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Ontological status of time in chemistry

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Abstract

While temporal considerations are of prime importance for chemical reactions, as well as for molecular stability, most chemical concepts (outside of the field of chemical kinetics) are not explicitly formulated on a diachronic basis (Earley ~~in Found Chem~~ 14:235, 2012). It will be argued here that a formulation explicitly incorporating temporal and epistemological considerations enables us to treat chemical reactions and chemical substances on ontologically equivalent terms, instead of assigning a more fundamental status to the latter. After all, in collision theory, a chemical substance is just a collision complex (a “resonance”) that takes too long. How long qualifies as “too long”, and “too long” in relation to what, are crucial questions that distinguish chemical substances from chemical reactions, and reversible reactions from irreversible ones, thereby introducing anthropocentric considerations into these distinctions. Too long for a lab chemist is very different from too long for an astrochemist studying chemical reactions between chemical substances in inter-stellar space on cosmological timescales. Examining several physical and chemical properties on the basis of which chemical substances are distinguished from one another, the role of temporal and anthropocentric considerations in defining molecular properties is emphasized. I conclude with some observations on the much-debated reduction of chemistry to other disciplines, arguing that such reduction depends on our aesthetic choices as to what kinds of observations demand explanation, and what kinds of explanation are acceptable.

AQ1

Keywords

Collision theory
Chemical dynamics
Ontology of time
Reduction of chemistry
Process structural realism
Anthropic principle

Introduction

The ontological status of time has been a topic of considerable philosophical speculation over the ages. The subjective nature of perceived temporal duration has led to questions as to whether time is no more than a creation of the mind, an ordering device or an illusion (Ballard 1984; Eddington 1928, 1939; Hoffmann 1972; Hoyle and Hoyle 1963; Hoyle 1966; Jaffe 2018; Schuster 1986; Wesson 2010). Other questions include whether time has an origin, a unique “beginning” (Hawking 1988; Penrose 1989) or whether it is cyclic, whether it is continuous or discrete, the relation between time and entropy or the so-called “arrow of time” (Eddington 1928, 1939; Everett 1957; de Witt 1970; Hoyle and Narlikar 1974; Petkov 2007; Schuster 1986; Wesson 2010), and whether there can be multiple time dimensions (Bars, Deliduman and Minic ~~et al~~ 1999; Bars 2000; Craig and Weinstein 2008; Velez 2012). Considerations of the epistemology of time and its relationship to space led Einstein (1905a, b) to formulate his Special Theory of Relativity in terms of two postulates:

1. The laws of physics are the same in all inertial frames; there is no preferred inertial frame (the Principle of Relativity);
2. The speed of light in free space has the same value in all inertial frames (Principle of Constancy of the Speed of Light).

AQ2

For observers in different inertial frames, where one is moving with a constant velocity relative to the other, time and space are inter-related through Lorentz contraction and time dilation. This welding of space and time results in a hybrid measure of separation interval, called the Minkowski spacetime metric, where covariance of the theory requires that time and space be interchangeable. Einstein subsequently generalized the treatment to include accelerated frames of reference

or objects moving in gravitational fields, in his General Theory of Relativity. Here I will focus on the consequences of the ontological status of time for the formulation of chemical theories, explanations and concepts.

Chemical substances and reactions are the objects of discourse in chemistry

In our conventional thinking, the ontological entities of chemistry may be classified as either chemical substances or reactions. Table 1 summarizes their essential ontological properties:

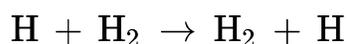
Table 1: Chemical Substances and Chemical Reactions

Chemical Substance	Chemical Reaction
Object	Process
Stable	Dynamic
Formed by and undergoes reactions	Converts chemical substances into other chemical substances

AQ3

It is conventional to consider the former (chemical substances) as the more “fundamental” constituents of matter and of the theory. Chemical reaction networks are constructed by considering chemical substances as nodes or vertices of a graph, with chemical reactions forming the edges or connections between them. Process realism (Earley 2008) takes the alternate viewpoint of considering processes as of more fundamental significance. In his book *The Order of Time*, Carlo Rovelli (Rovelli 2018; Paetz 2010) also posits that events, rather than particles or fields, are the basic constituents of the universe.

