



TECHNICAL NOTE

TERNARY NUCLEATION: KINETICS AND APPLICATION TO WATER–AMMONIA–HYDROCHLORIC ACID SYSTEM

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Abstract—The ternary nucleation of an ideal mixture of three alcohols and a non-ideal mixture of water, ammonia and hydrochloric acid, which is relevant in atmosphere, have been investigated theoretically. In the ideal mixture of three alcohols, the nucleation rates obtained using simplified kinetic approach are compared with the nucleation rates given by a detailed kinetic model. The simplified model is seen to underestimate nucleation rates by 2–3 orders of magnitude. This is mainly due to the crude estimate for the Zeldovich factor in the simplified model. We have proposed a modification to the simplified model. The improved model gives order-of-magnitude estimates for the nucleation rates. The ternary nucleation of water–ammonia–hydrochloric acid is studied with the improved model. The results have been compared with binary nucleation of water and ammonium chloride. The results show that water–ammonia–hydrochloric acid mixture is effectively a two-component system. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

Formation of atmospheric aerosols by homogeneous nucleation has recently received growing theoretical and experimental interest. Conventionally, the formation of new atmospheric aerosol particles is assumed to occur most commonly via homogeneous heteromolecular nucleation of sulfuric acid and water vapors (see, for example, Raes and Van Dingenen, 1992; Russel *et al.*, 1994; Kulmala *et al.*, 1995a). Recently, it has been proposed that e.g. the ternary nucleation of water, ammonia and sulfuric acid occurs easier than the binary nucleation of water and sulfuric acid (Coffmann and Hegg, 1995). However, there are situations where ambient conditions do not favor water–sulfuric acid nucleation. We can also expect that nucleation of some other species occurs via multicomponent routes in the atmospheric conditions. Such species may be, for example, water–ammonia–nitric acid or water–ammonia–hydrochloric acid.

Besides water–ammonia–sulfuric acid system ternary or multicomponent nucleation has been investigated in some earlier studies: Ohta (1982) studied the kinetics of ternary nucleation, Kremer (1978) and Trinkaus (1983) developed general theory for multicomponent nucleation kinetics, Van Dingenen and Raes (1993) have studied nucleation in ternary water–MSA–sulfuric acid system. However, in the studies mentioned above a thermodynamically inconsistent way to evaluate composition and size of critical cluster is used. Viisanen and Strey (1996) have studied experimentally the nucleation of water–*n*-nonane–*n*-butanol–mixture. In the present study we consider ternary nucleation and investigate the accuracy of a simplified model, which can be used as a part of aerosol dynamics models. In our study thermodynamically consistent model is used to evaluate the composition of the critical cluster. It is known, that in binary systems (see Kulmala *et al.*, 1997) there is a clear discrepancy between the nucleation rates predicted by thermodynamically consistent and inconsistent theories.

For an ideal mixture of three alcohols, we have used the most rigorous analytical treatment for the nucleation kinetics and studied the effect of various kinetic simplifications on nucleation rates. As a practical example thermodynamically consistent and kinetically simplified ternary nucleation model has been used to study the nucleation of

water–ammonia (NH₃)–hydrochloric acid (HCl) clusters in the atmospheric conditions. Korhonen *et al.* (1997) have studied the nucleation of the same system as a binary nucleation of water–ammonium chloride particles. In this paper we studied the difference between ternary and binary systems.

2. THEORY

According to the thermodynamically consistent, the so-called revised classical nucleation theory (Wilemski, 1984) the critical cluster composition in three-component systems is obtained as a simultaneous solution of the equations

$$\ln\left(\frac{p_1}{p_1^s}\right)v_2 = \ln\left(\frac{p_2}{p_2^s}\right)v_1, \quad (1)$$

$$\ln\left(\frac{p_3}{p_3^s}\right)v_2 = \ln\left(\frac{p_2}{p_2^s}\right)v_3, \quad (2)$$

where p_i and p_i^s are, respectively, the actual vapor pressure and the saturation vapor pressure of component i , and v_i is the partial molar volume of component i .

The radius of the critical cluster is given by the Kelvin equation:

$$r^* = \frac{2\sigma^*v_i^*}{kT \ln(p_i/p_i^s)} \quad (3)$$

and the free energy of critical nucleus formation is

$$\Delta G^* = \frac{4}{3}\pi r^{*2}\sigma^*, \quad (4)$$

where σ is the surface tension of the solution. The asterisk refers to the critical cluster.

