I Have Found You an Argument

The Conceptual Knowledge of Beginning Chemistry Graduate Students

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Twenty years ago a paper entitled "The Grim Silence of Facts" was published in *the Journal* (*1*). It began as follows.

> While grading a beginning graduate inorganic examination some time ago, I was startled to discover that the student believed silver chloride to be a pale green gas. . . . A little later the student launched into a long, plausible explanation as to why silver chloride was a pale green gas.

This paper stimulated an on-going discussion of the proper balance between the theoretical principles we expect students to understand and the factual knowledge on which they are built. It might now be time to examine the conceptual knowledge that chemistry majors construct during their undergraduate experience.

For the last three years a conceptual knowledge exam has been given to entering graduate students at Purdue during the orientation program for new teaching assistants. The number of questions on the exam and the wording of these questions has gradually changed, but responses to these questions have now been obtained for a sample of up to 132 graduate students. Some of the questions and the responses they elicited are described below. A complete list of the questions and the answers he would give to these questions can be obtained by writing the author.

What Are the Bubbles in Boiling Water?

Osborne and Cosgrove found that the majority of secondary-school students believe that the bubbles in boiling water are made up of either "heat", "air", or "oxygen and hydrogen" (*2*). The first question examined the extent to which graduate students in chemistry give similar answers. It was phrased as follows: "Assume that a beaker of water on a hot plate has been boiling for an hour. Within the liquid, bubbles can be seen rising to the surface. What are the bubbles made of?"

Slightly more than 70% of the graduate students answered that the bubbles contain water vapor, steam, or molecules of water. Almost 20%, however, suggested that these bubbles consisted of air or oxygen and 5% indicated that they contained a mixture of H_2 and O_2 gas.

Many students followed the advice of Samuel Johnson, who was quoted as saying: "I have found you an argument; I am not obliged to find you an understanding" (*3*). Others, however, tried to explain their answers. The following are typical explanations of the assumption that boiling water contains bubbles of air.

> These are air bubbles. With increasing temperature, the solubility of air in water decreases and since at room temperature there is always some air dissolved in water, it gets pushed out of solution.

Or:

> Most of the containers have small packets of air trapped inside. And so when the water is boiling this air gets heated and the hot air rises up which is seen in the form of bubbles.

What Is the Relationship between Temperature and Heat?

There is an extensive literature devoted to the analysis of student's concepts of heat and temperature (*4–8*). The following item was used to probe the hypothesis that students' misconcepts about these topics are resistant to instruction: "One way of raising the temperature of an object is to heat it. Does this mean that adding heat to an object always raises its temperature?"

More than 80% of the sample said "no". This means, however, that slightly less than 20% said "yes". Some of the explanations indicated significant confusion about the concepts of heat and temperature.

> To add heat is like giving energy—and sometimes you can give energy to an object but it won't give it back; this is an endothermic reaction. When an object is heated and the temperature raises, it means that the reaction is exothermic.

Others used thermodynamic principles to reach incorrect conclusions.

> $q = nC\Delta T$ heat = mass × specific heat × ΔTemp. Therefore ΔT = heat/mass × specific heat. If heat is added to an object then q is positive, mass is positive, and the specific heat is positive. Therefore ΔT must be positive and the temperature rises.

Or:

> Yes, at constant volume the internal energy is equal to $C_v dT$. Therefore, $dT = dU/C_v$, at constant pressure it is $dT = dH/dT$, which implies that the greater the change in U or H, the greater the change in T.

The following quotation summarizes the most common explanation of why the answer to this question is "no".

> No, as in the case of boiling water. One may continue to add heat, but the temperature of the water doesn't continue to increase above the boiling point. The excess heat energy is converted into kinetic energy and water molecules vaporize as they escape the surface of the water.

Is Heat Conserved?

