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— Review —

ON THE SYNERGISM OF HOMOGENEOUS CATALYSTS

By

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Abstract

The qualitative analysis was made for the synergism phenomenon of homogeneous catalysts. The classification of those phenomena based on mechanism of interactions between two catalysts and two substrates is proposed. Some examples conforming this classification are given.

Introduction

“Activation” of one catalyst by another in heterogeneous catalysis is well known. It leads to a disproportionate increase of the reaction rate with changing the composition of mixed catalysts or to the so-called synergistic effect. In homogeneous catalysis the synergism phenomenon is seldom met. Here, as well as in heterogeneous catalysis, in detail are described the cases of increasing the activity due to the compounds which by themselves are not catalysts of reactions in given conditions but their introduction into the reaction medium increases the catalyst activity. Such compounds have been named activators¹⁾ (or promoters in heterogeneous catalysis).

Interest on the synergistic effect considerably increases at present due to the new possibilities revealed by this phenomenon, *e.g.*: elucidation in detail of the mechanism of reactions or their separate stages, identification of possible intermediate products, increase of activity and/or selectivity of catalytic systems for certain reactions. The latter is particularly important in practice (chemical engineering) so long as now in industry complex catalytic systems are already used which involve the synergistic effect.

The present paper discusses problems of synergism of the action of several (two, as a rule) homogeneous catalysts. In some cases one of the catalysts may not display an appreciable catalytic activity in reaction conditions; nevertheless, it catalyzes the reaction under study at different ligand concentrations, temperature, etc.

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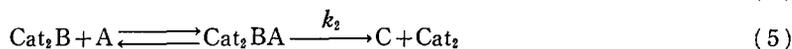
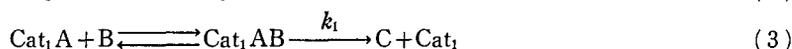
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Let us examine in general schemes the catalysts action in the cases when they display the synergistic effect.

For example, the simple reaction

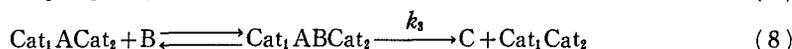


is accelerated by Cat_1 and Cat_2 catalysts, the limiting stage in both cases being the intermediate product decomposition :



The synergistic effects in the given reaction will be observed in the following cases :

1. Cat_1 and Cat_2 catalysts interact with each other forming a new, more active catalytic system

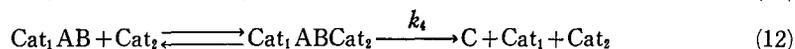


Here the following condition must be fulfilled :

$$k_3 > ik_1 + jk_2 \quad \text{or} \quad k_3 \gg ik_1 + jk_2 \quad (9)$$

where i and j are the coefficients determining the partial concentrations of catalysts.

2. Cat_2 catalyst interacts with the intermediate compound formed by Cat_1 and initial substrates and accelerates its decomposition :



The obligatory condition is

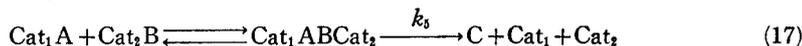
$$k_4 > ik_1 + jk_2 \quad \text{or} \quad k_4 \gg ik_1 + jk_2 \quad (13)$$

Analogous effect will be observed if the intermediate compound is formed by Cat_2 catalyst with substrates, and Cat_1 accelerates its decomposition, *e. g.*



3. Cat_1 catalyst forms intermediate compound with substrate A while Cat_2 catalyst forms $Cat_2 B$ compound with B ; interaction of two intermediate products proceeds with higher rates than in cases of "simple" catalysis (2-5).

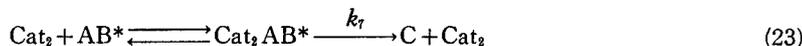
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The obligatory is the condition :

$$k_5 > ik_1 + jk_2 \quad \text{or} \quad k_5 \gg ik_1 + jk_2 \quad (18)$$

4. Catalysts do not react with each other neither during the initial, prereaction period nor after the formation of intermediate compounds but one of the catalysts interacts with an intermediate substrate species initially activated by another catalyst accelerating the formation of reaction products :



Obligatory conditions are

$$k_7 > k_6 \quad \text{or} \quad k_7 \gg k_6 \quad (24)$$

Thus, all known to us cases of synergism of homogeneous catalysts may be divided into four types. Here are examples confirming such classification.

