JOURNAL OF CHEMICAL EDUCATION

Article

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Mental Rolodexing: Senior Chemistry Majors' Understanding of Chemical and Physical Properties

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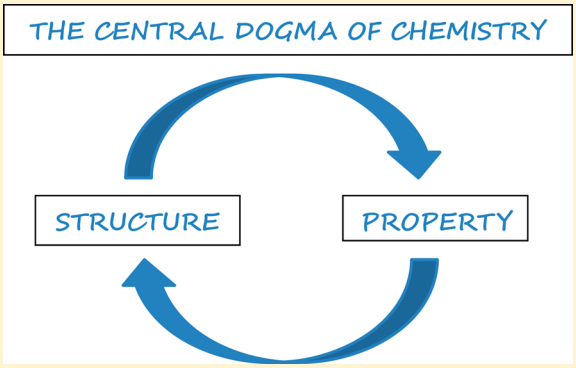
Supporting Information

ABSTRACT: Using a constructivist framework, eight senior chemistry majors were interviewed twice to determine: (i) structural inferences they are able to make from chemical and physical properties; and (ii) their ability to apply their inferences and understandings of these chemical and physical properties to solve tasks on the reactivity of organic compounds. The latter included predicting the behaviors of natural products under acidic, basic, nucleophilic, and electrophilic reaction conditions and designing molecules based on a set of constraints. Content analysis of the data revealed that the students' conceptualized a substance's phase (of matter) at ambient temperature and pressure primarily on molecular size and intermolecular forces, but did not consider molecular shape or any thermodynamic factors. This oversight of molecular geometry also manifested itself in the students' conceptions of molecular polarity and solubility in water, both of which were based solely on the presence of heteroatoms. Furthermore, the students were unable to articulate their conceptions of chemical characteristics such as acidity/basicity and nucleophilicity/electrophilicity. In the application tasks, the participants experienced considerable difficulty with components requiring them to integrate multiple concepts. These results are interpreted in the context of lingering concerns that current chemistry/science instructional practices lead to students developing knowledge bases consisting of numerous isolated facts with relatively few connections between them. We conclude with some suggestions for helping students in undergraduate organic chemistry courses to develop more robust and integrative conceptual frameworks.



KEYWORDS: *Second-Year Undergraduate, Upper-Division Undergraduate, Chemical Education Research, Organic Chemistry, Constructivism, Molecular Properties/Structure*

FEATURE: Chemical Education Research

A fundamental outcome of chemistry is a better understanding of how structures of and interactions between individual molecules affect macroscopic, or observable, behaviors of substances. To borrow a phrase from biology, structure–property relationships may be thought of as the Central Dogma of Chemistry. The structure part of this dyad is usually expressed in various diagrammatic representational forms which, at a minimum, show the atomic connectivity of the molecule. Properties refer to the physical and/or chemical characteristics of a substance that, individually or as a group, can be used to differentiate one substance from all others. Examples of physical properties include melting point and boiling point, and those of chemical properties are acidity and basicity. Practicing chemists use this connection in both directions; that is, they infer a property from a given structure and infer structure from a given property.

Our interest in structure–property relationships arose from prior work in representational competence. Consistent with a large body of research from many other disciplines, we found that organic chemistry graduate students attended almost exclusively to the surface-level features of electron-pushing diagrams of reaction mechanisms.[1]

This result led us to question the extent to which students' issues with representations were due to difficulty with understanding or disembedding symbols or due to misunderstanding of the structural features implied by chemical or physical properties. To shed some light on this issue, we conducted a qualitative study of 8 senior chemistry majors as they worked on tasks in which they were asked to provide structural features given physical and chemical properties. In addition to presenting the results of the research, we discuss the instructional implications of our findings.

BACKGROUND

In recent years, Cooper and co-workers reported multiple research studies regarding students' understanding of structure–property relationships.[2−4] Among other outcomes, this work resulted in the Implicit Information from Lewis Structures Instrument (IILSI) and a learning progression and curriculum

DOI: 10.1021/ed500360g
J. Chem. Educ. XXXX, XXX, XXX−XXX

for general chemistry students.[2,3] In the course of developing the IILSI, Cooper, Underwood, and Hilley[3] noted that a minimum of seven operations would be required to infer a physical property such as boiling point of a substance given its molecular formula. Each of the operations, in turn, requires students to draw upon several pieces of declarative and procedural knowledge. For example, inferring molecular shape from a Lewis structure would involve, ostensibly, determining the number of regions of electron density around the central atom(s), using VSEPR Theory to deduce an electronic geometry and, finally, and extrapolating the molecule's shape from its electronic structure. Considering that there are six more operations that are of similar complexity in their reliance on multiple chemical principles, it is safe to conclude that inferring a physical property from a molecular formula or even its Lewis structure may amount to a complex task requiring the students to integrate a diversity of ideas and skills.

However, several reports—notably, *How People Learn*[5] and *Disciplinary-Based Education Research*,[6] both commissioned by the National Research Council (NRC) of the National Academies of Science—and commentaries indicate that typical pedagogical practices in chemistry/science education at the secondary *and* tertiary levels are unlikely to help students achieve a level of integration of concepts needed to proficiently make inferences such as the type described in the previous paragraph. For example, both of the NRC reports contend that STEM instruction often does not address the students' prior knowledge.[5−7] One of the main consequences of this practice is that students end up learning the material as "isolated abstractions"[5] and are unable to, subsequently, process the concepts in a way that helps them understand the proverbial, "big picture".

Additionally, manuscripts written by some of the imminent scholars of chemical education research echo the concerns mentioned in the previous paragraphs. In one such instance, Sevian and Talanquer open their essay with the sentence, "Dominant approaches to the teaching of chemistry in many countries tend to present the discipline as a collection of somewhat isolated topics: atomic structure, chemical reactions, chemical bonding, thermodynamics, kinetics, etc."[8] This statement is particularly disturbing since the most effective understanding of chemical processes results from the integration of *all* of the topics noted by the authors. Similarly, in their description of a novel general chemistry curriculum, Cooper and Klymkowsky[9,10] observed that the prevailing trend for producing instructional materials for general chemistry courses—including textbooks—is based on a 50-year-old framework. The authors conclude, "that the result is a collection of facts or algorithms that can be searched on the Web."[9]

Although brief, the sources cited in this overview each reviewed significant swathes of the science/chemical education research literatures. As such, it can be inferred that current chemistry/science instructional practices lead to students developing knowledge bases consisting of numerous isolated facts with relatively few connections between them.

The conclusion raises additional concern since one of the hallmarks of experts is their well-organized and coherent domain knowledge as summarized in *How People Learn* (ref 5, p 31)

1. Experts notice features and meaningful patterns of information that are not noticed by novices.
2. Experts have acquired a great deal of content knowledge that is organized in ways that reflect a deep understanding of their subject matter.
3. Experts' knowledge cannot be reduced to sets of isolated facts or propositions but, instead, reflects contexts of applicability: that is, the knowledge is "conditionalized" on a set of circumstances.
4. Experts are able to flexibly retrieve important aspects of their knowledge with little attentional effort".

