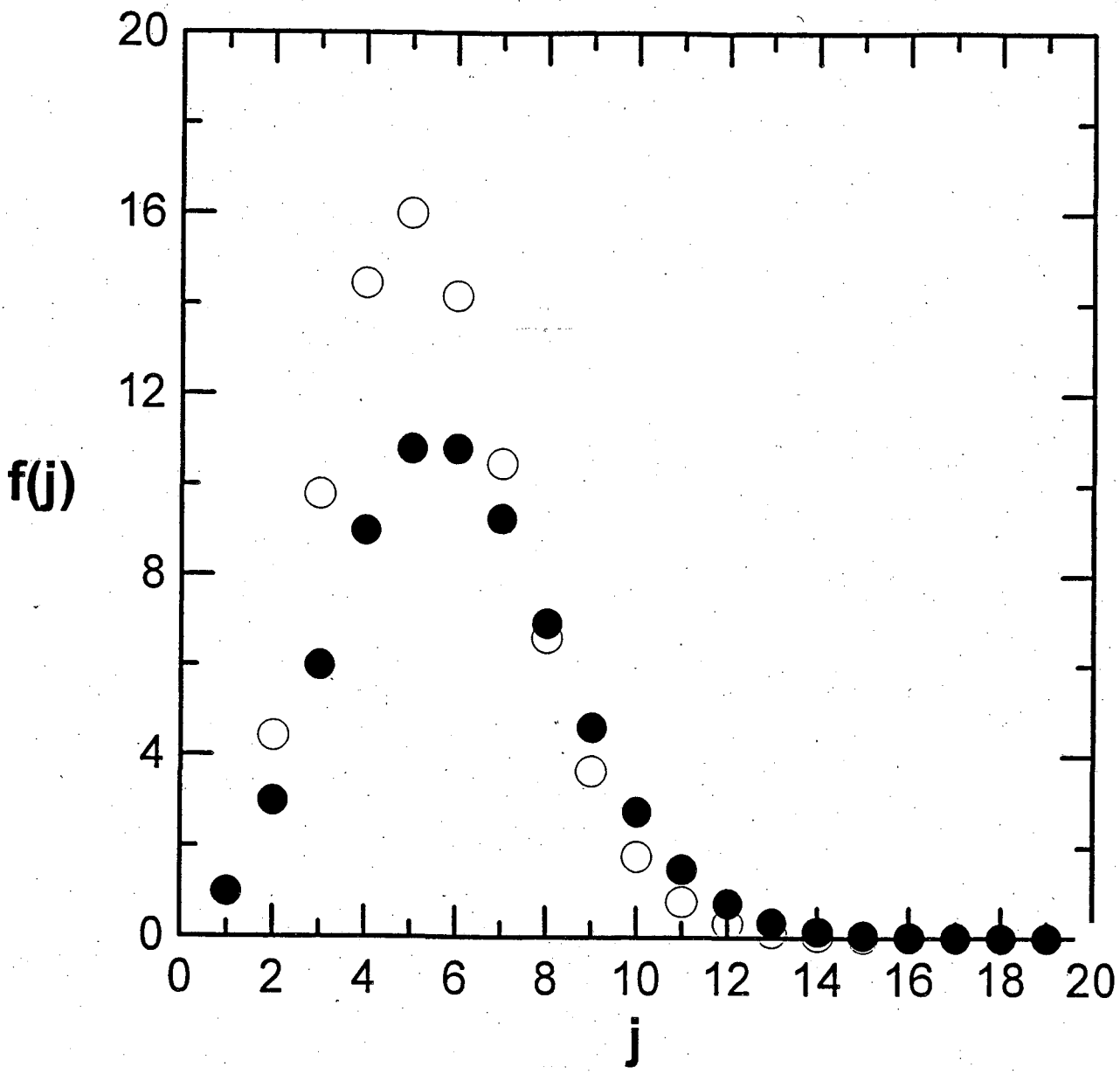
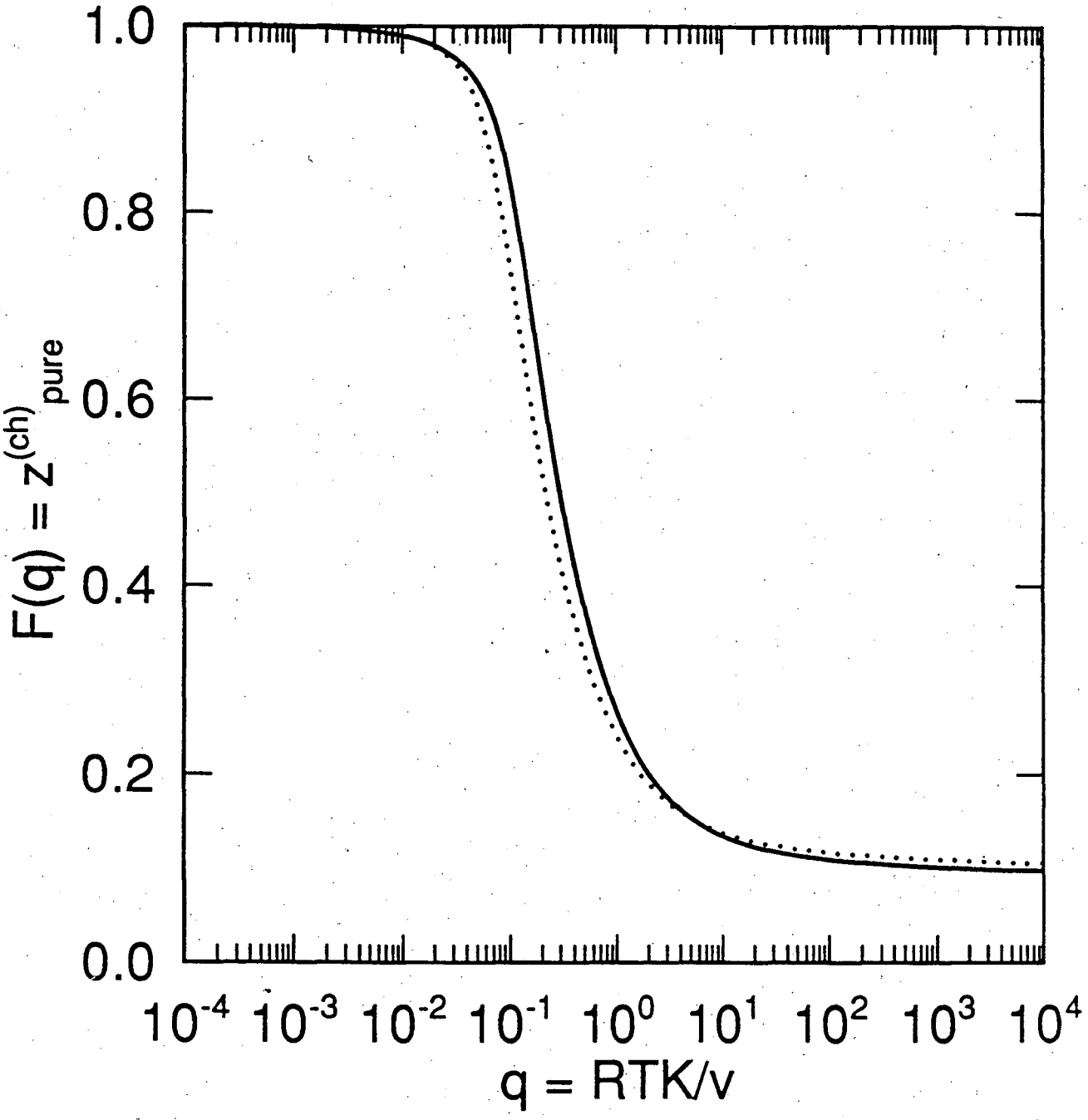


Fig. 