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Adsorption of H_2S on Alumina at Low Coverages

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Isotherms of H_2S adsorbed on γ-Al_2O_3 from H_2S/H_2 mixtures were determined at 260–560°C, and over a range of H_2S partial pressure from 1 μ to 4.4 mm. Saturation coverages of 39–107 μ moles H_2S/g Al_2O_3 were observed. Isosteric heats of adsorption, ΔH, ranged from -25 to -38 kcal/mole, depending on the degree of predrying of the alumina. Entropy calculations indicate that mobility of the adsorbed H_2S is highly restricted.

The number and strength of adsorption sites suggest that they are Lewis acid sites formed by stripping oxygen anions from a spinel surface, exposing incompletely coordinated aluminum cations. H_2S, like water and ammonia, reacts as a base at these sites, and forms an Al–S bond.

INTRODUCTION

Hydrogen sulfide has been known to modify or poison supported metallic catalysts. However, its interaction with the catalyst support has received scant attention. Many supports, such as activated alumina, themselves possess catalytically active sites of the Lewis or Bronsted acid type. Basic adsorbates, such as ammonia and water, react vigorously with these sites. While hydrogen sulfide is not generally considered as a base, this term is only relative. One can visualize hydrogen sulfide adsorbing on alumina in a fashion analogous to water, albeit with a different energy.

The sensitivity of analytical methods for determination of hydrogen sulfide permits one to examine the adsorption isotherm at very low partial pressures and surface coverages. In this region the isotherm reflects adsorption on the strongest sites, those which have an important influence on catalytic activity.

This paper describes measurements of the adsorption of hydrogen sulfide on alumina from hydrogen sulfide–hydrogen mixtures and considers the results in terms of reaction of hydrogen sulfide as a basic adsorbate at isolated Lewis acid sites.

EXPERIMENTAL

Isotherms of H_2S over γ-Al_2O_3 were developed by measuring the H_2S partial pressure in an H_2S/H_2 mixture, containing a known amount of H_2S, when in equilibrium with the solid phase. Range of partial pressures covered was 1 μ to 4.4 mm. The amount of H_2S adsorbed varied between 3 and 100 μmoles per gram of Al_2O_3.

The equilibration apparatus was an all-glass recirculation loop comprising an electromagnetic pump, a heated tube holding the γ-Al_2O_3, and a gas sample bulb of calibrated volume. The last could be isolated from the gas recirculation loop by three-way stopcocks at either end.

Thirty milliliters of γ-Al_2O_3 was charged to the apparatus and heated to a desired pretreatment temperature. Hydrogen was purged through the loop to flush out all air, and also to subject the alumina to a drying pretreatment in hot perfluent gas. Duration and temperature of this pretreatment varied as noted below. Hydrogen was electrolytic, deoxygenated over UOP nickel-kieselguhr catalyst at 300°C, and dried to below 10 ppm H_2O over Drierite and solid sodium dispersion.

The alumina was brought to test temperature, and the hydrogen pressure to slightly below atmospheric. The gas sample bulb was isolated from the system and H_2S was added, the amount being measured by a phosphoric acid manometer. The H_2S/H_2 mixture was recirculated over the alumina for 4–16 hours. The gas sample bulb was again isolated and its contents flushed into a titration flask with argon. H_2S was titrated with mercuric acetate, employing dithizone indicator. With a platinum-tipped microburette, it was possible to measure 1 ppm H_2S, corresponding to 1 micron partial pressure. Check determinations were made by back-flushing the argon in the sample tube with hydrogen, connecting the sample tube back into the recirculation loop, and re-equilibrating.

The H_2S inventory of the gas phase at the completion of an equilibration was calculated by dividing the H_2S content of the gas sample by the mole fraction of the total gas phase included in the gas sample bulb at the particular furnace temperature used. The difference between gas phase H_2S inventory and H_2S added originally gave the solid phase inventory, or coverage. Coverage was varied by adding more H_2S to the system, or by purging it with dry hydrogen and titrating the amount removed.

