Paper

Turkish chemistry undergraduate students' misunderstandings of Gibbs free energy

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Abstract

This study is aimed at identifying and classifying Turkish chemistry undergraduates' misunderstandings of Gibbs free energy. In order to fulfill this aim, open-ended diagnostic questions and semi-structured interviews were used, conducted both before and after the topic was taught. Diagnostic questions were answered as pre-tests and post-tests by about forty-five students who took physical chemistry courses from two different chemistry education departments in two different universities in Turkey. Twenty-two 'pre-interviews' and five 'post-interviews' were carried out just after the administration of the tests. Seven different misunderstandings were identified. Although some of the findings of this study confirm the previous research findings, it goes beyond them by identifying new misunderstandings and suggests places where these misunderstandings may originate. The results have implications for tertiary level teaching, suggesting that a substantial review of teaching strategies is needed.

Introduction

Ever since the classical studies of Piaget, there has been an interest in the conceptions of physical science held by young children.[1] Even a casual observer of the field of science education over the last two decades knows that this has been a period of unprecedented exposure of the ideas held by children, adolescents, and adults, about a wide range of scientific phenomena.[2, 3] Research in this domain has attempted to answer questions such as, which misunderstandings occur, what are their origins, how extensive are they and, of course, what can be done about them?[4] It is quite understandable why students' ideas concerning chemical phenomena have become a research focus. Many students both at secondary level and at university struggle to learn chemistry and many do not succeed.[5] Research now shows that many students do not understand fundamental concepts correctly[2] and also many of the scientifically incorrect ideas held by the students go unchanged from the early years of the schooling to university, even up to adulthood.[4] By not fully and appropriately understanding fundamental concepts, many students have trouble understanding the more advanced concepts that build on them.[6]

The constructivist theory of learning suggests that knowledge is constructed through a process of interaction between an outside stimulus and conceptions that already exist in the learner's head. During this process, some of the existing conceptions are modified and some new ones created. Different views on the nature of students' understanding, and differences in the methodologies employed to discover students' conceptions led researchers to make different claims. One of the widely discussed theories in science learning is that 'children's conceptions are genuinely 'theory-like', that is having a coherent internal structure and being used consistently in different contexts'.[7] This notion is articulated by McCloskey,[8] and supported by Engel Clough and Driver.[9] McCloskey argues that people develop well-articulated naive theories on the basis of their everyday experiences. Furthermore, he argues that these naive theories are consistent across individuals. On the other hand, diSessa[10] raises issues to do with the nature of misunderstandings. He questions the views of McCloskey and argues that people hold loosely connected, fragmented ideas, some of which reinforce each other but none of which have the rigour of theory. In diSessa's words, students have 'knowledge in pieces'. diSessa goes on to suggest that there is evidence in his work of students making up explanations spontaneously at the point which they are faced with a question, drawing where they can on core intuitions based on everyday experience. (He calls these notions phenomenological primitives, or p-prims.) Later work, for example that of Southerland et al.,[11] provides additional support for the notion that students make up explanations spontaneously. Therefore, students' explanations may not be misunderstandings; rather they are spontaneous constructions that might be scientifically correct or incorrect. Southerland et al.[11] also argue that, if it is accepted that some students reason from core intuition, a great deal of variability in students' explanations is to be expected.

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Many high school and university students experience difficulties with fundamental thermodynamics ideas in chemistry.[12] Despite the importance of thermodynamics as one of the foundations of chemistry, most students emerge from introductory courses with only very limited understanding of this subject.[13] Gibbs free energy is thought by students as one of the most difficult ideas in chemistry. There have been a limited number of researches carried out upper secondary level[14] and university.[6, 12, 15, 16,]

Johnstone et al.[14] observed that A-level students had some serious misunderstandings about Gibbs free energy. It was found that nearly a quarter of the subjects thought that if a reaction had a large Gibbs free energy change it would occur rapidly. The researchers also thought that there was a misunderstanding, which was not tested, that the net rate of the reaction in a system tends to zero as equilibrium is approached. They suggested that this was because of the fact that the value of ΔG tends to zero. It was also suggested that the reason misunderstandings of thermodynamics ideas arose among high school students was because of the fact that they are not mature enough to appreciate the conceptual subtleties of the subject. The remedies for these kinds of misunderstandings might include the suggestions[14] that students should avoid using too much mathematics during the learning of the ideas of thermodynamics, and also that students should be helped to make the correct connections with their existing knowledge.