To further probe the students' conception of heat, they were reminded that mass and energy are both conserved and then asked: "Is heat conserved?" The majority (60%) said "no". But 40% said "yes". The most common explanation was: "Heat is a form of energy and is therefore conserved." The next most common was: "Heat is a form of energy and therefore is not conserved." Two examples of another common explanation are given below.

> Heat is conserved. When something is cooled, it heats something else up. To get heat in the first place though, you may have to use energy. Heat is just one form of energy.

And:

> Yes, heat is transferred from a system to its surroundings and vice versa. The amount lost by one system equals the amount gained by the surroundings.

What Happens to the Weight of an Iron Bar When It Rusts?

It is not surprising that many secondary-school students believe that nails lose weight when they rust (*9*). In spite of the expectation that BS chemists would not make the same mistake, the following question was used on the conceptual knowledge exam: "What would happen to the weight of an iron bar when the iron rusts? Does it increase, decrease, or remain the same?"

As expected, most (81%) of the graduate students concluded that the weight of the bar would increase, as long as the rust was not scrapped off the bar. Approximately 10%, however, argued that the weight would decrease for reasons other than the loss of rust. Another 6% concluded that the weight of the bar would remain the same.

A typical explanation for the assumption that the weight of the bar would increase is given below.

> The weight increases assuming none of the rust falls off the bar. This is due to the formation of iron oxides.

Explanations for the decrease in the weight of the iron bar are more interesting.

> It decreases—the iron oxide that is forming is less dense than iron.

Or:

> As iron rusts, its weight decreases. Thus mass lost shows up as energy (i.e., if you had a closed system you could measure the change in energy. The energy would increase as the mass decreased.)

Explanations for why the weight remains the same are equally interesting.

> Remains the same. A chemical reaction neither creates nor destroys matter. It changes it. Oxidation causes the rusting. It does not create or destroy the iron, it changes its form.

And:

> It would be the same, since the metal is only being oxidized.

A small percentage of students were not able to answer this question. Only one explained why:

> The weight would change according to the difference in the densities of Fe(s) and Fe_3O_2(s).

How Does Salt Melt Ice?

Many of us who teach chemistry are asked practical questions, such as: "How does salt melt ice?" Because the primary goal of our TA orientation program is to help beginning graduate students learn how to function as teaching assistants, the following item was used on the comceptual knowledge exam. "In the winter, some people scatter salt on icy driveways. Explain how placing salt on the surface of ice can melt the ice."

The most common answers were based on simple colligative property explanations: salt lowers the freezing point of water or the melting point of ice. 10% of the students who invoked a colligative property explanation, however, concluded that salt *raises* the freezing point/melting point of water/ice.

Other explanations were based on thermodynamic arguments, such as the idea that salt dissolving in water is an exothermic process.

> The salt that is added goes into solution in some of the water that is present. Due to this, a certain amount of heat of solution is released. This helps in melting the ice.

Mechanical explanations were also popular.

> The weight of the salt on the surface of the ice disrupts the lattice structure and the ice melts—this is analogous to the blades of ice skates . . . .

Or:

> The weight of the salt on the ice surface generates heat to melt some of the ice which then dissolves the salt to give a liquid which has a lower freezing point than water.

And:

> When you put salt (or anything really) on the ice, it disrupts the crystal structure of the ice. The water molecules can no longer get into a nice perfect array, and so the ice becomes a liquid.

As were explanations based on chemical reactions.

> Placing salt on the ice will encourage or initiate the formation of an aqueous base, NaOH, thereby causing the one bond between oxygen and hydrogen to break and resulting in the formation of NaOH + HCl.
>
> $$\text{rxn: } NaCl + H_2O \rightarrow NaOH + HCl$$

A limited number of answers to this item provided a method for getting the salt into the crystal, so that colligative property explanations might succeed.

> The salt lowers the melting point of water. Even though the salt is scattered on the ice, as cars drive on it or even when people walk on it, the pressure of their weight melts a slight amount and the salt works to melt it. During the day, sunlight warms the ice enough to bring it to its melting point when salt is in the mixture. Ionic substances lower the ability of water molecules to bind to one another, lowering the melting point.

