MOLECULAR MOTION AND PHASE TRANSITION IN HYDROQUINONE CLATHRATE COMPOUNDS

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ABSTRACT . Distinction between the host-guest and guest-guest inter-
action in the roles they play in determining the physical properties of
the clathrate compounds is discussed. It is shown that the latter
causes cooperative effects and phase transitions. Experimental data on
the phase transitions and molecular motion in the hydroquinone clathrate
compounds are reviewed. Dipole interaction between the guest molecules
is shown to have a correct magnitude of energy to explain the experimen-
tally found transition temperatures. Possibility of quantum effects in
the clathrate property is discussed in relation to the free rotation and
ortho-para conversion of the hydrogen sulphide and other guest molecules.

1. Introduction

Clathrate compounds are usually formed between molecules that have no
specific affinity to each other. They are held together by subtle,
usually weak, interactions of the van der Waals type. It is generally
accepted that the interaction, the host-guest interaction, explains
most of the important properties of the clathrate compounds. The host-
guest interaction is the nearest neighbour interaction and thus is
naturally the first to be considered. Actually, thermodynamic calcu-
lation taking only host-guest interaction into account gave satisfactory
description of the stability of many of the clathrate compounds [1].
However, there is a very specific property of the clathrate compounds
that shows the existence of guest-guest interaction. That is the phase
transitions in clathrate crystals. Phase transitions in clathrate
compounds are of interest because they show that molecules not in direct
contact with each other interact with a large enough energy to determine
some of the bulk properties of the substance.
    Study of phase transitions in general is a vast field of research
in chemistry and physics. Great variety of phase transitions are known
to occur in substances of very different nature such as ferroelectric,
ferromagnetic, order-disorder, superionic and superconducting crystals.

However, the molecular interaction that is responsible to the occurrence
of a particular transition is rarely known. Ferroelectric, antiferro-
electric and other phase transitions in dielectric and molecular
crystals are among the most complicated in their microscopic mechanism
[2]. The clathrate compounds offer possibility of studying phase tran-
sitions in the substances in which molecular interactions are relatively
well-specified. It should be mentioned parenthetically that guest-guest
interactions play an essential role in a theory of   clathrate for-
mation [3]. The effects considered there are those of more drastic
change (presence or otherwise of the guest molecules in the neighbouring
cavities) than discussed in this paper.

     In the hydroquinone clathrate compounds the guest molecules are
separated by the rigid hydroquinone lattice. The interaction among
them is primarily electrostatic, perhaps with an additional effect of
the van der Waals force.

     Long range electrostatic interaction between polar molecules is
one of the most interesting in their experimental and theoretical sig-
nificance. The dipole moment of a molecule is a well-defined quantity
and can be determined experimentally. Because it varies from the zero
of a homonuclear molecule to a large value of a strongly polar molecule
such as hydrogen cyanide and acetonitrile even among the small molecules
that can be enclathrated in the hydroquinone cavity, we can study a
wide range of strength of the interaction in a series of the clathrate
compounds.

     The dipolar correlation is the principal interaction in the classi-
cal theory of dielectric properties of matter. In fact, neutral matter
is equivalent to an assemblage of electric dipoles as far as its elec-
trical properties are concerned [4], and various approximations have
been proposed to deal with the dipole interaction [5]. However, be-
haviour of dipolar substances at the temperature at which the thermal
energy is comparable with the dipole interaction is not understood well.
It is therefore desirable to study properties of substances which under-
go phase transitions due to the dipole interaction.

     Low temperature properties of hydroquinone clathrates of small polar
molecules are also of interest because of the possibility they offer
to the study of low-lying rotational levels of the molecules. In the
neat (i.e., non-clathrate) crystal of hydrogen chloride, hydrogen
sulphide and other small molecules, strong intermolecular interaction
prohibits rotation of the molecules. But a cavity is formed by the
rigid host lattice for each of the guest molecules in the clathrate.
Therefore, they can rotate rather freely in the approximately spherical
potential of the wall.

