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An analysis of the difficulties associated with determining that a reaction in chemical equilibrium is incomplete

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Abstract

There are inherent difficulties in a subject like chemistry particularly the notion of a *chemical reaction*. In this paper the difficulties are discussed from a teaching and learning perspective and from a history of chemistry perspective. Three teaching/learning studies of the incompleteness of the iron(III) thiocyanate reaction in chemical equilibrium are reviewed and it is shown that a recent historical study of the iron(III) thiocyanate reaction has the potential to challenge the interpretation of the incompleteness of the reaction. This establishes a controversial context where students can be introduced to epistemic thinking, that is, how to interrogate chemistry data and form a conclusion which resonates with what we know about the nature of science. A curriculum suggestion for pre-service chemistry teachers is provided.

Keywords Complete reaction · Incomplete reaction · Affinity · Phlogiston · Epistemology · Controversy

Introduction

It was Henry Bent (1986) who suggested that a falling match was easier to describe than a burning match. The inference was that a chemical reaction is more difficult to describe and understand than a falling object. This is borne out in the history of science. While classical physics reached the status of an exact science by the beginning of the eighteenth century, it wasn't until nearly two hundred years later that chemistry was to approach this status (Henry 2015). What contributed to the exactness of a science was the extent to which it could mathematize or quantify its concepts. This proved difficult for chemistry in the eighteenth century and it wasn't until the development of *chemical thermodynamics* and *kinetics* toward the end of the nineteenth century and early into the twentieth century that a clearer understanding of chemical reactions was possible. The publication of Newton's *Principia* in 1687 and *Optics* in 1704 marked physics as a mature and exact science (Henry 2015). In the preface to his *Principia*, Newton (1999) was to alert chemists to the difficulties they

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would face in trying to understand the nature of substances and their chemical changes with the same rigour with which he was able to treat the earth and its planets.

> We derive from celestial phenomena the gravitational forces by which bodies tend toward the sun and toward the individual planets. Then the motions of the planets, the comets, the moon, and the sea are deduced from these forces by propositions that are also mathematical. If only we could derive the other phenomena of nature from mechanical principles by the same kind of reasoning! For many things lead me to have a suspicion that all phenomena may depend on certain forces by which the particles of bodies, by causes not yet known, either are impelled toward one another and cohere in regular figures, or are repelled from one another and recede. Since these forces are unknown, philosophers have hitherto made trial of Nature in vain. But I hope that the principles set down here will shed some light on either this mode of philosophizing or some truer one.

A scan of the history of chemistry from the eighteenth century to the twentieth century gives some credence to Newton's understanding and I will focus on three ideas presented over this time period.

Three historical ideas

By the beginning of the eighteenth century chemists were attempting to understand the nature of a chemical reaction through the concept of *affinity* but this concept proved difficult to quantify. The construction of Tables of Affinity (Geoffroy 1719) during the eighteenth century helped to organise the large variety of chemical reactions and substances in a form which was at least partly helpful to the chemist. For example, metal displacement reactions known in the eighteenth century could be organised into a column with the following metals going in order from top to bottom: iron, tin, lead, copper, silver, mercury, gold. This means that iron can displace tin from a solution of its salts, tin can displace lead from a solution of its salts, lead can displace copper from a solution of its salts, and so on. In terms of the concept of *affinity*, one could express the relationships in the column as: iron has a stronger affinity for the salts of tin than tin has for the salts of iron, tin has a stronger affinity for the salts of lead than lead has for the salts of tin, and so on. But such tables had their critics like Antoine Grimoald Monnet (1734–1817) who said that (1775, p. 55), "substances act on each other according to the state in which they happen to be, rather than according to their respective affinities….and the system of affinities is a beautiful chimera, better fitted to amuse our scholastic chemists than to advance that science." Monnet's point is a pertinent one although chemists did find some benefit from the Affinity Tables. The difficulty in achieving consistency in orders of affinity eventually led to their demise in the nineteenth century.

Secondly, another concept popular in the eighteenth century to explain chemical reactions was the principle of *phlogiston* or *inflammable* principle promoted by Joseph Priestley and the principle of *acidity* or what became known as *oxygen* by Antoine Lavoisier. Priestley and Lavoisier were different, not so much in their practice, if by practice we mean the laboratory apparatus and manual skills brought to the task. They were different in the worldview of chemical change they brought to their practice. Kuhn (1970, p. 118), in his chapter ten on worldviews, observes that, ''Lavoisier saw oxygen where Priestley had seen dephlogisticated air and where others had seen nothing at all''. Jackson (2005, p. 38) suggests that the different worldviews of chemical change arose from different scientific traditions: ‘‘Just as Priestley and Lavoisier were born into different classes, they were heir to competing scientific traditions-quality versus quantity; a deep search for essence versus a faith in things that could be measured’’.

One way to illustrate the different worldviews is with the example where steam is passed over heated iron. In terms reminiscent of the times, the reaction can be represented as follows:

$$\text{Iron} + \text{Steam} \rightarrow \text{Iron calx} + \text{Inflammable air}$$

Priestley describes the French understanding of this reaction at the time as follows.

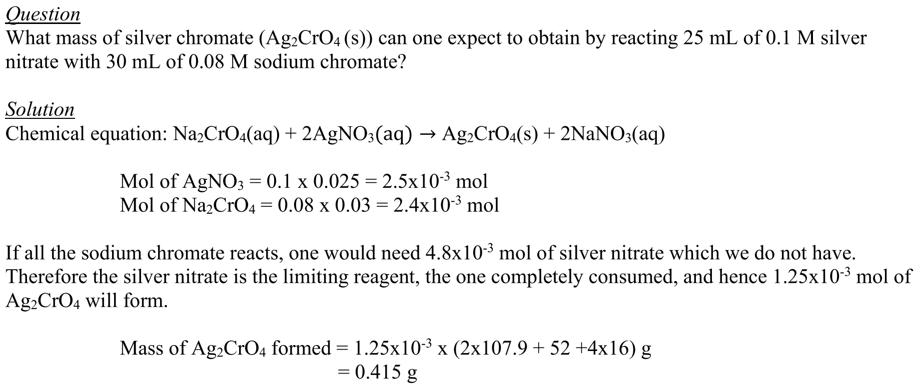
‘‘Water, they say, is completely decomposed when it is made to pass over red hot iron, the iron imbibing the acidifying principle (oxygen), and the remainder going off in the form of inflammable air (hydrogen)’’ (Priestley 1790, p. 546). The bracketed words in the quote have been inserted to enhance the clarity. According to Priestley's understanding however, since metals consist of the metal calx and phlogiston, the iron releases its phlogiston when heated, leaving behind the iron calx (what the French called an oxide of iron), and the phlogiston combines with water to produce inflammable air (what the French eventually called hydrogen). Again, bracketed sections have been inserted for clarity. This is a fundamentally different way of understanding the reaction. To Lavoisier, the iron metal was a simple substance or element; to Priestley, it was a substance made up of calx and phlogiston. To Lavoisier, water was made up of two simple substances; to Priestley, water was a simple substance or element. To Lavoisier, what triggered the reaction was an engagement between the heated iron and the steam; to Priestley, what triggered the reaction was the release of phlogiston from heated iron.