Banerjee[12] carried out a research with sixty third-semester college students (B.Sc. Ed.) in order to find out their ideas of chemical equilibrium and thermodynamics. An achievement test on thermodynamics and equilibrium was developed and given after 12 weeks to assess the conceptual understanding and problem-solving abilities of the students. Many widespread misunderstandings were revealed. One of those was that in an equilibrium reaction, a high negative value of ΔH and positive value of $T\Delta S$, make the right-hand side of the equation negative. Hence, ΔG is negative and the reaction is spontaneous. In this explanation, the problem lies behind the interpretation, although the logic is correct. The tendency to lower Gibbs free energy is solely a tendency toward greater overall entropy. Systems change spontaneously solely because that increases the entropy of the universe, not because they tend to lower energy. ΔG is a measure of the change in the entropy of the universe caused by the reaction. The equation: $\Delta G = \Delta H - T\,\Delta S$ gives the impression that systems favour lower energy, but this is misleading. ΔS is the entropy of the system and, $\Delta H/T$ is the entropy change of the surroundings. Total entropy tends toward maximum for spontaneous reactions.[12] The second misunderstanding was identified from the question: '*Draw a graph of Gibbs free energy versus the extent of the reaction: A → B*'. Students thought that Gibbs free energy would increase or decrease linearly to make the reaction spontaneous either in the direction A → B or B → A depending on whether A (reactant) or B (product) initially had more Gibbs free energy. Bannerjee comments that students were not able to conceptualise that Gibbs free energy has the lowest value at the equilibrium position. The researcher also argues that these kinds of misunderstandings should not be thought of being confined to this sample, they might be widespread among students and even teachers.

Carson and Watson[15] conducted a qualitative research with twenty first-year undergraduates drawn from a cohort of 100 students attending a university chemistry department in England. Their results suggest that students found Gibbs free energy an obscure concept even after the lecture course. Students were familiar with the concept but showed no understanding. The only aspect students knew was that it had to be negative for a reaction to be possible. In a study, carried out by Selepe and Bradley[16] with student teachers in South Africa, it was reported that students' understanding of Gibbs free energy was rather superficial. Six out of ten students said that Gibbs free energy is the energy taken out or lost by the system during a reaction. In addition, two out of ten argued that Gibbs free energy is the energy that has not been used to make the reaction to occur and that Gibbs free energy is the internal energy that makes substances react.

In a recent study Thomas[6] studied students' misunderstandings in thermodynamic concepts in physical chemistry. It was reported that students considered that ΔG^{θ} is the same as ΔG except that ΔG^{θ} is measured at a standard temperature (298K) and standard pressure (1 bar), whereas, ΔG is measured at any particular temperature and pressure. It was also reported that students confused ΔG (the change in Gibbs free energy between two states) with Gibbs free energy itself so that the Gibbs free energy of the system either asymptotically approaches zero or goes to zero at equilibrium. In another study it was reported that students perceived Gibbs free energy as the thermal energy transferred into or out of the system.[17]

The purpose of the study

This study is aimed at identifying and classifying Turkish chemistry undergraduates' misunderstandings of Gibbs free energy

In order to fulfill this aim, open-ended diagnostic questions and semi-structured interviews were used, conducted both before and after the topic was

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taught. Although some of the findings here confirm those reported previously, it goes beyond them by identifying new misunderstandings and suggests places where these misunderstandings may originate. This is particularly important in order to be able to take corrective action.

Methodology

This study is part of a continuing research project.[18] A diagnostic questionnaire consisting of open-ended questions on key chemical ideas in thermodynamics, including three questions on Gibbs free energy, was developed and applied twice as 'pre-test' and 'post-test' with seven months interval to a total of about forty five students who followed physical chemistry courses in two Chemistry Education Departments in two different universities in Turkey. Physical Chemistry is introduced in the third year and the course contents were similar in both departments. One of the participating universities is situated in western and the other is situated in eastern Turkey. The administration of the diagnostic questionnaires was carried out by the researcher in a lecture hour (50 minute). Students were not permitted to take the diagnostic questionnaires out of classroom or discuss it with their friends and their lecturers.

In this study it was accepted that a good diagnostic question is one that generates information that accesses respondents' thinking about the ideas being explored (Sozbilir[18]; p.331). The three diagnostic questions used in this study tested the following ideas related to Gibbs free energy:

- The magnitude of $\Delta_r G$ indicates how far the reaction is from equilibrium at a given composition but it does not give any information about the rate of a reaction.
- A more negative value of $\Delta_r G$ indicates the greater the probability that the reaction will occur, and also the more negative value of $\Delta_r G^0$, the larger positive value of the reaction equilibrium constant, K.
- The Gibbs energy change tends to become zero when the system approaches equilibrium and is zero at equilibrium.
- Thermodynamic quantities tell us nothing about rates of reactions.

A sample question can be seen in Appendix showing the ideas are being tested and the expected answer (For the complete diagnostic questionnaire see Sozbilir[18] pp. 385-405). The first analysis of the students' responses to the diagnostic questions identified a set of misunderstandings about Gibbs free energy. Following this, frequencies of the misunderstandings were determined and tabled.