2. HOST-GUEST AND GUEST-GUEST INTERACTIONS

Thermal excitations in crystals may be classified into cooperative and
non-cooperative interactions. The non-cooperative interaction is that
of rotational, vibrational and orientational degrees of freedom of the
guest molecules in the clathrate lattice. Such excitations can take
place even if there is only one guest molecule in the crystal, because
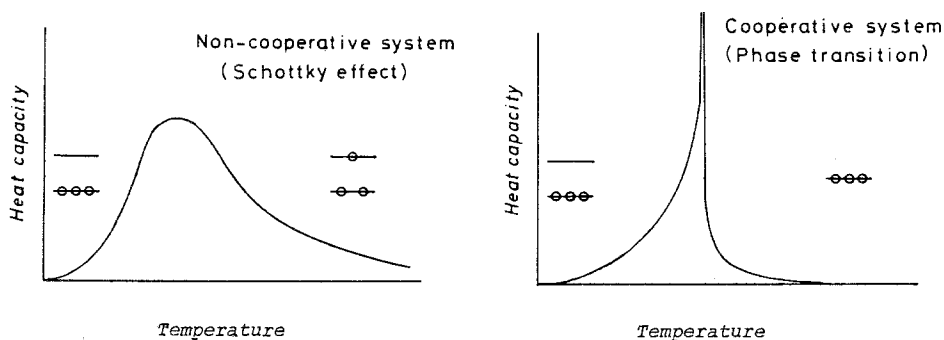
Fig. 1. Heat capacity of non-cooperative and cooperative systems
(schematic).

the energy levels that the guest molecule occupies are provided by the
host lattice. In the simplest form it causes a Schottky effect in the
heat capacity as shown schematically in Fig. 1. The non-cooperative
effects are primarily associated with the host-guest interaction. The
cooperative excitation is the excitation of the orientation of guest
molecules relative to each other. We assume that the host lattice
structure is such that one guest molecule by itself has two equivalent
and alternative orientations in the cavity. If one puts another guest
molecule in a neighbouring cavity, it destroys the equivalence of the
two orientations of the original guest molecule because of the inter-
guest interaction. The energy of the different orientations of one
molecule depends not only on the presence of the second molecule but
also on the orientation of the latter. There are great numbers of guest
molecules in the crystal. Consequently energy levels of the whole
crystal are complicated beyond possibility of exact calculation. How-
ever, it is known that this type of excitation can be described as an
orientational excitation of an arbitrarily chosen central molecule in
the average field produced by the neighbouring guest molecules. The
heat capacity of such a system has a sharp peak as shown in Fig. 1.
The central molecule feels an orienting field which is proportional to
the average orientation of the neighbours. But the central molecule
exerts an orienting effect back on the neighbours exactly in the same
way as it is exerted on by the neighbours. Thus at the lowest tempera-
ture the molecules determine the most favourable orientation for them-
selves without being dictated to do so by the host lattice. This co-
operative effect breaks down at a higher temperature as the orienting
field is exceeded by thermal motion. Since neither of the two orien-
tations of a guest molecule is preferred at the higher temperature,
symmetry of the crystal is different from that of the crystal at low
temperatures. The low temperature phase is called an ordered phase.
It changes into a disordered phase, which has the higher symmetry and
higher entropy than the ordered phase, at the transition temperature
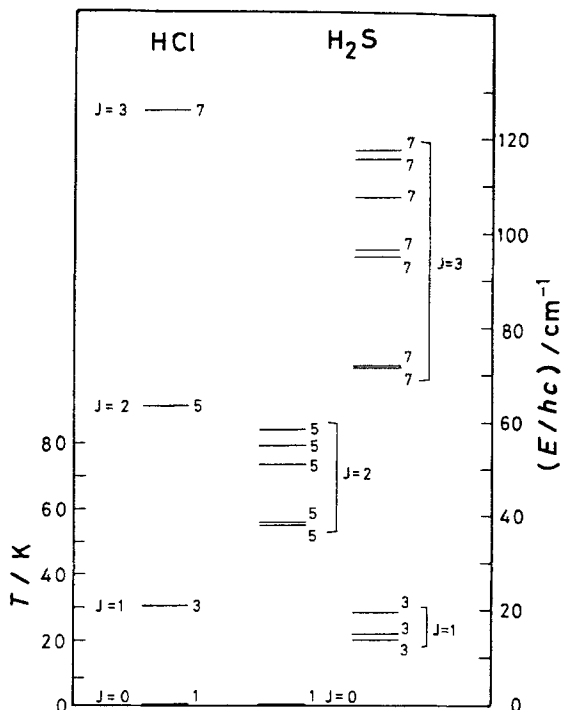determined by the magnitude of the guest-guest interaction.