1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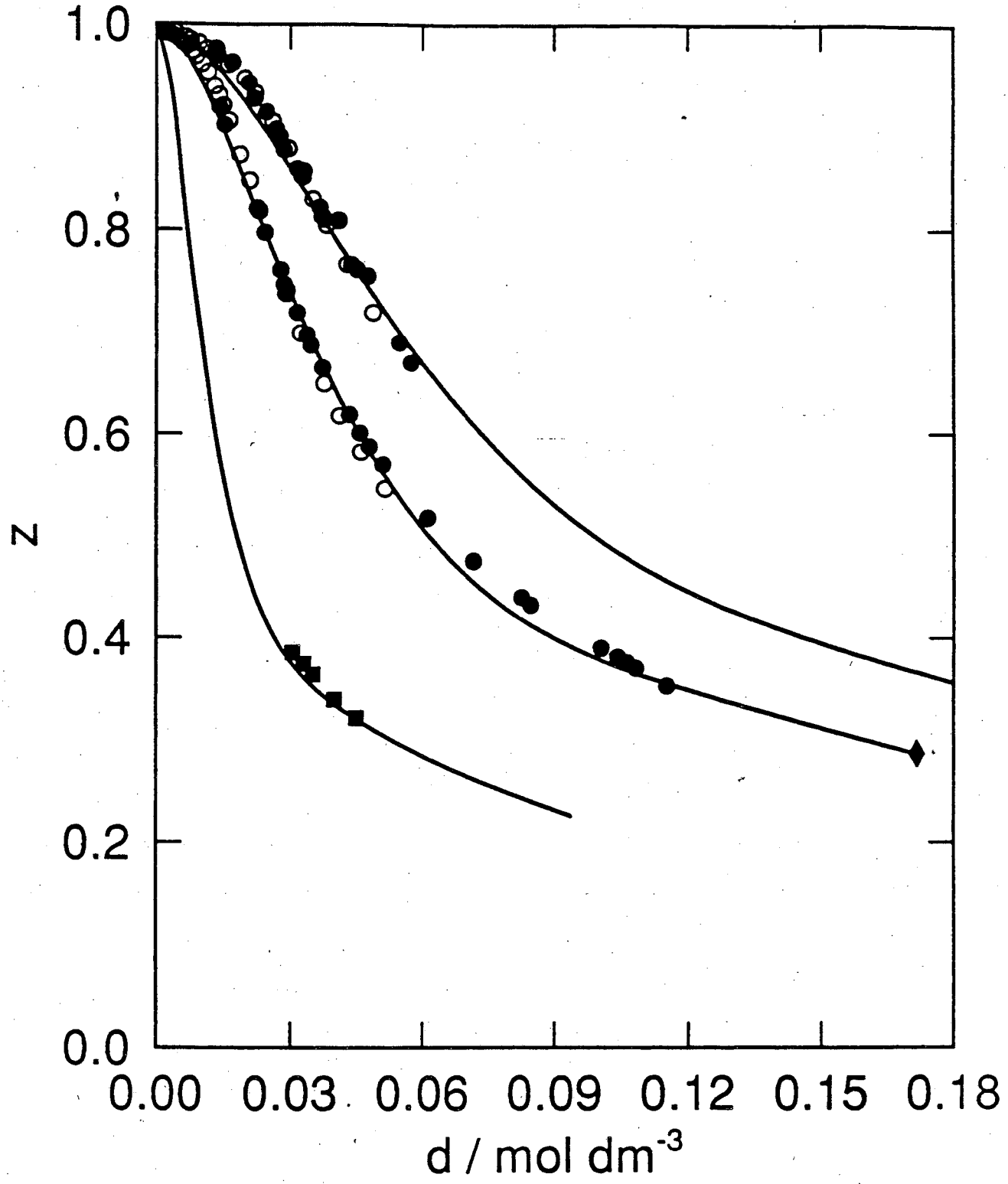
q = RTK/v

Fig. 2