How Does a Barometer Work?

Many years of observing teaching assistants led to the hypothesis that the following item would be a useful addition to the conceptual knowledge exam. "A barometer can be built from a long, thin tube of glass that is sealed at one end. The tube is filled with mercury and then inverted into a small pool of mercury. Explain how this barometer works."

A significant number of students were unable to produce an answer. One of the most popular explanations might be described as the "one-force model".

> There is no force pushing down on the mercury column inside the tube, but the mercury in the pan has the force of atmospheric pressure pressing down on it. The downward force on the pool, causes a column of mercury to be supported, the height of which depends on the pressure exerted on the pool.

Some students invoked a model which assumes that a gas is trapped at the top of the tube of mercury.

> (Student drew a figure that indicated that there is "trapped gas" at the top of the tube.) As pressure from the atmosphere increases, the pressure on the Hg should force mercury higher up the column until increased pressure from the compressed trapped gases balances the outside pressure. Lower outside pressure will lead to a falling Hg level inside the tube as the trapped gas will expand to yield a lower internal pressure.

Explanations, such as the following, which were based on a dynamic equilibrium between opposing forces were unfortunately rare.

> Because the open end of the tube is inverted into the mercury end of the dish, no air is allowed into the upper end of the tube. Therefore, only the weight of the Hg column (no air in the tube) will press against the pool of Hg. This weight will balance against the atmospheric pressure pressing on the pool of mercury.

Or:

> The atmosphere exerts a pressure on the pool of water [sic], which then gets pushed up the tube until the pressure exerted down by the column of mercury is the same as the pressure exerted up.

How Does a Hot-Air Balloon Work?

Several years ago, the following question was used on an hour exam in a general chemistry course for science and engineering majors. The distribution of answers was almost random; the fraction of the student population choosing each answer was essentially the same.

Which statement best explains why a hot-air balloon rises when the air in the balloon is heated?

(a) As the temperature of the gas increases, the average kinetic energy of the gas molecules increases, and the collisions between these gas molecules and the walls of the balloon make the balloon rise.
(b) As the temperature of the gas increases, the pressure of the gas increases, pushing up on the balloon.
(c) As the temperature of the gas increases, the gas expands, some of the gas escapes from the bottom of the balloon, and the decrease in the density of the gas in the balloon lifts the balloon.
(d) As the temperature of the gas increases, the volume of the balloon expands, causing the balloon to rise.
(e) As the temperature of the gas increases, hot air rises inside the balloon, and this lifts the balloon.

When the same question was given to the graduate students, the distribution of answers was no longer isotropic. Each answer was chosen, however, by a significant fraction of the total sample who completed this item: A(8), B(6), C(40), D(8), and E(18).

How Does a Pressure Cooker Work?

The following item was used to probe the students' ability to extend their knowledge of chemistry to real-world examples. "Long before we had microwave ovens, people used pressure cookers to increase the speed at which food cooks. Explain how a pressure cooker works."

One of the most popular answers was based on the ideal gas law. Several examples are quoted below.

> We know $P_1T_1 = P_2T_2$. So if the pressure is doubled, the temperature should be doubled, increased heat leads to quicker cooking.

Or:

> Pressure cookers are based on the principle that $P \propto T$, i.e., pressure is directly proportional to temperature. When volume kept constant thus if you increase the pressure the temperature also increases and it takes less time to cook.

Other answers invoked pressure as a direct means of cooking food faster.

> Food cooks faster because the pressure is high. This means that there are more impacts of molecules per surface area, which in turn generates more heat.

Or:

> Cooking is actually a way of denaturing the proteins in food. Temperature is a way of physically denaturing, but so is pressure. So therefore temperature and pressure work together to cook the food.

A popular explanation was based on the assumption that a pressure cooker is a closed system, which is inherently more efficient.