Fig. 2   Rotational energy levels of HCl and H_2S molecules.
(G. Herzberg, Molecular Spectra and Molecular Structure,
I, p.58; II, p.42 and 489, van Nostrand, 1945 and 1950)

THE HYDROQUINONE HYDROGEN CHLORIDE CLATHRATE COMPOUND

A gaseous hydrogen chloride molecule has rotational energy levels shown in Fig.2.   The lowest excited state lies 21 cm^{-1} above the ground state.   Far infrared absorption occurring at 10 - 20 cm^{-1} was assigned to the transition from the ground to the first excited state [6,7,8]. Raman spectra also showed occurrence of rapid rotation of HCl molecule in the cavity [9].   We measured heat capacity of the compound on the samples whose occupancy x was 0.68 and 0.75 [10]. Phase transition was not found between 1.5 and 20 K.   The sample x = 0.727 studied calorimetrically did not undergo phase transitions between 15 and 300 K either [11].   The rotational heat capacity at temperatures below 7 K was reproduced well by a free rotor heat capacity of two degrees of freedom. The only disposable parameter in the fitting was the moment of inertia of the molecule I = 3.29 x 10^{-47} kg m^2.   This is compared with the moment of inertia of the free molecule, I = 2.65 x 10^{-47} kg m^2.   The dielectric constant of the clathrate with x = 0.56 increased as the temperature decreased down to 10.4 K.   Below that temperature, the dielectric constant decreased.   The Curie-Weiss behaviour shows that the guest molecules are rotating or orientationally disordered at the higher temperature.

The spectroscopic, calorimetric and dielectric data are thus consistent with the large angular freedom of the guest. However, it should be mentioned that X-ray and neutron diffraction showed that the guest molecules are ordered in the cavity forming a hydrogen bond with the host lattice [12]. A unanimous conclusion has not been reached about the nature of the molecular motion in this compound.

THE HYDROQUINONE HYDROGEN SULPHIDE CLATHRATE COMPOUND

A free molecule of hydrogen sulphide has energy levels shown in Fig. 2. Since the two hydrogen atoms in the molecule are equivalent, there are ortho and para species of hydrogen sulphide. If the molecule rotates freely in the clathrate cavity, the distinction between the two species should be relevant to the low temperature property of the compound.
    The heat capacity of the hydroquinone hydrogen sulphide clathrate (x = 0.95) was measured between 1 and 300 K [13]. A peak occurred at (7.6 ± 0.1) K. No anomaly was found above that temperature.   The rotational entropy evaluated at 15 K (twice the temperature of the heat capacity anomaly) was closer to the rotational entropy of a normal (3 : 1) mixture of the ortho and para molecules than to the equilibrium entropy.   Thus the protons of the hydrogen sulphide molecule do not change their spin state in the clathrate compound at low temperature. This conclusion is based on the assumption that the free rotational energy levels are relevant to the motion in the cavity at all. Low temperature far infrared spectra appear to show that they are [7,8]. It is desirable to have direct evidence from other experimental methods such as neutron diffraction and scattering. The dielectric constant of the hydrogen sulphide clathrate increased as the temperature decreased down to 10 – 15 K [13]. It decreased at the lower temperature. The temperature of the maximum of the dielectric constant depended on the occupancy x. However, it was always higher than the temperature of the heat capacity peak. The mechanism of the phase transition at 7.6 K will be discussed below.

