The Nature of Chemical Existence

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I

In *The Nature of Physical Existence* (hereafter, NPE), Ivor Leclerc described "the modern concept of nature," and identified as one of its main features the doctrine that the physical existent is "matter, conceived in the Gassendist way as impenetrable, solid atomic bodies." (NPE, 227) After discussing the relationship of this outlook to earlier viewpoints, and how the modern system became dominant with the triumph of Newtonian science, Leclerc argued that it is now necessary to replace "the modern concept of nature." It is his contention that progress in important areas, including science, may be limited by continued use of approaches and categories that no longer have an adequate metaphysical basis. Professor Leclerc then provided a "prolegomena to a new concept of nature," involving a novel specification of physical existence:

The problem is how precisely are many substances to be conceived as constituting one substance. The theory being here advanced conceives the acting of substances as acting on each other. Now when the acting of the substances on each other is fully reciprocal, I wish to suggest, these actings combine to one single act, with one single form... It is in virtue of this combined acting, constituting a one acting, that the compound entity acts as a whole, that is, as one, with reference to, and on, other wholes. (NPE, 311)

The key concept in this proposal is "fully reciprocal" acting, further explained as follows:

If the acting of a particular substance in response to the acting on it of another be more strongly a passive response or reception than itself an acting on, that is, if the feature of acting on in this relationship be recessive by contrast with the aspect of reception, the relation will not be a unity of a substantial kind, but one in which the recipient substance will be quite changed but will remain substantially quite distinct. (NPE, 312)

In a paper published in 1982 (1) I proposed that certain chemical systems, called dissipative structures, ought to be considered to be unified active entities – that these coherences have as much claim to be "physical existents" as entities of any other class.

In *The Philosophy of Nature* (hereafter, PN) Professor Leclerc provided further discussion of the modern corpuscular concept, including analysis of the important role of chemical thought and practice in the origin, development and spread of this doctrine. He also generously reviewed my suggestion concerning the ontological status of dissipative structures, but he expressed the opinion that the chemical systems I had discussed were better regarded as "societies" rather than as single acting entities. He also provided further specification of his own proposal for a new concept of nature:

Moreover, as Leibniz and, even more clearly, Kant recognized, physical acting is at once an "acting" and a "reacting," so that when, say, an entity A acts on entity B, B reacts to A both by receiving an effect from A and being affected by A in respect of what it becomes, of its definiteness or character. By this reciprocal transaction there is thus both an exertion of "force" by A's acting, and a "bond" between the two entities by virtue of the two entities acting and reacting. This means that physical acting effects a relation in the full sense of "connecting." This, 1 venture to suggest, is the philosophical explanation of the physical "bonds" (sometimes spoken of as "forces") which hold a number of entities together to constitute a composite whole.

By reason of the mutual actings and reactings, compound wholes are constituted which have a unity and thereby also a determinate character, which is definitely more than those of a mere aggregate. This means that the actings of the constituents combine to constitute the whole a new physical existent. Since the combined acting of the constituents effects a unity which transcends the constituents per se, the combined acting must have the *whole* entity as its subject-for the combined acting is not reducible to the constituents severally as its subject. Thus, from the combined acting and reacting of the constituents there emerges a new integral entity in the full sense of itself per se capable of acting. By such a compound entity's entering into integration with other such entities, still more complex entities emerge. (PN, 166-167)

Aristotle remarked that those "who dwell in intimate association with nature and its phenomena" may have insights that are philosophically important. *(De Generatione et Corruptione* **I,** 316a 6) Both NPE and PN clearly illustrate that chemical concepts and experimentation have historically been intimately involved with philosophic understanding of nature. This paper will give some examples of what sons of things are held to exist (and not to exist) by contemporary chemists and reconsider the ontological status of compound entities.