TABLE 1
PROPERTIES OF ALUMINAS

	Alumina A	Alumina B
Surface area (m^2/g)	175	137
Pore volume (cc/g)	0.46	0.24
Pore diameter (Å)	106	70
% Na	—	0.14
% Cl	0.11	—
% S	<0.01	<0.01
Dehydration of cyclohexanol at 290°C; GLC peaks in product	7	1
Color with anthraquinone	Yellow	White

Two commercial aluminas were examined, designated A and B (Table 1). They exhibited a decided difference in acidity, probably due to differences in preparative procedure. Alumina A reacted with the weak Benesi (*1*) indicator, anthraquinone, to give the yellow acid color. When used to dehydrate cyclohexanol at 2 LHSV and 290°C, it isomerized the olefin product to a mixture of cyclohexene and methylcyclopentenes (*10*). Alumina B did neither.

These aluminas were also characterized by the severity of pretreatment in perfluent dry hydrogen to which they were subjected immediately before the adsorption experiments. Temperature of pretreatment was either 500 or 580°C, and was always higher than the temperature of adsorption. Duration was 16 hours in the majority of cases. In the earlier portion of the work only 2 hours were allowed. With one exception, aluminas pretreated at the same temperature gave consistent isotherms.

RESULTS

Table 2 gives adsorption data for H_2S on aluminas A and B; alumina A was studied the more thoroughly. The several subscripts refer to tests in which a fresh charge of alumina was introduced to the system and pretreated for the time and at the temperature specified. The data for each isotherm are listed in the order of increasing H_2S partial pressure. However, the points were taken in various sequences. In some cases the isotherms span a sufficient coverage range to permit calculation of the saturation coverage, v_m. In other cases where the data lie in a rather short range of coverage, they are useful as a basis for calculation of isosteric heat of adsorption.

Saturation Coverage

Saturation coverages (v_m) were calculated as the reciprocal of the limiting slope of the Langmuir hyperbolic plot of p/v vs. p. Figure 1 shows these plots for samples A_1, A_3, and A_5. Values are included in Table 2. Except for alumina A_5, they cluster around 50 μmoles/g. On a spinel (100) surface of 175 m^2/g, this corresponds to 2% of the anionic sites, a rather sparse distribution of the adsorbed H_2S. One would expect the density of adsorbing sites to increase with severity of pretreatment, on the basis that the sites are produced by dehydration of the alumina. In fact, an increase of v_m to 106 μmoles/g was observed

TABLE 2

ADSORPTION ISOTHERMS FOR H_2S ON γ-Al_2O_3

Temp. (°C)	Coverage, v (μ moles H_2S/g)	H_2S partial pressure, p (μ Hg)	Temp. (°C)	Coverage, v (μ moles H_2S/g)	H_2S partial pressure, p (μ Hg)
Sample A_1 (2 hr @ 500°C)			Sample A_4 (16 hr @ 580°C)		
300°	22.0	21	360°	20.3	1.5
	22.7	32		—	—
	22.8	32	430°	17.5	17
	40.5	157		17.5	19
	40.7	158		20.1[a]	35
	44.6	260		20.1[a]	36
	44.9	233		—	—
	45.1	216	500°	17.6	133
	45.4	269		17.8	124
	48.7	428		19.6[a]	140
	49.3	424		19.8[a]	180
	52.9	871		—	—
	54.2	992	560°	17.9	569
	55.4	1250		18.7	548
	v_m = 62				
360°	22.0	253			
	22.3	234			
Sample A_2 (16 hr @ 500°C)			Sample A_5 (16 hr @ 580°C)		
300°	5.3	3.4	300°	31.1	28
	5.3	2.5		54.5	110
	11.8	8.6		54.6	118
	18.4	32		67.4	315
	18.5	30		67.9	337
	50.8	371		80.6	817
	51.3	389		81.6	942
360°	25.2	271		90.6	1850
	25.6	263		92.8	2240
	45.3	1540		95.6	2820
	47.4	1890		98.2	3830
				v_m = 107	
Sample A_3 (16 hr @ 580°C)			Sample B (2 hr @ 500°C)		
500°	3.9	9.7	250°	48.7	113
	3.9	9.2		48.8	108
	8.9	40	300°	35.6	194
	9.0	54		35.7	194
	13.8	95		37.8	304
	13.9	101		38.1	297
	19.8	185		48.7	904
	20.1	201		49.4	973
	24.4	284		v_m = 56	
	24.8	314	360°	30.3	869
	v_m = 39			31.0	935
560°	7.2	184		35.7	1590
	7.4	184		37.0	1600
	7.8	157		38.4	1950
	21.2	1040		40.1	2550
	22.7	1160		42.0	3020
				44.2	4430
				v_m = 50	

[a] Values obtained on ascending leg of temperature survey.