THE HYDROQUINONE METHANOL AND HYDROQUINONE HYDROGEN CYANIDE CLATHRATE COMPOUNDS

The methanol compound has a phase transition at 66 K for x = 0.97   as shown by a sharp heat capacity anomaly [14].   The temperature of the peak decreased as the occupancy decreased. This provides   a piece of evidence which proves that the phase transition is caused by the interaction between the guest molecules.   Dielectric anomaly occurs also at the transition, showing that orientation of the guest molecules changes at the transition temperature (see Fig. 3)   By the use of   proton, deuteron and carbon 13 NMR, it was found [15] that the orientation of the guest molecule is more complicated than had originally been believed to be [14].   The new model was supported by   X-ray crystallography [16].
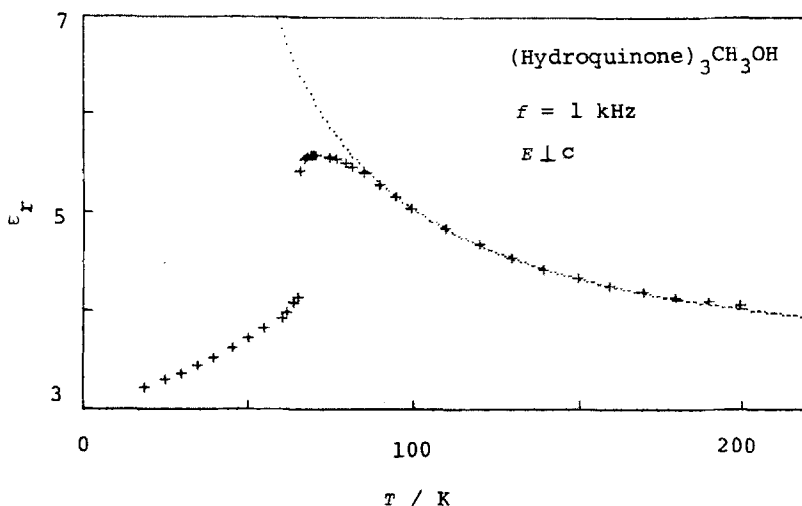   The hydrogen cyanide compound undergoes a phase transition at 178 K

Fig. 3   Dielectric constant of the hydroquinone methanol
          clathrate.

[17].   The heat capacity and dielectric constant have an anomaly at the
temperature.   The transition entropy value was consistent with the two
fold orientational disorder in the high temperature phase.   This com-
pound is an ideal model substance to study the dipole interaction be-
cause of the large dipole moment of the guest molecule and its small
size which does not distort the host lattice.   However, the experi-
mental data available are limited to those mentioned here. In particular
the structure below and above the transition are not known.

THE HYDROQUINONE ACETONITRILE CLATHRATE COMPOUND

No phase transition has been reported in this compound.   However, the
guest molecules can reorient themselves in the cavity at room tempera-
ture as the dielectric measurements showed [18,19],   On the other hand,
the guest molecules are orientationally ordered according to the X-ray
structural analysis [20].   The crystal may undergo a phase transition
at a higher temperature if thermal decomposition does not prevent the
crystal reaching the high enough temperature.

THE GUEST - GUEST DIPOLE INTERACTION

Previously we showed that the dipole-dipole interaction between the
guest molecules has an appropriate magnitude to explain the phase tran-
sitions in the hydroquinone clathrate compounds [14,17].   We have now
two more substances to compare with the model: the phase transition in
the hydrogen sulphide compound and the ordered structure of the aceto-
nitrile compound.   A Monte Carlo calculation showed that no phase tran-

sitions occur in the hydroquinone clathrate compounds if only the dipole interaction is considered [19].   It was suggested that anisotropic polarisation of the host lattice and higher order interactions need to be taken into account.   In the previous paper we calculate the energy of the most stable orientation of the guest molecules and leave it for the molecules to find that orientation without following the process of stabilisation as the Monte Carlo calculation did.

   In our calculation we regard the host lattice as an isotropic medium and limit the calculation to hydrogen sulphide, hydrogen cyanide, methanol and acetonitrile, avoiding other guest molecules such as methyl chloride for which orientational dependence of the interguest van der Waals interaction might be large.

   Figure 4 shows the transition temperature of the hydroquinone clathrate compound plotted against the square of the dipole moment of the guest molecule.   The data on the hydrogen sulphide, methanol and hydrogen cyanide compounds are those of the heat capacity anomalies.   The transition temperature of the acetonitrile compound, if it exists, lies above the room temperature.   One finds a good proportionality between the transition temperature and the square of the dipole moment.

