The use of pre-lectures might also, of course, be having more subtle effects. The confidence and motivation of more poorly qualified students will almost certainly be enhanced by learning experiences where their weaknesses were being taken into consideration. Motivation has been shown to be very important in influencing performance[11]. In addition, the use of pre-lectures could also be having a subconscious effect on the lecturers by heightening their sensitivity in checking the pre-knowledge of the students during the presentation of new material.

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Undergraduate Students' Understanding of Enthalpy Change

PAPER

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The study described in this paper is an investigation into the conceptions held about chemical thermodynamics by first year chemistry undergraduate students. Twenty students were interviewed on two occasions, each for about one hour and asked to explain temperature changes in three simple chemical reactions. The first interview sought to identify knowledge retained from A-level; the second interview followed a lecture course on chemical thermodynamics. Students' conceptions about enthalpy change are described and examples of students statements are given; it is clear that students come to the university with a very limited understanding of enthalpy change and have no knowledge of pV work. The impact of the lecture course on their conceptions is discussed; most students still held the same conceptions about enthalpy change although there was more awareness of pV work. Some quantitative information is given but the qualitative data show the range and variety of the alternative conceptions. Finally, the implications of the findings on the teaching of elementary chemical thermodynamics is discussed.

Introduction

This paper reports on part of a larger study which arose out of a concern of a chemistry department about the effectiveness of a first year course of chemical thermodynamics for undergraduate chemistry students. Although students were performing reasonably well in end of module examinations, informal discussion with tutors indicated that their understanding of basic thermodynamic concepts seemed weak. Similar views have been expressed in the literature[1,2]. The result is that, for many students, the study of thermodynamics is regarded as a chore whose equations are to be learned by rote in order to do calculations and to pass examinations.

A possible cause of the problem is a mismatch between the assumptions made by the teaching staff of the students' prior knowledge and understanding and the conceptions actually held by the students. Many previous studies of students' understandings of scientific concepts[3,4,5] have shown that students often hold conceptions which are different from the accepted science concepts and that when students construct new meanings, they are influenced by their own pre-existing (and often incorrect) conceptions. In this report, the term 'concept' is reserved for an accepted statement; the term 'conception' is used to refer to an individual's version of a concept and may be correct or not. The term 'alternative conception' is used to describe all conceptions that differ from the accepted version. Such alternative conceptions range from those that are very different from the accepted view to those that are merely incomplete.

The aim of the complete study was to explore students' understanding of thermodynamic concepts before and after they attended a lecture course and thus to throw light on the development of their conceptions with a view to drawing conclusions about possible improvements in teaching strategies. This paper deals with the enthalpy component of the thermodynamics teaching.

At the time of this study, enthalpy changes (especially Hess's Law calculations) are included in the core A-level syllabus. The syllabus demands little more than a knowledge of the term enthalpy change, that constant pressure is required (in all processes), and specific definitions of enthalpy change of formation, $\Delta H°_f$ and enthalpy change of combustion. It is often argued that reactions occur because the products have a lower enthalpy than the reactants (i.e. ΔH is negative). This leads to difficulties in understanding why endothermic reactions occur spontaneously[5,6]. Students also have difficulties in identifying exothermic and endothermic reactions. Boo[7] found that about one sixth of her sample of A-level students thought that copper reacting with air was an endothermic reaction. Similar results were reported by de Vos and Verdonk[8] in the context of a candle burning. Students confused the activation energy with the total enthalpy change of the reaction.

Studies at university level have indicated that students have difficulty in coping with the abstract nature of the concepts and their complex relations. Rozier and Viennot[9] point out that most thermodynamic problems are multi-variable usually involving changes in pressure, temperature and volume. According to Rozier and Viennot[9], students treat the system as if the changes occur as a series of sequential steps and consider first (for example) the effects of pressure change, then of temperature change rather than dealing with both at the same time. They describe this type of reasoning as linear causal reasoning, an example of concrete operational thinking. Cachapuz et al[5] also reported this kind of reasoning in 17 year-olds, with students explaining an endothermic reaction as a two stage process in which energy is envisaged as being absorbed in bond-breaking, followed by energy release in bond formation.

Difficulties in dealing with the abstract nature of the concepts involved in thermodynamics is highlighted by Dixon and Emery[10]. They developed a way of categorizing concepts in order of abstraction. Energy, work and heat occur on the third level of abstraction (two levels above temperature, for example) while enthalpy is found at a higher level again, the fifth level.