The new nomenclature suggested by French chemists of the late eighteenth century involved replacing *dephlogisticated air* with *oxygen* and the *calx of iron* with *ferric oxide*. In hindsight one tends to dismiss the idea of *phlogiston* as irrelevant even for eighteenth century chemistry but the French Academie of the time expressed some reluctance at accepting the new nomenclature for apparently good reasons according to Crosland's (1962, p. 185) report.

> Whereas many experiments were put forward in support of the latter (antiphlogistic theory), was it not also true, they (the committee) said, that the phlogiston theory was supported by a series of convincing experiments? The old phlogiston theory was no doubt incomplete, but were there not also some difficulties in the new theory?

The fact that even the French Academie was not comfortable in dismissing outrightly the phlogiston theory resonates with Hasok Chang's (2012) claim that the transition from the phlogiston theory to the oxygen theory was by no means a smooth process and chemistry's progress during the nineteenth century would have been richer and more productive if the two models had been allowed to coexist for a little longer. The driving principles for chemical reaction that resided within a substance were eventually to become quantified as *free energy* in the late nineteenth century when the concepts within *chemical thermodynamics* were applied to chemical reactions.

Finally, towards the end of the eighteenth century there were two different views emerging as to the impact of affinity on a chemical reaction. The Swedish chemist, Torbern Olof Bergman (1735–1784), suggested, after a study of many reactions, that if A reacted with B, it did so completely. This idea resonates with the conception of



Question

What mass of silver chromate (Ag_2CrO_4 (s)) can one expect to obtain by reacting 25 mL of 0.1 M silver nitrate with 30 mL of 0.08 M sodium chromate?

Solution

Chemical equation: $Na_2CrO_4(aq) + 2AgNO_3(aq) \rightarrow Ag_2CrO_4(s) + 2NaNO_3(aq)$

Mol of $AgNO_3 = 0.1 \times 0.025 = 2.5\times10^{-3}$ mol
Mol of $Na_2CrO_4 = 0.08 \times 0.03 = 2.4\times10^{-3}$ mol

If all the sodium chromate reacts, one would need 4.8×10^{-3} mol of silver nitrate which we do not have. Therefore the silver nitrate is the limiting reagent, the one completely consumed, and hence 1.25×10^{-3} mol of Ag_2CrO_4 will form.

$$\begin{aligned}\text{Mass of } Ag_2CrO_4 \text{ formed} &= 1.25\times10^{-3} \times (2\times107.9 + 52 + 4\times16)\ \text{g} \\ &= 0.415\ \text{g}\end{aligned}$$

Fig. 1 A stoichiometric calculation showing the limiting reagent reacting completely

a chemical reaction portrayed to chemistry students in their early chemistry education such as that shown in Fig. 1.

On the other hand, the French chemist, Claude Louis Berthollet (1748–1822), believed that A need not react completely with B. Many of the reactions studied by Bergman were precipitation reactions like that shown in Fig. 1 and Berthollet suspected that the apparent complete reaction was due to insolubility factors rather than affinity. In 1855, John Hall Gladstone (1827–1902) summarized the Bergman and Berthollet views as follows (Gladstone 1855, p. 181).

> A mixture of two salts in solution, which do not produce a precipitate, affords a case where this requisite is fulfilled. Let AB and CD be such salts. According to the one view, when mixed they will either remain without mutual action, or, should the affinities so preponderate, they will become simply AC and BD, the excess of either original salt remaining inactive. According to the other view, A will divide itself in certain proportions between B and D, while C will do the same in the inverse ratio, the said proportions being determined not solely by the differences of energy in the affinities, but also by the differences of the quantities of the bodies.

While Bergman classified a substance's innate capacity to engage in a chemical reaction as its 'elective affinity', Berthollet also considered that quantity of a substance determined its capacity to engage in a chemical reaction as suggested in the Gladstone quote above. Lindauer (1962) suggests that with the development of thermodynamics in the nineteenth century, the equilibrium constant for a reaction came to serve the function of Bergman's 'elective affinity' and the activity of a species as the product of the activity coefficient and concentration came to represent Berthollet's 'chemical mass' or 'active mass' as quantity's contribution to chemical affinity. It is important to realise that Berthollet's use of the term 'mass' is different to what one nowadays understands by the term. So Gladstone, without any knowledge of the concept of chemical equilibrium, set about checking the Bergman and Berthollet ideas of completeness and incompleteness respectively with a reaction which did not involve the formation of a precipitate. The reaction Gladstone chose to study was the iron(III) thiocyanate reaction. Furthermore, the colour produced on adding thiocyanate to a compound of iron was unique amongst iron compounds so there was no mistaking the fact that the deep red colour indicated the presence of the thiocyanate of iron and not some other compound of iron. Later, Waage and Guldberg (1864) were to draw upon the work of Gladstone in developing the 'law of mass action' or what came to be known as 'the equilibrium law'.

Gladstone and the iron(III) thiocyanate reaction

How did Gladstone perform his experiments with the iron(III) thiocyanate reaction? Using modern terminology, the stoichiometric chemical equation he considered would be equivalent to the following:

$$\mathrm{Fe_2(SO_4)_3(aq) + 6KSCN\,(aq) \rightarrow 2Fe(SCN)_3(aq) + 3K_2SO_4(aq)}$$

Gladstone also talks about the chloride of iron in which case the chemical equation would be written as:

$$\mathrm{FeCl_3(aq) + 3KSCN\,(aq) \rightarrow Fe(SCN)_3(aq) + 3KCl\,(aq)}$$

Gladstone (1855, p. 183) set about comparing the colours of iron(III) thiocyanate mixtures in clear glass vessels, relying on his assistant to make the final judgment: "My own observation was always checked by that of my assistant, and if we differed I generally adopted his view, since having no idea of what result was to be expected, his judgment was more impartial". Given that the chemical equations indicated that the ratio of iron to thiocyanate was 1:3, the test with iron(III) thiocyanate was described as follows (Gladstone 1855, p. 183):

> The first object to be determined evidently was, whether on mixing three equivalents of sulphocyanide of potassium with one equivalent of the ferric salt, say the chloride, the full depth of colour possible from the combination of all the sulphocyanagen with all the iron was actually obtained. That this was not the case was seen at once, for on the addition to such a mixture of either more sulphocyanide of potassium, or more chloride of iron, the colour was increased.

Thus Gladstone resolved the situation in favour, in his mind, of Berthollet's view, which turned out to be an important criteria for the concept of chemical equilibrium. Gladstone uses the term 'equivalent' in the sense of a 'quantity' rather than the way the term was used later in the nineteenth century. Today, one might talk about the mole ratio of iron to thiocyanate being 1:3. The naming of compounds was different in 1855 to that used today. Thus potassium thiocyanate was known as 'sulphocyanide of potassium'. What is interesting is that the 'incompleteness' of the iron(III) thiocyanate reaction, the Berthollet view supported by Gladstone, has also been used by chemistry educators to support the incomplete nature of a chemical equilibrium.

Chemical ideas and controversy

Since the eighteenth century, then, every time a new understanding of a chemical reaction was suggested, it was met with disagreement and controversy. The concept of *affinity* had its supporters (Geoffroy) and its detractors (Monnet); the concept of *phlogiston* had its supporters (Priestley) and its detractors (Lavoisier); and the concept of *incompleteness* had its supporters (Berthollet) and detractors (Bergman). It must be remembered that both supporters and detractors were highly skilled chemists of the time. There is no surprise then to learn that our students also have great difficulty understanding what is meant when the term *chemical reaction* is used in chemistry education.