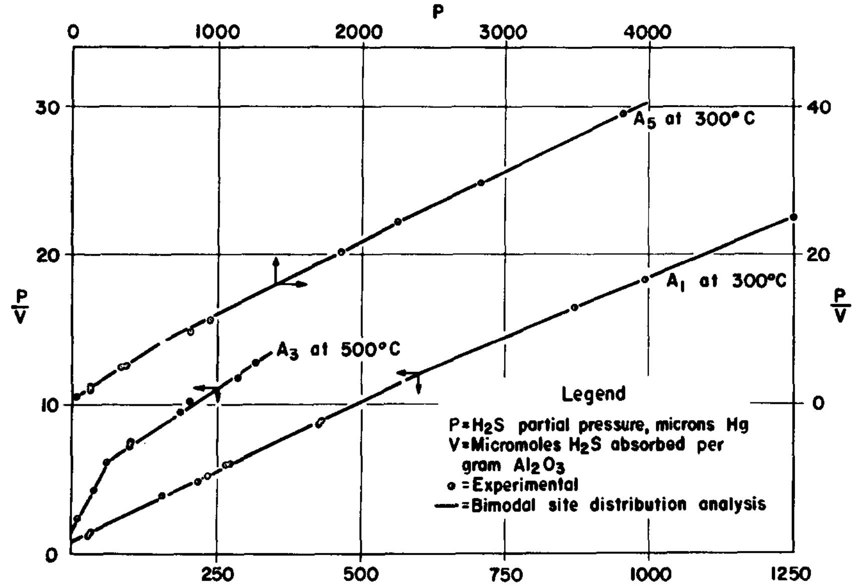

FIG. 1. Langmuir plots of H_2S—γ-Al_2O_3 isotherms.

for alumina A_5 pretreated at 580°C. Alumina A_3, also pretreated at 580°C, showed a v_m of only 39 μmoles/g when measured at 500°C instead of 300°C. This suggests a heterogeneous surface, some of the sites of which become ineffective for adsorption of H_2S as the temperature is raised. Unfortunately, of the three aluminas (A_3, A_4, and A_5) pretreated at 580°C, A_5 gave an isotherm inconsistent with the other two. The reason for the difference in v_m between aluminas A_3 and A_5 therefore cannot be unequivocally assigned to difference in temperature of measurement of the two isotherms.

Heat of Adsorption

Isosteric heats of adsorption were calculated as:

$$-\Delta H = 4.576 \frac{\log p_2 - \log p_1}{1/T_2 - 1/T_1}$$

where p_2 and p_1 are H_2S partial pressures at temperatures T_2 and T_1 and at the same coverage.

Table 3 gives values of the heats of adsorption calculated from the partial pressure data of Table 1. Pairs of pressure data were selected which involved a minimum of interpolation along the isotherm to adjust them to corresponding coverages.

The 500°C pretreated aluminas A_1, A_2, and B all exhibited a heat of adsorption near —25 kcal/mole over a range of fractional coverage, θ, between 0.3 and 0.7. The 580°C pretreated aluminas, A_3 and A_4, gave higher heats of adsorption, 30–38 kcal/mole, which varied with coverage.

The isostere for alumina A_4 was extended over a wide temperature range, from 360–560°C. Figure 2 shows this isostere adjusted to $\theta = 0.5$, based on $v_m = 39$ μmoles/g, the value obtained for the similarly pretreated alumina A_3. Figure 2 includes for comparison isosteres of the 500°C pretreated aluminas estimated at $\theta = 0.5$ by interpolation of the isotherms and use of the —25 kcal value for heat of adsorption.

