Thermodynamics Think-In

by Justin R. Read, Scott H. Kable

Experiment Overview

Thermodynamics is one of the topics in the introductory chemistry syllabus that many students find obtuse (Sozbilir, 2004), with a range of different approaches to teaching thermodynamic concepts having been described in the literature (Arnold and Millar, 1996; Williamson and Morikawa, 2002; Greenbowe and Meltzer, 2003), including in domains other than chemistry (Nasr and Thomas, 2004; Meltzer, 2004). The subject was developed empirically over the course of more than 100 years and, as such, can suffer from lack of cohesion and old-fashioned conventions. In Australia, many students now enter university with less preparation in mathematics than previous generations. As many treatments of thermodynamics do so from a mathematical basis, these students miss out on understanding the power and usefulness of thermodynamics and have difficulty in translating thermodynamic concepts from one application to another.

All University Chemistry laboratory courses will invariably have one or more experiments at the Introductory level that teach students thermodynamics concepts – in the recent review by Domin (1999), for example, all laboratory manuals examined included calorimetry experiments, and the majority also included experiments on chemical kinetics. That are also a large number of lecture demonstrations that have as an aim to reinforce and illustrate a particular thermodynamics concept.

Thermodynamics Think-In is a collection of existing, short, observational experiments that have, as a central theme, the concept of driving forces in chemical reactions. The mix is fairly eclectic, ranging from everyday objects, such as a chemical hot pack, to commercially available oddities – such as the "Drinking Duck", which was the subject of a recent study by Lorenz (2006) – to various sets of known and unknown chemicals in sealed tubes. The students heat different tubes, cool others in liquid nitrogen, compress and expand gases and rubber bands. The experiments have been chosen with the intention of evoking strong situational interest for students, which keeps them engaged with the exercise. The practical is structured around careful observation and peer discussion – intended to promote cooperative learning – leading up to a demonstrator conference. In addition to the development of a deep understanding of elements of thermodynamics, the practical is strong on the development of thinking skills and other generic attributes.

Aims and Objectives

Theoretical and Conceptual Knowledge: The most important concepts that the students will learn in this practical relate to the thermodynamical properties that allow us to predict the direction of spontaneous chemical change. These concepts range from simple Le Chatelier's Principle, to more challenging concepts of chemical entropy. Students will learn, by experiment and experience, that temperature changes are often associated with chemical change, but that spontaneous changes can be accompanied by either an increase or decrease in temperature (exothermic or endothermic processes). This leads to the introduction, or reinforcement of chemical entropy (depending on whether the students have had the lectures on entropy at this stage of the semester). The concept of entropy is developed in one of the early experiments, usually with a lot of help and guidance from the demonstrator. The students apply their knowledge in later experiments to explain what they observe, and thus need to transfer their understanding into new contexts; the design of the exercise is intended to promote transfer via the high-road rather than via the low-road. (Salomon and Perkins (1989, p. 113, emphases in original) defined these as follows: "*Low-road transfer* depends on extensive, varied practice and occurs by the automatic triggering of well-learned behaviour in a new context. *High-road transfer*occurs by the intentional, mindful abstraction of something from one context and application in a new context.") Successful explanation shows both students and demonstrator that the knowledge has been transferred from one chemical context to another. Students also learn about phase diagrams, the thermodynamics of phase changes and the effects of pressure and temperature on equilibrium.

Scientific and Practical Skills: The development practical skills is not a focus of this practical, although the students do encounter, often for the first time, liquid nitrogen and gas syringes, and get to practice their skills with bunsen burners, glassware, and handling of acids.

As has been noted elsewhere in the literature (Russell *et al.*, 1997; Kozma, 2003; Treagust *et al.*, 2003; Wu, 2003; Han and Roth, 2006), an important scientific skill in chemistry is the ability to switch between a macroscopic (observational) picture of a chemical process and an appropriate molecular interpretation of the process. This practical is very strong in the development of this skill. Thermodynamic quantities and properties are often expressed in macroscopic terms as ΔH, ΔS, ΔG, etc. These are crucial properties for the prediction of chemical reactions; in the present context on the direction of chemical change. However, a deeper understanding of these principles is attained from a microscopic, molecular interpretation. Students are quizzed about their explanations at both levels.