Another source of difficulty for students trying to understand thermodynamics is that instead of treating energy changes as processes, they frequently treat energy (and heat) as matter. Chi et al[11] divide all scientific entities into three different ontological categories: Matter, Processes and Mental States (each of these categories subsumes a hierarchical series of subcategories). Pinto's[12] study of undergraduate physics students' understanding of thermodynamics shows that they had difficulties in distinguishing thermodynamic process and entities. For example, students had difficulties in envisaging doing work as a process of transferring energy and instead often viewed it as a form of energy. A similar finding, reported widely in the literature (e.g.[13]), is that the way students think and argue about heat would often place heat in the ontological category of Matter whereas it should be categorized as a Process (as the process by which energy is transferred between a hot object and a colder one). The representation of heat change as the symbol 'q' in thermodynamic equations reinforces this view, that heat is Matter, as it differentiates it from enthalpy change, represented by ΔH. Chi et al[11] maintain that, if the concept to be learned occurs in a different category from that in which a student's thinking would place it, then learning is more difficult. i.e. to shift his/her thinking into a different category – in the case of heat, from the Matter category into the Process category – is difficult to achieve. Chi et al[11] see this mismatch as being more important than the abstract nature of the concepts or that concepts are represented by mathematical expressions in accounting for the difficulty of learning some concepts.

Methodology

A sample consisting of 20 first year university chemistry students was chosen at random from the total year 1 cohort of 100 students. Students took a course of 13 one hour lectures at the rate of two lectures per week in the second semester of their first year. There were also 6 examples classes held once each week. The students had been successful at A-level and had grades A, B or C for chemistry.

The course developed both classical and statistical approaches. For example, internal energy and entropy were defined in terms of energy levels. On the other hand, enthalpy was dealt with entirely from the classical standpoint. Certain assumptions were made about students' knowledge and understanding; no explanations were given of the meaning of heat and work. Enthalpy was defined mathematically through its relationship to internal energy, ΔU

i.e. $\Delta H = \Delta U + p\Delta V$.

pV work was also defined mathematically in terms of the relationship

$$w = -\int_{v_1}^{v_2} p_{surr}\,dV$$

Examples class problems were relevant to the lectures; all were numerical problems.

Each student was interviewed for just over an hour before attending the lecture course and examples classes and then, again, after the course, shortly before their examination on the course. Four of the students failed to attend the second interview and could not be followed up because of imminent examinations. The data which follow refer only to the 16 students who attended both interviews.

Three familiar chemical reactions were performed in front of each student; questions were asked about the reasons for the temperature change and why the reaction happened for each reaction in turn before moving on to the next reaction. Each reaction was chosen to illustrate different thermodynamic ideas. The reactions were:

- the neutralization between 2 mol dm^{-3} hydrochloric acid and 2 mol dm^{-3} sodium hydroxide. This is exothermic and there are no visible changes other than temperature rise as shown on the thermometer.
- the reaction between magnesium and 2 mol dm^{-3} hydrochloric acid. This again is exothermic and the visible changes include the effervescence due to the evolution of hydrogen, the 'disappearance' of the magnesium and the rise in temperature as shown on the thermometer. It was hoped that the evolution of a gas would provoke the student into making comments about work being done by the gas.
- the dissolution of ammonium chloride in water. This is endothermic and the only visible change is dissolving of the ammonium chloride and the fall in temperature as read on the thermometer. This reaction was included because, at A-level, explanations in use at that level often fail when applied to endothermic reactions. Such explanations include the notion that chemical reactions proceed from reactants to products, from a higher to a lower level in energy terms.

Each reaction was carried out and students were encouraged to comment on observable changes, take temperature readings and to write appropriate equations. They were questioned about each reaction in turn about what had happened to produce the temperature change and why the reaction happened. If the students did not mention the terms enthalpy change, internal energy, entropy and free energy during the interview, they were asked specifically about them after all the reactions had been discussed. Questions asked about the chemical reactions were deliberately open questions so that the student could decide the terms within which to frame a response. The interview focused on the quality of students' understanding of the thermodynamic concepts and so supplementary questions were asked to explore students' responses and meanings. All interviews were tape-recorded and transcribed. The researcher also attended all the lectures and examples classes and made field notes about the content of these teaching sessions and the methods used.