1. *First-type reactions.*

Among numerous works on redox reactions catalyzed by complexes of metals and ligands only those pertain to the type under study in which ligands (usually anions) are catalysts of given reactions. These processes are widely studied at our institute under the guidance of Prof. D. V. Sokolsky.²⁾

Thus, for example, halogen ions (Cl^- , Br^- , J^-) catalyze the process of phosphine oxidation to phosphoric acid³⁾ :



However, phosphine does not react directly with an oxidizer molecule (Ox).

With no metal complexes being present, the following reaction takes place :



X_2 is formed as a result of reaction



where Red is a reduced oxidizer form. Reaction (26) may be written down according to the following stages :

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On the basis of large experimental material scientific workers of our institute Ya. A. Dorfman *et al.* propose two groups of metal complexes one of which catalyzes reaction (27). These are Cu^{+2} , Fe^{+3} , Au^{+3} , V^{+5} , Pt^{+4} , Ce^{+4} , Mo^{+4} , W^{+6} compounds. Another group of metal ions (Cu^+ , Ag^+ , Hg^{+2} , Au^+) activates phosphine.

Considerable synergism in the given reaction is displayed by $Cu(II, I)$ and $Fe(III)$ complex compounds and halogenide ions. The authors explain the observed regularities by the fact that due to the complex formation between metal ion, ligand and substrate molecule (PH_3), electron is transferred from a ligand orbital to a central ion orbital; as a result, the radical is formed (*e.g.* J^0 , Cl^0 , *etc.*) which attacks a substrate molecule in the inner sphere or outside it and oxidizes it. The greater is the ion ability to donate an electron, the higher is the rate of the catalytic process. Thus, rate constants of the reaction (25) catalyzed by Cl^- , Br^- , J^- ions in the presence of $Cu(II)$ ions are $1:10^2:10^6$ respectively.²⁾

Particularly interesting is the reduction of $Cu(II)$ ions by phosphine. As a matter of fact, the catalysis here is realized by three species:

- $Cu(II)$ ions (generation of X^0 active species);
- $X^- - X^0$ ions (intermediate PH species is generated by reaction (28));
- $Cu(I)$ ions which activate PH_3 molecule.

Synergism appears due to the first catalysts pair whereas due to $Cu(I)$, autocatalysis is observed.

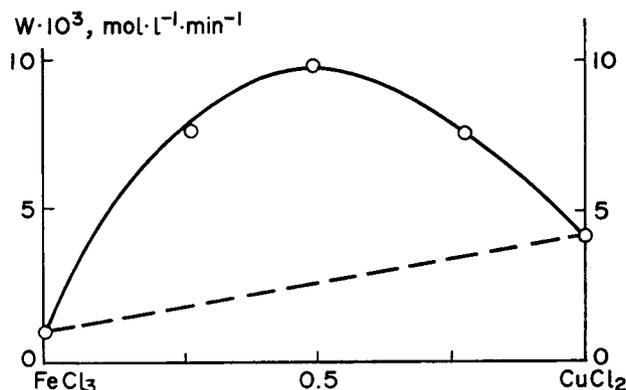


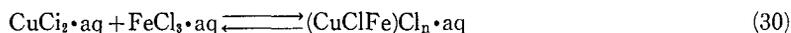
Fig. 1. Dependence of the rate of SO_2 oxidation on the composition $CuCl_2 + FeCl_3$ catalyst, $SO_2 + H_2O + O_x \longrightarrow H_2SO_4 + Red$
 $Cat_1 = CuX_2$; $Cat_2 = FeX_3$.

