The Transition State in Chemical Reactions.

Opening Contribution to a Discussion on the Transition State in Reaction Kinetics, held by the Chemical Society on February 4th, 1937.

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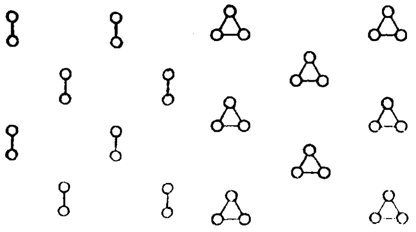
IN the time following the announcement of Bohr's theory there was an inclination to think of reactions as " quantum jumps " and to seek the origin of chemical inertia in restrictions which cause certain electronic transitions to be " forbidden." The catalytic decomposition of ozone, for example, was compared with the breakdown of metastable atomic states, such as parhelium, caused by collisions with a wall.

Theory to-day has returned to the older view that chemical reactions consist mainly in a rearrangement of atoms. Take, for example, the decomposition of ozone. A comparison between the arrangement of the atoms of ozone and oxygen in the condensed state shows us that the change consists in a rearrangement of oxygen atoms from one pattern into another (Fig. 1). And the same is true for all chemical reactions : they are not mere changes in electronic states, but generally consist in the breaking up of one molecular grouping and the formation of another in its stead. The causes of chemical inertia must, therefore, be sought in forces which bar the path of atoms trying to break away from old molecules to form new ones. It is the transitions between the old and the new grouping that we will have to consider if we wish to discover the principles of reactivity.

Let us examine the decomposition of ozone into oxygen from this point of view. In ozone we see three bonds linking each molecule, and gaps separating the molecules from one another. In oxygen we have pairs of atoms separated by gaps from other pairs. In both cases the difference between the larger atomic distances, which I have called gaps, and the smaller atomic distances, which correspond to bonds, is well marked. This distinction is characteristic of all definite chemical states.

To rearrange ozone into oxygen, bonds will have to be strained and ultimately severed by gaps. It follows that half-way between ozone and oxygen the distinction between bond-distances and gap-distances will be effaced. This geometrical feature of the transition state can be demonstrated on a pair of ozone molecules decomposing into oxygen. The colliding ozone molecules approach each other to a distance corresponding to the gaps in liquid ozone. Suppose that they are disposed to each other as shown in Fig. 2*a*; then the decomposition will occur by one atom breaking off from each ozone molecule and joining up to form an oxygen molecule. Fig. 2*c* shows the completed reaction, and Fig. 2*b* the transition state. In this state the separation of the atoms which have gone half-way to form a new oxygen molecule is anomalous and the distances separating these two atoms from the others are also anomalous : they are all larger than normal bonds and smaller than normal gaps.

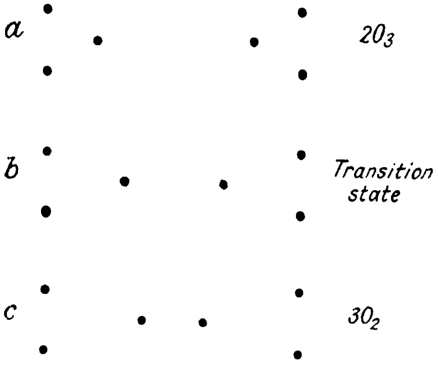
FIG. 1.



Oxygen, (110) *plane.* *Ozone, a possible pattern.*

FIG. 2.

Decomposition of ozone (crude picture).

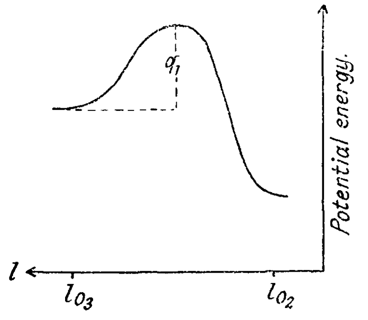


This transition state can be formed by starting either from a pair of ozone molecules or from three oxygen molecules. In either case we must start by straining the bonds initially present; so from which ever side the transition state is approached, its formation involves expenditure of work. It follows that the reaction on its way through the transition state is accompanied by an initial rise and a subsequent fall of the potential energy; the two chemical states are separated by an energy barrier as shown in Fig. 3. We can now redefine the transition state more precisely by identifying it with the configuration which corresponds to the top of the energy barrier.