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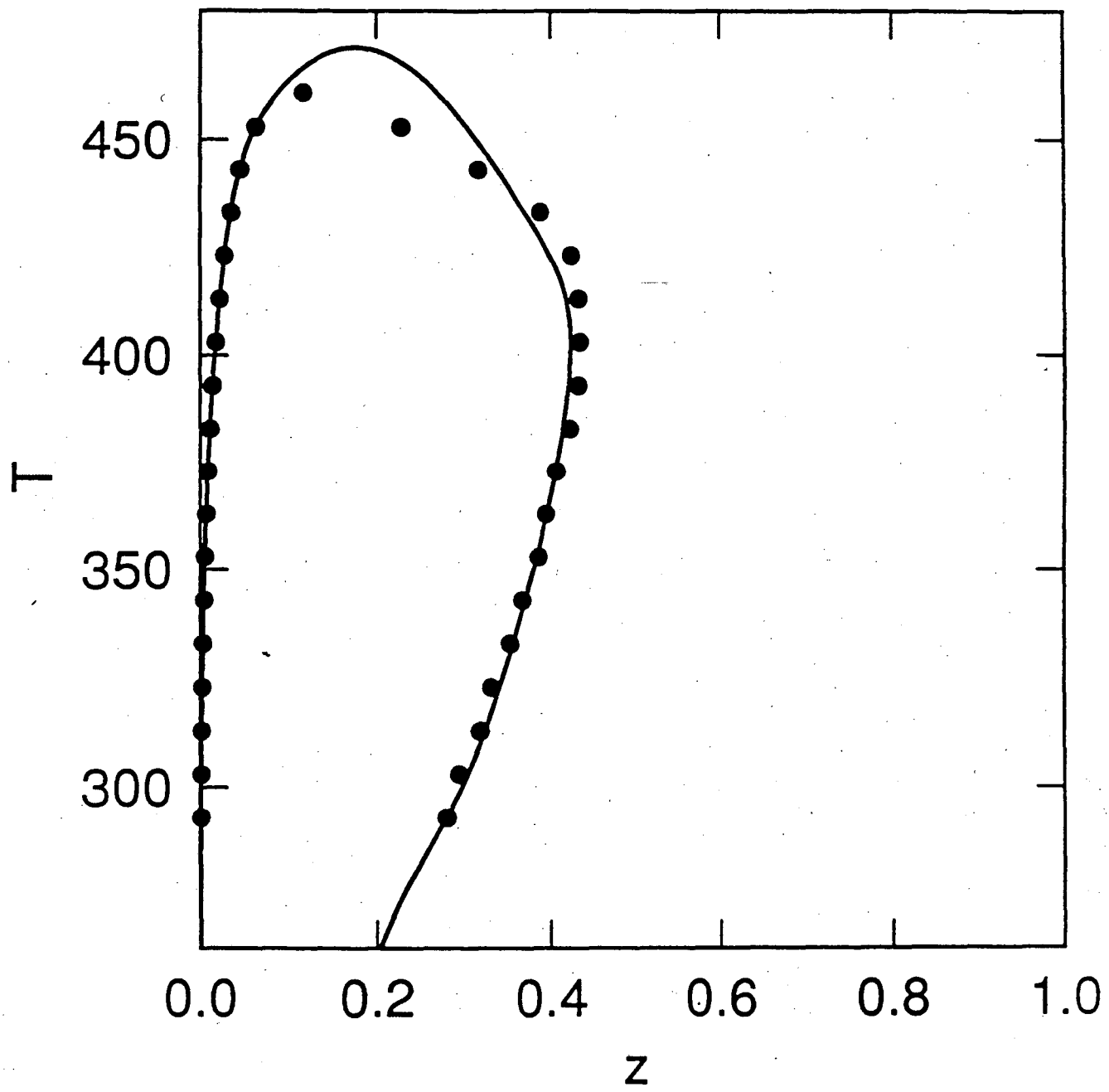


Fig. 4