Thinking Skills and Generic Attributes: This practical is built around the students' ability to observe and explain. They make no measurements, no calculations, and are not required to prepare any chemical quantity with any accuracy. Instead, they need to work out a scientifically rational explanation for their observations through a process of cooperative learning (Cohen, 1994; Gilies, 2006). The benefits of cooperative learning have been described elsewhere (Springer *et al.*, 1999; Bowen, 2000; Barbosa *et al.*, 2004), as have applications in general (Kogut, 1997), organic (Carpenter and McMillan, 2003), and physical Chemistry (Towns and Grant, 1997). In order to take both promote peer-interactions and thereby increase motivation (Paris and Turner, 1994), and to take advantage of the known qualitative superiority of collective over individual reasoning (Moshman and Geil, 1998; Moshman, 2004), consensus between students is an integral part of this practical. The observed phenomenon is first discussed between the pair of students to obtain agreement about the observations themselves. Mostly, the experiments can be repeated over and over to allow multiple chances to observe the effect and to obtain agreement. Following this, the pair must devise a chemically relevant explanation that they can agree on, and that both understand. This explanation needs to be written down in clear scientific language. After this has been completed the students may summon the demonstrator to a "conference". The students must describe their observations and then explain to the demonstrator the basis of their theory in a coherent and scientifically appropriate fashion. The demonstrator will generally challenge their theory or observations by pointing out aspects that are not consistent, or extend their understanding by introducing new data. Questions will also be asked of each student, ensuring that both students can rationalise their observations, and ensuring that students are interacting in a truly collaborative way.

Students may not progress to the next experiment before testing their theory at the demonstrator conference. Some of the experiments also have different levels of detail (and subsequent tests) to keep the most enlightened students engaged and appropriately challenged.

The whole process of this laboratory session is rich in the development of thinking skills and other generic attributes. No student, in 12 years of running this practical, has been able to explain all of the observations first time around. The thinking process is supplemented by verbal and written communication skills by the requirement that both students must agree on the explanation, and that their explanation must be written and explained to the demonstrator in clear scientific language. Sometimes this process also involves negotiation skills (!) and very often develops teaching skills in the situation where one student has grasped a concept before the other. Learners at similar cognitive levels have the opportunity to effectively co-construct an understanding of new material (Palincsar, 1998), and can also help to provide a 'scaffold' assisting each to reach a higher level of cognitive functioning (Clarkson and Brook, 2004). Vygotsky (1978) coined the term "Zone of Proximal Development" to describe such a circumstance; this zone refers to the difference between the level of cognitive achievement possible for a student working alone, and that which the student can achieve when their learning is scaffolded (John-Steiner and Mahn, 1996). In the final experiment of each set of five, the student pair is asked to explain the chemical thermodynamic basis behind what seems initially to be not a particularly chemical system. This develops the ability to apply fundamental knowledge into a general situation whilst simultaneously providing concrete examples of the 'real world' relevance of chemistry.

Level of Experiment

The experiment is run with an Advanced class at first yeat undergraduate level, but may also be suitable for students beginning second year study of physical chemistry.

Keyword Descriptions of the Experiment

Domain
physical chemistry

Specific Descriptors
thermodynamics, entropy, enthalpy, phase diagrams, equilibrium

Course Context

The student cohort is one of the advanced streams of Chemistry 1 at this university. Students work in pairs on these experiments and discussion between students is an integral part of the learning experience. Most commonly, we employ one demonstrator per 8 students (4 pairs), although over the 12 years of the experiment we have used up to one demonstrator per 16 students (8 pairs). A student / demonstrator ratio of 8:1 is very comfortable and allows the demonstrator to circulate to other experiments. A ratio of 16:1 works reasonably but is hard work for the demonstrator.