A number of interviews were carried out just after the pre-test and the post-test in order to support the data obtained from the questionnaires. The interviews held after the pre-test (twenty-two interviews) sought to reveal the students' understanding of all the key ideas that were investigated in the entire study, including Gibbs free energy. Five post-interviews sought to explore the students' understanding of Gibbs free energy in detail. Therefore, there are more pre-interviews than post-interviews. The interviewees were all volunteers and the interviews took place in a staff office on one-to-one basis. Each interview was tape recorded and then transcribed fully. Students' permission to tape-record the interview was sought in each case. Interview times varied between half an hour and 45 minutes. Students were not told about the content before the interviews, but they were aware that they would be covering the same topics as the questionnaire. The interviews were not carried out as a free-standing study and so were not subjected to rigorous analysis. Selected extracts from these interviews are reported here to illustrate and support the evidence found from the questionnaire data.

Results

An overview of the undergraduates' misunderstandings before and after teaching is given below, followed by detailed examination of some of the students' responses. Table 1 shows the percentages of the misunderstandings identified before and after teaching. The percentages in the tables may be seen as reasonable low. However,

Table 1. Common misunderstandings about Gibbs free energy

No	Misunderstandings Identified	Pre-test n=46	Post-test n=44
1	The slower the reaction, the smaller change in Gibbs energy	6%	13%
2	The bigger the Gibbs energy change, the faster a reaction occurs.	6%	<5%
3	The smaller $\Delta_r G^\theta$, the faster the reaction occurs.	<5%	34%
4	The bigger $\Delta_r G^\theta$, the faster the reaction occurs.	20%	11%
5	The reaction with bigger $\Delta_r G^\theta$ goes towards full completion.	<5%	6%
6	If a reaction occurs fast, it goes towards full completion.	<5%	11%
7	Incorrect drawings	16%	23%

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the percentage of blank responses was as high as 50% for some of the questions, indicating that students have almost no knowledge of Gibbs free energy. This high blank response rate lowers the percentages of misunderstandings revealed. In the quotations from students' responses such as ($OT_2/E/S_{13}$); **OT** and **ST** stand for the pre-test and the post-test respectively, **E** and **B** stand for the institutions where the data collected and **S** stands for the student. In the quotations from the interviews such as ($SI/B/S_1$); **OI** and **SI** stand for pre-interview and post-interview respectively, **E** and **B** stand for the institutions where the date collected and **S** stands for the student. In addition, **R** and **I** stand for the researcher and the interviewee respectively.

The slower the reaction the smaller change in Gibbs free energy:

This misunderstanding increased from 6% in the pre-test to 13% in the post-test. Students simply argued that if a reaction takes place very slowly, the change in Gibbs free energy must be less indicating a belief that there is a relationship between the reaction rate and magnitude of Gibbs free energy change in the students' mind. This misunderstanding suggests that students cannot differentiate between the kinetics and the thermodynamics of a chemical reaction.

Some of the responses quoted below reflect the students' views.

"Since the reaction proceeds slowly, Gibbs free energy change must be negative and close to zero ($ST_1/E/S_{11}$)".

"... because Gibbs free energy change must be very small as the reaction occurs very slowly ($ST_1/B/S_{13}$). "

The bigger Gibbs free energy change means the faster the reaction occurs:

The students simply argued that if the Gibbs free energy change of a reaction is large, the reaction takes place faster; this is exemplified by one respondent's answer below.

"The bigger the Gibbs free energy change the faster the reaction occurs. Gibbs free energy changes must be small for the reaction [transformation of diamond to graphite] as the reaction occurs very slowly ($OT_1/E/S_{11}$)."

The student directly related the magnitude of Gibbs free energy to the rate of reaction. This misunderstanding was also highlighted by Johnstone et al.[14] who reported that one A-level student in four considered that a reaction for which the Gibbs free energy change is large occurs rapidly (p.249). It is apparent from the findings of this study that undergraduates in Turkey also hold the same misunderstanding. The above two misunderstandings possibly originated from an analogy with the macrophysical world that 'the further things fall, the faster they go', or even 'the more energy provided, the higher the velocity'. Undergraduates seemed to confuse the common sense ideas of physics with chemical thermodynamics, due to a poor understanding of Gibbs free energy and chemical thermodynamics.[14] The interviews that took place after teaching also provided evidence that students thought along similar lines, as shown by the responses to the diagnostic questions:

"R: ... could you tell me, can we make a guess about the rate of a reaction by looking at the magnitude of a reaction Gibbs free energy value?"

"I: if... one... If a reaction occurs spontaneously yes... rate of a reaction... I am telling what I think right now."

"R: OK, that's OK."

"I: If a reaction does not occur spontaneously, it means, it occurs at low rates."

