

DIFFUSION OF ZINC IN DOPED NaCl CRYSTALS

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INTRODUCTION

The bivalent cationic (hereafter b. c.) admixtures move through the lattice of alkali halides by changing places with the neighbouring vacancy, so their diffusion is possible only when they form neutral complexes: admixture — cation vacancy. The complexes are formed as a result of electrostatic interaction between excess positive charge of admixture and virtual negative charge of the cation vacancy. Lidiard [1] examined theoretically the dependence of the diffusion coefficient of b. c. admixtures in alkali halides on their degree of association, i. e. on the ratio of the complex number to the total number of ions of the given admixture. When the admixture forms a very diluted solid solution then in a simple model the association — dissociation reaction determining the number of complexes obeys the law of mass action

$$(1) \quad \frac{\text{(complex concentration)}}{\text{(free admixture concentration) \cdot (free cation vacancy concentration)}} = K(T)$$

where $K(T)$ is the reaction constant depending on absolute temperature, on the number of possible complex orientations and on the association energy of these complexes. It follows from Eq. (1) that the association degree of the admixture in „pure“ crystals depends on its concentration, hence its diffusion coefficient will also depend on the concentration.

The b. c. admixtures are built substitutionally into the lattice of most of the alkali halides. In order to preserve the charge neutrality the same number of cation vacancies is formed simultaneously. If the b. c. admixture Zn diffuses into the crystal containing another b. c. admixture M in a substantially higher concentration, the number of free vacancies will practically be determined by the concentration and association energy of admixture M. This number will be high in comparison with a „pure“ crystal and it will not depend on the concentration of admixture Zn. The association — dissociation reaction will be displaced toward the higher complex concentration and the association

degree of the admixture Zn will practically not be dependent on its proper concentration. The diffusion coefficient of the admixture Zn will not depend on Zn-concentration and it will grow with increasing M-concentration.

The aim of this paper was:

- 1) to prove the concentration independence of the diffusion coefficient of zinc (hereafter D) in doped NaCl crystals,
- 2) to compare the effects of different b. c. admixtures on D ,
- 3) to analyze diffusion without vacancy gradient,
- 4) to obtain information about D at higher association degrees of Zn. An estimation of the association energy of added admixtures and of zinc should be possible by comparison of the shape of diffusion isotherms (D versus admixture concentration at the constant temperature T).

The formation of bigger agglomerates of admixtures with vacancies [2] and the formation of vacancy pairs the concentration of which is negligible [3], was not taken into account here.

Theoretical

a) Diffusion in „pure“ crystals

According to Lidiard [1] at high concentrations c_{zn} of the diffusing ions, when $4K_{zn}c_{zn} \gg 1$ (1) and, therefore, the degree of association is high, D reaches its saturated value D_0 . At lower concentrations D decreases with the decreasing concentration of the diffusing ions. When $c_{zn} \ll c_M$, where c_M is the total concentration of b. c. impurities in the crystal, it may be expected, that D will be independent on the concentration c_{zn} (see b) below). In this case Eq. (1) may be written

$$(2) \quad \frac{p_{zn}}{(1 - p_{zn})(1 - p_M)c_M} = K_{zn},$$

where p_{zn} and p_M are the association degrees of the diffusing ions (zinc) and of b. c. impurities (predominantly Ca), respectively. When $p_M \ll 1$ and $K_{zn}c_M \ll 1$ which may be expected at small c_M and at higher temperatures, then

$$(3) \quad p_{zn} \doteq K_{zn} c_M$$

and

$$(4) \quad D \doteq D_0 K_{zn} c_M$$

(1) K_{zn} is the reaction constant of the Eq. (1) for complexes of the diffusing ions.

since, according to Lidiard [1],

$$D = D_0 \frac{d(p_{Zn} c_{Zn})}{dc_{Zn}}$$

If the diffusion is traced by means of an isotope with high specific activity which enables to lower c_{Zn} , it may be expected from Eq. (4) that the D obtained will be independent on c_{Zn} and approximately proportional to the concentration of the b. c. impurities present. The values of D should be substantially lower than those previously published [4, 5].

