Group Theory and the Near-ultraviolet Absorption Spectrum of Gas-phase Benzene: An APCELL Experiment [1]

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Modern physical models, such as quantum mechanics, provide powerful means by which to describe and rationalise molecular properties. However, as the size (the number of electrons and nuclei) of the molecule increases, brute-force treatments employing such models can rapidly expand to ungainly proportions, which make the problem extremely difficult to conceptualise.

One way to simplify such problems is to employ the techniques of group theory. Group theory is a branch of mathematics that has a vast number of applications in the physical sciences. In chemistry, it permits aspects of molecular problems to be categorised in terms of molecular symmetry, with a consequent reduction of the apparent complexity. This, in turn, vastly aids the interpretation and conceptualisation of experimental and theoretical data.

One of the most striking achievements of the application of group theory has been in the realm of spectroscopy. With the development of quantum mechanics, spectroscopic data can be analysed to yield a great deal of very precise information about molecular structure and dynamics. But the extraction of this information can be extremely taxing, even for the simplest of systems, unless group-theoretical considerations are employed.

Twenty years ago, courses concerning chemical applications of elementary group theory constituted a standard component of university-level chemistry education. But they have become increasingly unfashionable, to the extent where modern treatments of molecular symmetry often exclude any significant formal treatment of group theory. Thus, for example, orbital, state and vibrational irrep (irreducible representation) labels are sometimes presented with no further explanation than to say that they imply something about the symmetry of the orbital/state/vibration.

The reasons for the demise of group theory are not entirely clear. It could be argued, particularly with the rise to prominence of biochemistry and molecular biology, that group theory is of only peripheral relevance to 'modern' chemistry. We would not be surprised to learn of a preponderant view among university chemistry educators that the theory is only really useful for providing a convenient system of labels, and that any deeper understanding of these labels, including the way in which they are determined, is an esoteric irrelevance. Equally, we would be unsurprised to find that many students who have been exposed to group theory see it as nothing more than a set of abstruse, theoretical exercises of little or no direct relevance to practical aspects of chemistry.

Several years ago, we designed a third-year laboratory exercise to refute these contentions, at least in the context of spectroscopy. Our aim was to illustrate that group theory is of genuine utility in the analysis of real data that would otherwise remain intractable. The experiment requires students to measure and assign the $^1B_{2u} \leftarrow {}^1A_{1g}$ electronic absorption spectrum of benzene, which occurs in the near-ultraviolet, between 220 and 285 nm. The spectrum has a moderately complicated appearance, due to vibrational structure with line shapes modified by rotational dynamics. However with the help of group-theoretical methods and application of physical intuition, students can make considerable sense of the structure and use it to partially characterise the excited state.

We chose the analysis of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene for a number or reasons:

- benzene is cheap, readily procured and easy to handle (with moderate care);
- benzene is a prototypically simple and relatively symmetric polyatomic molecule, with vibrational modes of several symmetries;
- the spectrum, which can be measured by using a conventional absorption spectrophotometer, exhibits a degree of structure that would be difficult to assign without the aid of group-theory;
- the molecular point group (D_{6h}) is sufficiently complicated to challenge the students without making the group theoretical manipulations too arduous;
- the third-year students' familiarity with the shape and electronic (p-orbital) structure of benzene should aid their ability to recognise, and make sense of, relationships between the theoretical results and the chemical concepts.

[1]The complete documentation for this experiment is freely available on the APCELL web site [www.apcell.org]. It includes the educational template, a set of student notes, demonstrator notes and technical notes to allow ready implementation into a new laboratory.

Educational Template

Section 1 - Summary of the Experiment

1.1 Experiment Title

Group Theory and the Near-ultraviolet Absorption Spectrum of Gas-phase Benzene

1.2 Description of the Experiment

Students measure the $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption spectrum of gas-phase benzene. With the guidance of the demonstrator and the student notes provided, they interpret the spectrum and assign individual vibronic bands. On the basis of these assignments, they measure some of the excited-state vibrational frequencies and relate them to physical differences between the electronic ground and excited states.