"R: Can we decide (rate of a reaction) by looking at the Gibbs free energy value? Let's say we have two reactions, one has positive Gibbs free energy one has negative Gibbs free energy. What do you think in this case?"

"I: At first glance, It seems positive...because it has positive Gibbs free energy, it means it occurs more rapidly. The other one must be slower because it has negative Gibbs free energy."

"R: You are saying that if $\Delta G > 0$ it occurs faster! What about the case where both of them have negative ΔG. Let's say both of the reactions have negative ΔG, one of them has -20 KJ/mol and the other one has -40 KJ/mol. In this case which one do you think occurs more rapidly?"

"I: The one with a bigger magnitude."

"R: Which one, 40?"

"I: No, -20, because it is bigger than -40 mathematically. "

"R: Why that so?"

"I: Only because of the mathematical value of them. The bigger value is bigger, and the smaller value is small. I decided according to the mathematical value of them. I don't know any more about Gibbs free energy. Mathematically it (means -20) is bigger. ($SI/E/S_4$)"

As seen from the beginning of the preceding discussion, the interviewee was not aware of the spontaneity of a reaction. She argued that if a reaction does not occur spontaneously, it occurs at low rates. She may have had the misunderstanding that spontaneous reactions occur quickly. Selepe and Bradley[16] argued that students perceived 'spontaneous' as 'immediate or rapid action' and as a result it was thought that slow reactions were not spontaneous. Subsequently, the interviewee also showed no understanding of the positive and negative values of Gibbs free energy. This is interesting, because at the beginning of the

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interview she displayed some knowledge about Gibbs free energy: stating that if $\Delta G > 0$ reaction does not occur, if $\Delta G = 0$ reaction is at equilibrium and, if $\Delta G < 0$ reaction occurs spontaneously. In answer to a subsequent question, the interviewee approached the problem from a solely mathematical standpoint and did not consider any chemical aspects. She simply compared the magnitudes of Gibbs free energy values mathematically. She also admitted that it was a guess, because the interviewee also declared that she did not know anything more about Gibbs free energy. This way of reasoning perhaps explains the source of the above misunderstandings in that students look at the mathematical values without an understanding of the underlying chemical ideas.

The smaller $\Delta_r G^0$, the faster the reaction occurs:
This particular misunderstanding was widely identified in the post-test responses. 34% of the students argued that the rate of the reaction is directly proportional to the magnitude of the Gibbs free energy change by stating that the smaller $\Delta_r G^0$, the faster the reaction occurs. The answers showed that there is a strong belief among the undergraduates, that the Gibbs free energy change of a reaction gives an indication of the rate of the reaction. Some of the responses are quoted below:
"We can compare the rate of the reactions. The reaction with small change in Gibbs free energy occurs faster... ($OT_2/B/S_1$)."
"To become spontaneous $\Delta_r G^0$ must be smaller than zero. The smaller the Gibbs free energy the faster the reaction happens. So, the second reaction occurs faster than the first one ($ST_2/B/S_5$)."

Although it was not clear why the respondents thought in this way, one can speculate from the nature of the students' responses. These showed two different approaches. The misunderstanding in the pre-test, that *the bigger $\Delta_r G^\theta$, the faster the reaction occurs* changed in the post-test to the misunderstanding that *the smaller $\Delta_r G^\theta$, the faster the reaction occurs*. This significant shift can be explained by examining the students' reasoning. In the pre-test, students tended to use their everyday experiences to explain phenomena such as the rusting of iron, whereas in the post-test they mostly tended to explain the phenomena in terms of phase changes occurring in the reaction and energy exchange accompanying the reaction. This shift suggests that teaching may replace particular misunderstandings with others rather than eliminating them. Hence, teachers and lecturers should be aware of this reality. Students developed a new way of approaching the problem as well as developing new misunderstandings.

The bigger $\Delta_r G^0$, the faster the reaction occurs:
This misunderstanding is the opposite of the above. However in contrast to the above, this was identified in 20% of the pre-test responses and dropped to 11% in the post-test. Students simply argued that if the Gibbs free energy change is bigger, then the reaction occurs faster as quoted below:
"The bigger the Gibbs free energy the faster the reaction happens ($OT_2/B/S_{11}$)."
"The first reaction $[CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}]$ *occurs fast. Since its $\Delta_r G^\theta$ is big. In addition, transformation from gas to liquid happens faster compared to solid ($ST_2/B/S_{16}$)".*
"The Gibbs free energy change of first reaction is bigger. Therefore the kinetic energy becomes more, I think, the first reaction occurs faster ($OT_2/E/S_{12}$)."