b) Diffusion in NaCl + MCl_2 crystals

In a doped crystal the formation of free vacancies and complexes may be described by the following equations: a) for the dissociation of the lattice on free cation and anion vacancies with molar concentrations x_{pos} , x_{neg} , respectively,

$$(5) \quad x_{pos} \cdot x_{neg} = K_0^{-1};$$

b) for complex formation of the diffusing b. c. ions

$$(6) \quad \frac{p_{Zn} c_{Zn}}{(1 - p_{Zn}) c_{Zn} x_{pos}} = K_{Zn};$$

c) for complex formation of the uniformly built-in admixture M_{++}

$$(7) \quad \frac{p_M c_M}{(1 - p_M) c_M x_{pos}} = K_M$$

K_0^{-1} , K_{Zn} , K_M are the respective reaction constants depending only on temperature;

d) the charge neutrality condition must be fulfilled

$$(8) \quad x_{pos} = x_{neg} + (1 - p_{Zn}) c_{Zn} + (1 - p_M) c_M$$

According to literature [6, 7] pure NaCl at 590 °C contains $(5-7) \cdot 10^{-6}$ mol fr. free vacancies. From Eq. (5) and from published data [7] it can be shown that in doped crystals $x_{neg} \ll 5 \cdot 10^{-6}$ mol. fr.; x_{neg} may be neglected in Eq. (8) which can then be written more simply

$$(9) \quad x_{pos} = (1 - p_{Zn}) c_{Zn} + (1 - p_M) c_M$$

Eqs. (6), (7), (8) lead to one cubic equation for $p_{Zn}(c_{Zn}, c_M, K_{Zn}, K_M)$.

The measured diffusion profiles (Fig. 2) show that in doped crystals, when $c_M \gg c_{Zn}$, D does not depend on c_{Zn} . According to [1] and Eq. (6) in this case p_{Zn} and x_{pos} should be independent of c_{Zn} . The Eq. (6) will be more simple

$$(10) \quad x_{pos} = (1 - p_M) c_M.$$

In this case it is sufficient to solve two equations

$$(11) \quad \frac{p_{Zn}}{1 - p_{Zn}} = K_{Zn} c_M (1 - p_M),$$

$$(12) \quad \frac{p_M}{1 - p_M} = K_M c_M.$$

Solving Eqs. (11), (12) we get

$$(13) \quad p_{Zn} = \frac{K_{Zn}}{2K_M} \cdot \frac{\sqrt{1 + 4K_M c_M} - 1}{1 + \frac{K_{Zn}}{2K_M} [\sqrt{1 + 4K_M c_M} - 1]}$$

and for D

$$(14) \quad D = D_0 \left\{ \frac{1 - \frac{K_{Zn}}{1 + \frac{K_{Zn}}{2K_M} [\sqrt{1 + 4K_M c_M} - 1]}}{1 + \frac{K_{Zn}}{2K_M} [\sqrt{1 + 4K_M c_M} - 1]} \right\}$$

From Eq. (14) it may be seen that D will be little dependent on K_M i. e. on the association energy of the admixture added and $\lim_{c_M \rightarrow \infty} D = D_0$. With increasing association energy of different admixtures their concentration being equal, D will slightly decrease.

Experimental

The NaCl crystals used were grown in nitrogen surroundings by Kyropoulos' method. The b. c. admixtures were added to the melt as chlorides. The Cd and Zn contents in crystals were determined by colorimetry, the content of Ca and of naturally present impurities by spectral analysis. The ratio of admixture concentration in the melt and in the crystal differs from the ratio given by Dreyfus [8]. The total concentration of b. c. impurities is in the range $(1-3) \cdot 10^{-6}$ mol. fr., the alkalinity of samples is lower than 10^{-4} mol. fr. Crystals with $CdCl_2$ content higher than 0,03 mol-% were „milky“. Samples cleft off the latter were heated before diffusion for six hours at the temperature of diffusion annealing and then rapidly cooled. After this treatment the samples were practically clear.

The $ZnCl_2$ layer (labelled by Zn^{65}) approximately 2μ thick was evaporated on to one surface of samples measuring $14 \times 14 \times 5$ mm. Two samples were coupled so that their active surfaces were adjacent and heated at 590 °C in an N_2 atmosphere. After diffusion annealing 3 mm from the sides of the samples were cleft off.