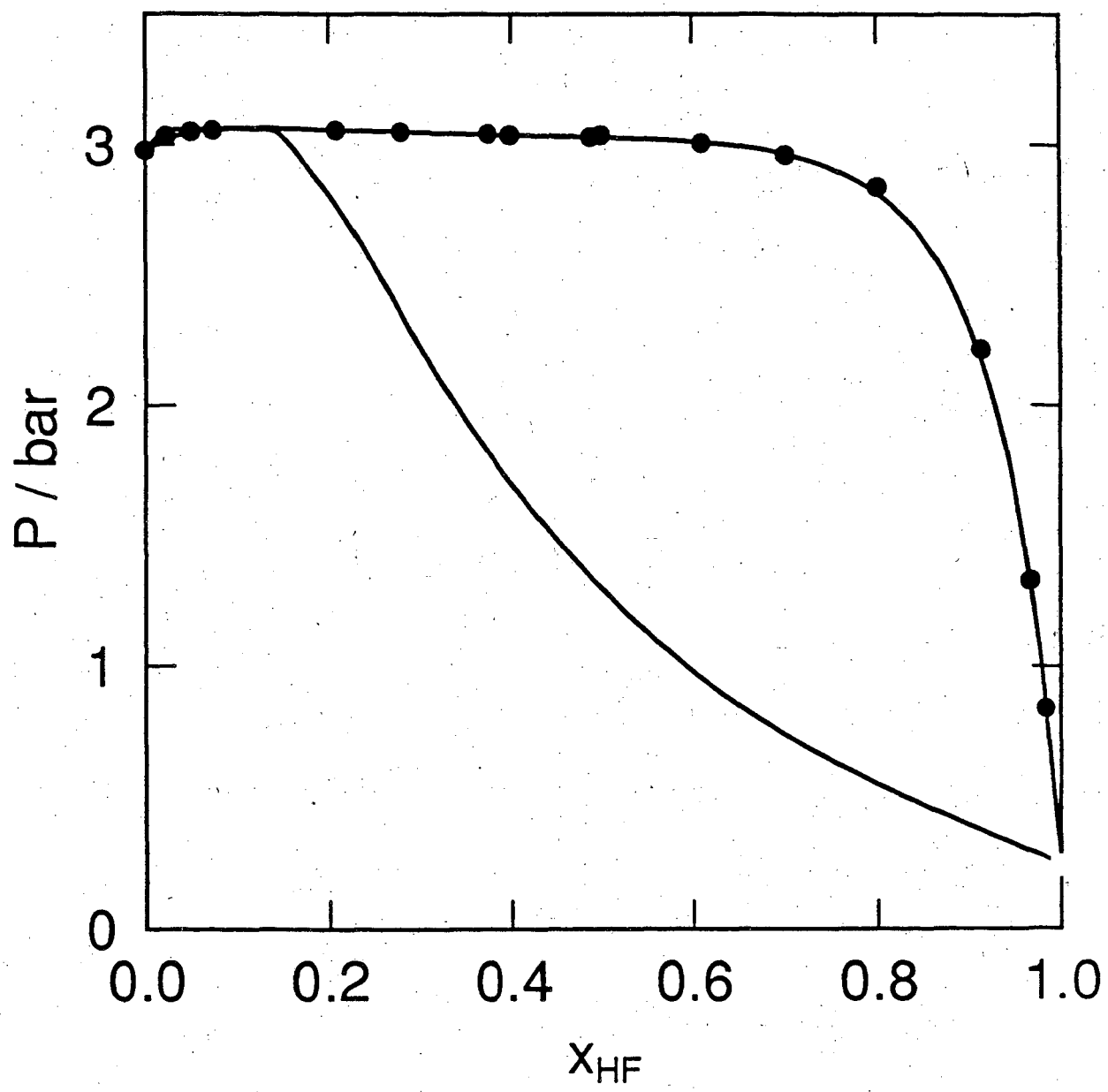


Fig. 5

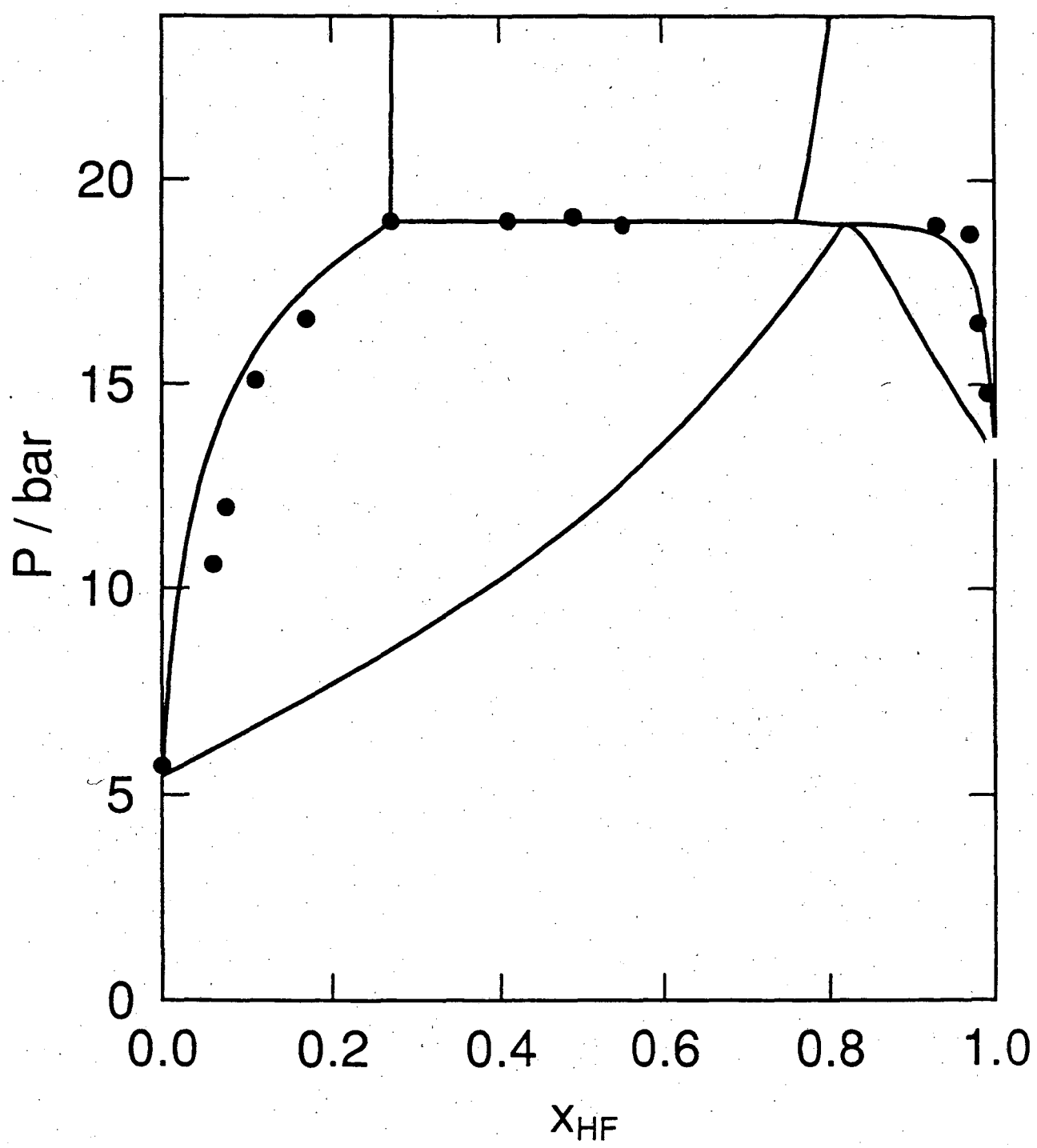