Figure 2 also illustrates the anomalous result obtained with the 580°C pretreated alumina A_5. At $\theta = 0.5$ the partial pressure of H_2S over this sample at 300°C was 100 μ. This value was much closer to the isosteres for the 500°C pretreated aluminas than that for the 580°C pretreated aluminas. It appears as though in one case the 580°C pretreatment increased the number of sites, while in the other two it increased

TABLE 3
HEAT OF ADSORPTION OF H_2S ON ALUMINA

Alumina	Temp. range (°C)	v (μ moles/g)	$\theta = v/v_m$	$-\Delta H$ (kcal/mole)
A_1	300/360	22	0.36	25.0
A_2	300/360	46	(0.75)[a]	24.3
A_3	500/560	7.5	0.19	37.7
	500/560	20	0.50	33.3
A_4	500/560	20	(0.50)[b]	29.5
B	300/360	36	0.64	25.2

[a] v_m assumed same as for A_1.
[b] v_m assumed same as for A_3.

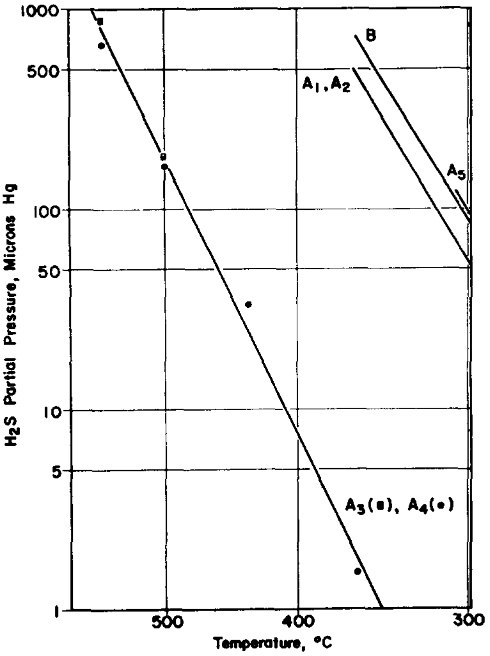

FIG. 2. H_2S—γ-Al_2O_3 isosteres at $\theta = 0.5$.

their strength, without increasing their number.

The difference in acidity between aluminas A and B was not reflected in any difference in the heats of adsorption of H_2S. From this we conclude that the sites are not intimately associated with the Cl^- and Na^+ impurities.

DISCUSSION

Mechanism of Adsorption

Tamele (*13*) suggested that incompletely coordinated aluminum atoms occur on the surface of a crystal lattice. Such lattice configurations are, like $AlCl_3$, strong Lewis acids, due to the electron-accepting ability of the incomplete coordination sphere. They form on the surface of γ-alumina as a result of exhaustive dehydration and readily react with basic adsorbents, such as NH_3 and H_2O.

Well-dried alumina also adsorbs indicator dyes from solution and converts them to the conjugate acid form. We observed that adsorbed H_2O or H_2S both prevented development of the acid color in the case of dicinnamal acetone ($pK_A = -3.0$). While it is difficult to determine whether conversion of the dye to its conjugate acid is due to interaction with a Lewis or with a Bronsted acid site, nevertheless the experiment clearly showed that H_2S reacts as a base with the acid sites of alumina, whatever their nature.

Reaction of H_2S with a surface proton would create a hydrogen bond between the surface and adsorbate. The energy available from this interaction cannot account for the high heats of adsorption observed at low coverages. Reaction of H_2S at a surface Lewis site would create an Al–S bond and more nearly satisfy energetic requirements.

A different picture of surface activity was proposed by Cook (*2*), who accounted for the energy of adsorption by relief of surface strains in the ionic lattice. The strain theory, like the simple acid-base reaction, involves chemical bond formation by displacement of electrons. However, it is less specific as to the nature of the bonds formed, and implies a broad spectrum of site energies.

Cornelius (*3*) used the surface strain theory to account for the rapid change in heat of adsorption of water on alumina with coverage. For an alumina calcined at 538°C, containing 1.075% H_2O, the initial isosteric heat of hydration was —105 kcal/mole. At 20 μmoles/g added water, the heat was —75 kcal/mole, and at 50 μmoles/g it was —53 kcal/mole. Ignoring the possibility of surface interaction, the results indicate an extreme polydispersity of adsorbing sites.