The equilibrium concentration of critical nuclei is

$$c_c^* = F \exp\left(\frac{-\Delta G^*}{kT}\right). \quad (5)$$

The pre-exponential factor F is here approximated by the sum of monomer concentrations, $F = (p_1 + p_2 + p_3)/(kT)$.

The general analytical expression (Trinkaus, 1983) for nucleation rate in many-component systems is

$$J = \frac{|\lambda|/\pi}{\sqrt{-\det(\mathbf{D}/\pi)}} c_c^*. \quad (6)$$

The elements of matrix \mathbf{D} are given by

$$\mathbf{D}_{ij} = 1/(2kT) \delta^2(\Delta G(i, j, k))/(\partial i \partial j)|_*. \quad (7)$$

These elements are essentially the second derivatives of formation free energy of the cluster with respect to numbers of molecules in the cluster, evaluated at critical point. λ is the negative eigenvalue of the product matrix \mathbf{KD} [see equation (18)], and \mathbf{K} is the condensation matrix.

If only monomer–cluster collisions are accounted for, only the diagonal elements of condensation matrix \mathbf{K} are nonzero,

$$k_{ii}(i, j, k) = k(i^*, j^*, k^*; 1, 0, 0) c_i^1, \quad (8)$$

$$k_{jj}(i, j, k) = k(i^*, j^*, k^*; 0, 1, 0) c_j^1, \quad (9)$$

$$k_{kk}(i, j, k) = k(i^*, j^*, k^*; 0, 0, 1) c_k^1, \quad (10)$$

where c_i^1 is the concentration of type i monomers, and the rate of collisions between critical clusters and monomers, $k(i^*, j^*, k^*; i_1, j_1, k_1)$, is given by the kinetic gas theory (Friedlander, 1977)

$$k(i^*, j^*, k^*; i_1, j_1, k_1) = \left(\frac{3}{4\pi}\right)^{1/6} (6kT)^{1/2} \left(\frac{1}{M_1} + \frac{1}{M^*}\right)^{1/2} (V_1^{1/3} + V^{*1/3})^2, \quad (11)$$

where M^* , M_1 , V^* and V_1 are, respectively, the masses and the volumes of the critical cluster and the cluster (in this case monomer) colliding with it. To take cluster-cluster collisions approximately into account Binder and Stauffer (1976) have derived the following expression for the elements of the symmetric condensation matrix \mathbf{K} :

$$k_{ij} = \sum_{i_1, j_1, k_1}^{\xi} i_1 \cdot j_1 \cdot k(i^*, j^*, k^*; i_1, j_1, k_1) c_e(i_1, j_1, k_1), \quad (12)$$

where $k(i^*, j^*, k^*; i_1, j_1, k_1)$ is the rate of collisions between clusters of critical size (i^*, j^*, k^*) and size (i_1, j_1, k_1) , ξ is the cut-off size, above which the concentrations of the clusters are so low that their collisions with nucleating clusters are not taken into account.

For approximation purposes, the general expression (6) can be transformed to a form analogous to Stauffer's expression for binary nucleation rate (Stauffer, 1976; Ohta, 1982).

The conventional expression for the nucleation rate is

$$J = R_{av} Z c_e^*, \quad (13)$$

where the average growth rate R_{av} is defined as

$$\begin{aligned} R_{av} = \det(\mathbf{K}) / \{ \sin^2 \theta [\cos^2 \varphi (k_{jj}k_{kk} - k_{jk}^2) + 2 \sin \varphi \cos \varphi (k_{ik}k_{jk} - k_{ij}k_{kk}) \\ + \sin^2 \varphi (k_{ii}k_{kk} - k_{ik}^2)] + 2 \sin \theta \cos \theta [\cos \varphi (k_{ij}k_{jk} - k_{ik}k_{jj}) \\ + \sin \varphi (k_{ij}k_{ik} - k_{ii}k_{jk})] + \cos^2 \theta (k_{ii}k_{jj} - k_{ij}^2) \}, \end{aligned} \quad (14)$$