II

We begin with a straightforward case. When zinc metal is added to an aqueous solution of hydrochloric acid, bubbles of an odorless, colorless, flammable gas appear. A variety of evidence leads to the conclusion that this gas is molecular hydrogen, H2, (now frequently called dihydrogen)-a chemical substance that can be regarded to consist of two hydrogen atoms (each of which, in tum, consists of one proton and one electron). Rather complete discussions of "the covalent chemical bond" that holds the dihydrogen molecule together can be found in textbooks of physical chemistry studied by upper-division undergraduate science students. Mutual interaction of protons and electrons cause the distance between the two protons to be rather closely restricted. Bringing the two positively charged protons closer together than the "equilibrium internuclear distance" engenders forces that tend to push the protons apart, but separating them beyond the equilibrium internuclear distance evokes responses that tend to compress the molecule. Splitting the dihydrogen molecule so as to produce two hydrogen atoms would require a specific, if rather large, amount of energy (the "bond energy" of dihydrogen). The magnitude of that energy can be calculated quite precisely on the basis of well-established principles.

Here we have an example of the clearest kind of chemical existence, let us call it E1. Interactions between the pans of a sub-microscopic entity give rise to a specific configuration (spatial arrangement of components) of the system such that any deviation from that configuration engenders a response that tends to reduce that deviation (that is, to restore the *status quo ante).* This circumstance is the defining characteristic of chemical structure and of the primary meaning of "existence" for chemists. Chemical systems that have structure, in this sense of having the propensity of self-restoration after disturbance, are regarded as constituting independently existing entities.

The dihydrogen molecule undergoes continual deformations around the equilibrium configuration. Dihydrogen molecules vibrate incessantly and rotate continually, and, vibrating and rotating, they move rapidly, and frequently collide with each other and with the container. The total energy of motion (kinetic energy) of any sample of the gas is proportional to the (absolute or Kelvin) temperature. At ordinary temperatures, dihydrogen molecules are in rapid. random motion, but they split apart into atoms only exceedingly rarely, because the bond energy of the H-H bond in dihydrogen is larger than the energies molecules generally acquire at normal temperatures.

Diatomic molecules have only one structural parameter (the internuclear distance); the internal potential (non-kinetic) energy of the molecule is specified by that one parameter. Internal potential energy is a minimum at the equilibrium inter-nuclear distance and higher at all other values of that single important parameter. More complicated chemical structures follow the same principle. A molecule of a gaseous organic chemical (such as paradichlorobenzene, the active ingredient of mothballs) has many chemical bonds (like the bond in dihydrogen). At ordinary temperatures, each of these bonds stretches and contracts in an *oscillatory* manner and the angles between the bonds also vary as the molecule vibrates and twists. The large number of parameters involved does not change the situation in any fundamental way; the molecule is said to be *stable-that* is, to exist-because there is a specific arrangement of components that is automatically restored after every variation, no matter how complicated that variation might be.

A crystal-of rock salt (NaCl) or of diamond, for example-requires many parameters to specify its structure. Fortunately for crystallographers (and those who study large molecules) the symmetry of a crystal or of a molecule can introduce great simplifications, so that most of these parameters can be combined to yield a relatively small number of relevant parameters. Even such large aggregations as visible macroscopic crystals have the kind of structure described for dihydrogen-a specific arrangement of components that restores itself after disturbance from outside and also after internal fluctuations (generated by thermal energy) of *every* sort. The pattern of the macroscopic solid of a salt crystal is made up by the juxtaposition of identical microscopic "unit cells" that fit together so as to fill space.

The molecule of methane, CH4 can appropriately be considered as a carbon nucleus (six protons and about six neutrons, firmly bound together) associated with an "inner core" of two electrons and an eight-electron "valence shell" in which four protons are embedded. (Chemists think of electrons in molecules as diffuse clouds of charge, rather than as discrete negative particles.) A configuration in which the four HCH angles are all the same has lower potential energy than any other configuration; any deviation from that configuration engenders a response that tends to reduce the deformation from tetrahedral geometry. Methane has the geometry it does because of the tendency of electrons to associate in pairs, and from the mutual repulsion of the (negatively charged) electron pairs. At ordinary temperatures methane molecules translate and tumble and also vibrate in several different modes; each of the four bonds continually stretch and contract. The properties of macroscopic samples of methane are due to the microscopic properties of the molecules-methane is a gas because there are no regions of concentration of unbalanced charge (either positive or negative) in the molecule. The microscopic properties of the molecule, in tum, depend on characteristics of the electrons and nuclei that comprise the molecule.