When de Vos and Verdonk (1985a, p. 238) began a five-part series of studies to help improve fourteen and fifteen year-old students' understanding of chemical reactions, they already knew that, "these students, probably just like those in other countries, have great difficulty in grasping and understanding the concept of *chemical reaction*". For decades chemistry educators (Bradley 1964a, b; deVos and Verdonk 1985a) have advocated a laboratory-focussed chemistry course in the early years of a chemistry education leaving the role of models, theories, and formalisms till later. Such a course would focus on experiment and observation, particularly those involving chemical reactions, using the tools of guided inquiry to enhance student engagement. But this is a delicate process requiring time and energy with no guarantee of reward for the teacher or student.

An early focus on chemical reactions in chemistry education in part grew out of a series of articles on chemistry teaching written by J. Bradley and published in the *School Science Review* in the 1960′s. Bradley (1965, p. 65) views chemistry teaching as ''heuristic, historical, and formal''. By heuristic, he (Bradley 1964a, p. 364) means the ''kind of teaching and learning in which the pupil creates for himself the necessary concepts to interpret his own experience''; by historical, he (Bradley 1966, p. 707) means those ideas and experiments of the past which are ''still a part of the living body of the science''; and by formal, he (Bradley 1964a, p. 364) means ''that kind of teaching in which each essential type of experiment is carried out by the student, or shown to him, before the concept, or the item in a conceptual scheme or theory, is employed''. Formal teaching also included the presentation of information that could not be demonstrated by experiment which Bradley (1964a, p. 365) called ''the dishonest appropriation of goods which happen to be lying around (or)… intellectual theft''. So one can see how central experiment was to Bradley's teaching, but also his preparedness to use formal approaches to assist his inquiry methods and to incorporate a significant historical experiment if deemed necessary.

de Vos and Verdonk (1985a,b, 1986,1987a, b) followed Bradley's example and introduced the idea of *chemical reaction* to groups of three or four students (14 and 15 years of age) using a five-part series as follows. Part one involved students mixing lead nitrate (called minium to the students) with potassium iodide (unlabelled at this stage but later called courtoisite for the students) in a mortar with a pestle giving the bright yellow lead iodide (not labelled for the students). The key idea to communicate was that a new substance forms in a chemical reaction. This is more difficult to deduce than one might think. When copper is heated and forms a black layer of copper(II) oxide, students will observe that, "the copper turned black", without implying a new substance has formed. Black copper is still copper in the minds of some students. So when minium turns yellow, it is still minium to some students.

Part two uses the same reaction as Part one but with the minium and courtoisite separated in a petri dish of water. Some formalism is introduced here by way of the terms, *dissolution*, *migration*, and *reaction* (yellow line appears in the petri dish). In this case it is a little more difficult to suggest that the minium turns yellow. Part three looks at the heat effects accompanying a chemical reaction. Exothermic and endothermic reactions were chosen for which an activation energy was not critical. If heat is required to start a chemical reaction it can be difficult to distinguish between heat required and heat released. Part four introduced the formalism of the name 'molecules' to replace 'substance'. The problem that arises here is that students assign to molecules the same properties as observed in the bulk. So hot water has molecules that are hot and when a metal expands on heating, its molecules also expand. Part five deals with element conservation in a chemical reaction or conservation of mass. This involves the development of the skill of mass measurement along with experimental skill. To be taken up at a later date were the concepts of equilibrium thermodynamics and kinetics.

Chemistry educators (Van Driel et al. 1998, 1999; Chiu et al. 2002; Ghirardi et al. 2014) have been anxious to provide students with experimental support for the incomplete nature of a chemical equilibrium by, as it turns out, repeating Gladstone's experiment with the iron(III) thiocyanate reaction. Van Driel et al. (1998, p. 386) provide a typical student response to the experiment with the iron(III) thiocyanate reaction: "With respect to chemical reactions, however, they firmly believed that these conversions proceeded to completion. In line with what they had previously been taught about chemical reactions, they reasoned that the reactants would be converted completely". In cases where the iron and thiocyanate had not been mixed in the appropriate reaction ratio, students reasoned that at least one of the reactants, the limiting reagent, would be completely reacted. "As soon as one of the reactants is exhausted, however, the reaction is expected to stop and possible excess quantities of other reactants will be left over". Van Driel et al. (1998, p. 386) comment on the reaction of students to the iron(III) thiocyanate experiments: "The results of the above experiments usually created confusion among the students. In many groups, lengthy and heated discussion took place". After introducing students to the idea of incompleteness of chemical equilibrium reactions, "students were puzzled by the results of the experiments".

Precipitation reactions were not the only type of reaction considered to go to completion in a student's pre-equilibrium education. Acid–Base reactions performed in laboratory titrations, where at least one of the reactants is strong, also were expected to go to completion. This context must at least be partially responsible for the dilemmas students faced when presented with the idea of incomplete reactions.

Teaching and learning studies involving the iron(III) thiocyanate reaction

Three studies that used the iron(III) thiocyanate reaction to introduce secondary students to the idea that a chemical equilibrium reaction does not proceed to completion are now addressed. The most comprehensive of these studies is that reported by Van Driel et al. (1998).

The Van Driel et al. study (1998)

This study was conducted at the secondary school level with Grade 10 students in groups of 3 or 4 participants over three research cycles in which qualitative data was collected from audiotaped oral discussions from 9 groups, 6 groups, and 4 groups respectively and written responses examined from 35 groups, 80 groups, and 100 groups respectively. The students in each group were asked to mix a solution containing iron(III) ions with a solution containing thiocyanate ions to form a red solution. This red solution was then divided over three test tubes; more iron(III) was added to the first test tube; more thiocyanate was added to the second test tube; and the third test tube was used as a colour reference. An enhanced red colour was observed in the first and second test tubes and students were asked to provide an explanation for this result.

The report on student reactions to this experiment is illuminating (Van Driel et al. 1998, p. 387).

After having added iron(III) solution to the first of the three test tubes with the reaction mixture, students would immediately conclude from the observed darkening of the red colour that excess thiocyanate ions had been used during the initial preparation. Consequently, many had to be persuaded by their teacher to actually add the thiocyanate solution to the second test tube because they considered this experiment to be redundant. The fact that this experiment also led to an intensification of the red colour gave rise to heated discussions in many groups. As an example, the process in one group of three students (s1-s3) is described. Before the addition of thiocyanate ions, one student predicted:

S1 Well, nothing should happen in this case.

After the addition, the students responded as follows:

S2 Hey, this also gets darker.
S1 Wow!
S3 Yes.
S2 Well, how can this be?
S1 Do we understand this?
S2 No. I really don't understand this!
S3 Well, it seems both reactants are present in excess quantities because otherwise it would not have reacted.
S2 Ha Ha! That's quite impossible!…The other reactant is also present in excess, so they should react until nothing's left over.
S1 They should react with each other, shouldn't they? They should react until one of them is left over, while the other is exhausted, I think.

Obviously, these students didn't accept the possibility of both reactants being present in 'excess quantities'. Almost every student objected to this idea. When asked to explain the observed phenomenon in corpuscular terms, most students considered it illogical for some iron(III) ions and thiocyanate ions to react with each other, while others did not.