The annealing temperature was chosen sufficiently high in order not to be limited by low Cd solubility. At low Cd concentrations the effect of calcium naturally present is considerable. The diffusion profile was determined by the method previously described [4]. For the activity measurement of slices a single channel amplitude analyzer Tesla was used.

Results

By our experiments we nearly approached diffusion from an infinitely thin layer into a semi-infinite body. In this case, if D is constant, the following equation holds good:

$$(A) \quad c(x, t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

$c(x, t)$ being the Zn concentration in the depth x below the original surface after t -hours' annealing. Q is the surface density of Zn in the original active layer. As the evaporated layer does not dissolve in the crystal with infinite rapidity, a deviation of the profile measured from Eq. (A) in the layer adjacent to the surface may be expected. In greater depth, if D remains constant, the linear relationship between $\ln c$ and x^2 must be satisfied.

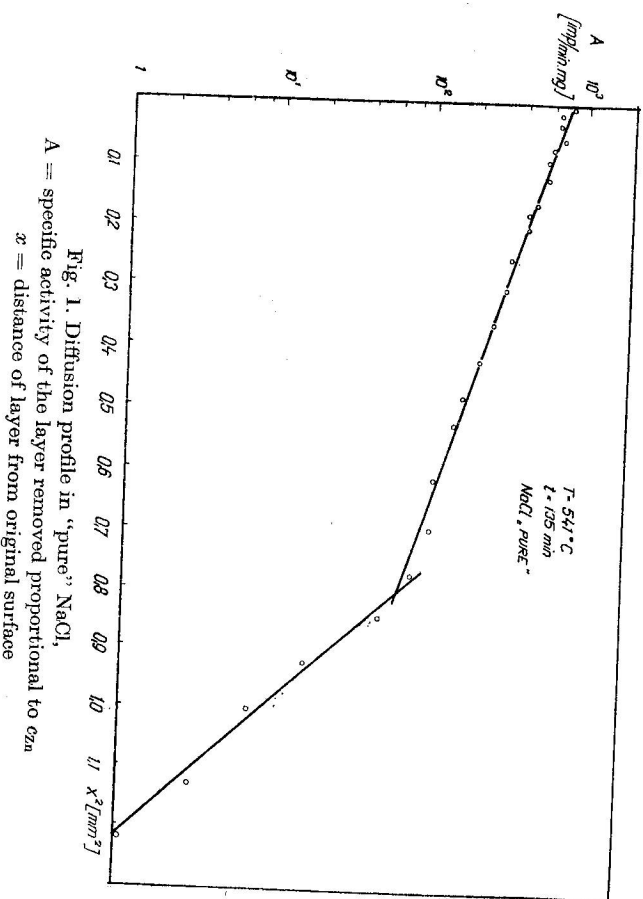


Fig. 1. Diffusion profile in "pure" NaCl, $A =$ specific activity of the layer removed proportional to c_{zn} , $x =$ distance of layer from original surface

In the case of diffusion into „pure“ crystals we observed an evident „knee“ to the lower D (Fig. 1) in all profiles, when Zn concentration dropped to the level of naturally present b. c. impurities, which is practically determined by the Ca^{++} concentration [5]. No temperature dependence of the zinc concentration in the knee was found.

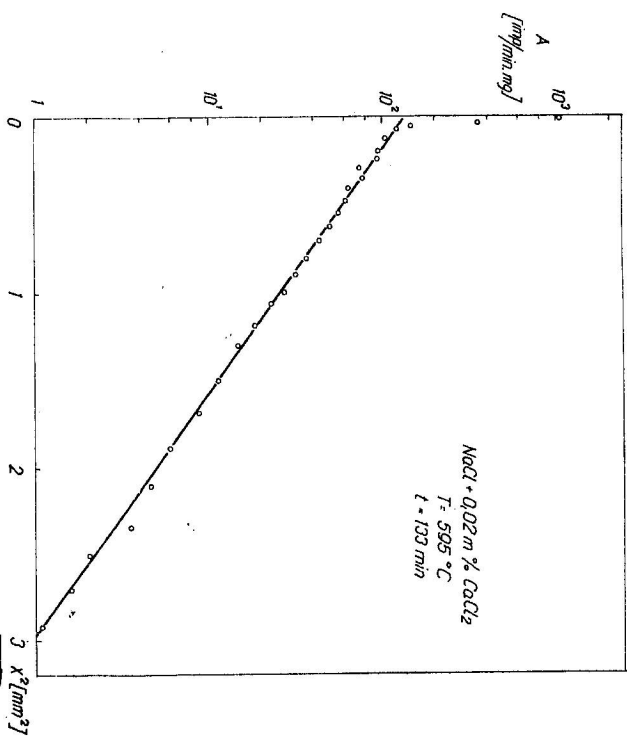


Fig. 2. Diffusion profile in doped NaCl if $c_{Ca} \gg c_{zn}$ ($M = Ca$ or Cd).