Each reasonably well-formed salt crystal may properly be regarded as a single entity, composed of sodium cations, Na+ and chloride anions, CI· distributed in a specific pattern. The cohesion of the crystal is due to electrostatic (Coulombic) interactions between the ions, and to the fact that the sizes of these ions are such that they pack neatly together in a lattice that has cubic symmetry. When the crystal dissolves in warm water the ions are not changed, they merely become surrounded by dipolar water molecules and disperse through the liquid in such a way that every region of liquid has very nearly the same number of positive cations and negative anions. What molecules and salt crystals have in common is not the nature of the interactions between components (covalent bonds within molecules are rather different from ionic interactions in salt crystals), but the circumstance that those interactions define specific, self-restoring structures-and, therefore, have chemical existence E].

III

Entities that have this strong (EI) sense of existence do not exhaust chemical ontology. There are many classes of entities that are recognized by chemists as having real, if sometimes transient, existence. We can only deal here with a few examples. Consider an experiment that is conceptually simple, although quite complex in practice-collision between two crossed beams, one a stream of molecules and the other a beam of atoms. Dihydrogen molecules can be made to collide with fluorine atoms; alternatively, beams of lithium atoms and hydrogen fluoride molecules can be crossed.] Experiments of this kind can be done in high-vacuum apparatus, and one can monitor the direction (relative to the directions of the initial beams) of emergence of the product molecules-HF molecules and H atoms in the first case and LiF molecules and H atoms in the second. By careful study of whether the reaction products emerge behind or in front of the position at which straightforward calculation indicates they should emerge, physical chemists often infer the existence of "complexes" that have short lifetimes, as low as one millionth of a millionth of a second (l0·12 second). For a brief time during the reaction the atom and the diatomic molecule constitute an aggregate; this grouping does not last long enough to undergo vibrational motion, but it does persist long enough to rotate as a unit-and that rotation has consequences in respect to how the distribution of product molecules is related to the initial beam directions. The action of the aggregate, as an aggregate, has discernible consequences; therefore, chemists consider that the triatomic "complex" exists. Let us designate this sort of existence (rotational, but not vibrational) as E2.

The next point of chemical ontology is best approached by considering an important and well-defined class of chemical entity called "the transition state." Entities of this class are remarkable in that (like Santa Claus) *they do not exist* (sorry, Virginia). Suppose a dihydrogen molecule is struck by a rapidly moving hydrogen atom. After the collision there will be an atom and a diatomic molecule (as there was before the collision), but it is possible that the loose atom may have come from the original molecule, and the projectile atom may be part of the final molecule, that is:

(l) H'+H-H ~ H-H'+H

Consider the situation half-way between the states indicated by the two sides of reaction (1)-the situation in which the new bond is exactly half-formed and the old one exactly half-broken. This specific configuration, uniquely defined for each specific reaction, is designated the "transition state" for the reaction. In favorable cases the configuration of this state can be precisely specified and accurately described. (Santa Claus would be a portly gentleman with a red suit and a white beard.) Bond lengths and the H-H-H angle can be accurately specified for the transition state for reaction (1) but that entity lacks the property that gives real chemical existence. There is one disturbance of the transition-state configuration that does *not* encounter a restoring force. (The variation that leads from the reactants' configuration to the products' configuration is different from all other variations.) The entity cannot "exist" in either of the two senses (El or E2) discussed above although (as Michael Polanyi first demonstrated over fifty years ago) fruitful chemical conclusions can be obtained 0.3by reflecting on its necessary properties (bond lengths, angles, etc.). Nevertheless, John Polanyi (Nobel laureate, son of Michael Polanyi) has predicted the absorption spectrum of the transition state of reaction (1). That is to say, he has given a detailed description of the *color* of something that does *not* exist-that cannot, by definition, exist in either of the two senses (E1 or E2) that we have already discussed. The paradox is resolved by noticing that absorption of visible light by a chemical species involves change of the *electronic* energy state of the system–one or more electrons use energy removed from the incident light to become "promoted" to a higher quantum energy state. Electrons are very much lighter that even the lightest atomic nuclei. Electrons move at the speed of light; atomic nuclei move much more slowly. The entire process of light absorption takes about 10-30 seconds-essentially *no* atomic motions occur in that short a time. The transaction that is responsible for color can take place thousands of times *during* the collision of two molecules, even during the brief impact of two rapidly moving molecules.