Analysis consisted of constructing a list of thermodynamic statements to represent a scientific view of the concepts being explored (this was a subset of all the concepts which were covered in the lecture course). The list was validated by an expert in thermodynamics and checked against the course content. All transcripts were read carefully and the students' statements compared with the list of scientific statements; correct and alternative conceptions were identified and noted.

Results

The analysis which follows shows the students' understandings related to the concept of enthalpy change before and after they did the lecture course.

Quantitative overview of the data

Ten statements giving a scientific view of what is meant by enthalpy change are listed in Table 1. These form a list of the

Table 1 *Enthalpy change* This table is a list of statments which covers (except for specific heats) the knowledge and understanding about enthalpy change which would be expected of a good student at the end of a course in elementary chemical thermodynamics.

1. Enthalpy change is the energy transfer which occurs during a chemical reaction and is measured as heat. It takes into account any pV work done (and no other types of work).
2. pV work is work done when a change in volume occurs during a chemical reaction. Work is done by the chemical system against the atmosphere when there is an increase in volume (e.g. a gas is evolved) or on the system by the atmosphere when there is a decrease in volume.
3. The enthalpy change, ΔH, is equal to q, the heat, only when the pressure on the system is constant and only pV work is possible.
4. Enthalpy is a function of state, that is, it is dependent only on the initial and final thermodynamic states of the reacting substances.
5. The thermodynamic meaning of state includes not only the physical states of the substances concerned (solid, liquid or gas) but also the temperature, pressure and volume.
6. Hess's law is a consequence of the first law of thermodynamics: if reactants can be converted to products by more than one reaction pathway, the total energy transfer will be the same no matter by which pathway. This can be summarised as:
   $\Delta H^{\circ}reaction = \Re\, \Delta H^{\circ}_{f}[products] - \Re\, \Delta H^{\circ}_{f}[reactants]$
7. The standard enthalpy change of formation of a substance is defined as the energy released or absorbed when one mole of the pure substance is formed from its elements in their standard states. (The enthalpy change of formation of an element in its standard state is defined as zero).
8. In order to calculate the enthalpy change for a reaction, the standard enthalpy changes of formation of all the substances involved are required.
9. Standard conditions are 1 atmosphere or 10^5 Pa, substances must be pure and in their standard state. The temperature must also be stated.
10. The standard state of a substance refers to the physical state of the pure substance at standard pressure.

Table 2 *Numbers of student conceptions*. These tables give an indication of the numbers of students who had correct ideas and alternative conceptions for each statement of Table 1 both before and after the lecture course.

(Before the lecture course) N = 16

Statement	1	2	3	4	5	6	7	8	9	10
No. correct	0	0	0	0	0	10	3	3	0	0
No. alt. Conc.	16	3	0	0	0	6	4	10	10	1
Do not know		13				3				

(after the lecture course)

Statement	1	2	3	4	5	6	7	8	9	10
No. correct	2	4	1	0	1	10	1	8	5	2
No. alt. Conc.	14	9	0	0	3	2	2	3	7	2
Do not know		4								

concepts defining enthalpy change, which a good student would understand at the end of the course in elementary thermodynamics.

When the interview transcripts were read a note was made each time a student made a statement showing that he or she has understood one of the statements in Table 1 or had an an alternative conception.

Table 2 shows the number of students who had correct conceptions and the number of students who had alternative conceptions, for each of the ten propositions in the list.

Where 'Do not know' is recorded, this means that when a student was directly asked, he or she made it clear that that concept was not known. 'Do not know' was not assumed by the researcher if a student omitted to mention the concept. Not all statements in Table 1 formed the basis for direct questioning; direct questions were only asked about enthalpy change (statement 1), pV work (statement 2) and Hess's Law (statement 6). For the other statements, the open form of the questions meant that students were free to refer to a concept if it seemed relevant to them.

Students sometimes changed their minds, even in the same context, from alternative to correct (and occasionally the other way round) providing evidence of more than one conception. Other students had more than one alternative conception. This accounts for the apparent discrepancy where there appear to be more than 16 students and why there are several boxes with no responses recorded.