No chemical equation for the reaction is provided in the 1998 paper, but in a subsequent report of the research (Van Driel et al. 1999) the equation is given in the form:

$$\mathrm{Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)}$$

This equation appears to be for the benefit of the readers because students in the study were "not informed about the structure of these ions" (Van Driel et al. 1999, p. 560). It appears the reaction was presented in the form:

$$\text{iron(III) ions} + \text{thiocyanate ions} \rightarrow \text{rhodanide}$$

According to the report (Van Driel et al. 1999, p. 561), it was only after much discussion, initial disagreements and reluctance, "that the vast majority of the students believed that both the forward and the backward reactions actually take place in a state of equilibrium", so that,

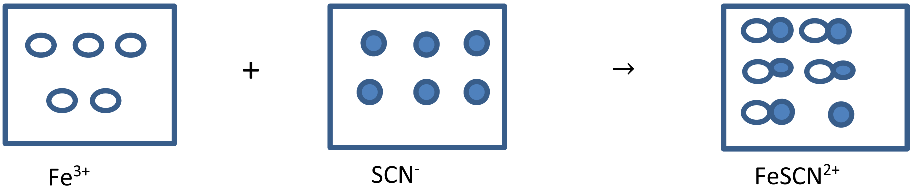


Fig. 2 Mental model of 5 of the 6 students interviewed before instruction for the iron(III) thiocyanate reaction

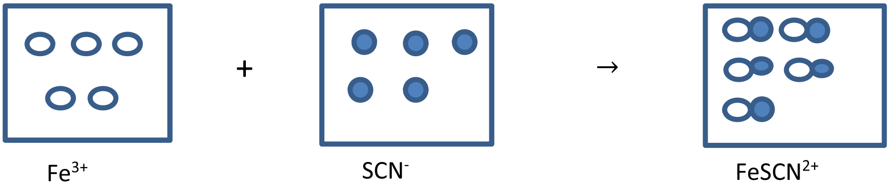


Fig. 3 The mental model of 1 of the 6 students interviewed before instruction

$$\text{iron(III) ions} + \text{thiocyanate ions} \rightleftharpoons \text{rhodanide}$$

Writing the chemical equation for the reaction in this form at least avoids the difficulty anticipated later in the history of the reaction of identifying the correct chemical formula for the red compound. The second teaching and learning study to consider is that by Chiu et al. (2002).

The Chiu et al. study (2002)

This study was also conducted with 10th grade secondary school students where they are challenged to explain the deepening red colour on addition of Fe(III) and SCN^{-} separately to two samples of the equilibrium, as in the Van Driel et al. (1998) study and Gladstone's study (1855). Here the emphasis is on students' mental models of chemical equilibrium. These mental models were ascertained by interviewing six students before instruction in chemical equilibrium and after instruction. The chemical equation was written as: $Fe^{3+} + SCN^{-} \rightarrow FeSCN^{2+}$, and students were told the reaction was reversible. Before instruction, five of the six student's responses were consistent with the mental model shown in Fig. 2. For example, when a solution of iron(III) was added to a solution of thiocyanate ions, the following dialogue took place.

Student: The solution turns red.
Tutor: Why?
Student: 'Cause Fe^{3+} reacts with SCN^{-}, and one of them was used up.

One of the six students chose the mental model shown in Fig. 3 where all the reactants are used up.

After instruction the authors claim that four of the six students had adopted the accepted mental model of a chemical equilibrium where neither reactant is all used up as shown in the mental model of Fig. 4. One student retained the mental model shown in Fig. 3 and the

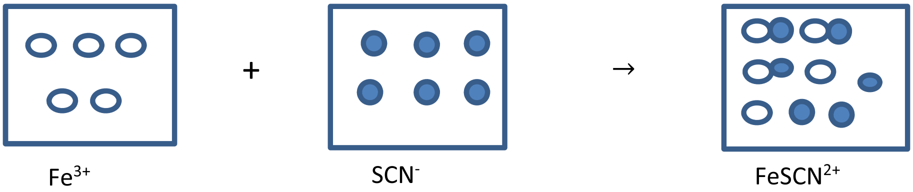


Fig. 4 The mental model of 4 of the 6 students after instruction

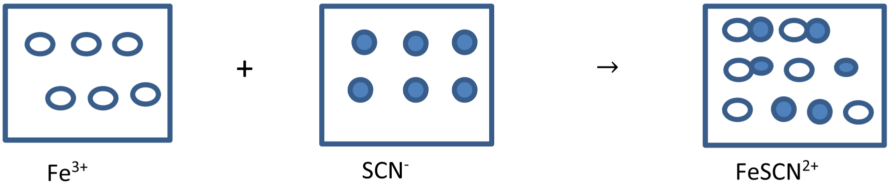


Fig. 5 The mental model of 1 of the 6 students after instruction

other student adopted a model where the total numbers of all three species are the same (Fig. 5). The conclusion was reached that significant conceptual change had occurred as a result of instruction. However, the nature of this study was such that the rich tapestry of student comments and initial unbelief that both reactants were not used up on reaction, shown in the Van Driel et al. (1998) study, was not manifest. Our final teaching and learning study is that by Ghirardi et al. (2014).

The Ghirardi et al. study (2014)

This study details the reaction of 54 seventeen year-old secondary school students to a teaching sequence of six activities designed to help students understand the concepts associated with chemical equilibrium. Activity 4 used the iron(III) thiocyanate reaction to help convince students that both reactants are incompletely reacted at equilibrium. The equation was written in the form, $Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$. After aqueous solutions of iron(III) nitrate and potassium thiocyanate were added to produce the red colour of iron(III) thiocyanate, crystals of iron(III) nitrate were added to a portion of the red solution and crystals of potassium thiocyanate were added to a second portion of the red solution and students were invited to provide an explanation for the deepening red colour in both cases. As in the Van Driel et al. study (1998), students found it difficult to accept the idea of incomplete transformation. Statements such as, “An excess of both reagents cannot be present”, and “how come both reagents are in excess” (Ghirardi et al. 2014, p. 62), are typical of student responses. Some students thought the reaction had not finished occurring so one might expect a deepening of the red colour with time. One group of students thought it was the iron of the added iron(III) nitrate that deepened the colour. “Students continued to be skeptical, so the teacher invited them to consider the idea of incomplete transformation as a simple working hypothesis”(Ghirardi et al. 2014, p. 62). This was the only way the teacher could move forward with introducing other aspects of chemical equilibrium. But is ‘incompleteness’ the only way of interpreting Gladstone’s experiments given the developments in chemistry since his time?

An historical perspective of the chemistry of the iron(III) thiocyanate reaction

What follows is a brief summary of a more detailed historical analysis of the reaction (de Berg 2019). While the iron(III) thiocyanate reaction was used as early as 1885 in chemical analysis (Thomson 1885) without any understanding of the nature of the reaction, by 1913 it was being described as an equilibrium reaction and written with arrows to illustrate both forward and reverse reactions as follows (Philip and Bramley 1913):

$$\mathrm{FeCl_3} + 3\mathrm{KCNS} \rightleftarrows \mathrm{Fe(CNS)_3} + 3\mathrm{KCl}$$

This was almost fifty years after the pioneering work of Waage and Guldberg (1864) on the law of mass action.

With the advent of the ionic theory in the late nineteenth and early twentieth centuries and the suggested use of partial forward and reverse arrows to indicate equilibrium where both the forward and reverse reactions were incomplete (Marshall 1902), the equation was written in ionic form in 1924 as a net ionic equilibrium equation where the dots are equivalent to positive charges and the dashes to negative charges for 3SCN (Bailey 1924):

$$\mathrm{Fe}^{\cdots} + 3(\mathrm{SCN})''' \rightleftharpoons \mathrm{Fe(SCN)_3}$$

By 1937, the ions were written as Fe^{3+} and SCN^- (Kielland 1937).