In the particular case of calculating the spectrum of the transition state of reaction (1), Polanyi *fils* imagined a large number of hypothetical experiments in which a hydrogen atom approached a dihydrogen molecule from some particular direction, at some specific speed. All the forces involved in this interaction are well understood; it was possible, in each case, to compute what the positions of each of the three atoms would be as a function of time during the course of each postulated encounter (the trajectory). He also could calculate the probability of an electronic transition for each possible configuration of the three atoms. These two types of calculation were then combined to yield the predicted electronic spectrum-the color-for the three-atom aggregate, although that aggregate does not exist in any strong sense. Entities having this third type of existence-let us designate it as E3-are capable of exhibiting electronic properties, although they do not persist long enough for vibration or rotation.

Perhaps this point can be clarified by another example. Solutions of diiodine in benzene have a distinctive color, due to absorption of light by a complex, an aggregation of one benzene molecule and one diiodine molecule. This complex *does not exist* in either the E1 or *Ez* senses. When diiodine is dissolved in benzene there will always be, merely by chance, some diiodine molecules that happen to be located directly alongside benzene molecules. When light falls on the system, electronic transitions will occur in which electrons are shuffled back and forth between the members of such chance pairs of adjacent and properly oriented molecules. (Light absorption will be much less likely for all other relative orientations of benzene-diiodine pairs.) Absorption of radiant energy corresponds to a color characteristic of a new entity, even though (on the time-scale of molecular vibration or rotation, 10.12 seconds) there is no third chemical entity present, only benzene and diiodine molecules. E3 is our designation of the type of the existence characteristic of the colored entities in these solutions, aggregations that exist for times of the order of 10-30 seconds (long enough for electronic transitions) but not for as long as 10-12 seconds (the time needed for vibration or rotation).

IV

Yet another strange sort of entity can be detected in simple gas-phase chemical reactions such as reaction (1). Sometimes, when reaction probability for such reactions is plotted against an experimental variable, a sharp spike of enhanced reaction likelihood appears in the graph at certain values of experimental parameters. These results are interpreted in terms of "resonances"-a type of existence that we will designate E4. Here, the details of the interactions between the several components of a system trap the components in a complicated pattern of motion, and hold them in intimate contact for more or less extended periods, although no specific chemical bonds are formed Such trapping requires that the total energy of the system be in certain restricted ranges, neither too high nor too low. (A homely analogy might be a ball shot in a pinball machine that gets trapped between several bumpers for a long time: if the ball were to stop moving it would at once escape the trap, but so long as it has kinetic energy in the appropriate range it may be held indefinitely.) Resonances in chemical systems come into existence when several components, with significant kinetic energy become entangled by the detailed nature of their interactions, in an aggregation that persists, as a coherent unit, long enough for that aggregation, as such, significantly to effect other events. We designate this sort of existence as E4. "Solitons" in physical systems and "exiplexes" in photochemical reactions6 also exist in related senses, but we will not discuss them here.

Analogous situations can be observed in condensed-phase chemical systems. One example is the Belousov-Zhabotinski (hereafter, BZ) reaction which involves interaction of bromate ion and a reducing agent (frequently malonic acid), usually in the presence of certain indicators and catalysts.7 This reaction is remarkable in that it proceeds in an *oscillatory* way, rather than merely changing from reactants to products directly. With the usual indicators present, the reaction solution turns red, then blue, then red, then blue, and so on. The system alternates between those two colors repeatedly, while the chemical energy of the reactants is released, with the production of low-energy products, including carbon dioxide. In the absence of stirring, intricate spatial patterns spontaneously develop; if the reaction is carried out in a continuously stirred tank, with reactants continuously supplied and the overflow removed, oscillations of color will continue indefinitely. An especially important feature of this system is that, within certain rather wide limits, perturbations (whether introduced externally or arising from within the system) are damped out-all conceivable fluctuations engender responses that tend to reduce the fluctuation, rather than amplify it. We designate this sort of coherence as E5. This sort of aggregation shares an important characteristic with the molecules and crystals that exemplify existence, E1. In both cases variations away from a reference arrangement are damped out; in the case of E1, the reference arrangement is a spatial configuration of component entities–in the case of E5 the reference arrangement is more complex and interesting. The E5 arrangement does not involve self-identical 'things' here and there at a specific time, but rather interactions of entities that are themselves undergoing continual change and are distributed over rather large regions. A further difference between E1 and E5 is that, in the latter case, the reference arrangement is not a single state definable without reference to the passage of time, but rather a sequence of states, each of which recurs after the lapse of a specific interval of time.