The height of the energy barrier q_1 counted from the initial state is the energy required to overcome the chemical inertia. This energy must be present in a collision to make it successful; it is approximately equal to the activation energy measured from the logarithmic temperature coefficient of the velocity constant k_1, *i.e.*, $q_1 = RT^2 . d \log k_1/dT$.

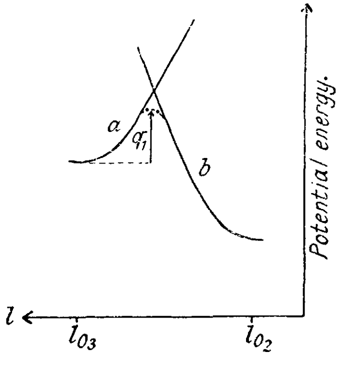
Our ideas of the transition state have acquired precision since London (Sommerfeld Festschrift, Leipzig, 1928; *Z. Elektrochem.*, 1929, **35**, 552) showed that the energy of a system composed of three or four univalent atoms can be defined for any configuration if the bonds which each separate pair of atoms can form with one another are fully known. London's method has been used for calculations of the energy and configuration of the transition state by Eyring and Polanyi (*Z. physikal. Chem.*, 1931, *B*, **12**, 279), but, although the results have proved illuminating in a general way, their value is restricted by the fact that it is difficult to judge the errors caused by the mathematical approximation involved in the theory.

FIG. 3.



l is the distance between the two oxygen atoms which change their position in Fig. 2. All reactions have such a " reaction co-ordinate " l, which describes the reaction path. The symbol l is used later in this general sense.

FIG. 4.



Curve a = energy of 4 strained ozone bonds.
Curve b = energy of 1 strained oxygen bond.

Fortunately, it is possible in many cases to calculate the energy and configuration of the transition state by means of another method, which is based on very simple assumptions. This method, suggested by Ogg and Polanyi (*Trans. Faraday Soc.*, 1935, **31**, 604), is applicable to reactions in which ions are formed or which are accompanied by other fundamental changes in electronic structure (Evans and Polanyi, *ibid.*, 1936, **32**, 1333) such as, *e.g.*, the change of bivalent into quadrivalent carbon.

The method can be demonstrated for the decomposition of ozone (without prejudice to the question whether it is truly applicable in this particular case) as follows: Starting from two ozone molecules in the configuration in Fig. 2*a*, we imagine the two oxygen atoms which lie on the horizontal axis displaced symmetrically in the direction of their position in Fig. 2*c*. We plot the consequent rise in energy while assuming that there is *no interaction between the two oxygen atoms*, and thus obtain the energy curve of the four strained ozone bonds (Fig. 4, curve *a*). Next, we start from the other side of the reaction, that is, from three oxygen molecules situated as in Fig. 2*c*, and pull the above two oxygen atoms apart towards their position in Fig. 2*a*. We again plot the rising energy, which will be merely that of a strained oxygen molecule if we *disregard all interaction between the two displaced atoms and the pair of oxygen molecules* flanking them on both sides. Thus we obtain curve *b* in Fig. 4. The reaction will occur at the point where the two curves cross; hence the energy and configuration at the crossing point can be identified with that of the transition state. It is true that, strictly speaking, the energy of the transition state is always lower than that given by the crossing point, since, on account of the quantum-mechanical " degeneracy " of this state the crossing point is cut off as shown by the dotted line in the diagram. An exact calculation of the " perturbation energy " which causes this depression would lead to the same solution as that proposed by London. The perturbation energy, however, is small, and can be neglected in reactions involving a fundamental rearrangement of the electrons; herein lies the practical justification of the method.

However, the main value of this treatment of chemical mechanism does not, perhaps, lie at present in its power to predict activation energies, but rather in the fact that it gives a clear picture of the transition state which leads to an understanding of various regularities of reactivity and, in particular, to a theoretical parallelism between variations of velocity constants and equilibrium constants.