We did not find a corresponding rapid change in heat of adsorption of H_2S over a comparable coverage range on aluminas pretreated at a comparable temperature. We must therefore conclude that the H_2S adsorption data do not indicate the extreme polydispersity in site energy suggested by the H_2O adsorption data. Following the Tamele Lewis acid model we visualize H_2S and H_2O adsorbing initially on dry alumina by a similar mechanism, transfer of electrons from the sulfur, or oxygen, to an incompletely coordinated, or "bare" aluminum ion. The rapid variation of heat of hydration can still be accounted for qualitatively by surface interaction, due to the relatively high polarization of the oxygen–hydrogen bond as compared to the sulfur–hydrogen bond.

In this model, the essential adsorption process is the formation of an Al–O or an Al–S bond. The heats of adsorption should be related to the bond energies, as reflected in the heat of formation of the bulk compounds (*11*). The ratio of heat of formation of Al_2S_3 vs. γ-Al_2O_3 from Rossini's tabulation (*12*) is 0.32. The more recent determination of $\Delta H°_f$ (Al_2S_3) by Kapustinskii (*6*) gives 0.45. The ratio calculated from Gattow's theoretical treatment (*5*) is 0.4. Using the highest value of the heat of hydration cited by Cornelius (—105 kcal), and our maximum value for H_2S adsorption, (—38 kcal), one obtains a ratio of 0.28. We conclude that the hypothesis of Al–S and Al–O bond formation is consistent with the thermochemistry of the bulk compounds.

Distribution of Adsorption Sites

While the energy distribution of surface Lewis acid sites does not appear to be polydisperse, the H_2S adsorption data indicate some degree of heterogeneity. For example, the heat of adsorption of H_2S on a given sample of alumina was constant over a fairly wide coverage range, but different values of the heat were obtained on different samples. Furthermore, the Langmuir plots of Fig. 1 definitely depart from linearity.

We have made a dual site analysis of these three plots to test the hypothesis that the distribution of Lewis acid site strengths on well-dried alumina is of low order of modality. This hypothesis is suggested by the infrared adsorption spectra of well-dried alumina, which show that the surface protons fall into discrete energy groups (*9*). It is plausible that these discrete variations in oxygen–hydrogen bond character arise from corresponding variations in distribution of aluminum in cationic spinel sites (*7*). For example, underlying a (100) surface hydroxyl, an aluminum cation may occupy one of the four nearest neighbor tetrahedral sites, or the nearest neighbor octahedral site, or none of these. Similarly, differences in Lewis acidity of a "bare" or incompletely coordinated aluminum ion on the surface may arise from a relatively small number of lattice configurations.

The dual site analysis used is that derived by McMillan (*8*). The Langmuir adsorption isotherm for bimodal site energy distribution is:

$$\frac{p}{v} = \left[\frac{a_1\theta_1 v_m}{1 + a_1 p} + \frac{a_2\theta_2 v_m}{1 + a_2 p}\right]$$

Here, v_m is the total number of sites, θ_1 is the fraction of stronger sites, θ_2 the fraction of weaker sites, and a_1 and a_2 are the energy parameters for the two adsorptions. If the heats of adsorption differ by a few kilocalories, so that

$$(1/a_2) \ll (1/a_1)$$

the isotherm approaches a combination of two straight lines, a low pressure and a high pressure section identified with the stronger and weaker adsorption, respectively.

The parameters for the low pressure line

$$(p/v) = (i/a'_1) + (p/b'_1)$$

are:

$$a'_1 = a_1\theta_1 v_m$$

and:

$$b'_1 = \theta_1 v_m$$

The parameters for the high pressure line

$$p/v = (1/a'_2) + (p/b'_2)$$

are:

$$\frac{1}{a'_2} = \frac{1}{v_m}\left(\frac{\theta_1}{a_1} + \frac{\theta_2}{a_2}\right)$$

and:

$$b'_2 = v_m$$

Values of these parameters calculated for the three isotherms of Fig. 1 by least square analysis are given in Table 4.