Students approached the problem from different points of view. Some approached it from a macrophysical point of view, as illustrated in the second quotation, by considering phase changes. In the first reaction the reactants are in the gaseous phase and the product is in the liquid phase, but in the second reaction $[4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}]$ the product is in the solid phase. Perhaps they thought that making a solid from the gas must take more time compared to making a liquid from gas reactants. In addition, some of them related Gibbs free energy to kinetic energy, as in the third quotation above. Students seemed to be confused between kinetic energy and entropy. Perhaps they thought about the relationship between Gibbs free energy and entropy hence they ended with the above misunderstanding, as entropy contributes to Gibbs free energy, and so Gibbs free energy must have a close relationship with kinetic energy, according to students.

The reaction with bigger $\Delta_r G^0$ goes towards full completion:
This particular misunderstanding was not evident in the pre-test but 6% of the post-test responses contained this misunderstanding. Students simply argued that if the Gibbs free energy change of a reaction is larger, it goes towards full completion. One of the respondents explained that if the Gibbs free energy change becomes large the reaction occurs rapidly, so it goes towards full completion. This kind of response suggests that students did not adequately understand the difference between reaction kinetics, thermodynamics and chemical equilibrium.

If a reaction occurs fast it goes towards full completion:
"If a reaction happens faster it produces more products and goes toward full completion ($ST_2/B/S_9$)."

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The above quotation and many similar others suggest that students have no understanding of reaction kinetics and of the equilibrium state, though every reaction has a different rate at different stages of the reaction. Students displayed the misunderstanding, that if a reaction occurs quickly, all the reactants will be converted into products. The probable origin of this misunderstanding is the assumption that all the reactions go to full completion. Perhaps students did not appreciate the fact that every reaction reaches an equilibrium point where the rates of the forward and reverse reactions are equal. That means that some of the products turn to reactants again. Alternatively, students may misunderstand the meaning of full completion of a reaction.

Incorrect drawings:

16% of respondents in the pre-test and 23% in the post test drew the incorrect representations shown in Figure 1 to reflect the Gibbs free energy change versus the extent of reaction for a hypothetical A → B reaction (see Appendix for the question).

In the post-test, one in four students drew the correct graph and provided a correct explanation. However, there were several incorrect drawings, as shown below. In a study conducted by Banerjee,[12] in response to a similar question undergraduates mostly drew the graph (d). The students argued that Gibbs free energy increases or decreases linearly to make the reaction spontaneous in either direction A → B or B→ A, depending on whether A (reactant) or B (product) had more Gibbs free energy to start with (p. 881). Banerjee[12] suggests that these incorrect ideas may originate from the fact that at equilibrium Gibbs free energy is at its lowest. The fact that the Gibbs free energy change tends to zero as the system approaches equilibrium and becomes zero at equilibrium, had not registered in the undergraduates' mind. A few respondents stated that Gibbs free energy becomes zero at equilibrium, indicating that students' confused Gibbs free energy change and Gibbs free energy itself because it is Gibbs free energy change that becomes zero at equilibrium.

The pre and post-interviews revealed some new misunderstandings about Gibbs free energy that were not identified through the diagnostic questions. In the pre-interviews, students were only asked what they knew about Gibbs free energy and why Gibbs energy is also known as 'free energy'. Students' responses showed either very little or no understanding of free energy. The only fact many students remembered was that it helps to estimate whether a chemical reaction occurs or not as illustrated below:

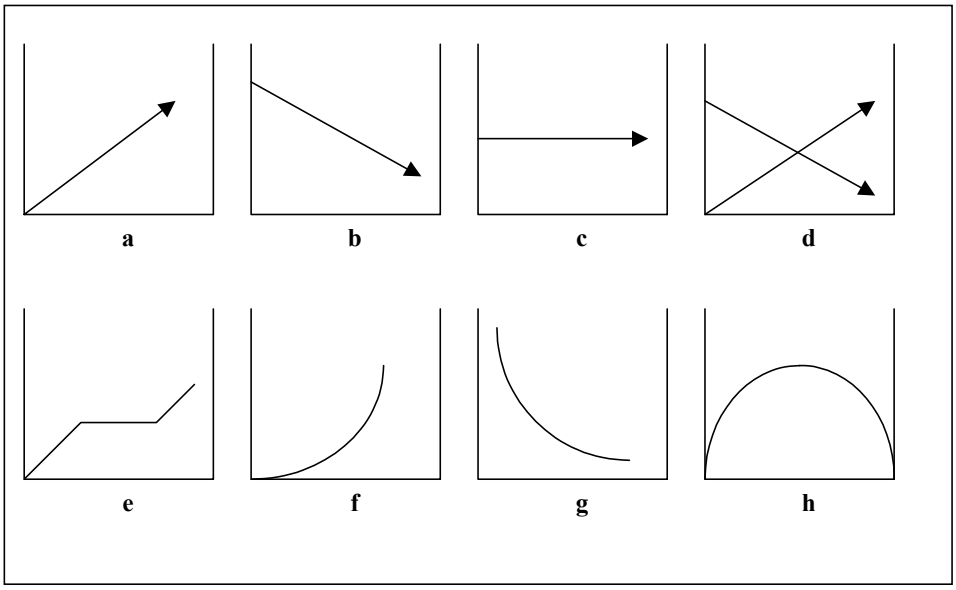
"R: Could you tell me what do you know about Gibbs free energy?"