Considering an equilibrium between ozone and oxygen, we would see the atoms passing back and forth between the configurations of Fig. 2*a* and *c*, passing on each occasion through the transition state, Fig. 2*b*. The transition state, which we will now call τ, thus takes part in the equilibrium, and we can apply to the " population " of τ (*i.e.*, the number of systems per unit volume which have configurations represented by τ) the fundamental considerations of statistics :

$$\text{Population } (\tau) = \text{birth-rate } (\tau) \times \text{average life } (\tau).$$

Now τ is formed either when a pair of ozone molecules decompose, *i.e.*, " reaction 1 " occurs, or when ozone is formed from oxygen by the converse " reaction 2." Birth-rate (τ) is, therefore, the sum of reactions 1 and 2 per unit of time. At equilibrium the numbers of reactions 1 and 2 are equal, and hence

$$\text{reaction rate } 1 = \tfrac{1}{2}\frac{\text{population } (\tau)}{\text{average life } (\tau)}$$

Since τ corresponds only to a single point on the co-ordinate l, the population and average life of τ are both infinitesimal quantities. Pelzer and Wigner (*Z. physikal. Chem.*, 1932, *B*, 15, 445), who first suggested such a statistical discussion of the transition state in a theory of the reaction $H + H_2^{\text{para}} = H_2 + H$, have shown that

$$\text{population } (\tau) = c'c''e^{-q_1/RT}\phi_1 \,.\, dl$$

where c' and c'' are the concentrations of the two reactants, q_1 is the activation energy, and ϕ_1 a probability factor which can be determined from the configuration and the elastic properties of the transition state. Wigner also pointed out that the average life (τ) is simply a thermal velocity divided by the infinitesimal length *dl*, *i.e.*, average life (τ) = v/dl. The velocity constant k_1 was thus obtained :

$$k_1 = \tfrac{1}{2}e^{-q_1/RT}\phi_1 v \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The novel feature of this expression is the appearance of $\frac{1}{2}\phi_1 v$ as a temperature-independent factor, *i.e.*, representing encounter number × steric factor. This is here derived from the configuration and elastic properties of the transition state. This magnitude, which we will briefly call the " collision factor," was calculated by Pelzer and Wigner (*loc. cit.*) for the reaction $H + H_2^{\text{para}} = H_2 + H$. Later, the factor ϕ_1 was given its general form by Eyring (*J. Chem. Physics*, 1935, **3**, 107) and by Evans and Polanyi (*Trans. Faraday Soc.*, 1935, **31**, 875). Eyring (*J. Amer. Chem. Soc.*, 1935, **57**, 985) used it successfully to calculate the collision factor for $2NO + O_2 = 2NO_2$.

More general conclusions can be obtained by introducing thermodynamic variables into equation (1). We define (Evans and Polanyi, *loc. cit.*; Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492, suggest a similar expression) an infinitesimal equilibrium constant

$K_1 . dl$ which determines the population (τ) as a function of the concentrations c' and c'' of the reactants, *viz.*,

$$\text{population } (\tau) = c'c''K_1 . dl$$

and, by the same process as that leading to (1), obtain

$$k_1 = \tfrac{1}{2}K_1 v \quad \ldots \ldots \ldots \quad (2)$$

Further, we define the free-energy difference F_1 and entropy difference S_1 by

$$\left.\begin{aligned} RT \log K_1 &= F_1 \\ \text{and} \qquad F_1 &= -q_1 + TS_1 \end{aligned}\right\} \quad \ldots \ldots \ldots \quad (3)$$

Starting from the opposite direction of the reaction, we have analogous magnitudes K_2, F_2, S_2, and q_2.

The collision factor $\tfrac{1}{2}\phi_1 v$ now assumes the form

$$\text{collision factor} = \tfrac{1}{2}e^{S_1/R}v \quad \ldots \ldots \ldots \quad (4)$$

We also note that the thermal velocity v can only change slightly at constant temperature, and we therefore set for any isothermic variable χ