With coordination chemistry emerging as a sub-discipline in the early twentieth century, a new nomenclature was needed to name its compounds and chemists had to distinguish between *primary valency* (charge number) and *secondary valency* (coordination number). So, while Fe^{3+} can be regarded as having a primary valency of ‘three’, in aqueous solution it had a secondary valency of ‘six’ since six water molecules could coordinate to the Fe^{3+} ion to give, $\mathrm{Fe(H_2O)_6}^{3+}$, with the name hexaaquairon(III). Consequently, the 1:1 complex was written as $\mathrm{Fe(H_2O)_5(SCN)}^{2+}$ with the name pentaaquathiocyanatoiron(III), the 1:2 complex as $\mathrm{Fe(H_2O)_4(SCN)_2}^{+}$ with the name tetraaquadithiocyanatoiron(III), and the 1:3 complex as $\mathrm{Fe(H_2O)_3(SCN)_3}$ with the name triaquatrithiocyanatoiron(III) and so on. These are the forms in which the complex is sometimes written in the reaction equations shown from 1958 to the present (Below et al. 1958). When the red species was now identified as a complex, the question which chemists needed to resolve was which of the complex species was responsible for the red colour.

There was considerable debate about the identity of the chemical species responsible for the red colour on mixing ferric ions with thiocyanate ions. Over 160 years, candidates included $\mathrm{Fe(SCN)_3}$ (Bailey 1927), $\mathrm{Fe\{Fe(SCN)_6\}}$(Schlesinger and Van Valkenburgh 1931), $\mathrm{Fe(SCN)_6}^{3-}$ (Macdonald et al. 1951), $\mathrm{Fe(SCN)}^{2+}$ (Frank and Oswalt 1947), $\mathrm{Fe(SCN)}^{+}$ (Woods and Mellon 1941), and $\mathrm{Fe(SCN)_2}^{+}$ (Perrin 1958). It is understandable why one of the first candidates was $\mathrm{Fe(SCN)_3}$ because this was expected from the stoichiometry of the reaction. The application of spectrophotometric and potentiometric methods led eventually to the identification of $\mathrm{Fe(SCN)}^{2+}$ or $\mathrm{Fe(H_2O)_5(SCN)}^{2+}$, and $\mathrm{Fe(SCN)_2}^{+}$ or $\mathrm{Fe(H_2O)_4(SCN)_2}^{+}$, as the dominant species up to thiocyanate concentrations of 0.25 M in aqueous solution (Laurence 1956; de Berg et al. 2016) and most likely $\mathrm{Fe(SCN)_3}$ for the red colour in organic extracts (Bjerrum 1985). When assigning the red colour to $Fe(H_2O)_5(SCN)^{2+}$ or $Fe(H_2O)_4(SCN)_2{}^{+}$, one can see that the iron(III) thiocyanate reaction is a ligand substitution reaction. Coordinated water is often not shown in the reaction equation for simplicity.

As one increases the thiocyanate concentration from 0.001 to 0.250 M for an iron (III) concentration of 1.5×10^{-4} M, the absorbance maximum shifts from 460 to 480 nm with a notable increase in intensity (de Berg et al. 2016). This is illustrated in Fig. 6. The 20 nm difference still leaves the solution with an intense red colour. In fact, the molar absorptivity of $Fe(SCN)_2{}^{+}$ is about double that for $Fe(SCN)^{2+}$ (de Berg et al. 2016). This fact leads immediately to an alternative interpretation of the Gladstone experiment when more thiocyanate was added to the iron/thiocyanate equilibrium mixture, and a possible alternative interpretation of the deepening red colour when more iron was added to the equilibrium mixture. This is shown in Table 1.

Epistemic approach for chemistry educators

The analysis shown in Table 1 is designed to show that one could have interpreted Gladstone's observations in terms of '*complete transformation*', for example,

$FeSCN^{2+} + SCN^{-} \rightarrow Fe(SCN)_2{}^{+}$, rather than Fe^{3+}(remaining) + SCN^{-} (additional) → $FeSCN^{2+}$ (more). The 'Assumptions' column in Table 1 is a clue as to what questions could be asked to try to resolve the controversy and suggested questions are shown in Table 2. At this point I would like to consider the structure of Tables 1 and 2 in terms of explanations, assumptions, and questions and what this structure might have to do with an epistemic approach to chemistry. Secondly, I will address the content of the tables.

Structure of Tables 1 and 2 and epistemology

There are at least three broad themes in science education research that are relevant to this iron(III) thiocyanate study: inquiry, argumentation, and nature of science (NOS). They emerged in the science education research literature over twenty years ago but are still topics of interest. The overlapping interdependent character of the three themes can be illustrated by the way in which scholars define the themes and dialogue about them. The link between inquiry and NOS is often described in two ways as learning science through inquiry or learning about science (NOS) through inquiry. According to Kelly (2014, p.

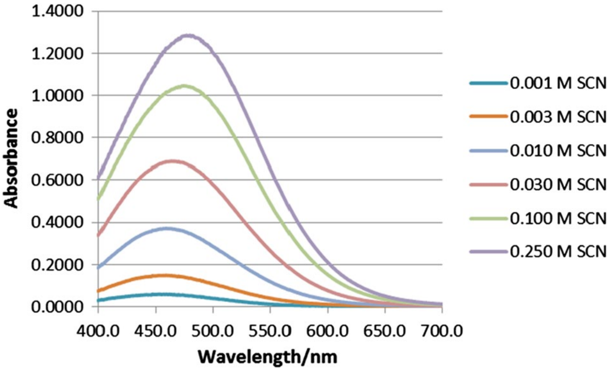


Fig. 6 Extrapolated spectra at zero time (initial spectra) for $[SCN^{-}]$ from 0.001 M (bottom) to 0.250 M (top), $[Fe^{3+}] = 1.5 \times 10^{-4}$ M at an initial ionic strength of 1.0 M

Table 1 Explanations for the increase or decrease in intensity of the blood-red colour of $FeSCN^{2+}$ when solid $Fe(NO_3)_3$, KSCN, and aqueous $HgCl_2$ are separately added to, $Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$, based on incomplete transformation (Berthollet) and complete transformation (Bergman)

Action	Observation	Explanation	Assumptions
Addition of $Fe(NO_3)_3(s)$	Blood-red colour intensifies with an absorption maximum at 460 nm	Bergman: $FeSCN^{2+} + Fe^{3+} \rightarrow Fe_2SCN^{5+}$ *Berthollet:* $Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$	*Bergman:* Fe_2SCN^{5+} exists and has a blood-red colour *Berthollet:* Residual SCN^- exists to react with added Fe^{3+}
Addition of KSCN(s)	Blood-red colour intensifies with an absorption maximum at 480 nm	*Bergman:* $FeSCN^{2+} + SCN^- \rightarrow Fe(SCN)_2{}^+$ *Berthollet:* $Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$	*Bergman:* $Fe(SCN)_2{}^+$ exists and has a blood-red colour *Berthollet:* Residual Fe^{3+} exists to react with added SCN^-
Addition of $HgCl_2(aq)$	Blood-red colour loses intensity and may disappear	*Bergman:* $FeSCN^{2+} + HgCl_2 \rightarrow FeCl_2{}^+ + HgSCN^+$ *Berthollet:* $Hg^{2+} + SCN^- \rightarrow HgSCN^+$ $FeSCN^{2+} \rightarrow Fe^{3+} + SCN^-$	*Bergman:* $HgSCN^+$ exists and does not have a blood-red colour *Berthollet:* $HgSCN^+$ exists and does not have a blood-red colour. The iron(III) thiocyanate reaction is reversible