> If we increase the pressure under which food is cooked, we have more collisions of heated air with the food, heating it faster. On an open stove, heat escapes into the surroundings, without affecting the food more than once.

Other explanations invoked complex thermodynamic models, which invariably led to the wrong prediction.

> $dP/dT \approx -\Delta H/\Delta V$, therefore dP is inversely proportional to dT, when P increases, T_{bp} decreases.

Or:

> Clausius–Clapyron equation: $\Delta H < 0$ always in this case, so as the pressure increases, the temperature decreases, thus the food cooks faster.

A remarkably small fraction of the explanations included arguments such as the following:

> As the pressure inside the sealed cooker builds, as a result of the vaporization of water, the boiling point of water is increased, thereby increasing the temperature at which the food cooks—*hotter temperature, less time.*

Why Does Sodium React with Chlorine?

The following item was used to probe the source of student's misconcepts. "Everyone knows that sodium metal reacts with chlorine gas to form sodium chloride. Explain why. In other words, what is the driving force behind this reaction?"

The first year this item was used, essentially all of the answers were based on simple thermodynamic principles, such as: "Because of a decrease in the Gibb's free energy of the system." During the next two years, the students were encouraged to look for explanations that helped us understand *why* the free energy decreases. A significant fraction of the sample was no longer able to answer the question, or invoked statements of the obvious, such as: "Because Na and Cl are very active," or "NaCl is a very stable material."

By far the most common explanation was based on the assumption that the octet rule drives chemical reactions.

> Chlorine wants to obtain another electron to achieve the most stable configuration where eight electrons are present in the outermost molecular orbital. Sodium donates an electron to chlorine and, thereby, allows both the chlorine and sodium atoms to achieve the eight electron configuration.

Or:

> This happens because every element wants to obey the octet rule and as such, when Na and Cl are brought together Na donates its single outermost electron to become more stable and Cl gladly accepts this single electron from Na and in the process NaCl is formed.

And:

> The driving force is for sodium and chlorine to have a filled octet. A filled octet corresponds to a more stable energy state than either sodium or chlorine exhibit. Thus sodium donates an electron to chlorine which give both a filled octet.

In spite of the fact that the net transfer of an electron from sodium to chlorine to produce Na^+ and Cl^- ions would be an endothermic process, a significant fraction of the students proposed arguments such as the following.

> Sodium metal is very unstable, it wants to give up electrons badly to become Na^+, which is much more stable. Chlorine gas readily accepts the electrons and becomes Cl^-.

This notion was so robust it led to errors in the remembered magnitudes of electron affinities and ionization energies.

> The electron affinity for Cl is greater than the energy required to pull an electron off of Na. Therefore Cl can remove an electron from sodium and the two resulting ions form an ionic salt.

A small, but significant fraction of the population invoked the lattice energy of NaCl as the driving force behind this reaction. No student, however, invoked the combination of the electron affinity of chlorine coupled with the lattice energy of NaCl as more than compensating for the energy required to produce a Na^+ ion and the energy required to break the Cl–Cl bond.

Why Do Both Icebergs and Steel Ships Float?

Research on misconceptions of density (*10, 11*) led us to investigate the students' responses to the following item. "Ice is less dense than water, but steel is almost eight times as dense as water. Explain why both the Titanic and the iceberg it hit were able to float on water."

One student admitted: "I've been searching for a good explanation for this one for a long time." A surprisingly large fraction of the sample population invoked miscellaneous buoyancy explanations, such as:

> The Titanic was equipped with flotation device which allowed the ship to have buoyance.

Other relatively innovative explanations were given,

> There is a force between the iceberg and Titanic—and this one plus the fact that ice is less dense than water prevent the Titanic from dropping.

Or:

> Ship is also propelled by an engine—when it took in water it sank.

And:

> The Titanic was made from titanium, not steel.

A popular explanation was based on surface tension: "The surface tension of water supported the boat." An equally popular explanation invoked the surface area of the ship.