It will be argued here that the distinction between a chemical substance and a chemical reaction or a collision complex is not always so straightforward. A simple example that encapsulates this dichotomy is the hydrogen exchange reaction:

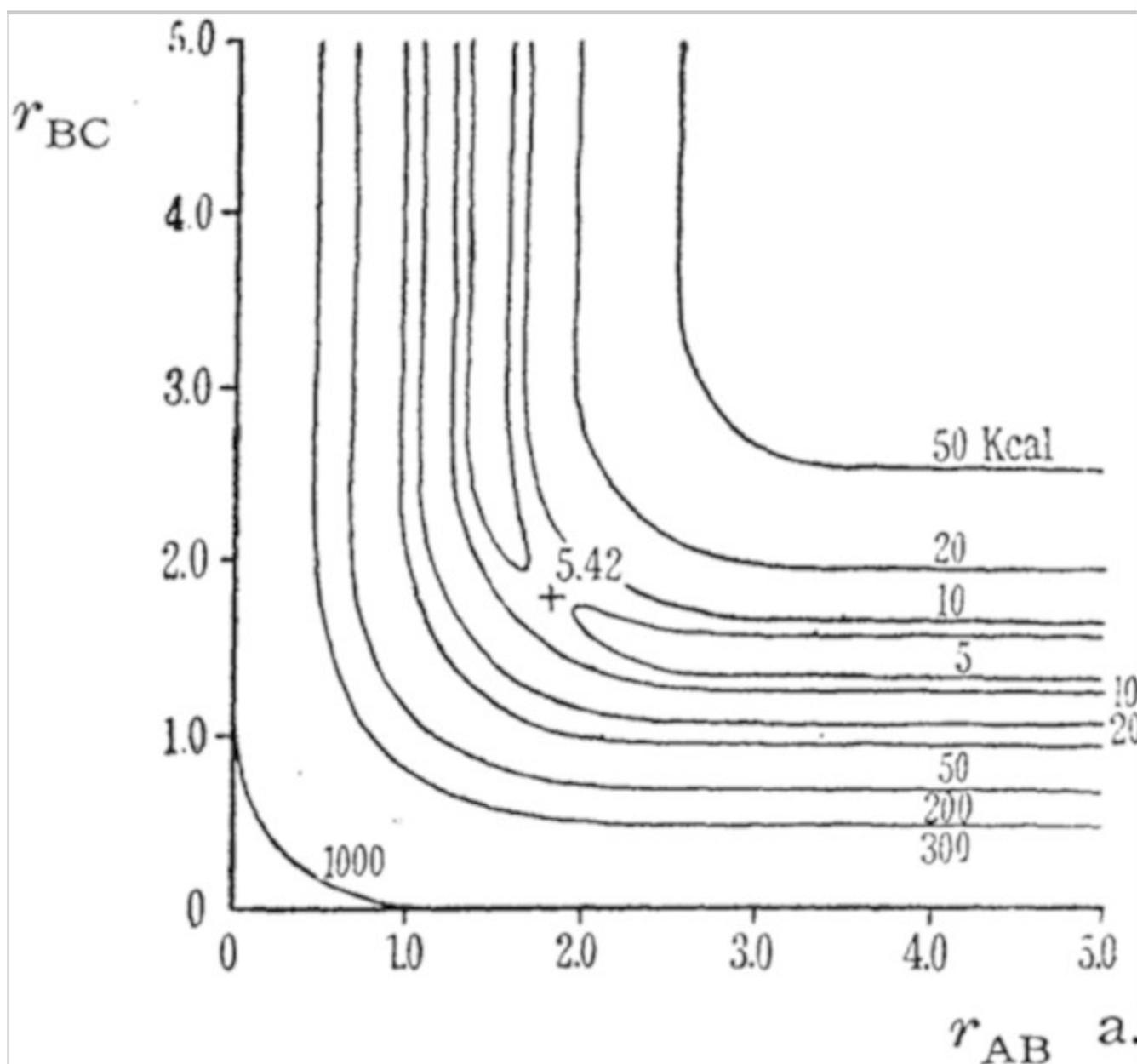


the simplest chemical reaction, which has been studied intensively for over 75 years. In the London-Eyring-Polanyi-Sato (LEPS) (Eyring and Lin 1974; London 1929; Polanyi and Schreiber 1974, 1977; Sato 1955a, b; Porter and Karplus 1964; Porter et al 1968; Varandas 1979) potential energy surface (PES) for the system (Fig. 1), H_3 forms a transition state for the collinear reaction. There is no minimum on the PES except at $r_1 = \infty$ or $r_2 = \infty$ (which correspond to dissociated H and H_2). So, does this represent a chemical reaction or is H_3 an unstable molecule? However, the mere existence of a minimum on the PES does not correspond to a stable chemical substance. If the zero point energy corresponding to the minimum is greater than the energetic barrier to dissociation, it will not correspond to a stable chemical substance. If the PES minimum can not sustain at least a few vibrational levels, the corresponding molecule will at best be metastable at all but the lowest temperatures, and will soon dissociate. Whether to treat it as a molecular system or as a collision complex is often a matter of choice or convenience. Thus quantum chemists often treat reacting partners or even weakly interacting chemical substances as a single “super molecule” in calculations.

Fig. 1

Potential energy surface for the system of three hydrogen atoms $H_A + H_B - H_C \rightarrow H_A - H_B + H_C$ in the linear configuration.

adapted from Sato (1955a, **b**)



How long is “Too Long”?