The aims of the experiment are to introduce the students to the practical application of quantum mechanics and group theory to the interpretation of reasonably complicated spectroscopic data. It is particularly relevant to students who are considering graduate- (including honours-) level study in physical chemistry. It introduces students to concepts that are commonly applied in (polyatomic) molecular spectroscopy and will help them to determine if they have an interest in pursuing research in this field.

This experiment is an effective learning tool since it requires the student to apply theoretical concepts that they have met in lectures to real data obtained from real chemical systems by using real equipment. The spectrum is reasonably complicated and most students are initially daunted by its appearance. The exercises incorporated in the experiment show that the joint use of group-theoretical and quantum-mechanical principles allows the experimenter to understand essentially all of the features of the spectrum and to deduce a good deal of information about the molecule. Moreover, the results are seen to be in accord with notions (for example bonding and antibonding orbitals) that students might reasonably be expected to have assimilated from other branches of chemistry.

1.3 Course Context and Students' Required Knowledge and Skills

This experiment was developed to illustrate the utility of group theory to the analysis of polyatomic spectra. It is best used in conjunction with lectures that have covered group theory to the level of (for example) Atkins, *Physical Chemistry*[1] or higher, covering representation theory, reduction methods, direct products, applications of group theory to the symmetry classification of molecular vibrations and determination of spectroscopic selection rules. It also requires knowledge of spectroscopic principles such as general selection rules, the Born-Oppenheimer approximation and the Franck-Condon principle. Students would be advantaged by previous exposure to the concepts of vibronic intensity stealing and hot bands. Some knowledge of angular momentum coupling, the Clebsch-Gordan series and the Pauli exclusion principle would also be helpful.

1.4 Time Required to Complete

Prior to Lab	none
In Laboratory	8 hours
After Laboratory	none

1.5 Acknowledgments

This experiment is based on a 1939 research paper by Sponer *et al.*[2] Papers by Atkinson *et al.*[3] and Stephenson *et al.*[4] provide other references for band assignments .

1.6 Other Comments

This experiment could be conducted in the large majority of teaching laboratories without the purchase or construction of specialised equipment. It requires a UV-visible absorption spectrometer, with resolution ~0.2 nm or better, a small amount of benzene and a pair of 1-cm quartz cells.

There are many possible variations of emphasis. Our intention was to design an experiment to complement an eight-lecture course on group theory, so the emphasis here was on the group-theoretical aspects of the analysis. Some of the information provided as supporting material, such as direct-product tables and determination of π-orbital symmetries, as well as determination of the symmetries of in-plane vibrational modes, could be set as separate assignments or tutorial exercises. Theoretical work could be extended to quantum-mechanical consideration of the π orbitals – from as simple as a 'particle-on-a-ring' model, through the Hückel approximation, to more sophisticated quantum-chemical calculations.

In the original version of the experiment, the vibronic bands are labelled according to the notation used by Sponer, *et al.*[2] Alternative labelling systems could be employed. For example, the vibrational-mode numbering scheme of Wilson, Decius and Cross[5] would have the advantage of emphasising the fact that several vibrational modes can be excited simultaneously.