"I: ...emm... it helps us to estimate whether a reaction happens or not. Enthalpy and entropy are used in calculation of Gibbs free energy. There is an equation.

$\Delta G = \Delta H - T\Delta S$. In this equation if $\Delta G < 0$, I think the reaction happens, if $\Delta G > 0$ it does not happen. If $\Delta G = 0$ it is in equilibrium (OI/E/S_1)"

A few of the interviewees demonstrated some knowledge of 'Gibbs free energy change' such as it is equal to 'maximum amount of work' without showing that they knew what is meant by

Figure 1. Incorrect drawings to reflect Gibbs free energy change versus extent of a hypothetical A → B reaction



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'maximum amount of work' or 'non-expansion work'. These suggest only a superficial understanding of the idea. However, when students' were asked a question about the nature of Gibbs free energy, the responses were mainly composed of guesses and showed little scientific understanding as shown below:

"R: Gibbs energy is called as Gibbs free energy as you know. Could you tell me why it was called as Gibbs free energy? Where may it come from?"

"I: It is a kind of energy when molecules are stable, they don't move, or it has in it when it is free... (OI/B/S_5)."

In another interview, one of the interviewees responded to the same question as follows:

"I: free [long silence] *it may be energy of substances when they are free (OI/E/S_5)."*

The interviewees' responses reflect the everyday meaning of word 'free', unlike what is meant by 'Gibbs free energy' in chemistry. At this point it is important to note that the nature of the Gibbs free energy is missed out in most of the textbooks, and also linked to this, it is not included in many physical chemistry courses. Most of the courses follow the quantitative problem-solving strategy in presenting physical chemistry to the undergraduates. Textbooks often describe Gibbs free energy in terms of its quantitative aspects with no explanations about its meaning. Under these circumstances, it is understandable if students don't understand the philosophy behind the Gibbs free energy.

The post-interviews demonstrated some additional misunderstandings about the concepts related to Gibbs free energy. These misunderstandings gathered around spontaneity and Gibbs free energy, and reaction rate and the magnitude of Gibbs free energy change. Students' understanding of the spontaneity of a reaction was limited, as they argued that if there is no external interference in the reaction it is spontaneous. Scientifically, a spontaneous process is one that has a tendency to occur, as determined by a negative Gibbs free energy change.[16] Students' understanding of 'spontaneous' shows parallels with meanings used in everyday language, as Ochs[13] argues. This can be seen from the following dialogue:

"R: What do you mean by spontaneous?"

"I: Without an external influence, if the conditions are available a reaction can happen without an external help, it happens spontaneously."

"R: Can you give me an example?"

"I: Yes, rusting, rusting of iron..."

"R: Could you tell me how can you understand whether a chemical reaction occurs spontaneously or not? Is there a criterion? If yes, what is the criterion?"

"I: Of course there is, reaction heat, reaction enthalpy. At constant temperature, I mean, in a spontaneous reaction, reaction enthalpy should be smaller than zero."

"R: Do you mean the reaction should be exothermic?"

"I: ... emm... exothermic, endothermic in fact it is not conditional at the end. I think enthalpy should be considered, we know like this (SI/B/S_{10})."

The interviewee's understanding of spontaneity is different from the scientific one. In many similar responses students repeated the everyday meaning of spontaneous. It is also clear from the dialogue that the interviewee did not understand the criterion for a spontaneous reaction, which is a widespread misunderstanding amongst the undergraduates. They perceive enthalpy as a criterion for the spontaneity of a reaction instead of Gibbs free energy. Similar findings were also noted by Selepe and Bradley.[16] Ochs[13] argues that the word spontaneous, as used in the context of chemical thermodynamics, is inconsistent and often misleading. It is commonly used without definition and its meaning varies amongst authors using it. The dictionary definitions do not fit the strict chemical definition of a negative change in Gibbs free energy.