In quantum field theory, all particles—and hence, in turn, all molecules—are excitations of a background quantum field. In collision theory, a molecule is just a collision (a “resonance”) that takes too long. But how long is “too long”, and “too long” in relation to what? These are crucial questions that distinguish chemical substances from chemical reactions, and reversible reactions from irreversible ones. Even in an exothermic reaction $A + B \rightarrow AB$ taking place *in vacuo*, with a negative heat of formation ($\Delta H_f < 0$), the atoms A and B will not “stick” to each other in empty space to form the molecule AB unless the system

has a way to dissipate the excess heat. The timescale at which this dissipation occurs is an integral part of the reaction kinetics. Thus all chemical reactions can be regarded as collision processes. The converse situation is the Einstein–Podolsky–Rosen (EPR) paradox ([Einstein, Podolsky and Rosen 1935](#)), where a correlated singlet (or a dissociating molecule) remains forever entangled, no matter how distantly separated the partners (or dissociation products), unless environmental perturbations are strong enough to cause decoherence of the quantum waves. See [Martínez-González et al. \(2019\)](#) for the relation of this discussion to the question of molecular structure.

It has always been recognized that chemistry depends not only upon chemical substances but also crucially upon the reaction conditions: most importantly temperature, pressure and time duration. Very different chemical reactions from what we encounter at [standard temperature and pressure \(STP\)](#) come into play under cryogenic conditions (such as in a helium matrix or in space), under high temperatures (such as in high energy collisions in the upper atmosphere, or on other planets), or at very low or very high pressures. Thus when considering reactions in the bulk, both temperature and pressure effects come into play, and the potential energy surface in the above considerations is to be replaced by the free energy surface. An endothermic reaction that is non-spontaneous ($\Delta H > 0$, $\Delta G > 0$) at low temperature may become spontaneous ($\Delta G < 0$) at high temperature due to the effect of the entropic ($T\Delta S$) term in $\Delta G = \Delta H - T\Delta S$ (if $\Delta S > 0$).