Prerequisite Knowledge and Skills

A qualitative understanding of high school chemistry concepts, such as enthalpy change and the application of Le Chatelier's Principle to predict the movement of equilibria, is required. The experiment develops students' understanding of entropy; it can be run either preceding lectures on this topic, in which case this serves as an introduction to the importance of entropy in determining spontaneous chemical change, or after lectures on the topic, in which case this serves to illustrate the influence of entropy with concrete examples.

Time Required to Complete

Prior to Lab: 30 min (for reading of experiment notes)
In Laboratory: 3 h
After Laboratory: 0 h

Experiment History

Thermodynamics Think-In has been running in the First Year Chemistry program at the University of Sydney since 1994. It was first developed by Dr Ian McNaught (now at the University of Canberra); the notes and experiments have undergone modest changes and additions since that time.

Comments

There are 10 separate experiments in this practical, organised in two sets of five. Student pairs perform one of the sets of five experiments in a prescribed order, from simple to more difficult, over 3 hours. The 10 experiments, and normal student observations are described below.

Experiment 1A (Thermodynamics of Rubber Bands, Part 1): Students place a rubber band against their lips and rapidly extend it so that the length is at least doubled. They then let the rubber band relax quickly, while still holding it against their lips. Students are asked whether they felt a temperature change (the change is small but distinctly noticeable). The students summarise their observations in chemical equation form by deducing the sign of ΔH for the equilibrium rubber band (extended) rubber band (relaxed).

Experiment 2A (Thermodynamics of Rubber Bands, Part 2): The students suspend a 1 kg block from a retort stand using 3-4 rubber bands. They then gently warm the rubber bands with a heat gun and watch whether the bands expand or shrink. Counter-intuitively, the rubber bands shrink when they are heated, as shown in the short video clip available on the Documents page.

Experiment 3A (Heating $I_2(s)$): Students are provided with two identical-looking tubes containing solid iodine. Using a gentle flame, each tube is warmed. The students are told that one tube is under vacuum, while the other contains air, but not which is which. In one tube the iodine sublimes, whilst in the other it melts.

Experiment 4A (Heating produces mixing and separation): Students are provided with two tubes – one contains roughly equal phenol / water which has two phases, and the other contains nicotine/water, which is miscible. Students heat both tubes together in a beaker of water. At about 80 °C the phenol/water mixture becomes monophasic while the nicotine/water phase separates.

Experiment 5A (Drinking Duck): The students must explain the thermodynamics principles behind how the famous “drinking duck” works (a video of one complete cycle of the drinking duck is available on the Documents page). The duck takes a drink from the bowl, then sways like a pendulum, slowly stopping, then tips over and drinks again. We use ethanol in the bowl rather than water to speed the duck up, especially on humid Sydney summer days! This is a good test of whether the students have developed a deep understanding of enthalpy, entropy, heat, temperature, and pressure.

Experiment 1B (Effect of temperature on the equilibrium between NO_2 and N_2O_4): Students are given three identical sealed tubes containing a mixture of nitrogen dioxide and dinitrogen tetroxide. They immerse one in hot water (~50 °C) and another in ice water. They are told that nitrogen dioxide is brown while dinitrogen tetroxide is colourless. The hot tube goes darker in colour than the room temperature tube, while the colder tube goes more pale. The experiment has been recently expanded to include cooling a tube in liquid nitrogen, in which case a bright blue product is formed.

Experiment 2B (Effect of pressure on the equilibrium between NO_2 and N_2O_4):Students prepare their own nitrogen dioxide from the reaction between nitric acid and copper turnings. They collect the gas in two 50 mL syringes. Both syringes are capped with blocked needles. Students quickly compress the gas with one plunger and observe the colour change. The gas initially goes darker, but then lightens over a period of a few seconds, though it remains darker than the control syringe.

Experiment 3B (ΔH and the direction of spontaneity): Students place a pool of water on a block of wood in the fume cupboard. In a beaker they mix given quantities of solid ammonium nitrate and barium hydroxide octahydrate and place the beaker on the pool of water. The beaker gets so cold that it freezes the water and the beaker sticks to the wood.

Experiment 4B (Cooling produces boiling and freezing): Students are provided with a sealed glass U-tube containing a little clear liquid. The students do not know that the liquid is water and that the tube has been evacuated. They tip the water into one arm of the tube and place the other in liquid nitrogen. The water will boil (often a sharp eruption), then the water will freeze.