Table 2 Some important questions arising from the Bergman and Berthollet explanations in Table 1

Bergman questions	Berthollet questions
1. Is there evidence that Fe_2SCN^{5+} exists and has a colour similar to blood-red?	1. In an equimolar reaction between Fe^{3+} and SCN^-, is there evidence of unreacted Fe^{3+} and SCN^- when the reaction has finished?
2. Is there evidence that $Fe(SCN)_2{}^+$ exists and has a colour similar to blood-red?	2. Is the iron(III) thiocyanate reaction reversible?
3. Is there evidence that $HgSCN^+$ exists and does not have a blood-red colour?	3. Is there evidence that $HgSCN^+$ exists and does not have a blood-red colour?

1364), “We can speak of learning science through inquiry, where inquiry is the means to learn knowledge and practice. Or we can view the pedagogy as inquiry about science where the intent is to communicate lessons about the nature of science”. As for the relationship between argumentation and NOS, Adúriz-Bravo (2014, p. 1444) reminds us that, “argumentation has been recognized by some traditions, authors and texts in philosophy of science as a key epistemic feature of the scientific enterprise”. This statement confirms that the construction and validation of scientific knowledge depends upon the process of argumentation, that is, a “process of logical reasoning that includes debate and persuasion” (Adúriz-Bravo 2014, p. 1443). In addition, “a school science that is structured around argumentation would convey important messages about the nature of science…”(Adúriz-Bravo 2014, p. 1446). Inquiry and argumentation are placed side-by-side by Duschl and Osborne (2002, p. 40) as they reflect upon the need for a science education that includes ‘how we know’ in addition to ‘what we know’: “A prominent, if not central, feature of the language of scientific enquiry is debate and argumentation around competing theories, methodologies and aims”.

It is interesting to reflect upon what elements might rightfully be considered to be common to the three themes. The National Research Council (1996) identified some of these elements when they identified inquiry as engaging learners in scientifically oriented questions, as formulating and evaluating evidence, as formulating and evaluating explanations, and communicating the results of such actions. Explanations and evidence also feature in one definition of argumentation as the “ability to relate explanations and evidences”(Jiménez-Aleixandre 2010, p. 11). Asti Vera and Ambrosini (2010, p. 6) associate the word ‘model’ with ‘explanation’ when they claim that, “some of the most important models of scientific explanation incorporate argumentation as a central piece in the scientific machinery”. Giere (1999) reminds us that the use of models has become recognized as important for scientific inquiry and can appear in different forms such as mathematical representations and chemical equation representations. The assumptions behind the construction of models is an important consideration when using models in explanations. History and Philosophy of Science (HPS) provides the context in which questions, explanations, evidences, models and assumptions adopt a specific format. In the case of the iron(III) thiocyanate reaction, the historical component grants us access to the controversy that raged between two well-qualified chemists, Bergman and Berthollet, in relation to the nature of a chemical reaction. The philosophical component reminds us of the interpretive flexibility of empirical evidence and what should count as evidence for the purpose of knowledge construction, that is, the epistemic criteria for evidence.

Why is it important to discuss inquiry, argumentation, NOS, and their common elements by way of a specific exemplar, the iron(III) thiocyanate reaction? One of the reasons why Kuhn's 'The Structure of Scientific Revolutions' (Kuhn 1970) has had a major impact in science education is Kuhn's use of specific examples to illustrate a philosophical point. For example, he examines the controversy between Lavoisier and Priestley in relation to the 'discovery' of oxygen in some detail to illustrate the difficulties associated with the use of the term 'discovery'. This is in spite of the misgivings some philosophers now have regarding some of Kuhn's conclusions. Giere (1988), in his 'Explaining Science', uses the example of Newton's laws of motion to illustrate whether such laws are empirical claims or definitions. Such specific examples have led scholars such as Rudolph (2000) and Irzik and Nola (2011) to caution against adopting a consensus view of science given disciplinary differences across the sciences which include conceptual differences, empirical differences, linguistic differences, differences in the models adopted, and problem solving differences. Kuhn (1970, pp. 50–51) illustrates this point with some clarity as follows:

> An investigator who hoped to learn something about what scientists took the atomic theory to be asked a distinguished physicist and an eminent chemist whether a single atom of helium was or was not a molecule. Both answered without hesitation, but their answers were not the same. For the chemist the atom of helium was a molecule because it behaved like one with respect to the kinetic theory of gases. For the physicist, on the other hand, the helium atom was not a molecule because it displayed no molecular spectrum. Presumably both men were talking of the same particle, but they were viewing it through their own research training and practice. Their experience in problem solving told them what a molecule must be. Undoubtedly their experiences had had much in common, but they did not, in this case, tell the two specialists the same thing.

The Bergman/Berthollet controversy of complete/incomplete transformation, as introduced by Gladstone (1855) and previously discussed in this paper, allows one to introduce some key epistemic issues that should inform and engage students in a study of the iron(III) thiocyanate reaction. The reader will observe what kinds of evidences, questions, explanations, models and assumptions, elements seen to be common to inquiry, argumentation and NOS, would resonate with a chemistry community whether found amongst professional chemists, upper high school science laboratories, or first-year university chemistry laboratories.

Dagher and Erduran (2014, p. 1205) have recently highlighted the importance of explanations in the teaching and learning of chemistry and claim they "are the backbone of scientific claims and are consequently a central target for epistemological disputes", such as that shown in Table 1 between Bergman and Berthollet. However, Dagher and Erduran (2014, p. 1204) lament the fact that, "despite the importance of laws and explanations in the science disciplines, (the) relevance of their epistemic nature to educational practice is seldom explored". The controversy outlined in Table 1 is designed to highlight one example of how the epistemic nature of explanations can enhance chemistry education in a practical sense.

While explanations are important ingredients of scientific theories, theories are not the only source of explanations. The explanations given in Table 1 are in the form of chemical equation models. An important question students need to address is how these models might help in making a choice between the Bergman complete transformation explanation and the Berthollet incomplete transformation (or what was to become the chemical equilibrium) explanation using "reasons and evidence" (Dagher and Erduran 2014, p. 1205). While a student's chemistry background may not have the depth to decide between the two explanations, they should be encouraged to provide a list of questions that they think will need to be answered if an informative choice is to be made. The 'Assumptions' column in Table 1 is a clue as to what questions could be asked and suggested questions, which might be generated by student groups for example, are shown in Table 2.