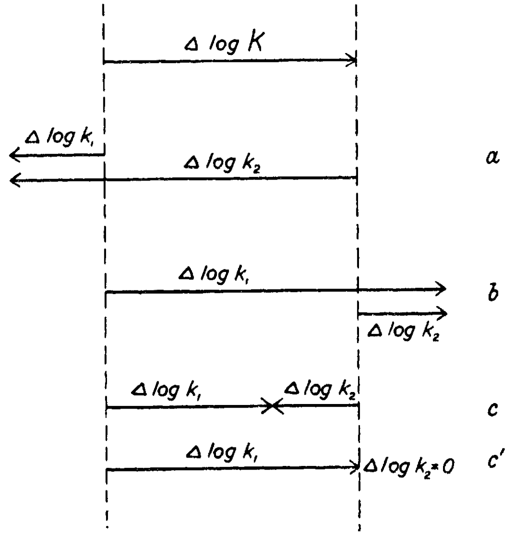
$$\partial v/\partial\chi = 0 \quad \ldots \ldots \ldots \quad (5)$$

and from (2), (3), and (5) we deduce (Evans and Polanyi, *loc. cit.**)

$$\partial F_1/\partial\chi \equiv RT . \partial \log K_1/\partial\chi = RT . \partial \log k_1/\partial\chi \quad \ldots \ldots \quad (6)$$

Before we proceed to apply this equation, we wish to call attention to the fact that the statistical discussion of the transition state implies a further revision of our ideas concerning its nature. The postulate that the transition state is only formed when a reaction occurs in either the forward or the backward direction implies that this state is the point of the reaction path having a minimum statistical probability. This point may not exactly coincide with the maximum of potential energy but corresponds to the maximum of the free energy.

Fig. 5.



A change in equilibrium constant $\Delta \log K$ can be made up in three ways by the changes in velocity constant $\Delta \log k_1$ and $\Delta \log k_2$. A similar classification holds for changes in heat $\Delta Q = \Delta q_1 - \Delta q_2$ and changes in entropy $\Delta S = \Delta S_1 - \Delta S_2$. The case *c* (and *c′*) is of particular significance.

The purpose of introducing thermodynamic variables relating to the transition state is to deal more easily with relationships between changes in equilibrium and changes in reaction rate. An equilibrium constant K is defined by the reaction velocity constants

$$\log K = \log k_1 - \log k_2$$

When K varies from one reaction to another, *e.g.*, under the influence of chemical substitution, or by a change of solvent, or else by a continuous factor such as hydrostatic pressure, then three alternatives are possible which are shown in Fig. 5, $\Delta \log K$ being the logarithmic change in equilibrium constant. The constituent $\Delta \log k_1$ and $\Delta \log k_2$ terms might behave as in *a* or as in *b* or as in *c*. A similar classification is possible for changes in reaction heat $\Delta Q = \Delta q_1 - \Delta q_2$ and in entropy $\Delta S = \Delta S_1 - \Delta S_2$. It has been found that many series of reactions behave according to *c* (or *c′*), which is due, as we shall presently see, to the fact that significant parameters of

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* The subsequent section of this paper is taken from the work of these authors.

the transition state have values lying somewhere between those for the initial and the final state of the reaction. The thermodynamic variables of the transition state permit us to define these parameters and to describe simply this interesting class of reaction.

Take, for example, reactions of the type A + B = AB, which might be the union of two atoms to form a molecule, or alternatively, the addition of two complex particles, *e.g.*, $2CPh_3 = (CPh_3)_2$. In both cases the configuration of the transition state might be expected to be intermediate between those of the initial and the final state and to lie close to the final state. The entropy of the transition state will, therefore, vary from one reaction of this type to another almost exactly as the entropy of the over-all reaction. In fact, a theoretical calculation yields

$$S_1 - S = R \,.\, \ln \frac{h\nu}{kT} \frac{h}{(2\pi m^* kT)^{1/2}} \dagger$$

where ν, the frequency of the bond A–B, and m^*, a compound mass, do not vary greatly from one reaction to another. Since, at the same time, S varies a great deal from one reaction to another, it follows that changes in S will be accompanied by almost equal changes in S_1. Such reactions are thus of the type c' with respect to variation of entropy.