As such experts are able to disregard the superficial contained in pictorial and diagrammatic representations and disembed information they deem relevant to the task at hand. In contrast, novices get mired in these surface-level features, often to the point of overloading their short-term memories. Furthermore, these differences in perception and knowledge organization hinder novices' abilities to effectively *reason* with the facts, especially in cases where information from multiple sources must be weighed against each other in order to make a well-reasoned decision.[5] It was based on these and other considerations that we were interested in better understanding students' conceptions of one of the foundational constructs of chemistry: structure−property relationships.

METHODOLOGY

Research Questions

Our study was guided by the following questions:

(1) What structural features do senior chemistry majors infer from chemical and physical properties?
(2) To what extent are senior chemistry majors able to apply their knowledge of structure−property relationships?

We took a qualitative approach to this study for primarily two reasons. First, it allowed us to conduct the study without any preconceived hypotheses about students' conceptions regarding structure−property relationships. Second, we were able to focus on describing the students' understandings rather than comparing specific parameters such as rate of success on tasks. The decision to pursue a qualitative methodology became an added benefit given the small participant pool.

Theoretical Framework

The theoretical framework for this study was constructivism which is based on the notion that learners actively construct their own knowledge by building upon prior experiences and conceptions.[11,12] More specifically, we adopted von Glasersfeld's position of radical constructivism in which learning is construed as a pragmatic activity in which one looks for a fit with one's unique perception of reality. Objects, therefore, do not have a stand-alone meaning. Rather, all meaning "is this construction of the individual's subjective reality..."[12] Constructivism was an appropriate choice for this study because the process of inferring structural features from a set of properties involves, at least on some level, eliciting the meaning participants give to these features and properties.

Critics of von Glasersfeld's radical constructivism attack it from multiple angles. Some cite shared meaning developed among the members of a group as evidence that sense-making cannot be solely in an individual's mind. Others argue that radical constructivism is a type of narcissism. Von Glasersfeld does not

DOI: 10.1021/ed500360g
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INTERVIEW PROTOCOL

Background Questions

- Participants were asked basic questions regarding academic background.
- What courses in organic chemistry have you taken?
- What is your overall perception of organic chemistry?

Structure-Property Questions (If you cannot think of a molecule that fits that class, then feel free to move on.)

- Can you please draw a hydrocarbon that is
  - **a liquid at** room temperature and atmospheric pressure?
  - **a solid at** room temperature and atmospheric pressure?
  - **soluble in water**?
  - **insoluble in water**?
  - **an acid**?
  - **a base**?
  - **a nucleophile**?
  - **an electrophile**?
  - *Note:* After each response the student was asked, "What was the reasoning behind your drawing?"

- Can you please draw a molecule containing only **carbon, hydrogen, and at least one oxygen atom** which is …? (*The center of reactivity **FOR ALL** these questions should be the oxygen.)*
  - *The same set of questions were asked for substances containing C,H,O as were for hydrocarbons.*
  - *Additionally, students were asked to name a substance containing C,H,O that would be a **gas** at room temperature and atmospheric pressure.*

- Can you please draw a molecule containing only **carbon, hydrogen, and at least one nitrogen atom** which is …? (*The center of reactivity **FOR ALL** these questions should be the nitrogen.)*
  - *The same set of questions were asked for substances containing C,H,N as were for hydrocarbons.*
  - *Additionally, students were asked to name a substance containing C,H,N that would be a **gas** at room temperature and atmospheric pressure.*

General Structure Questions

- In general what structural attributes do you associate with the following characteristics and why?
  - solid
  - liquid
  - gas
  - polar molecule,
  - solubility in water,
  - high or low boiling point,
  - high or low melting point,
  - nucleophilicity,
  - electrophilicity,
  - acidity, and
  - basicity
- What experiences do you think you have contributed to your current understanding of these concepts?

Box 1. Semi-structured protocol for Interview One. Students were asked to offer their reasoning for all of their responses, not just for the hydrocarbons.

question the existence of shared meanings. He acknowledges "that a human subject's experience always includes the social interaction with other cognizing individuals."[12] Furthermore, von Glasersfeld asserts that shared meanings arising from social interactions bring robustness to the individual's constructed knowledge. In the least, these interactions help a learner determine the extent to which her level of understanding of the newly learned material is consistent with the normative, or canonical, knowledge of the discipline. The latter position would refute the so-called narcissistic leanings of radical constructivism.

Participants and Setting

Eight senior chemistry majors were recruited on a voluntary basis one month before graduation at a large, research-intensive institution in the southeastern United States. The sample constituted 45% of the graduating class for that year and contained 4 women and 4 men, which accurately reflected the gender distribution of that class. Senior chemistry majors in their final term were purposefully chosen[13] because by that time they would have had the benefit of having taken all of the foundational coursework in chemistry, which was, indeed, the case with our participants.

Data Collection

Interview One. To reiterate, one of the motivations of this research was to examine the extent to which students' apparent weakness with interpreting representations was due to difficulty with understanding or disembedding symbols or due to misunderstanding of the structural features implied by chemical or physical properties. Since most studies in representational competence, including our previous one,[1] required students to select or infer properties from structural diagrams of chemical substances, we decided to give students the chemical and physical properties and asked them to supply representations of structures associated with the respective properties. Box 1 contains the interview protocol used for this translation task.

We purposely chose the most common of chemical and physical properties since that would minimize the likelihood of content-related difficulties for the participants. Furthermore, we did not want to ask students *only* general questions such as, "What structural features of a substance do you attribute to water solubility?" On the basis of previous experiences, the pitfall of only asking such questions is that the students' answers can often be verbalisms, which Vygotsky[14] defined as a "parrot-like repetition of words by the child simulating knowledge of the corresponding concepts but actually covering up a vacuum" (p 150).

DOI: 10.1021/ed500360g
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We addressed this potential problem by deciding to ask participants for specific examples in addition to general structural attributes.

This choice necessitated attending to several factors. Asking participants for substances without providing any other guidelines or boundaries would have resulted in tasks that were too high in extraneous cognitive load.[15] On the other hand, limiting the responses to a single functional group, for example, may have skewed the results if that functional group were a participant's weakest class of compounds. On the basis of these concerns, we chose to ask students about hydrocarbons and carbon, hydrogen, oxygen compounds, the latter including several functionalities including, carboxylic acids, esters, phenols, alcohols and ethers. With these two groups of compounds in place, there was a third consideration: since organic chemistry courses can often conjure legendary levels of memorization, there needed to be a class of compounds with which students would have had some exposure, but not to the extent that they may have memorized a large amount of information. Thus, we chose to ask students about carbon, hydrogen, and nitrogen-containing compounds since they are customarily covered in the context of other functional groups and not as a standalone topic as is the case of the oxygen-containing functional groups. Finally, to ensure that those who may not have been able to think of a specific compound would have an opportunity to explain their conceptions we ended the interview with a set of general questions as shown in Box 1.