and the Zeldovich factor is defined as

$$Z = \frac{-D'_{kk}}{\pi \sqrt{-\det(\mathbf{D}^*/\pi)}}, \quad (15)$$

where D'_{kk} is given by

$$\begin{aligned} D'_{kk} = D_{ii} \sin^2 \theta \cos^2 \varphi + D_{jj} \sin^2 \theta \sin^2 \varphi + D_{kk} \cos^2 \theta + 2D_{ij} \sin^2 \theta \sin \varphi \cos \varphi \\ + 2D_{ik} \sin \theta \cos \theta \cos \varphi + 2D_{jk} \sin \theta \cos \theta \sin \varphi. \end{aligned} \quad (16)$$

Direction angles θ and φ are the angles related to the critical point flow direction (θ is the angle between the flow vector and the k -axis, φ is the angle between the projection of flow vector to (i, j) -plane and the i -axis).

Kremer (1978) has shown that the direction of flow at the critical point is given by the eigenvector of the matrix \mathbf{KD} corresponding to the negative eigenvalue λ :

$$\mathbf{KD}\bar{\mathbf{T}}^* = \lambda \bar{\mathbf{T}}^*. \quad (17)$$

To use the given expression for the average growth rate and the Zeldovich factor, we need to know the number of various types of molecules in the critical cluster, not only the composition of the critical cluster. The total number of molecules in the critical cluster is evaluated by dividing the volume of the cluster by the average volume of a molecule:

$$N_{tot} = \frac{4\pi r^{*3}}{3(x_1 v_1 + x_2 v_2 + x_3 v_3)}, \quad (18)$$

where x_i is the mole fraction of component i in the critical cluster. This formula is sufficient for our purposes, although it does not take into account the surface enrichment properly. Accurate method for evaluating the total number of molecules is presented by Laaksonen

et al. (1993). The number of molecules of type i in the critical cluster is given by

$$N_i = N_{\text{tot}}x_i \quad (19)$$

The second derivatives of the Gibbs free energy are needed to obtain Zeldovich factor and critical point flow direction. To be consistent with equations (1) and (2), the surface tension derivative is set to zero when taking the first derivative of the formation energy.

The reference nucleation rates are calculated using equation (14) with cluster–cluster collisions neglected, and the effects of the following modifications used in literature are compared:

(1) The critical point flow direction is approximated by the direction of steepest descent given by the vector (i^*, j^*, k^*) ($\theta = k^*/\sqrt{i^{*2} + j^{*2} + k^{*2}}$ and $\varphi = j^*/i^*$).

(2) The correction to condensation matrix \mathbf{K} describing cluster–cluster collisions is taken into account.

(3) Kulmala and Viisanen (1991) have used the concept of virtual monomer and derived an approximate expression for the Zeldovich factor:

$$Z = \sqrt{\frac{\sigma^*}{kT}} \frac{v^*}{2\pi r^{*2}}, \quad (20)$$

where $v^* = v_1x_1 + v_2x_2 + v_3x_3$ is the volume of the virtual monomer, and x_i is the mole fraction of component i in the critical cluster. In the approach of Kulmala and Viisanen, the saddle point flow direction is calculated from steepest descent approximation.

(4) The Zeldovich factor in equation (16) behaves like $D/\sqrt{D^n}$, where D represents an “average” element of matrix \mathbf{D} , and n is the number of components in the system. Equation (21) is derived by reducing the many-component case effectively to one-component case, where the Zeldovich factor behaves like \sqrt{D} . We propose and test an improved model, where $Z = D^{1-n/2}$ and D equals the square of the Zeldovich factor given by equation (21). Thus, in the new model, the Zeldovich factor is given by

$$Z = D^{1-n/2} = \left(\frac{\sigma^* v^{*2}}{kT4\pi^2 r^{*4}} \right)^{1-n/2}, \quad (21)$$

and the steepest descent approximation is used for the saddle-point flow direction.

3. RESULTS

In the ideal ethanol–propanol–butanol system the second derivatives are numerically stable and the determinant of second derivative matrix \mathbf{D} is negative at the point given by equations (1), (2) and (20). Thus, expression (16) can be used for the Zeldovich factor. In the reference case, the eigenvectors of \mathbf{KD} are solved to obtain the critical point flow direction.