Section 2 – Educational Analysis

Learning Outcomes *What will students learn?*	**Process** *How will students learn it?*	**Assessment** *How will staff know students have learnt it? How will students know they have learnt it?*
Theoretical and Conceptual Knowledge		
(1) Group theory has 'practical' scientific applications. In this case, the analysis of an apparently complicated spectrum is substantially facilitated by an appreciation of molecular symmetry and group-theoretical concepts.	This is the general theme of the experiment. The students will learn this by analysing the spectrum and by completing exercises integral to the experiment. There is considerable scope for the supervising staff to extend the students and encourage them to link ideas that might normally be regarded as pertaining to 'separate' areas of chemistry (and physics).	Partly from student's reports and answers to the exercises. But this experiment is best conducted as a quasi-tutorial session with substantial interaction between staff and students. There are many opportunities to verbally test the student's depth of understanding and ability to integrate ideas.
(2) Principles for determining the electronic configurations and terms for a polyatomic molecules.	Consideration of discussion and completion of exercises. The students determine the ground- and excited-state configurations using the Aufbau principle. Then by using direct products of orbital irreps (including the concept of the 'hole-particle' convention) and the Clebsch-Gordan series, they determine the corresponding electronic term symbols.	Students should obtain the correct configurations and term symbols. Further, they should know what the degeneracies of the terms are and what the orbital and spin contributions to these degeneracies are. They should also be aware of the implications of the Pauli exclusion principle and the hole-particle formalism to these cases.
(3) Group-theoretical manipulations – character analysis, direct products and reduction of a representation.	By completing exercises for symmetry characterisation of electronic states and determination of selection rules.	Students should be able to use supplied tables to generate the correct results. See (4) and (5) below for specific criteria for the components of the exercises.
(4) Transitions that are formally symmetry forbidden can gain intensity through vibronic mechanisms, which can effectively be regarded as reducing the molecular symmetry.	Consideration of discussion and completion of exercises. Group theoretical exercises shows that the pure electronic transition $^1B_{2u} \leftarrow {}^1A_{1g}$ is formally forbidden in D_{6h} symmetry – but the experiment clearly shows that the transition carries intensity. Inclusion of vibration functions and determination of the corresponding vibronic symmetries shows how transitions between individual vibronic levels may be formally allowed, even when the pure electronic transition is forbidden.	Students should be able to show that only one of the pure electronic transitions arising from the LUMO ← HOMO excitation is allowed. Given that the near-UV transition is not the allowed one, they should be able to determine the vibrational symmetry (e_{2g}) appropriate for a transition between vibronic states to become formally allowed. Students should be able to the articulate the qualitative concept that the vibration can be effectively regarded as lowering the (instantaneous) symmetry of the system. Depending on student ability and the level of the associated lecture material, it might be appropriate for them to be able to discuss the process in terms of vibronic 'intensity stealing' from formally allowed electronic transitions.
(5) Spectroscopic principles (Born-Oppenheimer approximation, Franck-Condon principle) introduced in earlier lecture courses are illustrated and reinforced.	Observation and assignment of progressions in totally symmetric modes. Relating observed progressions to 'vertical' transitions between vibrational levels within the ground and excited state manifolds.	Students should be able to make the correct assignments and demonstrate and understand of the patterns of inter-band spacings and intensities.

(6) That finer spectroscopic details, such as 'hot' bands and 'sequence' bands, can provide important information about the nature of the electronic states and can be used to assist in making and/or confirming band assignments.	Consideration of bands that occur to the red of the main false origin. Recognition that, at room temperature and given the ground-state vibrational wave numbers, low-lying vibrational level of the ground electronic state will carry significant populations. Transitions from these levels will give rise to lower-energy transitions.	Using these concepts, students should be able to identify the position of the origin band and therefore determine the excited-state wave numbers for the Herzberg-Teller vibrational modes. They should be able to state the consequences of temperature changes and explains how the spectrum would be modified in the case of different excited-state vibrational frequencies.
(7) That different electronic states of a molecule are generally characterised by different physical parameters. That these differences are reflections (in the Born-Oppenheimer approximation) of the relative positions and shapes of the electronic potential energy surfaces. That these ideas can be rationalised in terms that relate to differences in the nature (type and strength) of the bonding in the molecules.	Determination of excited-state vibrational frequencies and comparison with those of the ground state. Consideration of these results in terms of the nature (relative bonding or antibonding character) of the molecular orbitals involved in the LUMO ← HOMO excitation.	Students should be able to make connections between changes of the vibrational wave number with ideas such as bond length and bond strength. They should be able to relate these ideas to the fact that the HOMO has greater bonding character than the LUMO, so one might expect the excited state frequencies of the C_6 skeleton to be lower in the excited state. One might also predict that the bond lengths would be greater in the excited state and (out-of-plane) flexion of the ring would be more facile.
(8) If group theory predicts that a process is symmetry allowed, there will usually (always?) be a physical mechanism by which the process really does occur.	Observation and assignment of the progressions built on a C-H false origin. One might not expect C-H vibrational coordinate changes to induce vibronic transitions involving the ring-based π-orbital system, but the false origin of this progression involves such a vibration.	Correct assignment of the vibronically active mode. A strong student might attempt to rationalise this observation rather than just stating the result.