Each participant was interviewed once with an audiotape using the protocol described above. The interview was semistructured to allow the interviewer to follow-up on interesting or important points brought up by the research participants. The participants had a copy of the organic chemistry textbook that was used for their course[16] and a copy of the Aldrich Catalog in case the students wanted to look up specific physical data. Of note, none of the participants consulted either resource. The participants were also offered paper and drawing implements. Although the protocol called for the participants to draw molecules for each question, only two students, given the pseudonyms Danielle and Sven, did so. Everyone else gave oral responses only; even after the interviewer suggested that they may want to draw out their answers. The interviewer wrote down salient observations during the course of the interview and recorded postinterview notes, as needed, immediately after the participant left the interview room.

Interview Two. Even before beginning the formal data analysis, it became apparent that the participants were able to offer general explanations for each of the chemical and physical characteristics in the protocol. However, they could only offer as specific examples substances with which they had direct contact. As such, there were only two nitrogen-containing substances that were cited by the students: ammonia and aqueous solutions of ammonia and pyridine, both of which they had used in teaching and/or research laboratories. The most likely reason for this result was the nature of the interview protocol, i.e., asking them for specific substances. To investigate this possibility, students participated in a second interview 2 weeks after the first one.

The protocol for this interview had two parts carefully designed to probe the questions raised by the results from the first interview. In the first part, they were given the two complex natural products shown in Box 2. The interviewer provided the structures one at a time on a sheet of unlined paper and asked the set of questions also shown in Box 2. To make sure that the students understood the difference between questions 1 and 2, the interviewer explained that structural features referred to more-global structural motifs. For example, paranolin could be said to have 4 fused rings as one of its structural features.

For each substance the interviewer asked:

1.) What structural features do you see?

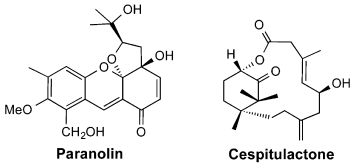
2.) What functional groups do you see?

3.) If this were to react with a strong acid, where would it react? How would it react, *i.e.* what would happen?

4.) How about with a strong base?

5.) How about with a good nucleophile?

6.) How about with a good electrophile?



Box 2. Natural products for which students were asked to describe structural features and general chemical reactivity.

Instead of asking students how each compound would react under specific reactions, information which could easily have been forgotten by the students since their previous organic chemistry courses, we chose to ask how the molecules would behave with a generic set of reagents. Thus, this first part of the second interview was used to probe students' ability to pick out the types of structural features they pointed out for the questions in the first interview.

The second part of the interview consisted of the two design tasks shown in Box 3. The goal for these tasks was to create a set of constraints that would rule out the common molecules that students chose in the first interview. For example, the molecular weight restriction for the water-soluble molecule in the second task would immediately rule out common substances such as ethanol—the majority of the students' choice for a water-soluble C,H,O-containing molecule in Interview 1—acetone, and common table sugar. The boiling point requirement would also exclude ethylene glycol or acetic acid. As such, the hope was that these constraints would require students to think not only about the relevant structural features for each of the constraints, but also to construct molecules consistent with each set of constraints.

For this interview, we used the think-aloud protocol to collect as much as possible of the participants' conscious thoughts and thought processes. Once again, the interviews were audiotaped and the interviewer recorded salient observations and postinterview notes. Since content knowledge can be a confounder when students work on problem-solving tasks, the participants were given a table of atomic weights and one containing the pK_a's of the common organic chemistry functional groups, These tables are shown in the Supporting Information. Students were also provided with a copy of an organic chemistry textbook and Aldrich catalog as in the first interview, along with paper and writing implements. Once again, none of the students chose to consult the textbook or catalog, even after being reminded by the interviewer.

Data Analysis

The data for this project were sorted into separate files for each participant, all of whom were given pseudonyms to protect their

DOI: 10.1021/ed500360g
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DESIGN TASKS

- Please draw a molecule of your choice using only C, H, N, O, and X (any halogen) having the following characteristics:
  - Molecular weight less than or equal to 150 g/mol
  - Water insoluble
  - High b.pt. (greater than that of water)
  - At least one proton with a $pK_a \leq 10$
- Please draw a molecule of your choice using only C, H, N, O, and X (any halogen) having the following characteristics:
  - Molecular weight between 60 and 150 g/mol
  - Water soluble
  - Low b.pt. (less than that of water)
  - No protons with $pK_a \leq 15$

Box 3. For each task, students were asked to provide a molecule that satisfied all of the constraints. They had access to the textbook they used in sophomore-level organic chemistry, an Aldrich Catalog, and a sheet of information shown in the Supporting Information.

confidentiality. The interviews were transcribed verbatim and were analyzed using a content analysis protocol used in one of our previous studies.[1] As such, the participants' answers to the questions were analyzed in two formats. In one, all of a participant's answers to the interview items were collected and evaluated for scientific validity of the examples offered and reasoning behind those responses. These data were then analyzed for emergent trends in reasoning patterns and for types of examples that were offered. Interviewer observations and postinterview notes were used to supplement the transcript data, as needed.

In the other format, all of the participants' responses to the same question were collected and evaluated on the basis of the same criteria for an individual's responses, i.e. scientific validity of example and reasoning. Again the set of responses were further analyzed for trends in the data. To ensure that the researchers' interpretations were in line with the participants' intent, three randomly selected participants were asked to do a member-checking interview at which time the researchers' interpretations of the data were confirmed by the three participants.[13]

RESULTS

Interview One

Tables 1−3 contain the students' answers to questions asking them to name specific compounds exhibiting each of the chemical and physical properties in the interview protocol. Although we did not expect students to cite somewhat esoteric cases such as azulene when asked for water-soluble hydrocarbons, we used categories like that one as a way to elicit their conceptions regarding the properties in the interview protocol.

Table 1. Students' Choices of Hydrocarbons Exhibiting Each of the Properties[a]

	Hydrocarbons			
	Liquid	Solid	Soluble in H_2O	Insoluble in H_2O
Bruce	Octane	C_{60}	Acetylide ion	Most of them
Danielle	Hexane	NoA	NoA	Most of them
Don	Octane	Decane	NoA	Most of them
Lauren	NoA	NoA	NoA	Most of them
Leah	Pentane	Long chain	Methane	Most of them
Raul	Hexane	Long chain	None	Most of them
Russell	Toluene	Long chain	None	Most of them
Sven	Octane	Long chain	None	Most of them

[a]NoA, no answer.