In this ideal solution, the activity coefficients equal unity, and the partial molar volumes equal to molar volumes of the pure substances. Surface tension of the solution is the mole fraction weighted average of surface tensions of pure liquids. The surface tensions and the saturation vapor pressures of pure compounds are given by Strey and Schmeling (1983) and Schmeling and Strey (1983). For densities of the pure substances we use linear fittings to Timmermanns’ data (Timmermanns, 1965).

Figure 1 shows the modified nucleation rates as a function of the reference rate. The rates are calculated with saturation ratios between 0.68 and 4 and temperatures between 223.15 and 298.15 K. Throughout the nucleation rate range, the steepest descent approximation works very well. The deviation caused by the correction describing cluster–cluster collision is negligible as expected for non-associating vapors.

The rates calculated with Kulmala–Viisanen approximation are 2–3 orders of magnitude lower than the reference rates. The improved model, where $Z = D^{1-n/2}$, overestimates the reference rates by less than one order of magnitude. Our test calculation for two binary

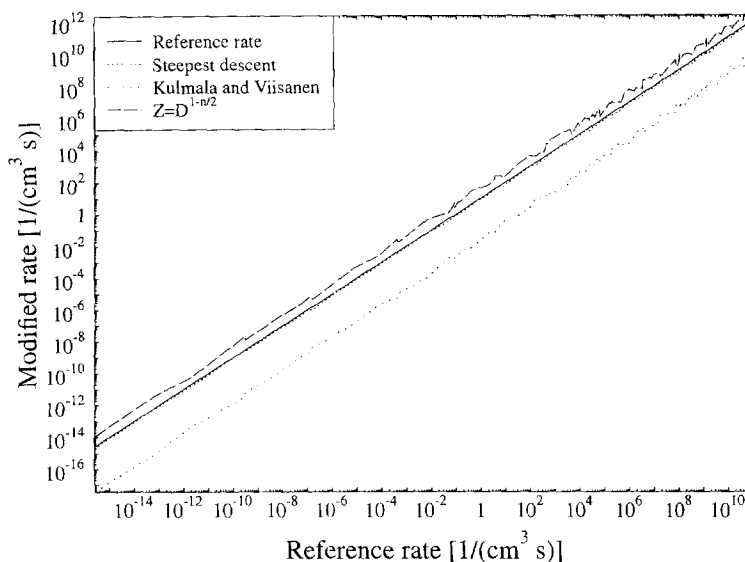


Fig. 1. The modified nucleation rates as a function of the reference rate in an ideal mixture of ethanol, propanol and butanol. The line corresponding to the cluster-cluster corrected rates cannot be distinguished from the line corresponding to the reference rates.

systems, an ideal mixture of ethanol and propanol and a nonideal mixture of water and sulphuric acid showed that in these systems the error in nucleation rate due to Kulmala-Viisanen approximation is 1–2 orders of magnitude. The improved model, which gives $Z = 1$ for binary systems, gives again order-of-magnitude estimates for the reference rates. As expected, that the deviation between Kulmala-Viisanen model and the most rigorous model for nucleation rate increases when the number of components in the system increases.

Water-ammonia-hydrochloric acid is one of the possible nucleation routes in the atmosphere. Recently Korhonen *et al.* (1997) have studied this nucleation route reducing ternary nucleation route to binary one (water-ammonium chloride). In the present study we investigate homogeneous nucleation in real ternary system.

The vapour pressures of pure substances are taken from Clegg and Brimblecombe (1988) and Kim *et al.* (1993). We have followed the earlier ternary nucleation studies of Van Dingenen and Raes (1993) and Coffmann and Hegg (1995) and solved activity coefficients in the ternary solution using the method presented by Kusik and Meissner (1978). The activity coefficients for hydrochloric acid and ammonium chloride in their water solutions and their temperature dependences are obtained from Jacobson *et al.* (1996). The water activities in hydrochloric acid-water and ammonium chloride-water systems are calculated using the data of Hamer and Wu (1972) for osmotic coefficients at 298.15 K and the temperature dependence presented by Jacobson *et al.* (1996). The activity coefficient of ammonium hydroxyl and water activity in water-ammonium hydroxyl system are estimated with the method presented by Bromley (1973) at 298.15 K.