Discussion

The key findings of this study can be summarized as follows. Many students were unable to answer the questions testing their ideas related to Gibbs free energy, as the blank response rate was as high as 50% for some of the questions. It was also apparent that a large number of students, who responded to the questions, demonstrated no understanding or included misunderstandings. The study confirms the earlier studies that undergraduate chemistry students' have serious misunderstandings about Gibbs free energy and often confuse key chemical ideas such as energy, enthalpy and entropy in thermodynamics (Sozbilir[18], Selepe and Bradley[16]). These results confirm that many find it difficult to grasp the advanced thermodynamic ideas with no or little understanding of the key underlying chemical ideas. Some misunderstandings could be correlated with some of the prerequisite concepts. Some of the misunderstandings about Gibbs free energy seemed to originate from a lack of understanding or ignorance of related ideas, such as equilibrium and reaction dynamics, energy, energy transformations and the change in energy involving in chemical reactions. The lack of knowledge of fundamental concepts, as it is well known, may generate subsequent misunderstandings. Therefore, care has to be taken to establish a secure knowledge of fundamental chemical ideas before teaching advanced ideas. For example, in this case, lecturers

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could check students' understanding of energy, the change in energy (i.e. establishing that the students are aware of the difference between G and ΔG, H and ΔH), enthalpy and entropy before teaching Gibbs free energy.

Very significant misunderstandings were concerned with using thermodynamic data to throw light on the kinetics of a reaction, since undergraduates failed to differentiate between kinetics and thermodynamics. There was also evidence that students had difficulty with the nature of Gibbs free energy itself. When students were faced with a question concerning the nature of Gibbs free energy, as discussed in the previous section, they failed to offer a meaningful explanation of it.

While it is difficult to be definite about the sources of misunderstandings, the following could play a significant part. As discussed earlier, some of the misunderstandings seemed to originate from the incorrect application of everyday experiences and definitions to chemical events and to the meanings of thermodynamic terms. In addition, some problems seemed also to have originated from the students' lack of mathematical knowledge since physical chemistry often involve a lot of complicated mathematics. A solution to this problem would be to teach the topics in a less mathematical way and to put more effort into the teaching of conceptual understanding. Moreover, application of algorithms without conceptual understanding could be a possible source of misunderstandings. In relying on memorization of scientific laws without understanding the underlying principles behind them is also another possible source for the misunderstandings. For example, the difficulty in recognizing the difference between 'Gibbs free energy' and 'Gibbs free energy change' is of this kind. This difficulty may also originate from the strategies applied during teaching. If no attempt has been made by the lecturers to help student to see the overall picture about the Gibbs free energy and related ideas, students would find difficult to conceptualize and differentiate the closely related ideas. The findings of this study suggest that lecturers should design these courses in such way that facilitates students to see clearly the difference between G and ΔG and also know that it is 'the change in Gibbs free energy' that becomes zero at equilibrium *not* Gibbs free energy.

The students' drawings also demonstrated a limited understanding of Gibbs free energy and displayed misunderstandings and confusions. Moreover, the results suggested that students were quite likely to develop new misunderstandings after teaching in some cases whereas some of the misunderstandings persist. The reinforcement of some of the misunderstandings rather than elimination of them after teaching deserves more consideration. As seen from Table 1, misunderstandings 1, 3, 6, and 7 increased after teaching rather than eliminated. This increase could in part be attributed to an increase in the number of responses after teaching. In the pre-test more than 50% of the responses were blank compared to the relatively fewer blank responses (less than 40%) in the post-test. For example, when 53% of the pre-test responses were blank, the misunderstanding that the smaller $\Delta_f G^\theta$, the faster the reaction occurs identified at less than 5% of the responses whereas it is identified in 34% of the responses in the post-test where only 30% of the responses were blank. As the number of responses increased, the possibility of revealing students' misunderstandings increased.

Finally, although some suggestions have been made about the possible sources of the misunderstandings, it should be borne in mind that tracing the origins of misunderstandings is a highly speculative enterprise. The origins of such conceptions are often hidden and therefore difficult to study using empirical methods.[20] The conceptual history of the individual should be traced in order to be able to produce strong evidence. However, the commonality of the misunderstandings across different cultures and populations suggest that outside effects such as instructional practices, textbooks and the excessive reliance on everyday language, should be considered as potential sources of misunderstandings.

Implications for teaching

Although the results of this study are based on a small sample in Turkey, it is likely that many of these misunderstandings would be found among physical chemistry students elsewhere. Therefore, these findings may provide some clues about the quality of student learning in typical physical chemistry classes. This study suggests that a substantial review of teaching strategies at tertiary level is essential. Physical chemistry instructors may sometimes overestimate students' understandings of the key chemical concepts and underestimate their difficulties in acquiring them. If instructors recognize the possibility of misunderstandings concerning basic concepts and difficulty of learning advanced level concepts on the basis of these misunderstandings they will be better able to teach difficult concepts. The research in this area suggests that attempts made in order to overcome students' misunderstandings should focus on 'identifying and modifying students' preconceptions' and 'teach students how to monitor and control their learning'.[20] Diagnostic questions are among the most frequently used technique for identifying students' preconceptions together with