The changes in S consist in a *decrease* with *increasing complexity* of A and B. Thus the reaction $2CPh_3 = (CPh_3)_2$ has a much smaller S than the union of two atoms. This obviously arises from the fact that two complex particles have to be linked up in a very particular way which makes AB an improbable state. The decrease in S_1 which accompanies the decrease in S explains the "slow reactions" of Moelwyn-Hughes and Hinshelwood (J., 1932, 230) in which the collision factor $\frac{1}{2}e^{S_1/RT}v$ [see equation (4)] has exceptionally small values. In fact, a number of "slow" reactions (and perhaps all of them) are additions of the type A + B = AB, in which A and B have complex structures.

We can also compare by this method the collision factor in solutions with that in the gas phase. For example, in the reaction $C_2H_4 + H_2 = C_2H_6$, if its entropy in the gas phase is S, then its entropy in solution, S^*, will be $S^* = S + s_{C_2H_4} + s_{H_2} - s_{C_2H_6}$, where $s_{C_2H_4}$, s_{H_2}, and $s_{C_2H_6}$ are the entropies of solution of ethylene, hydrogen, and ethane respectively. On introducing the measured data, *e.g.*, for carbon tetrachloride solution (Horiuti, *Z. Elektrochem.*, 1933, **39**, 22), it follows that S^* is greater than S by about 7·4 entropy units. Applying the same line of reasoning as before, we might assume that $S_1 - S$ is unchanged by the presence of the solvent, and hence that S_1 increases by the amount $S^* - S$. The corresponding change in the collision factor $\frac{1}{2}e^{-S_1/RT}v$ is a 30-fold increase as compared with the gas state. The presence of the solvent can thus increase the *a priori* probability of the reaction, *i.e.*, quite apart from any change in activation energy. The kinetic interpretation of this effect is to be found in the work done by the internal pressure of the solvent which helps the coalescence of two particles into one.

Considering that the formation of the transition state from two reacting molecules is a process similar to an addition A + B = AB, we might generalise this result as follows: The collision factor in solution as compared with the gas phase is determined by the sum $s_A + s_B - s_\tau$, where s_A, s_B, and s_τ are the entropies of solution of the reactants and the transition state respectively. If the sum $s_A + s_B - s_\tau$ has a positive value, as was the case for $s_{C_2H_4}$, s_{H_2}, and $s_{C_2H_6}$, the collision factor in solution will be greater than in the gas phase.‡ This might offer an explanation for numerous cases in which it has been found that the collision factor in solution is higher than the number of collisions which would occur between the reactants if they were present as gases.

In general, the collision factor in solution can be determined by the entropy of solution of the transition state. Attention has been recently drawn to the fact that entropies of solution of one solute in many solvents decrease linearly with the heat of solution; the same relation holds for some series of different solutes in the same solvent. Assuming that the latter relation holds true, at least approximately, for the reacting molecules and the transi-

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† This is equivalent to the assumption made by Polanyi and Wigner (*Z. physikal. Chem.*, 1928, *A*, **139**, 439), as pointed out by Evans and Polanyi (*loc. cit.*).

‡ This result has also been obtained in a somewhat different manner by Wynne-Jones and Eyring (*loc. cit.*).

tion state of their reaction, one would expect the collision factor to decrease with decreasing activation energy when a reaction is carried out in different solvents. This feature is, indeed, well marked in the influence of solvents on the rate of formation of quaternary amines from tertiary amines and alkyl halides (see data given by Moelwyn-Hughes and Sherman, J., 1936, 101).

The electrolytic evolution of hydrogen is a reaction in which both equilibrium and reaction rate vary together under the effect of an outside force, namely, polarisation. The relation between these two variations follows Tafel's over-voltage equation, which can be shown to express the fact that the reaction is of the type *c* with respect to log K. Tafel's equation can, accordingly, be deduced by assuming that the strength with which the electric field acts on the transition state lies intermediate between the strengths of its action on the initial and the final state.