There is a close analogy between E5 and E4. In both cases components are trapped in intricate more or less long-lasting behavior patterns by details of dynamic interactions that occur between components. In E4 resonances the components are single entities, such as atoms or molecules. E5 coherences are intrinsically more complex; vast numbers of several sorts of component entities are involved in the interaction. This complexity does not destroy the analogy, any more than the transition from a one-parameter diatomic molecule to a crystal or macromolecule alters the fundamentals of E1. In contradistinction to E1, E2 and E3, both E4 and E5 are *far from equilibrium* structures. These coherences require a source of energy (either internal or external) in order to come into being, and for their existence to be prolonged. In the BZ reaction, for instance, the high chemical energy of the reactants is dissipated as the reaction proceeds; this flux of energy keeps the oscillation in being. Such arrangements are called dissipative structures. A I flame in a gas jet is such an entity; it will continue to exist just so long as high-energy chemicals (gas and dioxygen) are provided. Flames (and instances of the BZ reaction) are chemical entities, in the sense that we designate Es. The interactions that give rise to E4 and Es have the property of filling time in a way that is quite comparable to the way in which extended crystal structures fill space. The type of existence designated E5 is a better model for entities of wide human interest than either the corpuscular model of the physical existent, or the E1 class of chemical existence typified by the hydrogen molecule. Human social groupings (The New York Yankees, for example) persist as recognizable entities over extended periods of time-and that persistent group identity has discernible consequences. Each of the human individuals that constitute those social groupings is always in the process of development and change. The continued existence of the group depends on the availability of resources (box office receipts for the Yankees) and also influences the types of development that are necessary or possible for component entities. The existence of such macroscopic coherences must be taken with full seriousness. There is no warrant for expecting that there is, anywhere or anywhen, some type of entity that is not composite in closely related senses. Existences of the class E5 need to be taken into account–they are *physical existents* if any such exist. In these cases, it is clear that the persistence of a unified center of effective action also depends on coherences of both smaller and larger scales; this is equally true, if less apparent, for other sorts of coherence. (In the institutional analog, invalids make poor Yankees; baseball's place in American culture is also important.) This is not a defect in the concept of E5; it is a general characteristic of being and of all beings whatsoever–or so I claim.

V

Everything that chemists deal with is composed of microscopic components – to that extent chemists warmly embrace the outlook that Leclerc designates as the "modern concept of nature." There is one important aspect of that worldview, however, that chemists do not, in general, share. Chemist *do not* *hold* that there is a single fundamental level of description-that *one* scale of time or size (or single group of classes of entities) which *all* interesting questions can be answered. According to L of the main features of the modern concept is the doctrine that t fact, *ultimate* components into which things can be resolved and I "atoms" which do, could, or should ground *all* explanations. Turn-of-the-century chemists identified these minima as the atoms of the elements, in mid-century, physicists sought a restricted set of truly "elementary particles”: in our own time, public-choice economists consider individual human agents to be ultimate: all of these attitudes may be regarded as manifestations of the complex of attitudes that Leclerc termed the "modern concept of nature.”

Ian Hacking has pointed out that ontologies that scientists use deprnds in important ways on the types of problems with which they deal.9 Chemists frequently need to worry about the spin of nuclei and consider prope vidual atoms and of such subatomic particles as electrons and nelltr are more likely to be engaged with more or less coherent aggreg molecules and the other entities that were discussed above, and with structures that form the primary subject matter of engineers or 0 Chemists agree that it may be possible to leam a great deal more abo nal structure of quarks, but would generally maintain that it is 110t lik information will be pertinent to the problems with which they are con