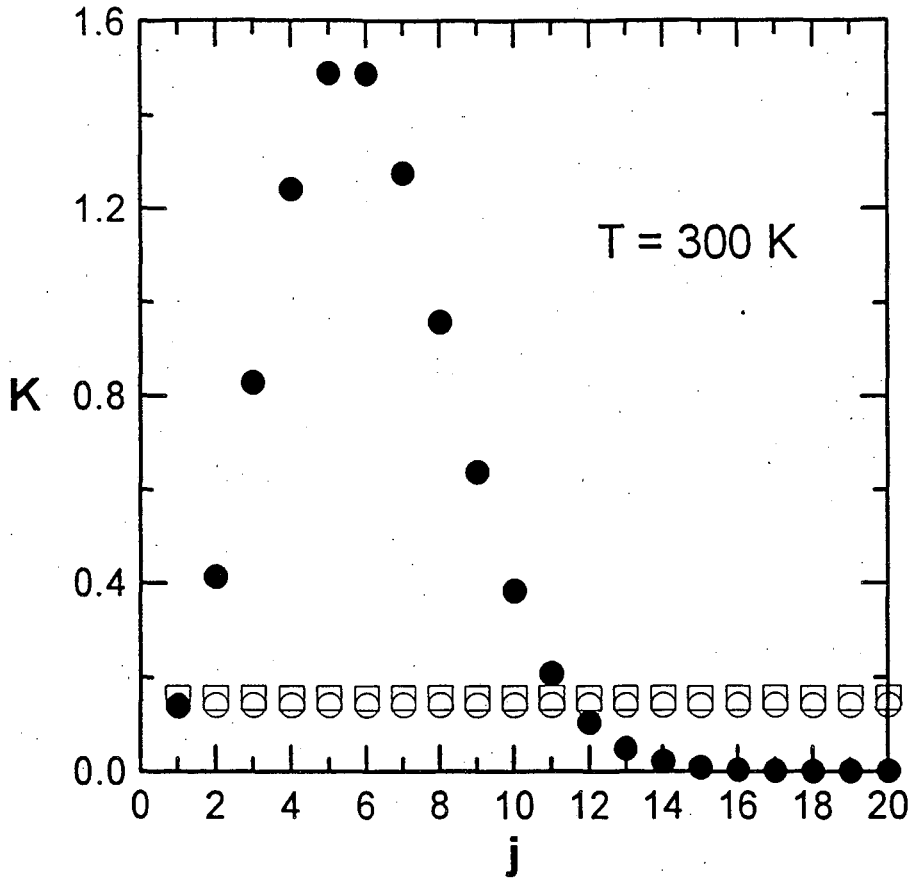


Fig. 6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