Suppose that we consider electrodes at which the rate-determining step in the discharge of hydrogen consists in the transfer of a proton from an oxonium ion to a metal surface where its charge is neutralised by union with an electron, then the free energy F of this process depends on the polarisation ε as does the free energy of the hydrogen electrode : $\partial F/\partial\varepsilon = nA$, where $n = 1$ is the number of electric charges carried by a proton, and A is Faraday's equivalent. Assuming that the effective charge n of the proton in the transition state has a value intermediate between 1 and 0 (which values correspond to the initial and the final state), we obtain

$$\partial F_1/\partial\varepsilon = \alpha nA\,;\ 0 < \alpha < 1$$

which by use of equation (6) immediately leads to Tafel's equation

$$\log i = \alpha nA\varepsilon/RT + \text{const.}$$

if we measure the velocity constant by the intensity of the current.*

Other proton transfers, occurring in acid-base catalysis $AH + B = A^- + {}^+HB$ (A = acid ; B = base), can be treated in a similar fashion, resulting in Brønsted's equation, which correlates dissociation constants with velocity constants. On the assumption that the variations of the free energy from one acid to another and from one base to another arise purely from variations in the intensity of the molecule's electric field, the derivation would be exactly the same as that of Tafel's equation. But it seems more appropriate to leave the exact nature of the parameter which causes the variations in the dissociation constants open, and, denoting this unknown parameter by χ, to define another parameter as the derivative of the free energy with respect to χ, denoting it by β, and β_2 for the initial and the final state respectively :

$$\partial F/\partial\chi = \beta_1 - \beta_2$$

Brønsted's equation then results if

$$\partial F_1/\partial\chi = \beta$$

has a value about half-way between β_1 and β_2, *i.e.*,

$$\partial F_1/\partial\chi = \alpha(\beta_1 - \beta_2), \text{ where } \alpha \sim 0{\cdot}5.$$

This gives $\partial F_1/\partial F = \alpha$, and hence, from equations (2) and (3),

$$\log k_1 = \alpha \log K + \text{const.}$$

which is Brønsted's equation if $\alpha \sim 0{\cdot}5$.

Clearly, this framework is appropriate to express also the other numerous cases of logarithmic proportionality between the constants of equilibrium and velocity preliminary to a detailed analysis of the relevant parameters χ and β.

Another promising field for these considerations is the influence of hydrostatic pressure π on reaction rate in solutions. According to van't Hoff, $\partial F/\partial\pi = V_1 - V_2$, V_1 and V_2 being the volumes of molar solutions of the reactants in the initial and the final state.

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* This derivation of Tafel's equation becomes identical with the derivation given by Horiuti and Polanyi (*Acta Physicochim. U.S.S.R.*, 1935, 2, 507) if we assume $F_1 = q_1$, which corresponds to the earlier definition of the transition state as being the maximum of potential energy (see above).

Assuming, as before, that for reactions of the type A + B = AB the configuration of the transition state is intermediate between those of the initial and the final state and nearly the same as that of the latter, we might expect to have

$$\partial F_1/\partial\pi = \alpha(V_1 - V_2)$$

where $0 < \alpha < 1$, and α is near to unity, resulting [equation (6)] in

$$\partial \log k_1/\partial\pi = \alpha(V_1 - V_2)/RT$$

and for the reverse reaction

$$- \partial \log k_2/\partial\pi = (1 - \alpha)(V_1 - V_2)/RT$$

The union of two particles to one molecule being generally accompanied by a reduction in volume, $V_1 - V_2$ should be positive, and hence the association should be accelerated and the dissociation impeded by hydrostatic pressure. The acceleration should be almost but not quite as large as the accompanying shift of the equilibrium, the difference between the two being equal to retardation in the rate of dissociation. This prediction has been fully confirmed by Perrin, Gibson, and Williams (*Proc. Roy. Soc.*, 1936, *A*, **154**, 684) for the reaction benzylmethylaniline + allyl bromide = phenylbenzylmethylallylammonium bromide. Thus it appears that the direction in the change in reaction rate caused by hydrostatic pressure can be predicted for reactions of the type A + B = AB, and the magnitude of the change can also be foretold closely enough from the densities of the initial and the final solutions.

One might try to go one step further by considering all bimolecular reactions as association reactions primarily leading to the fusion of the reacting molecules into a transition state. One might expect, therefore, all bimolecular reactions to be accelerated by pressure. It is true that this is confirmed by experience, so far. Nevertheless, this consideration can hold strictly, and can be formulated quantitatively, only if A and B unite to the transition state (AB) without any change in the solvation forces and changes in the density of the solution arising from this cause. Thus, predictions appear to be safe enough so long as no ions are involved in the reaction, but otherwise the theoretical analysis is more complex.

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