The density of the ternary solution is obtained using the method presented by Van Dingenen and Raes (1993). The density of ammonia-water solution is obtained from the fit that is made using the experimental data tabulated in CRC (1997), and the density of water-HCl is obtained from the fit which is made using the data presented in the International Critical Tables (1928).

The method presented by Van Dingenen and Raes (1993) for calculating the surface tension of the ternary mixture results in an expression that gives correct results in the limits of binary mixtures of water-hydrochloric acid and water-ammonia, but fails to give the surface tension of water-ammonium chloride mixture when there are equal amounts of ammonia and hydrochloric acid in the solution. For this reason we have modified the

equation for the surface tension of the ternary mixture (σ_{mix}), and use the following form:

$$\sigma_{\text{mix}} = \frac{X_{\text{LOW}}\sigma_{\text{NH}_4\text{Cl}}^{\circ} + (X_{\text{HIGH}} - X_{\text{LOW}})\sigma_{\text{HIGH}}^{\circ}}{X_{\text{HIGH}} + X_{\text{WATER}}}, \quad (22)$$

where X_{HIGH} and X_{LOW} are the mole fractions of ammonia and hydrochloric acid in the ternary solution, depending on which one is higher and which one lower in concentration in the solution, and X_{WATER} is the mole fraction of water in the ternary solution. $\sigma_{\text{NH}_4\text{Cl}}^{\circ}$ is the surface tension of the binary solution of water and ammonium chloride, calculated using the value $X_{\text{LOW}}/(X_{\text{HIGH}} + X_{\text{WATER}})$ for the mole fraction of the ammonium chloride. $\sigma_{\text{HIGH}}^{\circ}$ is the surface tension of the binary solution of water and HCl or NH_3 , calculated using the value $(X_{\text{HIGH}} - X_{\text{LOW}})/(X_{\text{HIGH}} + X_{\text{WATER}})$ for the mole fraction of HCl or NH_3 . We have used the mole fractions instead the mass fractions, because surface tension is dependent rather on the number of molecules than on the mass. The surface tensions of binary solutions of water–ammonia and water–ammonium chloride are taken from Kulmala *et al.* (1995b) and Korhonen *et al.* (1997). The surface tension of water–HCl solution is obtained from the fit to the data presented by Landolt–Börnstein (1960).

In water–ammonia–hydrochloric acid system the second derivatives of the formation energy at critical point are numerically unstable. In the critical cluster, the amounts of ammonia and hydrochloric acid molecules appear to be equal, and the droplet is actually a water solution of ammonium chloride. If some excess NH_3 or HCl molecules are brought to the solution, they tend to evaporate very strongly, and the saturation vapor pressures of NH_3 and HCl change by orders of magnitude, i.e. the partial derivatives of the vapor pressures with respect to numbers of molecules are almost infinite. Already at this point, the behaviour of the partial pressures suggests that the system studied is effectively a binary one. Since the second derivatives cannot be calculated reliably, the Zeldovich factor cannot be calculated using equation (16). We have to restrict to the use of the steepest descent approximation for the critical point flow direction and the approximative expression for the Zeldovich factor. We have used equation (22) for the Zeldovich factor, since it seems to work better than the original Kulmala–Viisanen approximation in the ideal ternary system as well as both in ideal and nonideal binary systems. The nucleation rate is calculated without the correction describing cluster–cluster collisions.

We have chosen the temperature range from -10 to 10°C for water–ammonia–hydrochloric acid nucleation study. The nucleating clusters are highly concentrated with the ammonia and hydrochloric acid. This causes considerable freezing point depression, i.e. clusters are liquid at temperatures clearly below zero Celsius degrees. Linear extrapolation of the data tabulated for freezing point depression of aqueous ammonium chloride (CRC, 1997) gives the depression to be *ca* 24.9°C when the molality of ammonium chloride is $7.405 \text{ mol kg}^{-1}$ (approximately the saturated solution). Thus, we assume that no ice formation occurs in the conditions studied. Furthermore, we have chosen the relative humidity for water vapor to vary between 97–99.9%, which ensures that we are clearly above the deliquescence point of ammonium chloride in all the cases studied. The ambient concentrations of HCl and NH_3 vary between 2 and 10 ppbv.