In doped crystals where admixture concentration was by several orders higher than the Zn concentration, the dependence of $\ln c$ on x^2 was linear in the whole measured Zn concentration range (Fig. 2). The linearity was preserved when the following admixtures were chosen 1) calcium, 2) cadmium in concentration not higher than $5 \cdot 10^{-2}$ mol-%, 3) cadmium in higher concentration if the samples were pre-heated (see Experimental).

We did not succeed in obtaining a linear dependence of $\ln c$ vs x^2 by means of Zn as admixture and thus in achieving a diffusion without a concentration gradient. The Zn solubility in NaCl at $590^\circ C$ is only $2.5 \cdot 10^{-4}$ mol. fr. [9] and when grown from the melt the Zn content in crystals was even much lower. The Cd doped crystals with $c_{Ca} > 5 \cdot 10^{-2}$ mol-% nonpre-heated had

compound diffusion profiles (Fig. 3). In the resulting dependence of D on Cd concentration (Fig. 4), therefore, only results obtained on pre-heated samples were taken into account.

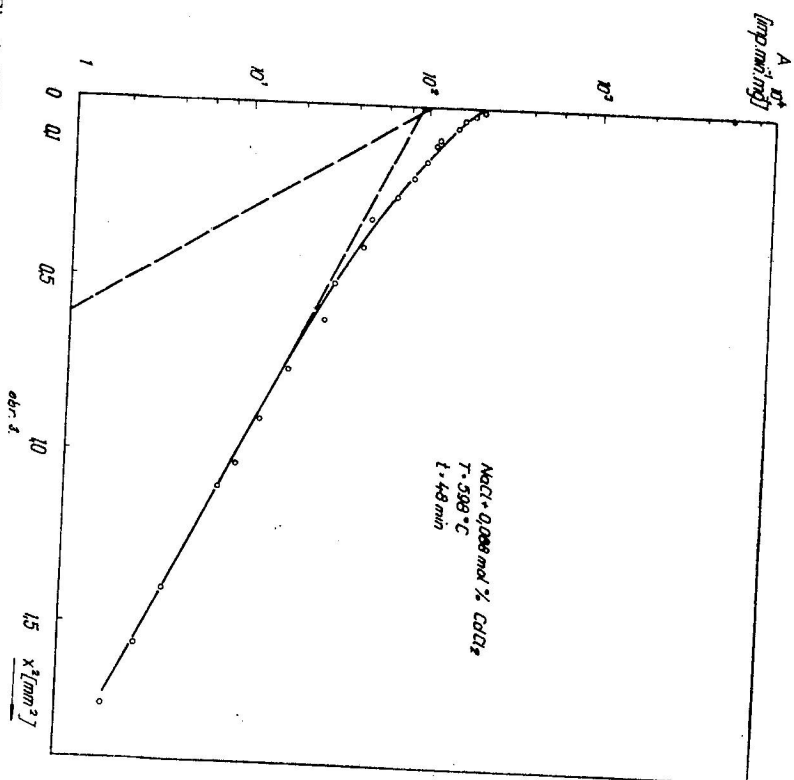


Fig. 3. Diffusion profile in doped nonpre-heated NaCl with high Cd content

Discussion

a) Diffusion in the „pure“ crystal
 The concentration independence of D observed in the range (5—20) · 10⁻⁵ mol. fr. Zn⁺⁺ (Fig. 1) follows from the linearity of $\ln c$ vs x^2 . It may be tentatively explained by D having reached the saturated value D_0 . A rough estimation shows that the necessary association energy of Zn⁺⁺ complexes should be at least 0.55 eV. The following facts, however, are against this explanation of the shape of the diffusion profile:
 1) according to Bassani and Furni [10] an association energy lower than 0.38 eV is expected,