> Steel (of the Titanic) is more dense than water, however, its weight is distributed over a large area.

Or:

> The weight of the ship is spread over such a large surface area that it is suspended on top of the water. It is also a shape that doesn't allow water on the top of the ship.

A remarkably small fraction of the population proposed explanations based on the idea that the average density of a ship filled with air might be less than that of the water it would displace.

> Anything less dense than water floats on it, so the ice floats. The Titanic is also less dense than water even though it is made of steel because the steel contains an air-filled area. So in essence it is like a steel balloon, and the steel balloon is less dense water.

Conclusion

The student responses are consistent with—but by no means test the validity of—the following assertions.

1. Knowledge is constructed in the mind of the learner (*12*).

   Students construct knowledge about the concepts we expect them to learn from lectures, laboratory experiments, textbooks, homework assignments, and so on. During this process they test the validity of the knowledge they construct within the domain in which it is defined. They have difficulty, however, applying their knowledge to areas where they have not been actively encouraged to apply it. All too often, this means they cannot extend their knowledge beyond the limits of the classroom into the real world.

   Evidence for the domain-specific character of chemical knowledge is easy to obtain. Ask students in organic chemistry to explain why acetylene is reactive. They will frequently invoke the C≡C triple bond. Then ask students taking inorganic chemistry why nitrogen is virtually inert. They will attribute it to the N≡N triple bond. Because we seldom ask students to extend their knowledge beyond the domain in which it is constructed, it is the rare student who recognizes the dissonance generated by assuming that the same argument can be used to justify diammetrically opposing behavior for systems that have the same number of valence electrons.

2. Misconcepts are resistant to instruction.

   The research being done to identify the concepts students build during their first exposure to chemistry is important for all of us because the misconcepts they build are so resistant to instruction that a significant fraction of the population retains them even after the 500 h of laboratory and 400 h of lectures that characterize the undergraduate experience in chemistry mandated by the ACS Committee on Professional Training.

3. Knowledge is not the same as understanding.

   Many of the responses we have observed can be explained by assuming that students all too often possess knowledge without understanding.

4. Misconcepts are often instructor-driven.

   Student misconcepts about physics come from prior experience with the world (*13–16*). They know, for example, that they must apply a constant force to keep an object (such as a car) in motion, regardless of what they are told by our physics instructor. In biology, there are media-driven misconcepts, such as the common notion that humans and dinosaurs coexisted. (Remember the Fred Flintstone cartoons?)

   In chemistry, there are two additional sources of misconcepts. Some result from the language we use. We use terms (such as "heat capacity") or phrases (such as "heat flows") that were meaningful in the context of the accepted theory at the time they were proposed, in spite of the fact that this theory is no longer accepted. The language often remains constant as science evolves, while the meaning of the terms changes until they become misleading.

   Other misconcepts in chemistry are instructor-driven. Some result from the way we simplify ideas so they can be learned for the first time. Explanations that help students make sense of the chemistry we expect them to learn for the first time are often remembered in place of the more correct, and far more explicit, discussions to which students are introduced at later points in their careers. Misconcepts are also created when students are not explicitly told—or are unable to understand—points that are obvious to their instructors. The following equations, for example, are both used as statements of the first law of thermodynamics.

$$\Delta E = 0$$

$$\Delta E = q + w$$

Both equations are legitimate, but the first describes the fact that the energy of the universe is constant,

$$\Delta E_{\text{universe}} = 0$$

whereas the second describes how the energy of a system can change.

$$\Delta E_{\text{system}} = q + w$$

Finally, instructor-driven misconcepts can be generated unintentionally when the limits of assumptions are not explicitly described. How many of us, for example, do calorimetry experiments in which we ask students to assume that the heat given off in a chemical reaction is equal to the heat absorbed by the water in which the reaction is run or by the water bath that surrounds the reaction? It is possible that this experiment reinforces the idea that heat is "conserved". That heat cannot be either created or destroyed.

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