Content of Tables 1 and 2

The questions on the Bergman side are quite feasible given that we now know of the existence of $Fe(SCN)_2{}^+$, and other possible ligand substitution reactions of coordination compounds unknown to Gladstone at the time. It turns out to be very difficult to answer Question 1 on the Berthollet side because reactants cannot be separated from the products in the aqueous solution reaction to test for the presence of unreacted Fe^{3+} and SCN^-. For precipitation equilibria like: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$, the system can be filtered to separate AgCl(s) from the other components. Addition of KI(aq) to the filtrate will precipitate yellow AgI(s) showing that residual $Ag^+(aq)$ must have been present in the filtrate. Reversibility is also more easily demonstrated with precipitation equilibria using radioactive isotopes. Adding labelled silver nitrate to the silver chloride equilibrium, for example, leads to the presence of radioactivity in the silver chloride precipitate demonstrating reversibility and a dynamic equilibrium. The Berthollet explanations also illustrate the importance of *quantity* in determining *affinity* as Gladstone affirmed. Adding excess ferric ion increased its affinity with the remaining thiocyanate ion to produce an enhanced amount of the red coloured species. On the other hand, Bergman explained the enhanced red colour in terms of an ongoing reaction rather than increased affinity of ferric ion for remaining thiocyanate ions. So deciding between the Bergman and Berthollet explanations is not a straightforward matter in the case of the iron(III) thiocyanate reaction. While Gladstone interpreted the changes in Table 1 in terms of the Berthollet explanation of incomplete transformation, it is also possible to consider the evidence in terms of Bergman's model of complete reaction. This is a case where two different interpretations of the same empirical evidence seems to apply. It is this context that helps one to engage in epistemic thinking.

Gladstone (1855, p. 185) also observed that, "A solution of chloride of mercury …very speedily removes the colour", and this is presented as the third item in Tables 1 and 2. The species, $HgSCN^+$, is a coordination compound on the way to producing the species $Hg(SCN)_2$ which is not very soluble in water. Both the Bergman and Berthollet explanations in Tables 1 and 2 rely on the production of this mercuric compound although other possibilities such as a combined coordination compound between $FeSCN^{2+}$ and Hg^{2+} or Cl^- could be posited but we have selected the simplest option for illustration purposes. For the first two cases in Tables 1 and 2 the Berthollet explanation does not depend on the formation of new compounds as required in the Bergman explanation but deciding between the two explanations can still prove difficult particularly for students. Berthollet and Bergman were both highly respected chemists of their day but differed in their understanding of a chemical reaction. So students should not be surprised if it is difficult to choose between the two approaches. If students realize that this situation is endemic to how knowledge is often generated in chemistry and they learn the art of asking the appropriate questions, that is, learn to interrogate chemical ideas, much will have been achieved in their chemistry education. It took studies of a large number of reactions to reach the conclusion that equilibrium reactions were incomplete transformations, reversible and dynamic and that the chemical affinity between two species depended not only on their innate or elective affinity as Bergman called it but also on the quantity of the species involved. So it is misleading to think that all the properties of chemical equilibria can be discovered by looking at just one reaction like the iron(III) thiocyanate reaction. It is probably more appropriate to think of the iron(III) thiocyanate reaction as a means of illustrating the principles of chemical equilibria rather than discovering those principles.

The explanations in Table 1 for both the Bergman and Berthollet models of complete and incomplete reactions are associated with a set of assumptions which could be considered just as important as the explanations from an epistemic point of view. Both the explanations and associated assumptions are deeply chemical in nature and reflect the understanding chemists have had about this reaction. It is doubtful that the students in the Ghirardi et al. study (2014) had in mind the formation of species like $\{Fe(SCN)_2{}^+\}$ or $\{Fe_2(SCN)^{5+}\}$ for the simple addition of SCN^- and Fe^{3+} to $\{Fe(SCN)^{2+}\}$respectively as an explanation for the deepening of the blood-red colour of the solution but these species have been either proposed or verified in the history of the reaction (de Berg 2019). Under normal circumstances students would not be aware of these facts from the history of the reaction.

The questions in Table 2 are the key to epistemic thinking and constitute the tools for interrogating Bergman and Berthollet and it is this very feature that should be given more space in our chemistry curricula. From an epistemological point of view, the development of the skill of asking relevant questions is just as important, if not more important, as a knowledge of the facts of chemistry.

A curriculum suggestion for pre-service chemistry teachers at the tertiary level

Given the experience of Ghiradi et al. (2014) and Van Driel et al. (1998), one could not expect high school students to generate the data in Tables 1 and 2 even with much guidance. There is also every reason to believe that first-year university students are also likely to experience difficulty in the topic of chemical equilibrium given the observations of Hildebrand (1946, p. 589).

> There seems to be no topic in freshman chemistry that presents more difficulties to students than chemical equilibrium. After trying for over 30 years to give clear answers to their questions, I have come to have a great deal of sympathy with them, realising that the subject is inherently a difficult one.

Undoubtedly, the incomplete nature of the reaction will be one of the issues. One is likely to have more success with pre-service chemistry teachers who have already completed their science degree and are about to confront the difficulties associated with epistemic issues as a preparation for a career in chemistry teaching. The following is a procedure that could help pre-service chemistry teachers appreciate the difficulty their students will experience when placing reactions that apparently proceed to completion (Bergman) alongside reactions that are incomplete (Berthollet). On this basis it can be helpful to students to show that reactions considered to go to completion for practical purposes are actually equilibrium reactions with residual concentrations, albeit small concentrations, of all reactants.

Reaction 1: Precipitation reaction between silver nitrate and potassium chromate

Procedure 1
In the case of precipitation reactions like that given in Fig. 1, have the students add two volumes of 1 M $AgNO_3$ to one volume of 1 M K_2CrO_4, shake the mixture and allow the orange product to settle.

Procedure 2
Write down a net ionic equation for this precipitation reaction.

Calculation 1
Calculate the mass of silver chromate (s) you expect to have formed.

Question 1
What assumption have you made in this calculation?

Question 2
How could you verify if your assumption was correct?

Statement 1
Berthollet considered that even precipitation reactions were actually equilibrium reactions.

Question 3
If Berthollet is correct what would this mean for the residual concentrations of Ag^+ and CrO_4^{2-} ?

Question 4
If the precipitation reaction is an equilibrium reaction, how would you go about proving there were residual concentrations of Ag^+ and CrO_4^{2-} after equilibrium had been reached?

Statement 2
Initially follow student suggestions here but remember one can filter the equilibrium mixture so as to physically separate the reactants from the products and show by adding a precipitating reagent to two portions of the filtrate that both reactants are still present.

Question 5
(a) What precipitating agents could be added to the filtrate to produce a different silver salt and a different chromate salt?
(b) What idea is guiding your choice of precipitating agent?

Statement 3
The following can be added to the filtrate divided into two portions. A few drops of 1 M KCl added to one portion produces a white cloudy solution of AgCl showing some silver ions were still present in the silver chromate equilibrium, and a few drops of 1 M $Pb(NO_3)_2$ added to the second portion produces a cloudy yellow precipitate of $PbCrO_4$ showing some chromate ions were still present in the silver chromate equilibrium. A table of solubility products guides the choice of precipitating agent.