Phases of Matter. The data in Table 4 indicate that students conceptualized states of matter primarily as a function of molecular weight and intermolecular forces (IMFs) with gases lying at one end of a continuum and solids at the other. According to the students, therefore, gases would be composed of small, or lighter, particles−primarily mono- and diatomic−exhibiting weak IMFs and solids would be composed of tightly packed particles with very strong IMFs. Consider, for example, the following quotes about solids from Leah and Sven:

> *I tend to associate, um, more of a crystal lattice structure with it. Although, I sometimes, then the next association would be, kind of, like, the metal with electron cloud type of association. And then, I have to, and then I might start thinking about phase shifts and how, you know, anything, any substance, could be a solid, but you just have to cool it long enough so that they're closely enough packed together. But they experience stronger intermolecular forces.*
>
> —Leah

> *Tightly packed, strong intermolecular forces, not fluid, soluble or insoluble in water, is it crystalline or not. Size. The bigger the size generally the more likely it is to be solid, um, look at the functional groups on it, cause the charges will indicate intermolecular interactions, and that's kind of all I would really look for. ... Generally just the bigger it is, um, the heavier it is, so the harder time it is going to have flowing, and it's also going to have more points to interact with the molecules around it to solidify it. ... No specific functional groups are associated with it being solid, however, if it's got something that produces a dipole, that would make me lean less towards it being solid, however, um, that's also a note for solubility.*
>
> —Sven

Interestingly, about half of the participants' explanations suggest that they may have even pictured a specific model of solids in their mind like Leah when she spoke of "a crystal lattice structure".

Although the participants could, for the most part, accurately propose substances that would be liquids under room temperature and pressure conditions, their responses seemed less definitive than those for either solids and gases. As an example, consider Sven's explanation for choosing octane as the example for a liquid hydrocarbon:

> *It's long enough to where I think that its heavy enough that intermolecular forces; there's enough to like stick them together because you have that chain of hydrogens interacting, kind of like Velcro almost, but it's not as strong as polar bonding, so I think it's going to keep it in a liquid state, because there's not enough energy to get it out.*

DOI: 10.1021/ed500360g
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Table 2. Students' Choices of C, H, O Compounds Exhibiting Each of the Properties[a]

	Substances Containing Only Carbon, Hydrogen, and Oxygen							
	Acid	Base	Nucleophile	Gas	Liquid	Solid	Soluble in H_2O	Insoluble in H_2O
Bruce	Acetic Acid	H_2O	H_2O	CO	Ethanol	Large polymer	Methanol	NoA
Danielle	Carboxylic Acid	NoA	Ketone	$H_2C{=}O$	Alcohol	NoA	Methanol	Decanol
Don	Methanol	Ketone	Ketone	$H_2C{=}O$	Acetone	Esters	Alcohols	Ketones
Lauren	Alcohol	NoA	NoA	NoA	NoA	NoA	NoA	NoA
Leah	Carboxylic Acid	Methanol	Methanol	$H_2C{=}O$	Ethanol	Triglyceride	Methanol	Fatty acid
Raul	Acetic Acid	Dimethyl ether	Dimethyl ether	$H_2C{=}O$	Methanol	Long-chain acid	Ethanol	Phenol
Russell	Carboxylic Acid	Ketone	Alcohol	$H_2C{=}O$	Alcohol	Long-chain ketone	Carboxylic acid	Ketones
Sven	Acetic Acid	Acetate ion	Acetate ion	CO_2	Ethanol	NoA	Ethanol	Ethers

[a]NoA, no answer.

Table 3. Students' Choices of C, H, N Compounds Exhibiting Each of the Properties[a]

	Substances Containing Only Carbon, Hydrogen, and Nitrogen							
	Acid	Base	Nucleophile	Gas	Liquid	Solid	Soluble in H_2O	Insoluble in H_2O
Bruce	Amino Acid	NH_3	NH_3	HCN	HNO_3	Amino Acid	Amino Acid	Pyridine
Danielle	NH_3/NH_4^+	Amide	Amide	NH_3	Propyl amine	NoA	NoA	2°/3° amine
Don	HCN	Methyl amine	Methyl amine	Methyl amine	1° alkyl amine	$(Pentyl)_3N$	Liquid Amines	Et_3N
Lauren	NoA	NoA	NoA	NoA	NoA	NoA	NoA	NoA
Leah	Me_3N^+H	Amine	Amine	NH_3	1° alkyl amine	Ammonium salt	Methyl amine	2°/3° amine
Raul	Amino Acid	Amine	Amine	NH_3	1° alkyl amine	NoA	Methyl amine	2°/3° amine
Russell	Pyridine	Amide	Azo Compound	NH_3	1° alkyl amine	NoA	Methyl amine	NoA
Sven	Amino Acid	Pyridine	NoA	Pyridine	NoA	NoA	Pyridine	NoA

[a]NoA, no answer.

Contrast this quote with that he offered on solids in Table 4. In that answer he offers clearer, benchmarks for the types of substances and IMFs exhibited by solid substances under ambient conditions. As another example, consider Bruce's comment at the end of the interview when he was asked the general structural features he inferred from knowing a substance was a liquid at room temperature and pressure:

> *Uh, a liquid at room temperature. Oh I can think of this, um, some kind of big polymer, just make some giant polymer. Under some giant pressure that'd be solid. Anyway so what I'm thinking is um, I want something, for a solid or for a liquid I want something intermediate between like natural gas, and some polymer.*

Bruce's description of a liquid as having characteristics between the extremes of solids and gases reflects the manner in which they are often presented in chemistry courses. We tend to present explicit scientific models of the structures of solids and gases but not of liquids, with the exception of solute−solvent interactions.

The participants' conceptions of states of matter were consistent across solids, liquids, and gases with respect to the roles played by intermolecular interactions and molecular weight. However, it is also important to note that none of the students ever considered molecular shape or any thermodynamic parameters in their explanations. Regardless, none of the participants, with a few exceptions, could apply their conceptions of the states of matter to less familiar contexts. Consider, for example, the following quotes from Danielle and Russell:

> *Uhh, solid. Well, what I'm thinking about is that, with the liquids I know that the reason that, it's a lot of intermolecular forces that I'm thinking about, so when I'm think of, like, like I know what would be a gas is because it's really small because those carbon chains don't overlap and like tug on each other at all, and so it's a liquid when you have a certain length of chain, they get wrapped around each other, so they have more interaction and that's why they're liquid. And so, now, I'm thinking about what to draw and thinking that you either have to get a really long carbon chain or it'd have to be something with, like, maybe, like, some functional groups on it.*
>
> —Danielle

> *And eventually there is going to be enough London dispersion forces or, yeah, that would interact and become a liquid at room temperature. They are not branched, so they lay flatter, so that was my reasoning behind that one. Toluene is just probably something that I saw in lab, or in a bottle, so I have no reasoning behind that, just recalling something and taking an educated stab at it.*
>
> —Russell

While Danielle clearly applied her understanding of the variables affecting states of matter in drawing a hydrocarbon that would be a solid at ambient temperature and pressure, Russell's answer of toluene suggested an apparent disconnect between the two—although toluene is a liquid at ambient temperature and pressure, it is an aromatic hydrocarbon unlike the linear ones he was describing. This disconnect became increasingly evident such that many of the students' choices for compounds containing carbon, hydrogen, and nitrogen did not actually contain any carbon atoms! It is important to note that although the students had resources like the Aldrich catalog at their disposal to look up given substances, none of them chose to do so.