Figure 2 shows the vapor pressure of HCl (which is set equal to the vapor pressure of NH_3) required to produce a nucleation rate having a value of $1/(\text{cm}^3 \text{ s})$, as a function of temperature. The relative humidity is 99%. We have compared our results to the results of Korhonen *et al.* (1997), which have been obtained assuming that the surface tension of the cluster is same as the surface tension of saturated water–ammonium chloride solution (their line *i*). Although Korhonen *et al.* (1997) have used quite crude approximations in their model for binary water–ammonium chloride nucleation, the present study gives almost the same results for the onset conditions as their model. Thus, this study supports the conclusions of Korhonen *et al.* (1997) that significant water–ammonium chloride nucleation in atmosphere is possible only in quite cold and polluted conditions.

Consistently with the results of Korhonen *et al.* (1997), the nucleation rate was seen to increase clearly with increase in the HCl and NH_3 concentrations, but depend only weakly

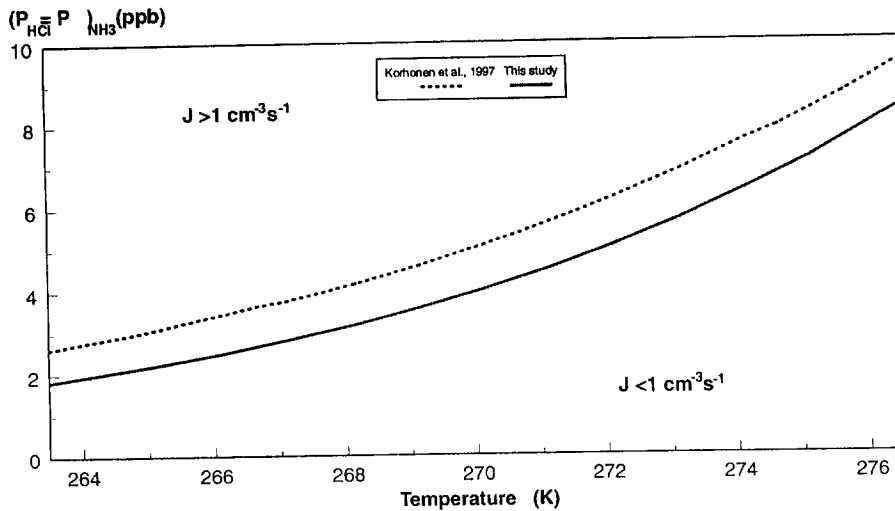


Fig. 2. The vapor pressure of HCl (set equal to the vapor pressure of NH_3) required to produce a nucleation rate having a value of $1/(\text{cm}^3 \text{ s})$. The relative humidity is 99%. The solid line: results from this study. The dashed line: results from Korhonen *et al.* (1997) (their line *i*).

on the relative humidity. Moreover, this result is supported by the measurements of Banic and Iribane (1980) who noticed that the presence of water does not affect the formation free energy of critical cluster significantly, but it affects the kinetics of nucleation.

4. CONCLUSIONS

We have used the thermodynamically consistent model for homogeneous ternary nucleation and tested the effect of different kinetic approximations using an ideal three-component mixture. The steepest descent approximation is found to be valid for a wide range of temperatures, saturation ratios and nucleation rates. The kinetic correction describing cluster-cluster collisions is found to be negligible. The Kulmala-Viisanen approximation for Zeldovich factor underestimates the nucleation rates by 2–3 orders of magnitude in all the cases studied. We have proposed an improvement to the Kulmala-Viisanen approximation, and tested the new model in ternary and binary systems. The improved model overestimates the nucleation rates slightly, but gives order-of-magnitude estimates in both three and two component systems.

The improved Kulmala-Viisanen model has been used for a water- NH_3 -HCl system relevant in the atmosphere. Our simulations show that in the newly formed aerosol particles the concentrations of ammonia and hydrochloric acid are equal, which means that we actually have a binary solution of ammonium chloride and water. Consistently with earlier studies, water-ammonia-hydrochloric acid nucleation in atmosphere is predicted to occur only in cold and highly polluted conditions.

In the present paper we have shown that thermodynamically consistent ternary nucleation model with simplified kinetics can be used in atmospheric conditions to obtain nucleation rates. The model for ternary nucleation is applicable also for other practically important systems.

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