Scientific and Practical Skills

To measure absorption spectra on a commercial spectrometer.	This skill will normally be well established through prior laboratory experience by this stage of a chemistry student's education.	A well-resolved spectrum with an appropriate signal-to-noise level is an indication of correct use of the spectrometer.
To determine peak positions and reinforce awareness of the relationship between wave length and wave number.	These tasks may be achieved either manually or automatically, depending on the intentions of the demonstrator and the capabilities of the instrumentation.	By obtaining 'correct' band and vibrational wave numbers. A student who obtains wildly incorrect values has (a) performed at least one part of the measurement and conversion incorrectly, and (b) has insufficient background knowledge or scientific common sense to realise their mistake.
To be aware of the types of features that might be apparent in electronic spectra of polyatomic molecules.	This is a general theme of the experiment learnt through completing the exercises and discourse with supervisor and other students.	From the overall appreciation of this aspect exhibited in the student's (oral and written) discussion, as well as the answers to specific questions set out in the exercises.
To recognise patterns in the vibrational structure of electronic transitions.	See (5) and (6) under Theoretical and Conceptual Knowledge	See (5) and (6) under Theoretical and Conceptual Knowledge

Relation and utility of molecular spectroscopy to other aspects of chemistry.	Exercises seek to connect the quantitative results of the experiment to qualitative concepts regarding molecular orbitals, bond strengths etc., that play important roles in all aspects of chemistry. Many students will be aware of these concepts from (for example) organic and inorganic courses.	See (7) under Theoretical and Conceptual Knowledge

Generic Skills

Development of intellectual skills.	Students have to integrate a number of complex spectroscopic, quantum-mechanical and group-theoretical concepts, to which they may have been previously exposed at different times and in different contexts	From the overall appreciation of this aspect exhibited in the student's (oral and written) discussion, as well as the answers to specific questions set out in the exercises.
To present relatively complicated analysis clearly and precisely.	Students have to organise the data in order to be able to make sense of it and to allow others to see that they have made sense of it. Many of the exercises ask for tables and/or plots.	The final results should be summarised in clearly presented tables and by spectral plots on which the various progressions and band assignments are clearly indicated.
Use of spread-sheet software.	Many sections of the analysis can be performed efficiently by using commercial spreadsheet software, such as EXCEL.	Correct application throughout the analysis.
Cross-checking of the results of theory-based manipulations of the data with chemical/physical 'common sense'. Modification of a scientific 'mind view' through exposure to problems from new perspectives.	One intention of the exercises is to encourage the students to 'surface' from their theoretical deliberations every now and then to check that their results are in accord with mind views built up through prior experiences in their chemistry (and perhaps physics) education. Where there is disagreement, the students must decide if they have made an error in their manipulations. If they (believe they) haven't made an error then they have experienced a new perspective, which could lead to modified (and perhaps more appropriate) mind views.	Absence of 'errors' and confident, clearly presented (oral and written) discussion are reflections of a student's ability to check for errors. The development of underlying mind views is essentially impossible to test objectively, but remains an important aim of this experiment.
Appropriate analysis of uncertainties.	Students are expected to determine statistical uncertainty wherever there are sufficient data. They need to employ correct methods for propagation of uncertainties when deriving results from experimentally measured data.	Correct application of error analysis throughout the analysis.
To help other students. To work with a colleague on a common problem.	Students work in pairs. They bring slightly different perspectives, which can be helpful when attempting to understand some of the theoretical concepts or when relating them to the experimental results.	This can only be judged by the surveillance by the staff members during the laboratory period.