While it may be tempting to chalk this discrepancy to verbalisms, which, according to Vygotsky, cover up mental vacuums,[14] the data suggest otherwise. Consider this comment from Raul, which is representative of responses provided by the participants when probed in follow-up questioning for the reasons why molecular mass can affect a substance's boiling point:

> *Uh, well basically because as you add more mass, or more weight, you increase London dispersion forces, so if you're just using a long carbon chain you are going to get more like tangling basically, which, in polymers, causes them to have specific properties.*

DOI: 10.1021/ed500360g
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Though his words may not have incorporated some of the associated scientific jargon, it is clear that Raul understood, at least to an extent, the effects of these factors even at the molecular level. As such, the participants' conceptions went deeper than the surface level understanding of some of the factors affecting the states of matter.

Polarity and Solubility. The research participants verbalized conceptions of polarity that were compatible with their understanding of properties that confer solubility of a substance in water. The main indicator for polar substances for the students was the presence of heteroatoms—atoms of elements other than carbon or hydrogen—as explained in Leah's and Don's quotes below:

> *Well, I, when I think polar, polarity, I generally think of carbon-based molecules will heteroatoms in them. And that's kind of my fall back place. My happy place. With polarity.*
>
> —Leah

> *Um, well the first thing I thought of was methanol, so definitely I would change from carbon and hydrogen to nitrogen, oxygen, fluorine, something like that. Something that will pull electron density way one way.*
>
> —Don

Don extended this idea later when asked about the general characteristics of water-soluble substances:

> *So, hydrogen bonding automatically, so nitrogen and oxygen are the big ones. I would say they're soluble in water. I would say not very large chains, because I feel like alkyls are not very soluble in water at all because they are so different from water which is so small. Yeah, so if you wanted to have an alcohol, which, they should all be soluble in water. But they, alcohols are even in, um, amino compounds, automatically I think of smaller, like, first of all methanol, ethanol, butanol, propanol. It just um, well we were always taught 'like dissolves like.*

As demonstrated in other studies,[4,17] the adage "like dissolves like" seems to have a lasting impact on students. However, the research participants in the current study also noted that the mere presence of heteroatoms does not automatically imply water solubility. For example, Don qualified the idea about the need of highly electronegative atoms by noting that the effects of those elements were also dependent upon the sizes of the hydrophobic, alkyl groups attached to said heteroatoms. The need for this balance was nicely articulated by Raul in the following quote:

> *Because, um, once you get to a certain, once you get enough carbons on there, and not, and you have a small number of oxygens, the hydrophobic properties outweigh the hydrophilic properties that the oxygen provides.*

In addition to the need for heteroatoms, the students cited two other characteristics when talking about the factors that promote water-solubility of substances. In the quote below, for example, Leah spoke of the need for ionic substances:

> *The first thing that I'm going to think is ionic compound. Um, and then, after that, I'm gonna think, um...*

Although ionic substances are often water-soluble, they are not universally so and, as such, should not be used as a determinant of this behavior.

More interestingly, perhaps, is the following quote from Bruce, who was among the half of the participants who believed in the

Table 4. Features Common to the Students' Conceptions of the States of Matter

State of Matter	Characteristics	Representative Quotes
Gas	small, or lighter, particles—primarily mono- and diatomic—exhibiting weak intermolecular forces	Leah: *"So I'm going to assume that it is a either unimolecular or dimolecular or that, that the first assumption. But then I'll broaden my outlook and say, oh, it could be slightly larger but it certainly doesn't have very strong intermolecular forces."*
Liquid	in between solids and gases in molecular weight and intermolecular forces.	Russell: *"At some point, um, the longer and longer your alkane gets, it will turn from a gas to a liquid, and um, the heavier that it gets, um, of course the longer it will be too, and it will just have more points that they can lay on top of each other, so it will have more, more forces interacting there."*
Solid	tightly packed particles with very strong intermolecular forces	Sven: *"Tightly packed, strong intermolecular forces, not fluid, soluble or insoluble in water, is it crystalline or not. Size. The bigger the size generally the more likely it is to be solid, um, look at the functional groups on it, cause the charges will indicate intermolecular interactions, and that's kind of all I would really look for."*

DOI: 10.1021/ed500360g
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importance of multiple carbon−carbon as regards water-solubility:

> *Well, so first I was thinking, "Well to be soluble in water you have to have a dipole: an inducible dipole or, um a charge, which would be able to dissociate or something". I was thinking, "Do I know any hydrocarbons that can do that?", and I was like, "Well not really, unless I start using um double and triple bonds, because then I can induce".*

Although much of what Bruce said is scientifically valid, carbon−carbon π-bonds are just not inducible enough to cause water solubility.

Finally, it is important to note that none of the participants invoked any geometrical constraints when considering molecular polarity and solubility. This last point is particularly important since carbon dioxide has two polar carbon−oxygen bonds but is nonpolar overall due to the fact that the individual C═O bonds cancel each other out, rendering the molecule nonpolar overall.

Chemical Characteristics. In general the students had much more difficulty identifying substances with specific chemical properties, which is consistent with our previous work with organic chemistry graduate students.[1] Although we had initially planned on asking students to name hydrocarbons exhibiting acidic, basic, or nucleophilic properties, the first three participants had substantial difficulty with it. As such, we excluded those items for the remaining interviews.

Regardless, there were many instances where students were unable to provide examples of compounds with the specified chemical characteristic, as shown in Tables 1−3. Moreover, the participants verbalized to a far lesser extent during this portion of the interview often not providing any explanations even when they did have a specific compound in mind. Interestingly, the students were readily able to recite the Brønsted-Lowery definition for acids as shown by the following quote from Leah:

> *Well, because acidity is based on how easily a compound donates hydrogen, er, donates protons.*

However, they were unable to apply the principles in the broadest sense that any molecule containing hydrogen atoms can, to some extent, be an acid, albeit a very weak one in some cases. Similarly, molecules bearing π-electrons or heteroatoms with nonbonding electron pairs can also exhibit basic behavior. One possibility as shown by the following quote from Don is that in the students' minds they may have interpreted the question as asking for strong acids at strong bases:

> *First of all I'm stuck on like HCl and HI and HBr. Strong acid so it's, no it wants to dissociate and be negative.*

Alternatively, one anonymous reviewer noted the participants' narrow conception of acids could result from viewing acidity as a simple "dichotomy", to quote the reviewer. Although our data cannot speak to this interpretation, it should be noted that the reviewer's observation is consistent with reports in the literature that students often lack the necessary epistemic development for constructing the more nuanced and relativistic understanding to which the reviewer alluded.[18]

Unfortunately, we are unable to infer from these data the reasons why students appear to have felt greater facility when asked about physical properties as opposed to chemical ones. However, we surmise that one possibility is that structure−physical property relationships are given far more attention in the undergraduate chemistry curriculum than the corresponding connections with chemical properties. Nonetheless, the results appear to be of concern that the students struggled with structure−chemical property relationships.