While all chemical reactions are, in principle, reversible, reversibility in practice depends upon the activation free energies, and hence on the rates, of the forward and reverse reactions. Even at a given temperature and pressure, catalysts may be used to modify the free energy landscape of a reaction. Enzyme catalysis exploits this feature to make otherwise irreversible reactions reversible, thereby recycling many of the chemical components in biochemical reactions. Reversibility in common discourse is thus essentially a question of whether or not the reverse reaction proceeds at an appreciable pace under the given conditions. But this (“appreciable pace”) is a subjective term. To a femtosecond spectroscopist, a millisecond is too long, whereas to a chemist studying reactions in interstellar space, a million years is, metaphorically, but the blink of an eye. The chemical reaction that is too slow to be of any practical use to a synthetic organic chemist may be the one that created the precursor molecules of life in interstellar space or

giant molecular clouds. Thus time scales effectively distinguish chemical substances from chemical reactions, and reversible reactions from irreversible ones. For determining whether or not a chemical reaction yields a desired product in the lab, in most cases we mean too long or too slow in relation to our lifetimes, thereby introducing anthropocentric bias into these chemical distinctions.

Anthropocentric bias in chemistry

Keserú et al. (2014) have argued, on the basis of a comprehensive analysis of organic reaction parameters in the chemical literature dating back to 1771, that anthropogenic limitations on reaction parameters are responsible for the fact that synthetic chemists have till date explored only a small fraction of the available chemical space. The reaction time is one of the key parameters defining the boundaries between the ontological objects of chemical discourse. Being able to study and monitor molecular interactions on the femtosecond scale has opened up new areas of chemistry that were hitherto unknown, as has the ability to use generated pressures and temperatures, and employ catalysts that effectively speed up chemical reactions.

We recognize that the “state of matter” (for instance, whether a substance is a solid, liquid or gas) is a function of temperature and pressure. Thus whether “water” is a liquid or solid depends upon whether we live in tropical India or in the interior or Antarctica. At low temperatures and high pressures, many other phases of “ice” come into being. Near the critical point, on the other hand, the distinction between liquid and vapour vanishes, and it becomes possible to continuously convert “liquid” water to its “vapour” without undergoing a phase transition. So chemists are generally careful to specify that water is a “liquid at STP.” But this anthropocentrism applies to other physical properties as well. Colour, state of aggregation and smell are three properties that chemists have traditionally used for characterization and identification of chemical substances. A brick red colour in a flame test is indicative of calcium, a smell of rotten eggs is diagnostic of hydrogen sulphide, that of bitter almonds is indicative of cyanide, while the colours of various precipitates have been used as diagnostic tests for ions such as silver, barium, copper, sulphate, etc. (Vogel 1968).

The subjective nature of colour, being a product of the reflectance of the object,

the incident radiation, and our perceptual system (the mechanics of human vision and the way our brains process information), was pointed out by Johann Wolfgang von Goethe in his *Theory of Colours* (1840). For instance, the visual systems of different species have different sensitivities to different wavelengths of light, and thus different colour spaces. So a substance that emits in the ultraviolet is not “colourless”, just colourless to us. Furthermore, sunlight has a nearly constant intensity between 400–700 nm, but this approximate constancy of the intensity of solar radiation at different wavelengths does not hold in other wavelength ranges, and not on other star systems. And since perceived colour is the complementary colour to the wavelengths absorbed from the incident light, it is also a function of which star system we happen to live in. To take another example, under intense irradiation and low pressure, benzene absorbs two photons at 391.4 nm and would thus appear purple (Johnson 1976). Thus it may quite legitimately be argued that “Benzene is a purple gas.”

AQ4

Here too, time enters the picture. Visual perception of colour is due to different kinds of cone cells in the retina, where the conversion of light energy to an electrical signal takes place through photoisomerization of a molecule such as retinal, through a potential surface conical intersection. This conformational change initiates a biochemical cascade, which in turn leads to the activation of phosphodiesterase (PDE), an enzyme that catalyzes the hydrolysis of cyclic guanosine monophosphate (cGMP) to 5'-GMP. The sodium ion channels in photoreceptors are cGMP-gated; so light-induced activation of PDE and degradation of cGMP causes sodium channels to close, which leads to the hyperpolarization of the photoreceptor's plasma membrane, and this change in membrane potential triggers an electrical signal which carries the visual information to the brain. Thus the electrical signal generated by the biochemical processes initiated by absorption of a photon by the cones in the retina generates activity in the visual cortex, which is sensed as the colour of the object. So colour perception, and visual perception in general, is the direct result of a cascade of biochemical reactions, starting with a light-induced photoisomerization in the retina. The eventual result of this biochemical cascade is a temporal, rather than amplitude, modulation in the firing of neurons in the visual cortex, *i.e.* the visual signal is manifested as the firing of more or less neuronal spikes per time interval. Thus it would be fair to say, in the spirit of Goethe, that colour is not just an inherent property of an object, but is equally the