Section 3 - Student Learning Experience

3.1 Did this experiment help you to understand the theory and concepts of the topic? If so, how, or if not, why not?

S1: Yes - group theory had already been covered in the lecture course and this experiment was a practical application of this theory to a real situation with visible results.
S2: Yes, we were able to see how what we had learned might be applied to something you could obtain experimentally (rather than theoretical diagrams).
S3: Yes, could apply theory and concept to data.
S4: Yes, it built on lecture material, and gave me a greater appreciation of it through the hands-on work.
S5: Yes, because it gave the origins of the numbers being used (e.g. the electronic and vibrational energy levels involved in each transition, with appropriate diagrams).
S6: Yes. By going over them again and get explained what was going on helped to understand the theory and concepts.
S7: Yes, actually putting theory into practice in a logical step-by-step fashion.
S8: Yes, it went through step by step in a practical way, to show us how to relate concepts to data.

3.2 How is this experiment relevant to you in terms of your interests and goals?

S1: Group theory and its application to molecular structure is an important part of understanding the chemistry of molecules. The analysis of absorption spectra is a useful skill to have, so this experiment had some relevance to the practical application of knowledge.
S2: My goal to understand the chemistry (and maybe quantum mechanics one day) is helped when I can see why and where the theory arises in actual chemical situations.
S3: It gave me a better understanding of UV absorption spectrum.
S4: It is part of a course that I need to complete for my degree. It may be the area I end up specialising in.
S5: It involves applied spectroscopy and group theory (two subjects which are difficult to understand). It requires analysis of a spectrum. These are topics which are central to physical chemistry, so they are definitely relevant.
S6: I believe it has helped me to understand group theory in more detail and it should help when coming to study for the end of year exam.
S7: Helps understanding of group theory - good for exams and possible further related work.

3.3 Did you find this experiment interesting? If so, what aspects of this experiment did you find interesting? If not, why not?

S1: To see a spectrum develop from a series of unidentified peaks to a series of assigned peaks and know *how* and *why* this happened was very interesting.
S2: Yes, interesting intellectual challenge to apply the concepts of the lecture course to real data. Not heaps of fiddling around with messy solutions and lots of actually thinking about the chemistry (and physics and maths) involved makes it one of my favourite labs.
S3: Related coursework to lab work; interesting to see it all come together.
S4: Matching the theory to the results was interesting, although it got a bit repetitive.
S5: I found the level of group theory used interesting, although without the associated lectures and assignment it would have been a bit tedious, because a certain level of understanding is needed beforehand. Group theory - and the fact that it works - is interesting.
S6: The experiment was interesting. It was good to obtain our own spectrum of benzene and analyse this.
S7: Yes - it is amazing what you can do with some maths and symmetry - very simplified.
S8: Yes, I could understand the concepts behind it. It relates well to the lecture course.

3.4 Can the experiment be completed comfortably in the allocated time? Is there time to reflect on the tasks while performing them?

S1: Obtaining the actual spectrum is very straightforward and takes a very short period of time. The analysis can be completed in the remaining time provided the background work has already been covered - i.e. could not do so without prior knowledge of group theory.
S2: Yes, if the machine's working fine and we have help (or have really learned what we are supposed to know).
S3: Yes.
S4: Yes, it can easily be completed in the allotted time.
S5: We finished in the allocated time without rushing too much. There was time to discover where the results obtained came from, and why they were what they were.
S6: Yes it can be finished in the required time and there is time to think about what is going on and what you are doing.
S7: Yes, good timing. Took me exactly the allocated eight hours working at a consistent, but not rushed, pace.
S8: Yes. But I still prefer to write up afterwards.

3.5 Does this experiment require teamwork and if so, in what way? Was this aspect of the experiment beneficial?

S1: Teamwork is not required although working together is helpful because you can explain the results to each other and increase your understanding.