Summary. Although the data indicate that students seemed to have self-consistent conceptions of some of the factors responsible for observed physical properties, the participants did not consider geometric requirements when articulating ideas about molecular polarity or the connections of structure to the states of matter. In the latter case, the students also did not mention any thermodynamic factors when describing parameters that determine whether a substance is a solid, liquid or gas under ambient conditions. Finally, the research participants appeared to be less adept at identifying compounds exhibiting the desired chemical characteristics or articulating reasons behind those behaviors.

Of all the results from this interview, the one that we found most intriguing was the students' apparent inability to apply their conceptions when responding to some of our questions. Certainly, one possibility could be that this phenomenon was an artifact of asking the students for a number of specific substances which, in turn, could have put them in a mindset that made it difficult to think on a general basis about the physical and chemical characteristics in question. Another possibility could be conceptual weakness on the students' part. While this option is likely the case to some extent, the data clearly demonstrate that the students *did* understand several of the topics covered in the interview. Not only were the students able to offer scientifically-valid reasons for the relationships between some molecular-level factors and the corresponding macroscopic behaviors, but they were able to do so consistently across all of the classes of compounds.

A third option to explain the students' apparent difficulty in applying their knowledge to less familiar contexts may be attributed to their science instruction. As mentioned earlier, several scholars have critiqued current STEM educational practices for promoting fragmented knowledge structures in students. It would follow then that such compartmentalized knowledge would, by its very nature, be difficult to effectively synthesize into meaningful combinations. The results from this interview point to at least two different strategies students appeared to use. In one, the participants seemed to propose hydrocarbons that would be solids under ambient temperature and pressure conditions using rule-based criteria that solids tend be made of particles of relatively high molecular weight and strong IMFs (Table 4). In another approach, the students just seemed to mentally go through a list of substances, as if they were looking through a "mental rolodex", and evaluate each substance to determine whether it would fit the task at hand. Consider, for example, the following statements:

> *I think about temperature and a level of excitation and pressure. ... Um, well, then I kind of compare it with all of the known gases that I just instinctively think of. And the ones that I'm going to think of, the gases at room temperature, are going to be oxygen, nitrogen, you know, hydrogen, those kinds of things. So I'm going to assume that it is a either unimolecular or dimolecular or that, that the first assumption.*
>
> —Leah

> *Just stuff that's got oxygen that's not soluble in water, um, kind of going through most of the solvents that I know. But at the same time, that's just, the wouldn't mix with water. I was thinking about ether, but I'm pretty sure that eats up water too, well, not eats up, but. And I'm trying to think solid things, but nothing's really popping into my head.*
>
> —Sven

DOI: 10.1021/ed500360g
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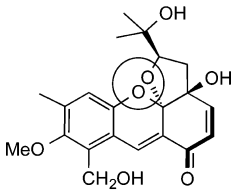
This approach can be very cumbersome since an individual may have to go through a large number of instances before arriving at an acceptable match. Additionally, a person would be limited to her experience which, especially for novices, tends to be limited. On the other hand, the first approach, which is reminiscent of rules-based reasoning, is inherently a flawed strategy for multivariate tasks such as the ones in this study.[19] It was to gain greater insight on the students' reasoning strategies that we asked them to participate in a second interview.

Interview Two

Paranolin and Cespitulactone. In this part of the interview, the students were highly successful at identifying the structural features of both natural products, including some of the more nuanced aspects. Consider, for example, the following comments from Lauren and Raul about the highlighted portion of the structure of Paranolin in Figure 1:



Paranolin

Figure 1. Bonds in bold are part of the conjugated system referred to by Raul and Lauren. The circled area indicates a ketal functional group. Instead of recognizing this group as a ketal, all of the participants thought there were two ethers present. Ketals are far more labile to acidic conditions than ethers which is a main reason why this distinction is important.

> *Um, the double bonds will give it resonance, so it's like the electrons can jump kind of around.*
>
> —Lauren
>
> *Um, other than the carbonyl and the benzene, there's two other double bonds, um, since they're only separated, each only separated by one single bond, I assume that there is some sort of resonance going on there.*
>
> —Raul

These quotes indicate that, like the rest of the participants, both of them were able to recognize the particular arrangement of bonds which is the hallmark of a conjugated system. Although neither used the domain specific term both of them correctly described the phenomenon using a term with which students tend to be far more comfortable, "resonance."

Additionally, all of the participants noted one or more of the geometric features of the structures. As examples, consider the following quotes from Russell about Paranolin and Lauren about Cespitulactone:

> *Umm, it's planar, for the most part; I see a carbonyl group. Umm, the first things that pop out...*
>
> —Russell
>
> *But this, this ring right here will be above the rest of this stuff. Um, if I'm thinking of the geometry right.*
>
> —Lauren

While it may be argued that Lauren's recognition of the three-dimensional structure was more readily cued by the solid wedges, Russell's inference of planarity certainly required structural recognition beyond the surface-level features of the representation. Regardless, this result is particularly noteworthy since none of the participants spoke at all about geometric constraints when talking about different physical characteristics during Interview One.

When asked to name the functional groups represented in the structures, all of the participants seemed easily able to identify all of them for both cases. The exception was the functional group called a ketal circled in Figure 1. This result is consistent with our previous research with organic chemistry graduate students who were also unable to identify or recognize this particular functional group and its close analogue called an acetal.[1,19] Unfortunately, we were unable to elucidate the reason behind this phenomenon during follow-up questioning.