Experiment 5B (ΔS and the direction of spontaneity and a commercial heat pack): Students are provided with a 500 mL measuring cylinder containing supersaturated sodium acetate. They place a few crystals of sodium acetate on top and watch the crystals grow until the whole measuring cylinder is solid. The cylinder gets quite hot. After explaining this phenomenon, the students set off a commercial sodium acetate portable heat pack; this commercial pack works the same way, but is initiated differently.

References

Ainley, M., Hidi, S. & Berndorff, D. (2002). Interest, learning and the psychological processes that mediate their relationship. *Journal of Educational Psychology,* **94,**545-561.

Arnold, M. & Millar, R. (1996). Learning the scientific “story”: A case study in the teaching and learning of elementary thermodynamics. *Science Education,* **80,** 249-281.

Barbosa, R., Jofili, Z., & Watts, M. (2004). Cooperating in constructing knowledge: Case studies from chemistry and citizenship. *International Journal of Science Education,* **26,** 935-949.

Bergin, D. A. (1999). Influences on classroom interest. *Educational Psychologist,* **34,**87-98.

Black, A. E. & Deci, E. L. (2000). The effects of instructors' autonomy support and students' autonomous motivation on learning organic chemistry: A self-determination theory perspective. *Science Education,* **84,** 740-756.

Bowen, C. W. (2000). A quantitative literature review of cooperative learning effects on high school and college chemistry achievement. *Journal of Chemical Education,***77,** 116-119.

Carpenter, S. R. & McMillan, T. (2003). Incorporation of a cooperative learning technique in organic chemistry. *Journal of Chemical Education,* **80,** 330-332.

Clarkson, B. & Brook, C. (2004). I can't understand why I didn't pass: Scaffolding student activities. In R. Atkinson, C. McBeath, D. Jonas-Dwyer, & R. Phillips (Eds). *Proceedings of the 21st ASCILITE Conference: Beyond the Comfort Zone* (pp. 191-196). Perth, WA: ASCILITE.

Cohen, E. G. (1994). Restructuring the classroom: Conditions for productive small groups. *Review of Educational Research,* **64,** 1-35.

Domin, D. S. (1999). A content analysis of general chemistry laboratory manuals for evidence of higher-order cognitive tasks. *Journal of Chemical Education,* **76,** 109-111.

Ertmer, P. A. & Newby, T. J. (1996). The expert learner: Strategic, self-regulated, and reflective. *Instructional Science,* **24,** 1-24.

Gilies, R. M. (2006). Teachers' and students' verbal behaviours during cooperative and small-group learning. *British Journal of Educational Psychology,* **76,** 271-287.

Greenbowe, T. J. & Meltzer, D. E. (2003). Student learning of thermochemical concepts in the context of solution chemistry. *International Journal of Science Education,* **25,** 779-800.

Han, J. Y. & Roth, W. M. (2006). Chemical inscriptions in Korean textbooks: Semiotics of macro- and microworld. *Science Education,* **90,** 173-201.

Hidi, S., Renninger, K. A. & Krapp, A. (2004). Interest, a motivational variable that combines affective and cognitive functioning. In D. Dai & R. Sternberg (Eds.). *Motivation, Emotion and Cognition: Integrative Perspectives on Intellectual Functioning and Development* (pp. 89-115). Hillsdale, NJ: Erlbaum.

Hidi, S. & Renninger, K. A. (2006). The four-phase model of interest development. *Educational Psychologist,* **41,** 111-127.

John-Steiner, V. & Mahn, H. (1996). Sociocultural approaches to learning and development: A Vygotskian framework. *Educational Psychologist,* **31,** 191-205.

Kogut, L. S. (1997). Using cooperative learning to enhance performance in general chemistry. *Journal of Chemical Education,* **74,** 720-722.

Kozma, R. (2003). The material features of multiple representations and their cognitive and social affordances for science understanding. *Learning and Instruction,***13,** 205-226.