S2: Not really since the practical part is almost completely automated. It's good to work with someone else (if they are at about the same level of understanding) on the interpretations (the description bits) to bounce ideas and explanations off one another.
S3: It was good to be working in pairs as if one person got stuck the other could help and also could work through problems together.
S4: Not really (require), but it was helpful to be working with someone.
S5: It can be done individually, but the input from more than one person is helpful, because some points can be difficult for one person to discover by themselves.
S6: I think it does require teamwork as some parts were hard and it is good to discuss what's happening with a partner who is on the same level as you.
S7: Not really. It can be discussed, but can also be done individually just as easily.
S8: Not as such. But it is always better to have someone to work with, especially when there is a lot of data analysis to be done.

3.6 Did you have the opportunity to take responsibility for your own learning, and to be active as learners?

S1: Yes - the exercises which lead to the assignment of the peaks in the spectrum are designed to increase your knowledge as you go. If you don't understand a part you can't continue because each question builds on the last. Thus you have to take responsibility for your own understanding and you learn as you go, and to see the results as you go too which is very helpful.
S2: Yes, it would be possible (given the fairly simple ways group theory can be manipulated) to get the right answers for most of the lab but not have that good an idea of the chemistry involved.
S3: Reinforced lecture notes and gave a better understanding of lecture material.
S4: Yes - we worked through the exercises. There were clues to let us work it out for ourselves.
S5: Yes, all the necessary information is presented, and processing it requires active learning.
S6: Yes I believe so.
S7: Yes, got to operate the computer program and manipulate data as required. Good supervision and instructions - had to think for ourselves, but help was available.
S8: Most of the work we knew (from lectures) or could access from notes.

3.7 Does this experiment provide for the possibility of a range of student abilities and interests? If so, how?

S1: Not everyone is interested in group theory to the same level. This experiment shows how it can be used as a tool, which is helpful for people who are not theoretically inclined. The design of the exercises is stepwise, each building on the last so someone of less ability would still be able to follow them through even if it took them more time than someone who was very interested and had a high ability in this subject.
S2: Range of interests - theoretical, analytical, cool machine to play with (even if ours was a bit grumpy). Range of abilities - there is a choice as to how deep you take your understanding of concepts and explanations involved.
S3: It can be used as an aid to better understanding the topic. Also there was support to explain concepts when you didn't understand.
S4: It was aimed at 3rd year honours students studying physical chemistry. Other people did a different part of the experiment.
S5: The benzene experiment would be baffling for any but the top students unless preceded by the similar assignment, so a different one involving iodine was given to those who hadn't done the assignment. This doesn't really cater for other interests, but spectroscopy is an essential part of chemistry, so interest doesn't matter, it is very useful.
S6: It does provide a range of interests as you get to learn about group theory but also spectroscopy. I think it does cover a range of abilities as it is explained carefully in the method.
S7: Yes, as can skim instructions if knowledgeable in this area or read if need more information. Would need some group theory background information though.
S8: There doesn't seem to be a large range of tasks in the lab.

3.8 Did the laboratory notes, demonstrators' guidance and any other resources help you in learning from this experiment? If so, how?

S1: The laboratory notes and exercises are well written and logical. They were very helpful. The demonstrator's assistance was helpful when we got stuck on a question or couldn't decide if the answer we had arrived at was correct.
S2: Yes, couldn't have done it without both of them. Would have been very tricky without lecture course I would imagine.
S3: Gave plenty of information to complete tasks.
S4: The notes given gave a lot of clues, but the demonstrator was really helpful in putting us on the right track, or telling us we were on the right track.
S5: It is a difficult experiment, but the notes and the demonstrator's help are valuable in showing where the peaks come from, and a lot is learned about spectra and how to interpret them.
S6: The laboratory notes and demonstrator were very helpful.
S7: Yes - good lab notes (relate well to our lectures) and good explanations when required.

S8: The lecture course was really helpful and the lab, in turn, helped concrete the concepts from the course

3.9 Are there any other features of this experiment that made it a particularly good or bad learning experience for you?

S1: Answering the questions/exercises and then seeing the results build up the assignment of the spectrum was a very good learning experience. The fact that we were using the theory to get a visible result in a real situation was what made it so good for me.