The students' predictions for the behaviors of each compound under general reaction conditions are shown in Figures 2 and 3,

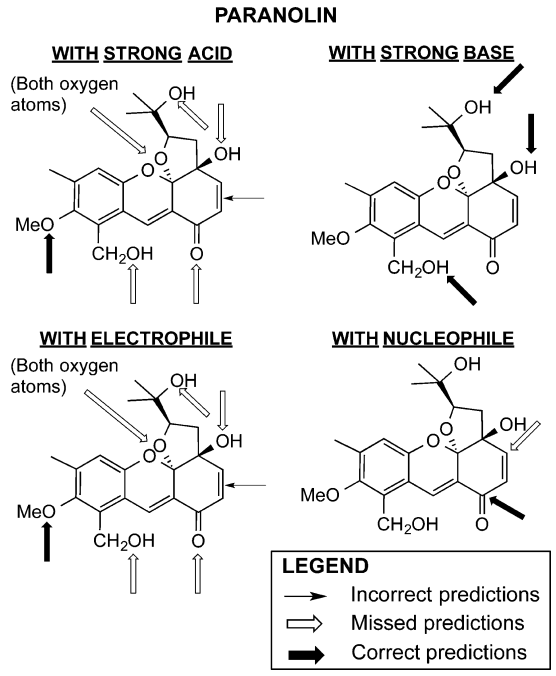


Figure 2. Expected reactivity of Paranolin in acidic or basic and nucleophilic or electrophilic conditions. Missed predictions refer to those that none of the students identified during their interviews.

respectively. There were two types of mistakes the students made: identifying an unlikely site of reaction or not recognizing a likely location where a reaction would have taken place. Though these missteps may seem arbitrary, they are all bound by a single underlying theme: an apparent misunderstanding of emergent properties.

Emergent properties are those that result from the non-linear interactions of two or more properties of systems.[20] In the context of molecules, when multiple functional groups are connected through electronic interactions such as resonance, they form systems whose reactivity cannot be predicted solely by "adding" the effects of the individual functional groups. In a sense, there is a gestalt to the systems' reactivity, and it was with predicting these combined behaviors that research participants struggled. Consider, as an example, the students' predictions of the reaction of Paranolin with a strong acid. Had the carbon−carbon double bond been attached to a simple alkyl group, then it would have reacted quite readily with the acid. In this particular situation, however, the attachment of the carbon−carbon double bond to the ketone in Paranolin would likely render it inert to the reaction conditions.

DOI: 10.1021/ed500360g
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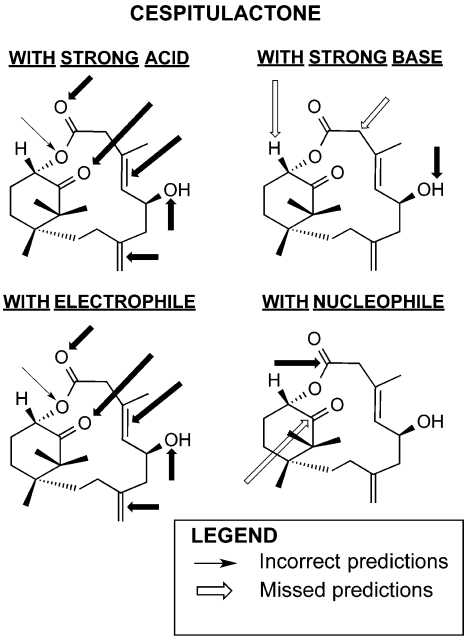

Figure 3. Expected reactivity of Cespitulactone in acidic or basic and nucleophilic or electrophilic conditions. Missed predictions refer to those that none of the students identified during their interviews.

As another example, the oxygen atom of the methoxy group could, at least in principle, be protonated under strongly acidic conditions. However, the conjugation of one of its nonbonding electron pairs with the aromatic ring would render it far *less* likely to do so than any of the other oxygen atoms in the molecule. The participants who predicted that it would be a primary site of protonation may not have had—based on data from Interview One—the epistemic sophistication to consider acidity and basicity as continua and, instead, assumed them to be dichotomous characteristics. However, it is also possible based, on the predictions in the previous paragraph, that the students may not have understood the emergent behavior of the entire *system* that included the methoxy substituent.

Design Tasks. Perhaps the most interesting data from this interview were collected in the context of these tasks. On one hand, students were able to match the individual constraints to the appropriate structural attribute. Consider, as examples, the following quotes from Don and Raul:

> *Uh, right now I'm just trying to think of something with probably an oxygen in it for hydrogen bonding purposes.*
>
> —Don

> *I know that if you continue to put more hydrophobic groups on it, it will become less and less water-soluble. ... Um, because generally is, I mean, since we're talking about organic chemistry, generally the larger an organic compound becomes, the less water-soluble it becomes. I mean, you get to polymers and they become virtually, like, virtually insoluble.*
>
> —Raul

As demonstrated by these quotes, the students' inferences from the constraints were consistent with the conceptions elicited in the first interview. Don's comment reflected the students' understanding that water-soluble organic compounds would likely contain heteroatoms as hydrogen-bond donors and/or acceptors. Likewise, Raul's remarks suggested his understanding of some of the factors that tend to promote hydrophobicity.

Although the students were adept at making the individual inferences, they struggled to integrate them and propose solutions to the tasks, as reflected in the following comment from Leah, who was the most articulate about this process:

> *Alright, well, here's what I'm thinking now. I've just drawn this structure, and I made sure that my weight was within limit, and I'm, kind of, uh, this isn't my final structure by any means, I'm just kind of doodling at this point. But I'm kind of reevaluating this by all the, um, things. So, I think, I'm pretty sure it's over and under the weight limit. It's very, very polar in lots of different directions, so I can't imagine it not being water-soluble, although I could surprised. I don't know about the boiling point though. And I'm thinking about that currently. But I'm also thinking about, I mean, the only, it wouldn't have a low boiling point? The proton here and because these are very electronegative elements, I was wondering if I might of done bad things to my pK_a here. So I was just kind of thinking about that. And... So those were my thought processes.*
>
> —Leah

Even though Leah appeared to have processed all the information to the point of producing a potential solution, she realized that her focus on the water solubility characteristic resulted in a compound that would likely have a high boiling point due to the presence of all of the hydrogen-bonding groups.

Consistent with the students' use of their "mental rolodexes" in the first interview, they seemed to have resorted to a similar strategy during this task as well:

> *I'm just going through a list of, kind of, structures in my head, thinking about what they might, what it might entail." [I: So what are the things?] "Well, I do love a good carbon—oxygen double bond. ... But then the, and then I was kind of kicking around boiling point, too. Thinking about, because I could just draw you some, like, amino acid or whatever and that would have, that would satisfy the molecular weight, the protons and the water solubility. But it wouldn't have a low enough boiling point.*
>
> —Leah

> *Ok, this is my best guess. Um cyclohexanone. ... Um, I think that from working in the ochem stockroom I've seen a cyclohexenone as a liquid at room temperature, so that's a check. I don't know if the boiling point was greater than water...*
>
> —Russell

> *Um, I'm thinking about, uh, insoluble water, liquid at room temp, higher boiling point, uh, than, ah, water. And going through the compounds that I know that have those characteristics and mainly, um, oils are, are that. However, uh, oils aren't, don't really have proton groups that are, ah, less than ten.*
>
> —Sven

In all, there were a dozen quotes during this part of the interview in which all eight of the participants alluded to searching through their minds' "rolodex" of compounds. As such, when asked to put several of these factors together to build a structure, the participants appeared to "scan" their minds to find compounds that would fit the constraints instead of designing a compound in the sense contemplated by engineers.[21] In a sense, the students used a reductionist strategy in which they simplified multivariate problems to a series of univariate ones, a method noted in other studies.[19,22] Over and above the potentially

DOI: 10.1021/ed500360g
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immense cognitive load demand, this approach cannot account for any interactions among the variables, which is one of the reasons that the students in this study were unable to provide solutions to the tasks that satisfied all of the constraints.