result of the thermodynamics and kinetics of these photochemical, biochemical and electrochemical processes, along the pathway from the eye to the brain.

While most humans have three kinds of cone cells, which have broadly overlapping ranges of sensitivity, there is some recent evidence for presence of a fourth kind of cone cells, with colour sensitivity lying between the standard red and green cones, in about 2–3% of women (Jordan et al. 2010). This condition of possessing four types of cone cells in the retina, resulting in a four-dimensional sensory colour space (which extends a bird's range of colour vision into the UV), is known as tetrachromacy, and is known among several species of birds, fish, amphibians, reptiles, insects and some mammals. It is believed that a genetic change in the past made most species eventually lose two of their four **types of cones**. Asking why something “is” a particular colour is thus a very different question from asking why it absorbs light at a certain wavelength. The latter question leads to a reduction to physics, while the former leads us to a reduction to biology: an object is perceived to be of a certain colour because our visual systems have evolved (and retained) the appropriate cone cells to perceive that colour.

When it comes to the sense of smell, the human nose and brain are capable of distinguishing roughly 1 trillion distinct scents. Most scents are composed of many odorant chemical substances. Odour perception is the result of binding of odorant chemical substances to olfactory receptors inside the nose. These olfactory receptors are G protein-coupled receptors (GPCRs), that are expressed in the cell membranes of olfactory receptor neurons, and are responsible for the detection of odorants. There are **around** 1,000 different odour receptors in the mammalian genome, which form a multigene family. But not all potential odour receptor genes are expressed and functional in humans. Humans have approximately 400 functional genes coding for olfactory receptors. Activated olfactory receptors trigger nerve impulses which transmit information about odour to the brain. Olfactory receptors display affinity for a range of odorant molecules, and conversely a single odocant molecule may bind to several olfactory receptors with varying affinities, depending upon the physicochemical properties of the molecule. Therefore smell is a direct consequence of the thermodynamics and kinetics of odorant-receptor binding.

The existence of such a large number of olfactory receptors, representing as

much as 3% of genes in the mammalian genome, is indicative of a functional, evolutionary advantage conferred by possessing such a sophisticated chemical analysis system in the nose. It is therefore a legitimate question to ask why carbon monoxide is odorless. Why did natural selection not design an olfactory receptor for this deadly gas, a common product of incomplete combustion in confined spaces? The taste of a chemical substance is similarly classified into sweet, sour, bitter, salty and umami, due to the different associated receptors. Flavor is a broader term, referring to the smell, texture, and taste of a chemical substance. Both taste and smell are important from an evolutionary standpoint, as they enable an organism to distinguish food from potentially deadly toxins. This reduces to seeking the explanation for chemical properties such as the smell and taste of a chemical substance, in terms of evolutionary biology.

Reduction to physics or to biology?

I argue that whether we choose to reduce a science to physics or to biology ultimately reduces to which kinds of questions we hold to be more fundamental: material or efficient causes, instrumental or functional causes. This reduction of some chemical questions to biology is not necessarily a return to the positivism of earlier centuries. Some physicists, for instance, argue for a reduction of the most fundamental unanswered question in physics, namely why the fundamental constants in our universe have the values they do, to the evolution of intelligent beings, and thus to biology—this goes by the name of the anthropic principle. However, such arguments have been criticized on the grounds that the anthropic principle does not meet Popper's (1959) test of falsifiability. But the relevance of the anthropic principle to the philosophy of chemistry stems from the fact that “intelligent life” (however that may be defined, but it is presumed to include beings like ourselves, capable of intellectually understanding chemistry and philosophy) depends critically upon the stability of molecular matter under the conditions found on earth, *i.e.* around STP. Under different environmental conditions (temperatures and pressures differing from STP by just one order of magnitude), many of the molecules of life, such as proteins, nucleic acids, lipids, and liquid water, are not stable.