It can be seen that before the lecture course the students had no knowledge of pV work (Table 1, items 1,2 and 3) and that there was a small increase in students' understanding of this aspect of the course. Some students also became familiar with the importance of specifying standard conditions (Table 1, items 9 and 10). The strongest change in the correct explanations was in item 8 (Table 1) which is about calculating enthalpy changes of reactions. There is a small decrease in the overall numbers of alternative conceptions used by students between the two interviews, but many alternative conceptions were expressed both before and after the lecture course. The tables, however, give little indication of the quality and variety of the conceptions expressed. This is given below in a more detailed qualitative description of students' responses.

Understandings before a lecture course

Before the lecture course no students gave a scientifically correct explanation of enthalpy change. Their explanations can be characterized as lacking in precision or discrimination, being devoid of any understanding of pV work and viewing enthalpy as a 'form of energy'. Most students (12/16) described enthalpy change as an energy change and failed to mention the limiting conditions (See proposition 1,Table 1).

Student 1: Enthalpy change... it's the change in energy from the start to *finish of a reaction*.

Other responses seem to assume that enthalpy is just another form of energy and simply give an example of when there is an energy transfer.

Student 8: It's when one mole of water's produced when you're adding an acid and an alkali.

A third group of responses is formed of statements where students seem to treat enthalpy, activation energy, internal energy and entropy simply as different 'forms of energy'.

Student 5: ΔH will be the energy which is supplied to the reaction.

Student 2: … whereas the enthalpy change is the change that internal energy undergoes it might get hotter in which case the enthalpy change will be an increase.

Student 1: [Interviewer: What do you understand by entropy?] I usually get confused with enthalpy like it's [i.e. entropy] just another word for enthalpy.

Underlying the notion of 'forms of energy' is the view that energy is a quasi-material substance. It was never explicitly stated but many statements make such an inference plausible. A search of the literature reveals that even experts cannot agree on a suitable definition for energy though everyone would agree that it is not material.

While most students seemed to be aware that enthalpy changes were associated with endothermic reactions (though they were often unsure about the sign convention), one student firmly believed that endothermic reactions did not have an enthalpy change.

None of the students associated work with chemical reactions. For many of them, work was a concept only learned at GCSE and not encountered since (especially if they had no A-level in physics) and the concept of pV work was entirely unknown during the first interview. Students were only asked directly whether work was done in the context of reaction B (magnesium and hydrochloric acid). Some students believed that work was done when bonds were broken or made or when atoms were ionized.

Student 17: yes I suppose there was, magnesium had to change from its atomic state to the ionic state.

Student 18: yea work was done by having to break the bonds in the HCl 'cos work done means energy given out...

Other students denied that any work was done. None related the work done to the evolution of the hydrogen.

Understandings after the lecture course

There was little change in the quality of student responses about enthalpy change between the two interviews. Only two students gave a full and correct explanation of the meaning of enthalpy change. Again, explanations lacked precision and discrimination. The commonest conception again fell into the category of incomplete definitions of enthalpy change; this type of response was give by 9/16 of the students.

Student 1: As I said it's the heat flow between system and surroundings.

There were again several explanations consisting of definitions restricted to a specific type of reaction, such as neutralization... The 'forms of energy' explanations also persisted in many explanations (4/16).

Student 2: That's the heat changes or energy changes taking place in a reaction so whether from potential with little satchels moving to kinetic energy when they've dropped their satchels and they start running around..

The biggest change in students' conceptions related to enthalpy was their awareness of the concept of pV work. Four students provided an acceptable explanation of the meaning of pV work. Eight students showed an awareness of work but this awareness was accompanied by an increase in the variety of different alternative conceptions. Four students, even when questioned about work in the context of reaction B, still maintained that no work was done.

Only one alternative conception was given by more than one student; three students argued as follows:

Student 13: [Interviewer: Under what conditions does the production of a gas do work?] In a closed system … that's a closed system with a piston if there's a gas being produced there's be an increase in pressure in here and this piston would move out. [draws a diagram to illustrate].

When this statement is analysed, it seems likely that these students cannot envisage a gas being able to do work unless it pushes out a piston, which then does the work against the atmosphere. This is probably a relic of the calculation which converts the relationship: work = F ∞ d
to the relationship: work = $p\Delta V$.

A similar conception was of work done being associated with a weight being raised:

Student 8: It's work when you change the height of a weight or something so the gas has been released it's changed its height because it's gone from being in solution to being a gas.