TABLE 4

Parameters of Dual Site Analyses of Isotherms for Aluminas

	Temp. (°C)	a'_1	a'_2	$b'_1 = \theta_1 v_m$ (μmoles/g)	$b'_2 = v_m$ (μmoles/g)	$\theta_1 = b'_1/b'_2$	$a_1 = a'_1/b'_1$	a_2	$RT \ln a_1/a_2 = \delta\Delta H$ (kcal/mole)
A_1	300°	1.248	0.434	53.3	61.8	0.86	0.0234	0.00130	3.3
A_5	300°	1.764	0.324	76.5	106.7	0.72	0.0231	0.00095	3.6
A_3	500°	0.605	0.216	12.9	39.4	0.33	0.0468	0.01157	2.4

The analysis gives an excellent fit to the experimental data. This is not unexpected with two additional parameters available. It requires a constant heat of adsorption for alumina A_1 up to $\theta_2 = 0.86$; and for alumina A_3 it requires a change in heat of adsorption at $\theta = 0.33$. Both requirements are consistent with the Clausius-Clapeyron calculations in Table 3.

The last column of Table 4 gives an estimate of the difference in heats of adsorption ($\delta\Delta H$) between the two postulated site types. The energy parameters are of the form

$$1/a = A \exp(\Delta H/RT)$$

Assuming the pre-exponential factor to be the same for adsorption on either type,

$$\delta\Delta H = RT \ln(a_1/a_2)$$

The differences, amounting to 2–4 kcal/mole, are at the limit of accuracy of our determination of isosteric heats of adsorption. The argument for a small number of Lewis acid site types must therefore rest on an analogy with the distribution of Bronsted acid sites as observed by infrared adsorption, and on the success of the bimodal distribution equation in fitting the data.

Entropy of Adsorption

The Lewis acid site model proposed suggests that the adsorbed H_2S is immobile. For entropically ideal site adsorption, DeBoer (*4*) shows that the differential entropy of adsorption at the standard state $\theta = ½$ should equal the translational entropy of the gas at the standard state of one atmosphere. This choice of standard state for the adsorbed species eliminates entropy of localization. A calculation of the entropy of adsorption gave the results shown in Table 5.

Three isotherms were examined, those for aluminas A_1 and A_5 at 300°C, and for alumina A_3 at 500°C. Free energy of adsorption at the standard state $\theta = ½$ was calculated as:

$$\Delta F^\circ = RT \ln [760/(p \times 10^{-3})]$$

where p is the partial pressure of H_2S (microns Hg) at a fractional coverage $\theta = ½$.

The standard differential molar entropy of site adsorption was calculated as:

$$\Delta S^\circ_i = -(\Delta F^\circ - \Delta H)/T$$

using the observed isosteric heats of adsorption. No heat of adsorption was available for alumina A_3. On the basis of its similarity to A_1, a value of —25 kcal/mole was assigned.

The standard translational entropy of gaseous H_2S at 760 mm pressure was calculated as:

$$_gS^\circ_{tr} = R(\ln M^{3/2}T^{5/2}) - 2.30$$

Comparison of the last two columns of Table 5 shows that the decrease of entropy on adsorption accounts for about two-thirds of the translational entropy of the gas.

A calculation of the entropy loss predicted on the basis of DeBoer's model of mobile adsorption, where the original translation entropy of the gas ($_gS_{tr}$) is replaced by the translation entropy of an ideal two-dimensional gas ($_aS_{tr}$), was also made. A different standard state is specified for this calculation; however, it happens here to be of the same magnitude as that used for the site model, and gave about the same entropy of adsorption, ΔS°_m. Comparison of observed and calculated values in the last two columns of Table 5 shows that the mobile model accounts for less than half of the observed entropy loss.

We conclude that entropy considerations support the model of H_2S adsorption at Lewis acid sites, with highly restricted mobility of the adsorbate between sites.

TABLE 5

ENTROPY OF ADSORPTION OF H_2S ON ALUMINA

Alumina	Temp. (°C)	v @ $\theta = 0.5$ (μmoles/g)	p @ $\theta = 0.5$ (μ Hg)	$-\Delta H$ (kcal/mole)	$-\Delta F^\circ$ (kcal/mole)	$-\Delta S^\circ_l$ observed (e. u.)	$_gS^\circ_{tr}$ calculated (e. u.)	$-\Delta S^\circ_m$ observed (e. u.)	$_gS^\circ_{tr} - _aS^\circ_{tr}$ (e. u.)
A_1	300	31	70	25	10.5	25.3	39.9	27.1	11.1
A_5	300	53	100	(25)[a]	10.2	25.8	39.9	28.7	11.1
A_3	500	20	180	33	12.8	26.2	41.3	27.7	12.4

[a] Assumed the same as for A_1.

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