Similar considerations apply *a fortiori* to biologists, who fre~ concerned with chemical matters, but rarely get into the physico-chemical arcana that many chemists relish, although biologists are more likely to deals and with questions of ecology, large-scale integrations of food chains and biogeography than are chemists. Maynard Smith's concept of the evolutionary stable strategy10 bears close and important analogies to the chemical concept of the dissipative structure. David Hull and others have engaged in vigorous controversy, which they unabashedly term *metaphysical,*11 concerning the "units of selection," i.e. what sort of entities ought to be considered fundament in discussions of biological evolution. As in chemistry, there is no *single level* of description that is fundamental. To the extent that chemists, biologists, and other scientists have abandoned the notion of a fundamental class of units adequate for all discussions – they have moved away from an essential metaphysical feature of the “modern concept of nature"

VI

In PN Professor Leclerc rejected my identification of dissipative structures (E5 in this paper) as integrated active entities because "those structures are wholes which are not per se agents." (PN, 168) In NPE (311), he states: "The action of one compound 'atom' on another is not, by the scientific evidence, an aggregate acting of the electrons and protons individually on each other, but of each 'atom' as a whole on others." This description does not apply to dissipative structures; if such a description were characteristic of compound individuals functioning as unified physical existents, then rejection of my suggestion would be well-founded. But I know of no scientific evidence to support the contention that the action of 'atoms' on each other differs in any way from the (properly weighted) sum of the aggregate actings of the components. It is difficult to conceive situations in which the two alternative descriptions would be discernibly different from each other, providing only that proper account be taken of the constraints that arise from the structures (internal to the existents) that define the entities in question.

Is the sound of a well-rehearsed chorus different from the arithmetic sum of the sounds made by the individual singers? Are the properties of the methane molecule merely the sum of the properties of the components? The sound of the chorus in performance is certainly different from the tumult that rises from the champagne party after the concert, but only because sounds emitted by the choristers during the performance are carefully coordinated, while the babble of the same people during the party has little or no organization. The sound of the chorus in both cases is the arithmetic sum of the sounds made by the chorus members.

Are the properties of methane merely the sum of the properties of the components? Again the answer is affirmative; providing one considers atomic kernels (nuclei plus inner electrons) and valence electrons as the components of the molecule then the properties of the molecule follow from the properties of the components, and of *the symmetry of the structure in which they are united.* This symmetry also depends on the components.

Crystals have extension because unit cells combine to fill *space:* networks of interaction that define existence E5 fill *time* in a quite analogous way. In these cases, sequences of states periodically recur in time, just as specific distributions of atoms periodically recur in the spatial arrangement of a crystal. In PN, Leclerc indicates that it was the question of the nature of extension that brought Leibniz to understand the crucial importance of relations (PN, 39,146) and that the same problem was the occasion of Kant's 1769 realization of the primacy of the perceiver and the activity of perception. (PN, 104) It seems that it will require a judicious *combination* of these two insights to understand the metaphysical significance of the new concept of nature that is emerging from contemporary science.

ls it the internal composition of an entity, alone, that decides whether the thing is a unified source of action or is not such a unified source? Or is it, instead, some characteristic of the percipient that determines whether a thing is one or many? 1suggest that the chemical examples crudely sketched in sections I to IV indicate that *both* the internal composition of an entity *and* the interactions of that entity with the external world are important in deciding whether a thing is a unified source of action or whether it is a multiplicity.

Does the benzene-iodine complex exist, or does it not? It depends on how one looks for the supposed entity. If the probe is visible light, the complex evidently exists, because there is a visible color, associated with the complex, that can be detected not only with a spectrometer but even with the unaided eye. Electronic transitions take only 10-30 seconds; the two molecules are near enough to each other for a long enough time for the color to be apparent. However, if one uses a slower technique, such as nuclear magnetic resonance or infrared spectroscopies, then all evidence indicates that there is no such thing as a benzene-iodine complex. The aggregation does not persist long enough to be detected by *those* techniques. The measurement technique does not *cause* the existence (however fleeting) of the aggregation: the preexisting properties of benzene and diiodine and the consequent characteristics of the properly oriented molecular pair formed by these two entities determines what there is for the measuring technique to discern. Existence is not a univocal concept; aggregations that are unified with respect to some measures are composite with respect to other interactions. Any adequate ontology must be able to deal with this general characteristic of existence.12

We are now at an intellectual watershed as significant as that of the seventeenth century-the scientific and social changes we are witnessing are equally far-reaching. Ivor Leclerc has delineated major philosophical problems that face contemporary culture, and has made an inspiring beginning toward their solution.

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NOTES

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