DISCUSSION

The senior chemistry majors in this study demonstrated an emerging sophistication in their conceptions of many of the physical properties that were part of the instruments. They understood the dependence of the states of matter on molecular mass/size and intermolecular forces. They could also use their understanding of intermolecular forces and polarity to explain solubility/insolubility of substances in water. However, until they were cued by the structural representations of the natural products in Interview 2, none of the participants considered geometric constraints when explaining their answers in the first interview; neither did they invoke any of the thermodynamic principles that govern these physical characteristics of substances. Of greater concern, perhaps, should be the students' overall lack of fluency with the chemical characteristics. Like those in our previous studies these research participants could name compounds belonging to each class, but could not articulate clear conceptions for virtually any of them.[1]

The students appeared unable to apply their knowledge of physical properties to some of the tasks in the second interview. First, the students seemed to have difficulty in understanding the emergent reactivity of chemical substances that result from electronic interactions between and/or close proximity of multiple functional groups and other structural features. For example, when asked to describe the behaviors of the natural products in Box 2 with different classes of reagents, the students made unlikely predictions especially in the cases of strong acids and electrophiles. The reactivities of the corresponding basic and nucleophilic sites on the natural products were dependent on their emergent behavior which resulted from the π-conjugation of multiple functional groups. Recall, that the students were *not* asked to predict the products of specific reactions or, for that matter, predict the results from the reaction of the natural products with the reagent classes; they were only asked to indicate plausible interaction sites of the natural products with the standard classes of reagents. This result, therefore, may help explain why students typically experience great difficulty with getting started with mechanism tasks.[23−25]

Second, the data from the design tasks, along with those from Interview One, are consistent with the concerns raised in the chemistry/science education research literatures about the limitations that students with fragmented knowledge structures may experience. The students were readily able to make the appropriate inferences from the individual constraints; however, they struggled to integrate these isolated pieces of information to propose valid solutions. Such a synthesis, which would involve balancing all of the constraints, was precisely the type of difficulty predicted by the research on the differences between experts and novices.[5] As such, the participants' strategy for the design tasks was to use the structural implication of one of the constraints to conduct a mental search for members of that category. They subsequently attempted to test one or more of the first set of compounds against each successive constraint. Consequently, the students did not *build* a structure using the constraints; they went through their "rolodexes" to determine the extent to which each example matched the constraints. Furthermore, the participants did not even attempt to modify a recalled substance that fit one or more of the constraints. Instead, they resumed their mental search for a more accurate match. Not only was this strategy a laborious one, it did not lead to successful results.

In sum, our results indicate that fragmented knowledge can be a major hindrance to successfully completing tasks requiring the combination of multiple chemical constructs, which are, in effect, at the heart of (almost) all real-world problems. In actuality, as shown by Cooper and colleagues,[3] concept integration is at the core of the most commonplace of chemical operations, such as predicting a relative boiling point from a molecular formula or Lewis structure. It should not be surprising, then, that some of the most predominant strategies used by students are rote memorization or just skipping parts of assignments.[25]

IMPLICATIONS

The results of this research support the "big picture" goal, as called for in the DBER literature, of advocating major changes in undergraduate STEM curricula. That discussion, however, should be left to a broader conversation and not as an outcome of a single research study. We offer more feasible instructional changes here; however, it is worth making a note about assessments before addressing those. One of the often cited best-practices of assessments, especially for multiple-choice or true/false questions, is that an item should cover only one idea.[26−28] This guideline does not call for "dumbing down" test items. Rather, it is to help instructors more accurately interpret student responses. It would appear, however, that adhering to this recommendation would likely rule out testing students on more complex problems such as the design tasks in Interview Two. To our knowledge, one of the best examples that reconciles this apparent paradox is offered by the National Board of Medical Examiners, who use scenarios to test students on real-world diagnoses while still following exemplary assessment practices.[26]

In the specific context of sophomore-level organic chemistry courses, we believe there are several things instructors may do to help students better integrate course material. All of these take advantage of the observation that a single molecule is a complex system of steric and multiple electronic variables.[19] The interaction of these characteristics is most explicitly showcased in the context of nucleophilic aliphatic substitution and elimination, i.e., S_N1/S_N2 and E_1/E_2.[16] This focus, however, does not carry over to other classes of reactions, all of whose outcomes are dictated by the interplay of steric and electronic factors. In these other contexts the focus tends to be on electronic factors with only sporadic allusions to steric effects when compared to the detail given both these factors in the discussion of S_N1/S_N2 and E_1/E_2 reactions. We recommend, therefore, that far more explicit attention be given to the interactions between steric and electronic effects throughout, thus steadily reinforcing this integration over an entire curriculum. It is even worth considering sacrificing some of the breadth for this added depth, given the level of retention exhibited by students in this and other studies.

Along with this added focus, we believe that instructors should consider giving students several intermediary tasks, similar to a learning progression, before asking students to propose entire reaction mechanisms. For example, they may give students small molecules and ask, as we did in Interview Two, for the sites on the molecule most likely to react with a given class of reagents. Exercises such as these would have the added effect of helping students go beyond the surface-level features of the representations, a problem consistently exhibited by students since the landmark studies of Kozma and Russell.[29,30] A second type of exercise representing such "baby steps" would be providing students with one step of a reaction mechanism and asking them

DOI: 10.1021/ed500360g
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what the outcome would be of just that step, emphasizing the reasoning behind their decisions over the product of the step.

Finally, we recommend that design tasks, such as those used in Interview Two, be incorporated courses to help students to learn to apply and integrate their conceptual knowledge. Schön[31] demonstrated that design activities are excellent vehicles for inducing the type of reflection in learners that can lead to robust learning. A basic characteristic of design tasks is that they are ill-defined to the degree that one does not, initially, even know what is(are) the problem(s) that need to be solved. Schön observed that the process of defining the problem(s) facilitates reflection on many, if not all, of the concepts related to the task.[31] Thus, design tasks can be used to develop a conceptual understanding in a way that can be conducive for integration rather than separation.

■ ASSOCIATED CONTENT

Supporting Information

Reference sheet containing atomic weights and pK_a values of common functional groups given to the participants in Interview Two. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to express their profound gratitude to the research participants for their time and efforts, especially during an intensely busy time of their final semester. We would also like to thank the thoughtful and constructive comments on earlier versions of this manuscript made by the three anonymous reviewers; their insight resulted in a vastly improved final product. G.B. would like to thank George M. Bodner and Daniel S. Domin for helpful conversations during the data analysis phase of the research project.

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DOI: 10.1021/ed500360g
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