	$2Ag^{+}(aq)$ +	$CrO_4^{2-}(aq)$ $\rightleftharpoons$	$Ag_2CrO_4(s)$	K=3.85x10^{11}
Initial moles	2.5x10^{-3}	2.4x10^{-3}	0	
Reacting moles	2.5x10^{-3}	1.25x10^{-3}	1.25x10^{-3}	
Remaining moles	0	1.15x10^{-3}	1.25x10^{-3}	
Reacting moles	2x	x	-x	
Equilibrium moles	2x	(1.15x10^{-3}+x)	(1.25x10^{-3}-x)	

$$K = \frac{1}{[Ag^{+}]^{2}.[CrO_4^{2-}]}$$

$$3.85\text{x}10^{11}.\ (2x/0.055)^{2}.(1.15\text{x}10^{-3}/0.055) = 1$$

$$x = 3.065\text{x}10^{-7}$$

$$[Ag^{+}] = 1.11\text{x}10^{-5}\ M$$

$$[CrO_4^{2-}] = 0.02\ M$$

$$\text{Mass of } Ag_2CrO_4(s) = 0.415\text{ g as } x <<< 1.25\text{x}10^{-3}$$

Fig. 7 Solution of the silver chromate problem in Fig. 1 using equilibrium principles

One can in fact calculate the residual silver and chromate ion concentrations if the problem in Fig. 1 is solved using equilibrium principles. This is shown in Fig. 7. There is an interesting interaction between complete reaction and incomplete reaction ideas in the solution of Fig. 7. Because the equilibrium constant is so large, one assumes that all of the limiting reagent reacts as shown on the 'reacting moles' line, but then one allows for an incomplete reaction by allowing an amount 'x' of Ag_2CrO_4 to react in a reverse reaction to give residual amounts of Ag^{+}(aq) and CrO_4^{2-}(aq). In other words, the mathematics shows why one was able to assume complete reaction of the limiting reagent in problems prior to learning about chemical equilibrium.

While the assumption of complete reaction on the second line in Fig. 7 allows one to find a mathematical solution for the equilibrium concentrations without having to solve a cubic equation, an unfortunate misunderstanding of the nature of chemical equilibrium may eventuate. This calculation may reinforce the idea that the forward reaction proceeds to completion before the reverse reaction proceeds, whereas what is being highlighted is that one can approach equilibrium from the reactant or product side.

Reaction 2: The reaction between ferric ions and thiocyanate ions to produce a coloured coordination complex

Statement 1

As far as the iron(III) thiocyanate reaction is concerned, one cannot physically separate the reactants from the products to show that iron and thiocyanate ions are still present at equilibrium. One has to infer this from observing what happens when extra iron and thiocyanate are added in turn to the equilibrium mixture.

Procedure 1

Have the students add equal volumes of 0.001 M $Fe(NO_3)_3$ and 0.001 M KSCN to a beaker. A soluble blood-red coordination complex forms. The students can be told that the simplest way to represent this reaction is: $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$.

The students may have already confirmed this as part of their laboratory course. The absorption maximum of the blood-red solution is around 460 nm.

Question 1
How can it be confirmed that residual Fe^{3+} and SCN^- exist at equilibrium?

Statement 2
Students can be introduced to Gladstone's three experiments shown in Table 1.

Procedure 2
Give students a copy of Table 1 with the assumptions column blank. Students complete the assumptions column for the Bergman and Berthollet chemical equation explanations.

Question 2
Is there evidence that Fe_2SCN^{5+} exists?

Statement 3
If Fe_2SCN^{5+} existed one would expect an absorption maximum to differ from 460 nm.

Question 3
Is there evidence that $Fe(SCN)_2{}^+$ exists?

Statement 4
The fact that the absorption maximum is different (480 nm) but close enough to 460 nm to maintain the blood-red colour is consistent with the existence of $Fe(SCN)_2{}^+$.

Question 4
Is it possible to decide which of the Bergman and Berthollet chemical equation explanations most likely applies to the addition of $HgCl_2(aq)$?

Statement 5
The fact that the Berthollet explanation involves a reaction between oppositely charged ions may lead to it being preferred.

For all the possibilities in Table 1 students could be challenged to choose what they consider might be the best explanation, giving reasons for their choice. This is where issues related to the nature of science could be brought to bear. The Berthollet explanation does not depend on the formation of new compounds as required in the Bergman explanation but deciding between the two explanations can still prove difficult for students. The universal character of the equilibrium law is an important consideration whereas Bergman's idea may only apply in a limited number of cases, for example, ligand substitution reactions of a certain type, whereas the equilibrium law applies across all reactions occurring in a closed system. Science is characterised by the use of as few laws as possible to explain the properties of nature. This means that the laws that are adopted need wide application across a variety of contexts and the equilibrium law fits this proposition well.

If one accepts incomplete transformation or the idea of chemical equilibria as a working hypothesis as Ghiradi et al. (2014) proposed to their sceptical students, then one has access to mathematical explanations for the situation described in Table 1. The mathematical explanations arise from the law of chemical equilibrium, historically known as the law of mass action. So while the function of chemical laws might be said to 'describe' a chemical situation, explanations can make use of chemical laws just like they can make use of chemical equation models as shown in Table 1. The law of chemical equilibrium can be expressed using the equilibrium constant, K, and species concentrations as:

$$K = \frac{\left[\mathrm{FeSCN^{2+}}\right]}{[\mathrm{Fe^{3+}}]\cdot[\mathrm{SCN^{-}}]} \text{ for the reaction: } \mathrm{Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)}$$

The reaction quotient, Q, has the same expression but with concentrations not necessarily equilibrium values. When solid $Fe(NO_3)_3$ is added to the equilibrium system, $[Fe^{3+}]$ increases which means $Q < K$. This means the numerator, $[FeSCN^{2+}]$, must increase to restore K. This can only happen if the forward reaction becomes momentarily favoured over the reverse reaction until $Q = K$. The same reasoning applies to the addition of solid KSCN. The addition of solid Na_2HPO_4 reduces the $[Fe^{3+}]$ making $Q > K$, so the reverse reaction becomes momentarily favoured over the forward reaction until $Q = K$. The qualitative equivalent of this quantitative approach has been called Le Chatelier's principle. The arguments here can be extended at the tertiary level to include the impact of adding non-reacting salts like $NaNO_3$ to the equilibrium system if activities (effective concentrations accounting for ionic strength) replace concentrations.

Conclusion

One lesson to be learnt from controversy, including the Bergman/Berthollet controversy, is that experimental evidence does not lead automatically to conceptual knowledge. The evidence needs interpretation through the provision of an explanation along with the assumptions implied in the explanation. The assumptions then lead to a set of questions with which to interrogate the proposed models. This kind of epistemic teaching and learning is what can move science education away from a 'rhetoric of conclusions' (Schwab 1962). The close relationship between the explanations, assumptions and questions is a feature of such an epistemic education.

Since the eighteenth century chemists have struggled to understand the nature of a *chemical reaction*. So it is no wonder that students of chemistry have also struggled. This paper has taken pains to point out that it wasn't only with the concept of *incompleteness* where the struggle lay, but also with other concepts like *affinity* and *phlogiston* in relation to chemical reactions. While chemistry educators have knowingly or unknowingly used the 1855 Gladstone experiment with iron(III) thiocyanate to introduce students to the idea of *incompleteness* of a chemical equilibrium reaction, work subsequent to 1855 showed the blood-red compound to be a coordination compound for which ligand substitution reactions can occur in excess complexing reagent. So in this specific case one could interpret the Gladstone experiment in terms of a complete reaction. It is suggested that this controversial scenario could form the content of a curriculum project for pre-service chemistry teachers where epistemic values such as questions, explanations and assumptions are encouraged. This can highlight the significance of the equilibrium law because of its universal character. Such an experience for pre-service chemistry teachers should encourage them to appreciate the difficulties inherent in teaching the topic of chemical equilibrium and to think of creative ways that might be applicable when teaching the topic themselves.

Compliance with ethical standards

Conflict of interest There are no conflicts of interest to declare relating to this manuscript.

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