This is clearly an attempt to make sense of definitions of work in text books which relate work to energy expended in raising weights.

In two conceptions it was argued that work was done because the temperature changed – up in one case, down in the other:

Student 19: … yes the formation of a gas caused work to be done because I think it's because you get a temperature rise in the gas given off.

A further conception suggested that, as gas leaves the system, it carries energy with it and identified this as work done. Other explanations proposed that work had been done because there had been a change of state:

Student 14: … well I suppose yea because it all changed.. it had changed its state.

As can be seen from the above examples, even though most students claimed to recognize the term pV work, its meaning remained far from clear.

During the second interview of this research, students were asked to explain what they understood by some of the common thermodynamic mathematical expressions such as $\Delta H = \Delta U + p\Delta V$. It was found that many of the students did no more than recognize the names of the symbols (and some not even that). In the case of this specific equation, 3 indicated that they understood what it meant, 5 students 'read' the symbols while 4 did not recognize the symbols correctly. On the whole, they appeared to have little understanding of the meanings of the equations.

Discussion

When students embark on an undergraduate course they have already developed frameworks for their ideas; these frameworks have been successful in coping with the requirements of A-level thermodynamics. Such frameworks are robust and resistant to modification or displacement by new conceptions.

One such framework which is particularly resistant to change is that of regarding energy as functioning in different inter-convertible forms. One of the difficulties which arise from this way of thinking about energy is that students incorporate new ideas such as enthalpy into this framework. While there was a small amount of improvement in the understanding of enthalpy as a result of the lecture course, it was clear that students did not see the meaning of enthalpy as problematical and did not, therefore seek to probe for any deeper meaning.

The lecturer for the first year course on chemical thermodynamics during which this research was carried out provided the researcher with a list of concepts which he would assume that students already knew. He assumed that students had a prior understanding of the concepts of heat and work. Neither concept was explained beyond introducing them as the symbols, q and w.The concepts of heat and work involve the use of words which are in everyday use and have different meanings for thermodynamics experts from these everyday meanings[14]. No assumptions were made about student knowledge of enthalpy, even though it is a concept which appears in all A-level syllabuses, but the lecturer was not aware of the prior ideas about enthalpy which the students had already developed.

Students' lack of understanding about work (and lack of any knowledge of pV work) means that it was inevitable that they would have had a limited knowledge of enthalpy at the beginning of the course.

Implications for teaching

In the constructivist view of learning, learners actively construct their own meanings which are affected by what they already know[15]. As Laurillard[16] points out, how students deal with new knowledge depends on the knowledge they bring with them to a lecture course; in this case, inadequate conceptions of enthalpy are already part of their mental 'baggage'. However, this is not the only influence on learning; learning is not a process carried out in isolation – learners construct their meanings as a result of interaction with the world around them. This interaction includes discussion with their peers, with their teachers and the more formal situations of the lecture theatre. The way lecturers present material is affected by their own private understandings, which are underpinned by an array of concepts, most of which are implicit.

It would seem essential, in the light of these arguments, that a lecturer needs to be aware at the outset of a course, of the alternative prior understandings students are likely to have. Actual student statements about concepts from research such as this can be used as problems to test future students' understanding and to encourage students to think about the problems for themselves.

There is clear evidence in this research that students do not understand the meaning of expressions like $\Delta H = \Delta U + p\Delta V$. It seems unreasonable to expect students to read into an expression like this all the meaning that is built into it and which is understood by expert thermodynamicists. It is important that thermodynamic entities are defined qualitatively and their effects talked about before they are defined quantitatively. Problems could be set that could be answered in qualitative terms and only later, when there is a reasonable understanding of the meanings attached to the thermodynamic entity should numerical calculations be introduced. This suggests a reversal from the usual procedure where calculations are set, students become proficient at manipulating the numbers to get the correct answer, with understanding following much later if at all.

It is worth pointing out that in the research exercise reported in this paper students were expected to apply their thermodynamic knowledge to real chemical reactions in a way which probed their understanding in depth. This is in contrast to the way in which assessment of thermodynamic knowledge usually takes place, that is, by expecting proficiency in performing calculations and in the rote learning of mathematical definitions. This implies that it is necessary not only to rethink the way thermodynamics is taught but also the way it is assessed.

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