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interviews, concept mapping and classroom discussions. The diagnostic questions used in this study (an example is given in Appendix) were found to be successful in identifying some student' misunderstandings. Therefore, it could be useful in the light of the evidence gained from this research that a systematic simple diagnostic test be used prior to teaching the topic in order to identify students' existing misunderstandings. Similar open-ended diagnostic questions, as given in Appendix, would be useful in identifying whether students hold the unscientific ideas such as confusion of G and ΔG, thinking that ΔG decreases or increases linearly in equilibrium and G is equal to zero at equilibrium rather than ΔG. Moreover, the other questions used in the study (see Sozbilir[18] pp. 385-405) were successful in identifying students' misunderstandings, such as confusing reaction kinetics and thermodynamics, and also the state of reaction equilibrium and reaction thermodynamic values. A practical alternative to diagnostic questionnaire would be classroom discussions, which can provide a wealth of information about the students' existing knowledge. Once students' ideas have been identified, the task of modifying those ideas begins. Several different successful conceptual change and cooperative learning approaches, including (for example conflict and confrontation, problem based learning, context based learning strategies etc) have been reported in the literature so far.[20] Accomplishing meaningful learning may be facilitated by a combination of individual, small-group and whole-class activities in which alternative explanations and descriptions of scientific phenomena are verbalized, justified, debated, tested and applied to new situations as suggested by Wandersee et al.[20]

Another possibility might be to focus on the quality of students' learning rather than quantity of concepts covered during the course.[6] Students may require extensive help to revise their thinking about the concepts and acquire the correct scientific meanings. Otherwise, although students correctly answer the examination questions, they may still hold on to their misunderstandings. It is also important to recognize the importance of the examination questions. In physical chemistry exams, questions mostly require quantitative solutions rather than qualitative discussions. It is suggested by Carson and Watson[15] that questions need to be of a kind that required students to demonstrate an understanding of the concepts involved. Mathematical calculations promote algorithmic learning rather than conceptual understanding. In the same vein, it might be useful to consider presenting first the nature of Gibbs free energy, the conceptual hierarchy up to Gibbs free energy and the relationships between the concepts qualitatively and then follow this with the quantitative aspects, as suggested by Carson and Watson[15]. Gibbs free energy could be defined as 'the quantity that tells us what changes are possible'. It tells us how to fix the circumstances so that a change becomes possible - for example Haber noticing that hydrogen and nitrogen could combine to make ammonia at high temperatures only if the pressure was made suitably high, but not at low pressures.[21] Here it is important to note that students may quickly misunderstand this statement if it is not mentioned that Gibbs free energy changes inform us about the spontaneity of a reaction only in the cases where temperature and pressure are constant. Otherwise students may adopt it as a general criterion and apply it incorrectly to every case. 'For non-isothermal cases there is no generally useful relationship between spontaneity and the sign of ΔG'.[22] Finally, as Millar[19] argues, 'the process of eliciting, clarification and construction of new ideas takes places internally within the learner's own head,... science should be taught in whatever way is most likely to engage the active involvement of learners'. Conceptual learning can be fostered by providing students with a variety of learning experiences.

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Appendix

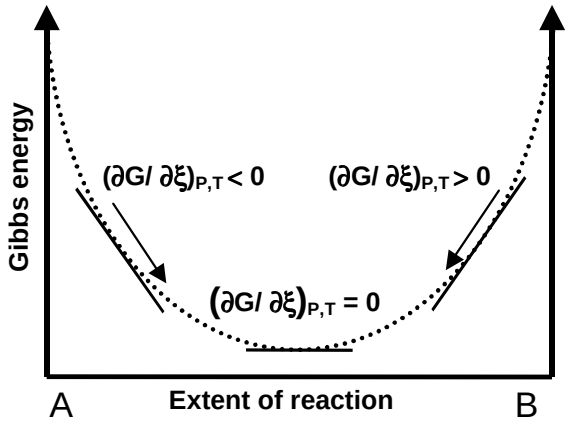
Gibbs free energy

(This question is adopted from Banerjee[12])



Draw a graph of Gibbs free energy versus extent of reaction **A → B** on the diagram is shown here. Discuss and interpret the graph as carefully as you can.

The idea being tested is: The Gibbs free energy change tends to zero when the system approaches equilibrium and is zero at equilibrium.



The expected answer is: The following graph was expected to be drawn.
As indicated on the graph, chemical reactions spontaneously approach the equilibrium state from both directions; A → B or B → A. The equilibrium state always has a lower Gibbs free energy than that of either reactants or products. As the reaction approaches the equilibrium the Gibbs free energy change decreases, and at the equilibrium state the change in Gibbs free energy becomes zero. At equilibrium, the entropy of the universe attains a maximum level compared to minimum Gibbs free energy.

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