$t = 25^\circ C$, $[Cat] = 0.05 \text{ mol} \cdot \text{l}^{-1}$, Broken line is the theoretical dependence $R = f(Cat)$ in absence of synergism

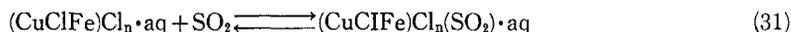
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First-type synergism is also found in the reaction of SO_2 oxidation to SO_3 on haloid copper (II) and iron (III) complexes in aqueous solutions (Fig. 1). This reaction is catalyzed by both haloid Cu (II) and Fe (III) complexes.⁹ We have shown that copper (II) chloride introduction into iron (III) chloride solution is accompanied by a considerable activity increase of the system. CuCl_2 - FeCl_3 system study by ESR and visible spectroscopy (400-800 nm) methods has shown that interaction takes place between components. From these data it follows that a binuclear complex is formed, the Cu:Fe ratio in which is 1:1.

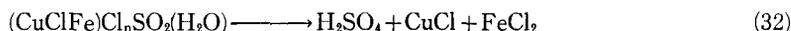
In general, the reaction scheme may be presented in the following way. In solution a mixed heteronuclear complex



is formed with which a dissolved SO_2 (or HSO_3^-) molecule interacts forming a sulphodioxide (or sulphite) complex



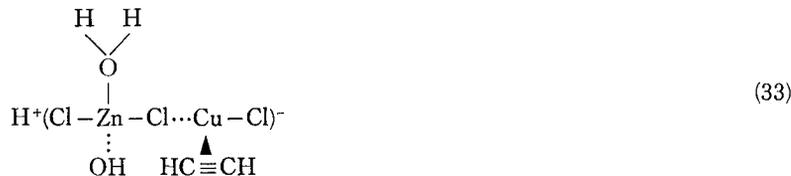
As a result of the inner-sphere redox-decomposition of the latter, S^{+4} oxidation to S^{+6} and central ions reduction to Cu (I) and Fe (II) take place



Oxidation of these ions by air oxygen makes this process cyclic.



O. N. Temkin and R. M. Flid have found that catalytic activity of the CuCl - ZnCl_2 aqueous solution in acetylene hydration reaction is much higher than the catalytic activity of its components.¹⁰ The authors suggest that the given system activates components according to the bifunctional mechanism. Thus, CuCl in the complex



activates acetylene as a result of π -complex formation, while OH^- group is added to acetylene C atom due to transference from a zink atom, *e. g.*



The preliminary formation of the above given complex is confirmed by the fact that in the system there is, practically, no free water, and CuCl is dissolved due to a complex formation with zink chloride.

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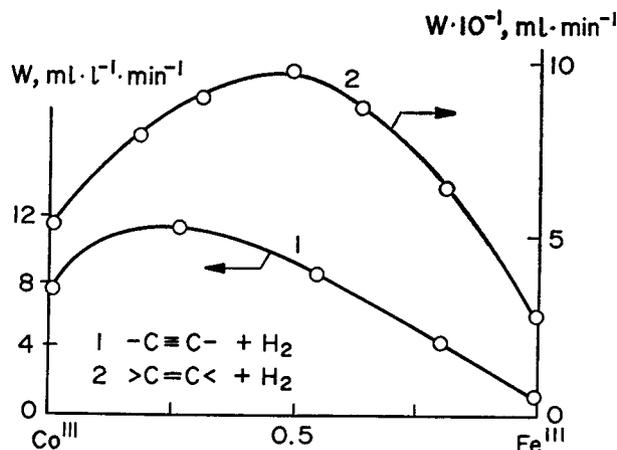


Fig. 2. Dependence of the rate of phenylacetylene hydrogenation on the composition $\text{Co}(\text{acac})_3 + \text{Fe}(\text{acac})_3$ catalyst,⁶⁾ $\text{C}_6\text{H}_5\text{C}\equiv\text{CH} + \text{H}_2 \longrightarrow \text{C}_6\text{H}_5\text{CH}=\text{CH}_2 \xrightarrow{\text{H}_2} \text{C}_6\text{H}_5\text{C}_2\text{H}_5$, $\text{Cat}_1 = \text{Co}(\text{acac})_3 + D$, $\text{Cat}_2 = \text{Fe}(\text{acac})_3 + D$, $D = \text{Al}(\text{C}_2\text{H}_5)_3$.
 $t = 25^\circ\text{C}$, $[\text{Cat}] = 0.28 \text{ mmol}$
 1 $\text{C}\equiv\text{C}$ bond hydrogenation
 2 $\text{C}=\text{C}$ bond hydrogenation