S2: The demonstrator was very patient. If I enjoy the lab it enables me to learn more rather than getting frustrated at the time I'm spending doing very little.

S3: There was a lot of material to read although this is needed.

S4: Given the work-through nature of the exercises, it was hard to write up as an experiment.

S5: There were some aspects which were difficult to see without help from the demonstrator, but generally it is good revision for an introductory course to group theory. It gives a much-needed application to some concepts which are difficult to understand.

S6: No

3.10 What improvements could be made to this experiment?

S1: I found this a well organised, logical experiment.

S2: Perhaps get to have a bit better idea how the machine works (or why it doesn't on occasions).

S5: More explanation of some of the terms could be given in the instructions, because it is not always known what is wanted in answer to a question.

S6: I think the experiment is good as it is.

S8: Allow students to take the spectra, just to show how to use the equipment.

3.11 Other Comments

S8: Lecture course + lab = good.

References

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3. G. H. Atkinson and C. S. Parmenter, The 260 nm Absorption Spectrum of Benzene: Remeasured Band Positions and Refined Assignments, *J. Molec. Spectrosc.* 73 (1978) 20-30.
4. T. A Stephenson, P. L. Radloff and S. A. Rice, $^1B_{2u} \leftrightarrow {}^1A_{1g}$ spectroscopy of benzene: Single vibronic level fluorescence studies, *J. Chem. Phys.* 81 (1984) 1060-1072.
5. E. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations*, W. B. Saunders (1971)

What does it mean? Pedagogical content knowledge

The Law of Equilibrium is usually expressed as follows:

> If a system that can be represented by the equation
>
> $$aA + bB = cC + dD$$
>
> is at equilibrium at a specified temperature, then
>
> $$\frac{[A]^a\,[B]^b}{[C]^c\,[D]^d} = K$$

It is my experience that many students interpret this with a rather limited meaning, expressed as follows using a real example:

> In a vessel in which a reaction occurs that can be represented as
>
> $$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$
>
> concentrations change as reaction proceeds toward equilibrium until, at equilibrium, the ratio $[NO_2]^2/[N_2O_4]$ reaches a constant value.

This statement is correct, but it hardly represents the full meaning of the law. The focus of this interpretation is on one particular reaction mixture. In any one mixture it is also true that

$$\frac{[NO_2]^4}{[N_2O_4]^{0.5}} = \text{a constant}$$

and

$$[NO_2]^{11}\,[N_2O_4]^{56} = \text{a constant}$$

In fact, at equilibrium any function of $[NO_2]$ and/or $[N_2O_4]$ attains a constant value – simply because both $[NO_2]$ and $[N_2O_4]$ attain a constant value.

The real significance of this law is that if we have numerous reaction vessels (A, B, C, ….) in which this reaction is at equilibrium at a specified temperature, they all have the same value of the ratio $[NO_2]^2/[N_2O_4]$ - even though the concentrations of each reactant species might be different from vessel to vessel.

ie,

$$\left(\frac{[NO_2]^2}{[N_2O_4]}\right)_A = \left(\frac{[NO_2]^2}{[N_2O_4]}\right)_B = \text{.....}$$

This is not true for any other function of the concentrations.

I speculate that language is at the heart of the problem. To chemists, the word *system* refers to the process: in this case, all reaction mixtures containing $[NO_2]$ and $[N_2O_4]$ are the same system. To students, the word *system* probably refers to each separate 'reaction mixture'.

Furthermore, the chemist's meaning of *constant* is similar to 'same as' as used above. Perhaps the student interpretation of *constant* is more like its everyday meaning – unchanging.

Should we re-state the Law of Equilibrium, perhaps as follows?

> In all reaction mixtures in which a reaction represented as
>
> $$aA + bB = cC + dD$$
>
> is at equilibrium at a specified temperature, then the ratio $\frac{[A]^a\,[B]^b}{[C]^c\,[D]^d}$ has the same value in all of those mixtures.

Bob Bucat