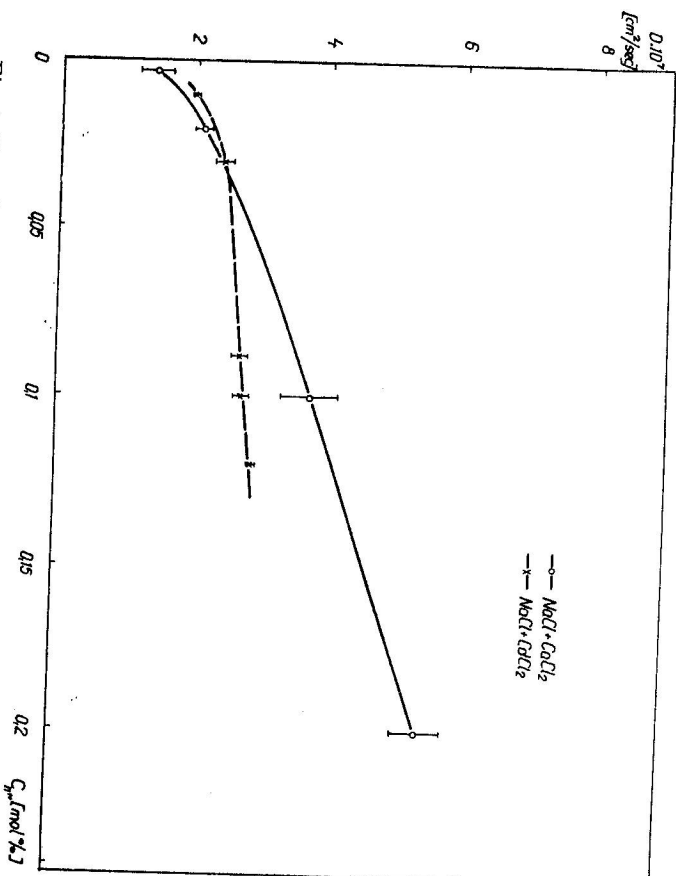


Fig. 4. Dependence of D in doped NaCl crystals on the admixture content

2) our further research (see Discussion b)) shows that D_0 is substantially higher,
 3) the concentration of the „knee“ is independent of temperature.
 We are proceeding, therefore, in the investigation of diffusion in crystals by a modified experimental method.

b) Diffusion of Zn in NaCl + CaCl₂ crystals

Fig. 5 shows the dependence of D on c_a computed according to Eq. (14) for experimental points in the range (2—20) · 10⁻⁴ mol. fr. Ca, for various K_{ca} given in literature (Table 2). Within the limits of errors the most suitable curve expressing Eq. (14) is d . But the points measured are better expressed by curve e , which demands a lowering of Zn association energy and an increase of D_0 at higher concentrations of admixtures. It is probable that the difference between the measured and computed shape is caused by a lowering of the effective association energy of Zn with growing admixture concentration when the interaction between free defects cannot be neglected any more. The rough estimation of the correction caused by this interaction given by Ikeda [13] for NaCl + CdCl₂ would support this explanation. An increase of D_0 with the