An interesting case of synergism of Ziegler-Natta type mixed catalysts for hydrogenation of acetylenic and ethylenic compounds was observed by D. V. Sokolsky and coworkers⁶⁾ (Fig. 2). The greatest rate increase occurred in the case of mixed $\text{Co}(\text{acac})_3 + \text{Fe}(\text{acac})_3$ catalyst with triethylaluminum (phenylacetylene hydrogenation). By the gamma-resonance spectroscopy method it has been shown that between mixed catalyst components an interaction takes place leading to stabilization of alkyl metal (III) complexes in the field of two and more nuclei of different metals (Fe, Co) and to other changes of composite complex properties. It has also been found that a quadruple splitting of iron is lower with mixed acetylacetonates, which indicates a symmetry increase of the iron electron shell as compared with complexes based on individual $\text{Fe}(\text{acac})_3$. In some authors opinion, it causes an increased stability of complexes formed on the basis of mixed acetylacetonates.⁷⁾

Considerable synergic effect is produced by proton- or electron-transfer catalysts forming multinuclear chains. Thus, Fanchiang and Goold⁸⁾ have informed of isonicotinamide and methylviologen synergism in the reaction of $\text{Co}(\text{en})_3^{+3}$ reduction by Eu^{+2} ion in aqueous solutions. Electron transfer in this case takes place along the chain consisting of four links.

Some other examples of synergism attributing to the first type may be given. The authors think that one of the reasons of synergism is a redistribution of electron density in a transient state which leads to the activity increase of the system.⁹⁾

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2. *Second-type reactions.*

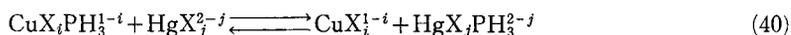
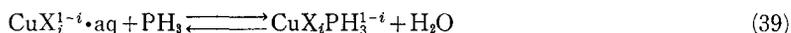
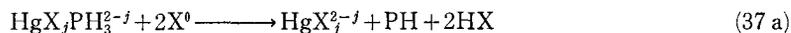
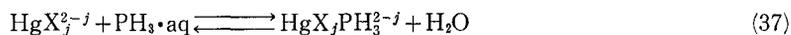
The greatest number of examples of this type synergism may be found among catalysts of hydrogen peroxide decomposition.

On the basis of large experimental material on this reaction B. I. Shpitalsky has substantiated some propositions of the theory of intermediate stages in homogeneous catalysis. In particular, he has found that an intermediate compound may be formed with the participation of several catalysts including H^+ and OH^- ions.

It has been shown¹⁰⁻¹²⁾ that a joint action of two catalysts in H_2O_2 decomposition is not additive; the rate is proportional to the concentration of a secondary intermediate product formed by one of the catalysts and H_2O_2 . As a result of these studies, a concept of "catalyzing a catalysis", (*e.g.* activation not of a substrate itself but an intermediate product formed by another catalyst) has been introduced into the theory of catalysis. Thus in catalysis by Fe(II) and tungstic acid salts (Na_2WO_6) the main intermediate product is pertungstate Na_2WO_8 , decomposition of which is accelerated by $FeSO_4$.

Synergism is also observed in Na_2MoO_4 and $CuSO_4$ *etc.* catalysis.¹³⁻¹⁶⁾ Various accounts for the mechanism of such catalysts action have been given.^{17,18)}

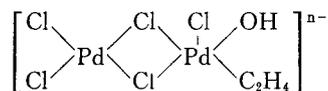
The effect of a considerable increase of phosphine oxidation rate in CuX_2 - $HgCl_2$ system may also be attributed to the second type (the reaction is given above). It has been shown that on adding the mercury (II) salt to $CuCl_2$ in 10^{-6} – 10^{-4} mole \cdot l $^{-1}$ concentration, the catalytic system activity increases 1-3 orders. The following reaction scheme accounts for the considerable rate increase of the process¹⁹⁾:



The important point in this scheme is interaction of the oxidized halide-ion, *e.g.* X_2 , with mercury (II) phosphine complex and an exchange reaction (40) due to which $HgX_jPH_3^{2-j}$ complex stationary concentration increases.