Krapp, A., Hidi, S. & Renninger, K. A. (1992). Interest, learning and development. In K. A. Renninger, S. Hidi & A. Krapp (Eds.). *The Role of Interest in Learning and Development* (pp. 3-25). Hillsdale, NJ: Erlbaum.

Lorenz, R. (2006). Finite-time thermodynamics of an instumented drinking bird toy. *American Journal of Physics,* **74,** 677-682.

Meltzer, D. E. (2004). Investigation of students' reasoning regarding heat, work, and the first law of thermodynamics in an introductory calculus-based general physics course. *American Journal of Physics,* **72,** 1432-1446.

Miles, M. B. & Huberman, A. M. (1994). *Qualitative Data Analysis: An Expanded Sourcebook* (2nd edition). SAGE Publications: London.

Mitchell, M. (1993). Situational interest: Its multifaceted structure in the secondary school mathematics classroom. *Journal of Educational Psychology,* **85,** 424-436.

Moshman, D. (2004). From inference to reasoning: The construction of rationality. *Thinking and Reasoning,* **10,** 221-239.

Moshman, D. & Geil, M. (1998). Collaborative reasoning: Evidence for collective rationality. *Thinking and Reasoning,* **4,** 231-248.

Nasr, K. J. & Thomas, C. D. (2004). Student-centred, concept-embedded problem-based engineering thermodynamics. *International Journal of Engineering Education,***20,** 660-670.

Palincsar, A. S. (1998). Social constructivist perspectives on teaching and learning. *Annual Review of Psychology,* **49,** 345-375.

Paris, S. G. & Turner, J. C. (1994) Situated motivation. In P. R. Pintrich, D. R. Brown & C. E. Weinstein (Eds.). *Student Motivation, Cognition and Learning* (pp. 213-237). Hillsdale, NJ: Erlbaum.

Russell, J. W., Kozma, R. B., Jones, T., Wykoff, J., Marx, N. & Davis, J. (1997). Use of simultaneous-synchronized macroscopic, microscopic, and symbolic representations to enhance the teaching and learning of chemical concepts. *Journal of Chemical Education,* **74,** 330-334.

Ryan, R. M. & Deci, E. L. (2000). Self-determination theory and the facilitation of intrinsic motivation, social development, and well-being. *American Psychologist,* **55,**68-78.

Salomon, G. & Perkins, D. N. (1989). Rocky roads to transfer – Rethinking mechanisms of a neglected phenomenon. *Educational Psychologist,* **24,** 113-142.

Schiefele, U. & Krapp, A. (1996). Topic interest and free recall of expository text. *Learning and Individual Differences,* **8,** 141-160.

Schraw, G., Crippen, K. J., & Hartley, K. (2006). Promoting self-regulation in science education: Metacognition as part of a broader perspective on learning. *Research in Science Education,* **36,** 111-139.

Sozbilir, M. (2004). What makes physical chemistry difficult? Perceptions of Turkish chemistry undergraduates and lecturers. *Journal of Chemical Education,* **81,** 573-578.

Springer, L., Stanne, M. E., & Donovan, S. S. (1999). Effects of small-group learning on undergraduates in science, mathematics, engineering, and technology: A meta-analysis. *Review of Educational Research,* **69,** 21-51.

Towns, M. H. & Grant, E. R. (1997). "I believe I will go out of this class actually knowing something": Cooperative learning activities in physical chemistry. *Journal of Research in Science Teaching,* **34,** 819-835.

Treagust, D. F., Chittleborough, G., & Mamiala, T. L. (2003). The role of submicroscopic and symbolic representations in chemical explanations. *International Journal of Science Education,* **25,** 1353-1368.

Vygotsky, L. S. (1978). *Mind in Society: The Development of Higher Psychological Processes.* Cambridge: Harvard University Press.

Williamson, B. E. & Morikawa, T. (2002). A chemically relevant model for teaching the second law of thermodynamics. *Journal of Chemical Education,* **79,** 339-342.

Wu, H. K. (2003). Linking the microscopic view of chemistry to real-life experiences: Intertextuality in a high-school science classroom. *Science Education,* **87,** 868-891.