A common philosophical article of faith held by many working physicists today is that physics deals not with “why” questions, but only with “how” questions. Biology, however, commonly seeks functional causes, rather than instrumental

ones, and thus often deals with “why~~ow~~” questions. But not all explanations in biology are framed as answers to “why” questions. While explanations in evolutionary biology are indeed framed as answers to “why” questions, explanations in molecular biology are framed as answers to “how” questions. Most philosophers relegate such answers to “why” questions to subordinate status. Thus, Alicia Juarrero (1999) has argued that “*the restricted notion of causality that was adopted with the rise of modern science is an impoverished one — quite inadequate for philosophical analysis of complex questions of properly philosophic interest.*” (Earley 2016).

AQ5

Periodicity, time and closure

Let us now briefly turn to the epistemology of time. If there were no periodic processes in the universe, no days, no years, no ticking clocks, we could not tell the passage of time. If, on the other hand, the universe comprised of only periodic processes, with no death, no ageing, no learning, we could not tell the passage of time either. So time can be perceived only through co-existence of periodic (cyclical) and acyclic processes. Of course, this co-existence of periodicity and aperiodicity is not just true of time: Restrepo, et al. (Leal and Restrepo 2018; Restrepo 2017; Restrepo and Villaveces 2012~~7~~) have argued that the formal structure of the Periodic Table is the result of two separate organizing principles: similarity and sequential ordering. Elements in the Periodic Table are not just copies of the ones above them in the group. This combination of periodicity and order is at the heart of the richness of chemistry.

Such notions of periodicity are employed by Earley to develop the theory of Process Structural Realism: “*Stability is achieved only when relationships internal to each item demonstrate such closure that states of the system repeatedly re-occur, so that the system persists through time.*” (Earley 2008) According to Earley, it is this closure that allows a substance to have ontological significance. “*Stability constitutes a closure of relationships that makes it possible for each chemical entity to retain its self-identity while undergoing interactions with the rest of the world.*” (Earley 2008) And elsewhere he states: “*What is fundamental is achievement of effective coherence—the level of size on which that achievement occurs is irrelevant.*” (Earley 2008) Of course, what Earley refers to here is the ontological relevance. But the time and length scales

are epistemologically relevant, because if an observer does not have access to the said time or length scales, then (s)he has not way of distinguishing between a chemical substance and a collision that takes place on a time scale too long to be observable. So from an epistemological standpoint, the distinction between a chemical substance and a chemical reaction would depend upon the time scale of this temporal closure. A process with a very long time scale for closure would be described by the observer as a (stable or metastable) chemical substance. Of course, since the duration of time is different in different accelerated frames of reference, according to the General Theory of Relativity, a process that is described as a chemical substance in one frame of reference could well be described by an observer in a different frame of reference as a chemical reaction.

Conclusions

In this essay, the ontological and epistemological status of the concepts of chemical substances, molecular stability, molecular collisions, chemical reactions, reversible and irreversible reactions, have been examined. It is shown that the distinction between a chemical substance and a chemical reaction is not always straightforward from an epistemological standpoint, and depends upon the time scales involved (generally in comparison to our own lifetimes). This leads to consideration of anthropocentric bias in the definitions and descriptions of chemical properties. The subjective nature of physical and chemical properties of chemical substances is pointed out, with the specific examples of colour and smell being discussed in detail. It is argued that the reduction to physics or to biology is a function of the kinds of scientific questions regarded as being more fundamental to the discipline. It is further posited that perception of time requires the co-existence of periodic and acyclic processes. Finally, these notions are related to and contrasted to the position of Process Structural Realism.

AQ6

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