A peculiar case of the second-type synergism is a so-called catalyst self-activation, *e.g.* when $Cat_1 = Cat_2$. Thus it is found that from a well-known reaction of ethylene oxidation to acetaldehyde by Pd(II) salts in $[Pd(II)] = 10^{-2}$ – $2 \cdot 10^{-1}$ mole \cdot l $^{-1}$ concentration range a second reaction route appears proceeding through binuclear complexes²⁰⁾:

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and the second reaction order with respect to catalyst is observed. Since before palladium (II) interaction with olefin binuclear complexes were not found, I. Moiseev suggested that such complexes are formed as a result of attacking Pd(II) ethylenic complex by Pd(II) ion.^{20,21)}

3. Third-type reactions.

This reaction type is well illustrated, in our opinion, by the amine oxidative carbonylation catalyzed by Pd(II) and Cu(II) complexes²²⁾:



N, N'-substituted ureas are reaction products.

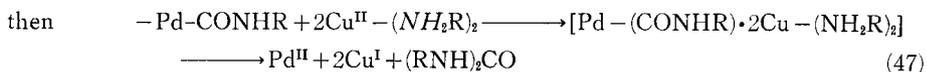
Formely it has been shown that Pd(II) complexes catalyze this reaction under conditions of regeneration of palladium reduced forms to the original state²³⁾:



Intermediate carbamoyl complex, (ClPdCONHR), forming in the course of reaction is very stable and in mild conditions is not decomposed to final products for several hours.

Cu(II, I) complexes are also reaction catalysts (41); however, the process in the initial stage proceeds very slowly owing to very weak CO activation by Cu(II) ions. Only with increasing the concentration of Cu(I) ions which activate CO molecule forming CuCOCl—type carbonyls, the reaction rate increases.²⁴⁾

Sharp rise of the process rate for 1-2 order occurs on adding catalytic quantities of Pd(II) complexes (Fig. 3).²⁵⁾ Here is a most probable mechanism scheme:



Synergism of the mixed catalyst action occurs as a result of sharp acceleration of palladium carbamoyl complex [-Pd-CONHR] decomposition under the action of Cu(II) amine complexes. The reaction route through Cu(I) and Pd(O) complexes in this case already plays no significant role due to a substantial difference in rate constants of these routes.

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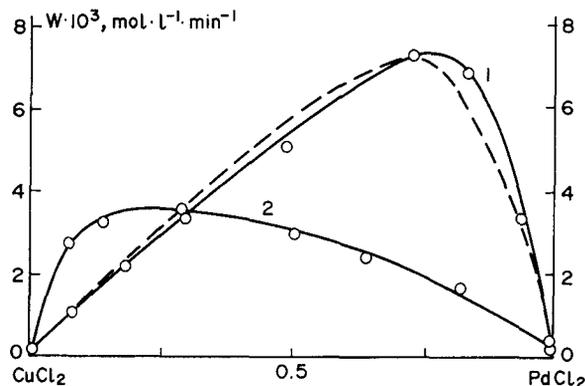


Fig. 3. Dependence of the rate of the oxidative carbonylation of amines on the composition $\text{PdCl}_2 + \text{CuCl}_2$ catalyst, $2\text{C}_5\text{H}_{11}\text{NH} + \text{CO} + \text{O}_x \longrightarrow (\text{C}_5\text{H}_{11}\text{N})_2\text{CO} + 2\text{H}^+ + \text{Red}$.
 $t = 40^\circ\text{C}$, $[\text{Cat}] = 0.5 \text{ mmol (CO)}$
 1 piperidine, 2 n-butylamine
 Broken line is the theoretical curve calculated by kinetic equation²⁵⁾