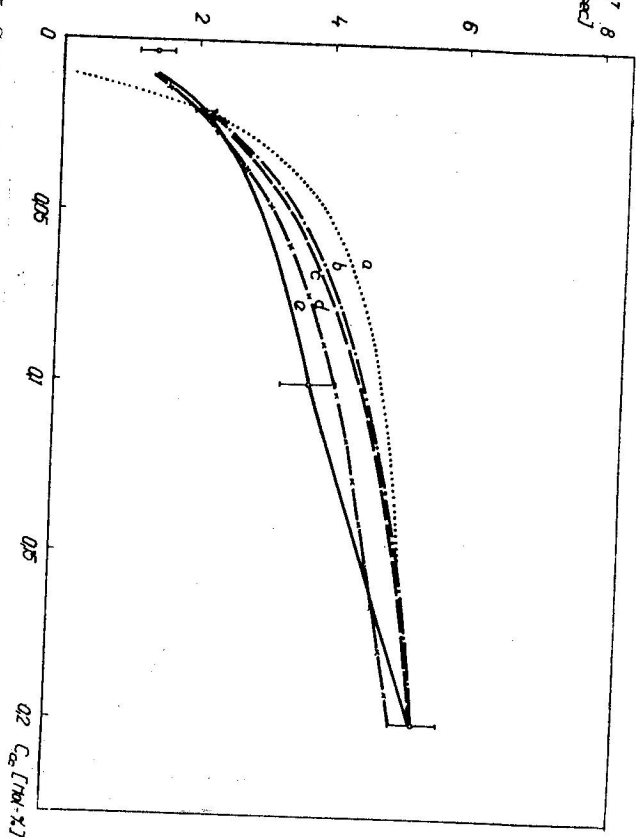


Fig. 5. Computed dependences of D on the admixture content in crystal for various association energies.

Ca concentration may be explained as a result of the growing defectivity of the lattice.

e) Diffusion of Zn in NaCl + CdCl₂ crystals

The slight dependence of D on the concentration of Cd higher than 3 · 10⁻⁴ mol. fr. is probably caused by the limited Cd⁺⁺ solubility. A further growth of the Cd concentration increases neither the number of free vacancies nor the D . Excess cadmium is precipitated in the form of a second phase or in the form of neutral agglomerates of cadmium ions and vacancies.

In nonpre-heated crystals with a high Cd content the concentration of Cd built in the lattice in the course of diffusion annealing probably remains low — close to solubility at room temperature. The rapidly diffusing component (Fig. 3) corresponds probably to the diffusion along the boundaries of the precipitates.

Conclusion

It has been shown that in doped NaCl crystals when the concentration of the built-in b. c. admixture is substantially higher than that of the diffusing admixture, the D is independent of the concentration c_{zn} . If the diffusion of

Table 1. Diffusion coefficients D and average concentrations of diffusing zinc \bar{c}_{zn} in various doped NaCl crystals

Sample	Admixture	Admixture content in melt [mol-%]	Admixture content in crystal [mol-%]	$D \cdot 10^7$ [cm ² /s]	$\bar{c}_{zn} \cdot 10^8$ [mol-%]
C 12	"pure"	—	0,003 ⁽³⁾	1,62	11
C 39	Zn	0,4	5 · 10 ⁻⁴	1,12	16
C 43	Ca	0,02	0,02	1,55	12
C 57	Ca	0,1	0,1	1,55	10
C 47	Ca	0,2	0,2	2,24	3
C 86	Cd	0,06	0,01	1,98	3
C 62	Cd	0,3	0,03	4,18	4
C 81	Cd	0,8	0,088	3,34	2
C 94	Cd	0,8	0,12	5,81	1
C 65	Cd	0,8	0,1	5,07	1
				2,00	1
				1,94	9
				2,44	5
				2,84	4
				2,60	5
				2,95	8
				2,87	7
				2,81	7
				2,86	8
				2,62	6

⁽³⁾ The total concentration of b. c. impurities

Table 2. Computed association energies of zinc complexes ΔG_{zn} (for different values of Ca⁺⁺-association energy ΔG_{Ca} obtained from literature) for curves in Fig. 5

ΔG_{Ca} [eV]	References	ΔG_{zn} [eV]	Curve in Fig. 5
0,08	[11]	0,42	a
0,38	[10]	0,38	c
0,24	[12]	0,39	b
0,5	—	0,4	d
0,38	[10]	0,25 for $c_{Ca} > 0,1$ mol-% 0,42 for $c_{Ca} < 0,1$ mol-%	e

a poorly soluble substance is investigated, where a diffusion without concentration gradient cannot be performed, it is more convenient to use doped crystals and so to achieve a diffusion without vacancy gradient. In "pure" crystals the D depends both on the concentration of the diffusing substance and on the purity of the crystal. In doped crystals the D depends only on the concentration of the admixture which is known.

The comparison of the diffusion isotherms for $\text{NaCl} + \text{CaCl}_2$ was possible only for small concentrations of Ca and Cd (Fig. 4). It suggested that the association energy of Ca complexes is the same or a little higher than that of Cd complexes.

The analysis of the shape of the diffusion isotherm in Ca doped crystals shows that the effective association energy of Zn complexes will decrease with increasing admixture concentration.

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