   The interaction energy U_{12} between two dipoles p_1 and p_2 is given by the following equation,

$$U_{12} = \frac{1}{4\pi\epsilon_0\epsilon_r} \left(\frac{\vec{p_1}\cdot\vec{p_2}}{r^3} - \frac{3(\vec{p_1}\cdot\vec{r})(\vec{p_2}\cdot\vec{r})}{r^5} \right)$$

Here, r is the distance between the two dipoles, $\epsilon_0 = 8.85 \times 10^{-12}$ Farad m^{-1} and ϵ_r, the relative permittivity of the medium.   The last quantity is taken as 3.2, the permittivity of the acetylene clathrate
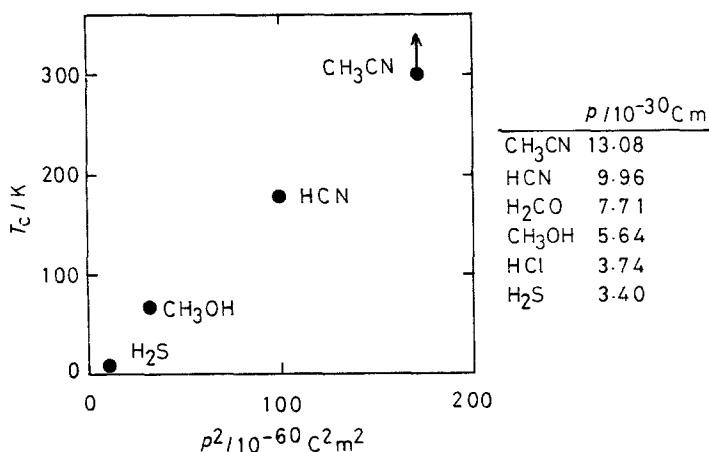

Fig. 4   Phase transition temperatures of hydroquinone clathcompounds plotted against the square of the dipole moment of the guest molecule.

$$L_z(R) = \sum_{r<R} (\frac{1}{r^3} - \frac{3z^2}{r^5})\sigma^3 F(r/R)$$
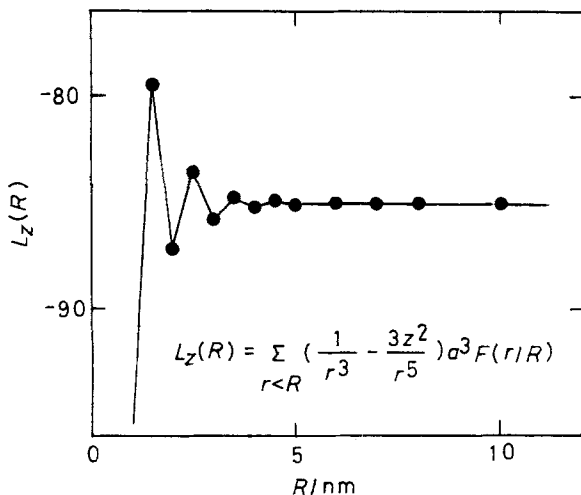
Fig. 5   Partial dipole lattice sum of the hydroquinone clathrate
          lattice plotted against the radius of the sphere in
          which the sum was taken.

compound.   The dipole lattice energy is calculated by summing the pair
interaction over all pairs in the lattice.   There were two difficulties
in doing so.   One is that not only the nearest neighbours but distant
neighbours contribute significantly to the sum.   Consequently, a large
number of terms had to be included.   The partial sum is plotted as a
function of the radius of the sphere within which the sum is calculated
(Fig. 5).   The convergence was accelerated by an auxilliary function
[21]. The limit of summation $R = 10$ nm was found satisfactory. The sphere
contained about 4000 dipoles.   The other difficulty is that the sum-
mation depends on the shape of the crystal in which the summation is
performed.   This is a fundamental difficulty of the dipole interaction.
For any interaction of shorter range than r^{-3}, the lattice sum is inde-
pendent of the sample shape.   The shape dependence of the dipole energy
is such that the dipole lattice is the most stable for a long needle
polarised along the axis and the least stable for a slab polarised per-
pendicular to the face of the slab.   We summed for the spherical sample.
Energy of the crystals of different shape can be calculated by the use
of the depolarisation factor.   The calculation was checked by doing
summation for a long ellipsoid polarised along the long axis.
        The result of the calculation is given in Table 1.   The four con-
figurations considered are (1) the z-polar, (2) the (1/3) z-polar,   (3)
the x-polar and (4) the x-antipolar.   The z-polar configuration is one
in which all the dipoles point to the same direction along the c-axis
of the clathrate lattice.   In the (1/3) z-polar configuration one of
the three sublattice has the orientation of the dipoles reversed ($i.e.$
pointing to the $-c$ direction).   The resultant polarisation is one third
the full polarisation.   The x-polar configuration has all the dipoles
pointing toward the a-axis.   The x-antipolar configuration is the same
as the x-polar except that every other dipole along the c-axis points