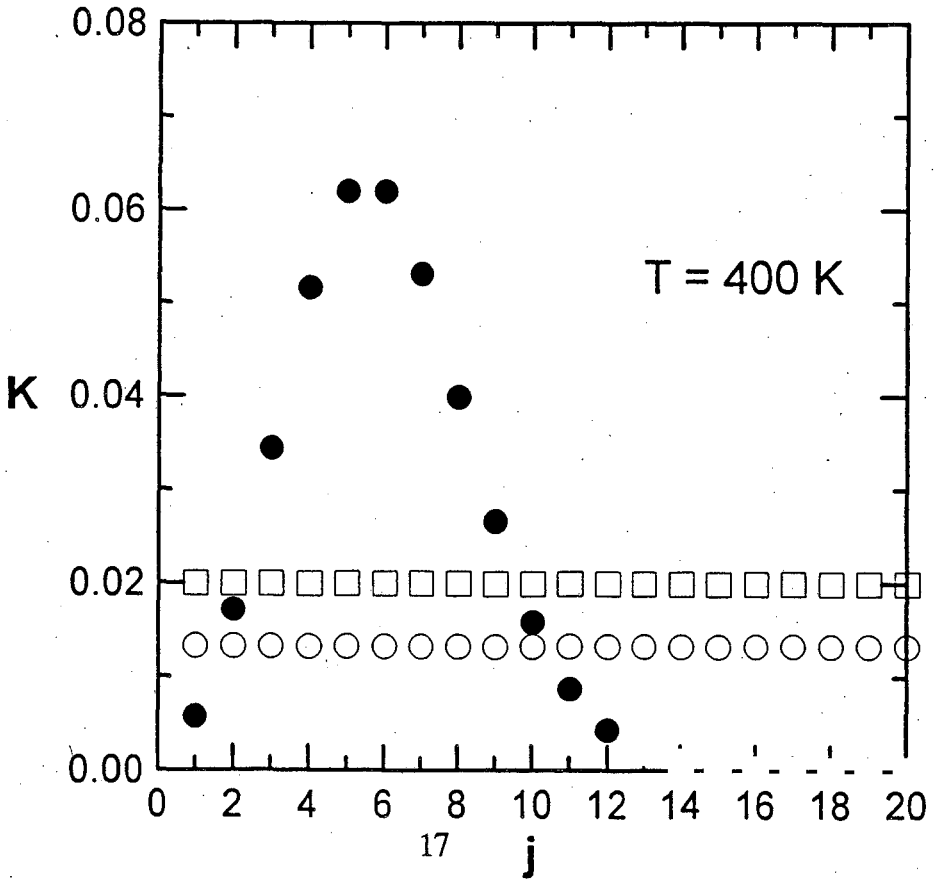
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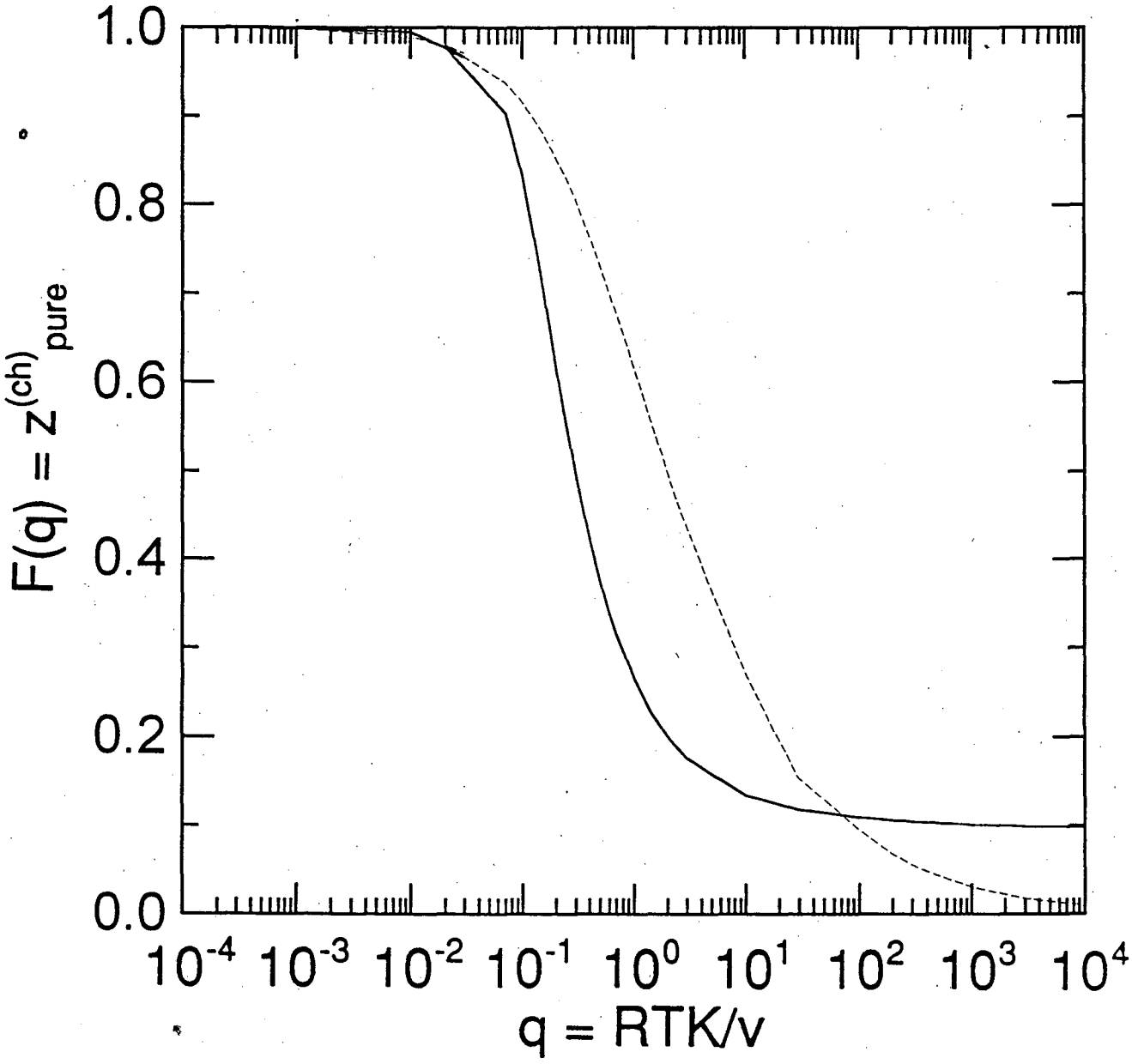
Fig. 7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F(q) = z(ch) pure
10-4 10-3 10-2 10-1 100 101 102 103 104
q = RTK/v

Fig. 8

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