Similar mechanism was found also in the reaction of CO oxidation by Pd(II) and Cu(II) complexes.²⁶⁾ We have shown that Pd(II) complexes are easily reduced by carbon monoxide, whereas CO reaction with Cu(II) proceeds appreciably only after Cu(I) emergence. Cu(II) ions actively interact with intermediate Pd(II) and Pd(I) carbonyl complexes causing their fast decomposition to Pd(II), CO_2 and CO.^{26,27)}

Thus, from the above given data it follows that the second catalyst being simultaneously an oxidiser and substrate activator interacts with an intermediate compound which includes the first catalyst and a second substrate molecule. Interaction between initial Pd(II) and Cu(II) complexes is not observed, *e.g.* first-type synergism is not possible.

4. Fourth-type reactions.

This type includes synergism of homogeneous catalysts of organic compounds oxidation by molecular oxygen. Among most frequently met catalyst pairs are cobalt and manganese salts. Thus, the Fig. 4 shows an example of Co(III) and Mn(II) acetates synergism in the reaction of chlorine-*p*-xylene and phenanthrene liquid-phase oxidation.^{28,29)} Both metals ions are catalysts of this reaction, though in given experimental conditions Mn(II) is little active. From the figure it may be seen that the maximum rate is achieved with Mn:Co=1:9 ratio. The authors account only for the descending curve (after the maximum) by the growth of chains breaking rate on manganese ions with increase of their concentration. It is interesting that on phenanthrene oxidation, the maximum is shifted to the other side and falls on 80% Mn.²⁹⁾

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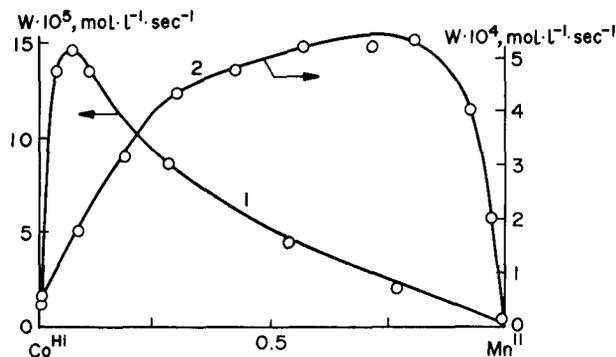
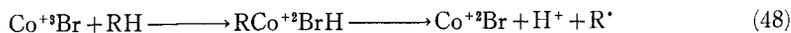
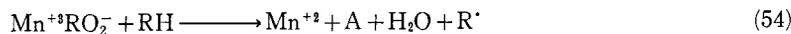


Fig. 4. Dependence of the rate of hydrocarbon oxidation on the composition $\text{CoAc}_3 + \text{MnAc}_2$ catalyst,^{28,29)} $\text{RH} + \text{O}_2 \longrightarrow \text{Products}$.
1 chlor-p-xylen, 2 phenanthren

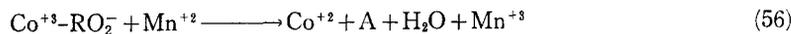
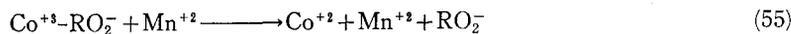
Mechanism of the synergistic action of these catalysts can be presented as follows.³⁰⁾ According to (48-49) reactions, RO_2 peroxide radicals are generated



which form with Mn(II)-salt the complexes reacting further according to the following scheme:



It is suggested that Mn^{+2} ions interact with $\text{Co}^{+3}\text{-RO}_2^-$ — complexes:



The latter reactions as well as Mn^{+2} interaction with $\text{Mn}^{+3}\text{-RO}_2^-$ complexes account for the decrease of the mixed catalyst activity with increasing the manganese concentration.

Synergism on these catalysts is also observed in oxidation reaction of other compounds.³¹⁻³³⁾

Synergism often appears upon inhibition in catalytic reactions of hydrocarbons oxydation by oxygen.³⁴⁾

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The classification given here comprises in our opinion the main types of interactions in homogeneous systems with two catalysts and two (or one) substrates which lead to the synergistic effects.

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