TABLE 1   Dipole lattice energy of the hydroquinone clathrate com-
pounds calculated for the four configurations. The energy
of the most stable configuration is given also in terms of
the temperature in the last column.

	sphere	needle	Sphere	needle	$-U\,k^{-1}$/K
		z-polar		1/3 z-polar	
CH_3CN	−2673	−4035	−3876	−4029	485
HCN	−1551	−2341	−2249	−2338	282
CH_3OH	−498	−752	−722	−751	90
H_2S	−180	−272	−262	−272	33
		x-polar		x-antipolar	
CH_3OH	+249	−6	−283	−283	34
SO_2	+220	−6	−250	−250	30
H_2S	+90	−2	−103	−103	12

z-polar   (1/3) z-polar

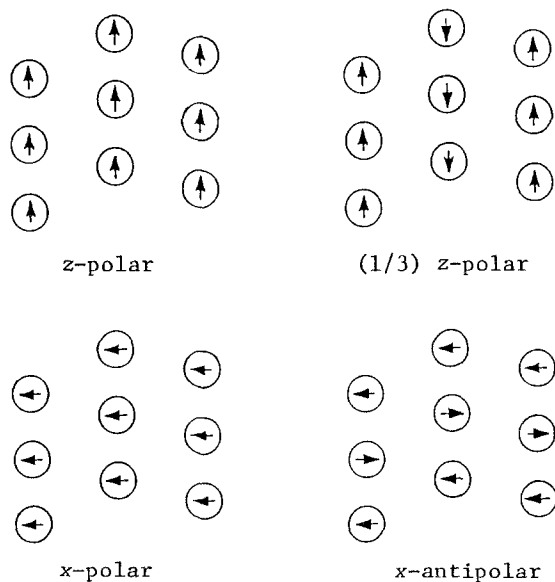x-polar   x-antipolar

Fig. 6   Four configurations of the guest molecules in the hydro-
quinone lattice for which the lattice energy was calcu-
lated.

to the opposite direction. The four configurations are shown schemati-
cally in Fig. 6. Table 1 shows that the 1/3 z-polar structure is the
most stable for the spherical crystal, the energy being -3876 J/mol for
the acetonitrile compound. This configuration is actually found in the
room temperature structure of the acetonitrile compound. The z-polar
configuration is the most stable for the needle, although the (1/3) z-
polar is the close second. The x-polar structure is not favourable
energetically (positive or very small negative energy). Therefore, if
the dipole moments are constrained in the plane perpendicular to the c-
axis (as in the sulphur dioxide compound), they will not align in the
same direction. The x-antipolar configuration has a negative energy
and thus a higher possibility. The energy of the antipolar configura-
tion does not depend on the shape of the crystal as is confirmed in
Table 1. The last column of the Table gives the energy of the most
stable configuration for each of the compounds in the unit of the
temperature. These values are to be compared with the transition
temperature. The calculated temperatures are larger than the observed
by a factor of about two. A part of this factor may represent a co-
efficient of lattice statistical origin. It should be noted that point
dipoles were assumed throughout the calculation.

A additional calculation showed that the correction for this
can amount to ten percent of the calculated lattice energy.

The calculation presented here showed that certain configurations
have lower energies than the others. The magnitude of the interaction
is large enough for the dipole-dipole energy to be the essential part
of the guest-guest interaction that causes the phase transitions, even
if other factors such as lattice distortion, van der Waals force and
hydrogen bonding may have to be considered in a more elaborate theory.

CONCLUSION

The dipole interaction model of the phase transitions in the hydro-
quinone clathrate compounds was conceived several years ago. It turned
out to be tenable in the light of the experimental data that became
available since. The clathrate compounds of hydrogen chloride and
hydrogen sulphide have been studied mostly by spectroscopic methods so
far to show that the small molecules rotate freely or quasi-freely in
the cavity. Low temperature calorimetric data are becoming available.
The entropic aspect of the rotational degree of freedom including the
effect of the nuclear spins can now be studied.

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