# Using Science Fiction To Teach Thermodynamics: Vonnegut, Ice-nine, and Global Warming

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When teaching general chemistry, it is often a challenge to keep the subject matter interesting for the students and fresh for the instructor. Taking examples from science fiction (1) or science in fiction (2) has been used as a way to boost interest in selected topics. While motivating the students is a worthy goal in itself, utilizing examples from another discipline such as literature may serve to show how seemingly remote topics such as chemistry and fiction are related to each other. A liberal education is about seeing the "big picture" and how each subject has an impact on other subjects. In addition, it is necessary to strengthen students' understanding of specific concepts by applying their knowledge to new situations. Using examples from science fiction certainly provides new situations to consider and also serves to reinforce the idea that the laws of nature are universal. Even if a situation is fictitious, concepts such as thermodynamics can still be applied.

While teaching thermodynamics to introductory students, I use an example taken from Kurt Vonnegut, Jr.'s, novel *Cat's Cradle (3).* In the story, an absentminded scientist<sup>1</sup> discovers a form of solid water, known as ice-nine, which is stable at room temperature. When a seed crystal of ice-nine is accidentally introduced into the ocean, the ocean immediately solidifies into ice-nine, eventually leading to the end of life on Earth. Any people who come into direct contact with icenine are likewise instantly "frozen". With only a brief introduction to the story, students are able to apply what they have learned about thermodynamics and make some rather interesting conclusions about the process of forming ice-nine. Using the information covered in a typical general chemistry course, it can be shown that the process of crystallizing all of the liquid water on Earth must be highly exothermic and lead to a significant increase in the global temperature.

Although ice-nine is fictitious, it does have some interesting ties to the real world (4). The author of the story, Kurt Vonnegut, Jr., graduated from Cornell University with a major in chemistry. Vonnegut took a job in the public relations office at General Electric where his older brother, Bernard, was working in the lab and had discovered how to use silver iodide particles for seeding clouds to precipitate rain and snow. The author Vonnegut credits the invention of ice-nine to Irving Langmuir, who pioneered the study of thin films and interfaces. While working in the public relations office at General Electric, Vonnegut came across a story of how Langmuir, who won the 1932 Nobel Prize for his work at General Electric, was charged with the responsibility of entertaining the author, H. G. Wells, who was visiting the company in the early 1930s. Langmuir is said to have come up with an idea about a form of solid water that was stable at room temperature in the hopes that Wells might be inspired to write a story about it. Apparently, Wells was not inspired and neither he nor Langmuir ever published anything about it. After Langmuir and Wells had died, Vonnegut decided to use the idea in his book, Cat's Cradle.

When covering thermodynamics in the general chemistry curriculum, I introduce a discussion of ice-nine to tie together the concepts of enthalpy, entropy, and spontaneity. While the thought of water spontaneously (and instantly) freezing at room temperature may seem so far beyond the realm of possibilities to even consider, such phenomena are seen with supersaturated solutions and super cooled liquids. To add a stunning visual effect to the discussion, a demonstration of a supersaturated sodium acetate solution (5) instantly crystallizing onto a watch glass containing a seed crystal, the so-called "pillar of salt", is shown to the students. We then consider the thermodynamics of the analogous but fictitious ice-nine. The question of whether the formation of ice-nine should be exothermic or endothermic may appear to be too difficult for many students at first, but if the question is presented stepwise, many students are able to come up with reasonable answers. The problem is presented in two parts (Parts A and B below). After working through the qualitative aspects of ice-nine formation and determining that the formation of ice-nine must be highly exothermic, we then consider some more quantitative aspects. The assignment is given in two parts since some of the questions in Part B contain answers to some of the questions in Part A. The questions below have been designed to lead the students through the thinking process one step at a time.

#### The Assignment

The students are presented with the following brief introduction to ice-nine and related questions in Part A prior to the discussion:

In the Kurt Vonnegut, Jr., novel *Cat's Cradle*, a hypothetical substance known as ice-nine destroys the world. Ice-nine is described as a crystalline compound, composed of  $H_2O$  molecules that are arranged in a different way than the molecules in "regular" ice. This alternate arrangement of  $H_2O$  molecules gives ice-nine its unique properties. For example, ice-nine is blue–white in appearance, and has a melting point of 114.4 °F. When a seed crystal of ice-nine is introduced into the ocean, it solidifies instantly. The event is described as follows (*3*):

#### I closed my eyes.

There was a sound like that of a gentle closing of a portal as big as the sky, the great door of heaven being closed sofily. It was a grand AH-WHOOM.

I opened my eyes-and all the sea was ice-nine.

The moist green earth was a blue white pearl.

The sky darkened. Borassi, the sun, became a sickly yellow ball, tiny and cruel.

The sky was filled with worms. The worms were tornadoes.

W

#### Part A

Consider the thermodynamics of the hypothetical process.

$$H_2O(l) \rightarrow ice-nine(s)$$

- 1. Based on the information above, will  $\Delta G^{\circ}$  for the formation of ice-nine from liquid water be positive (+) or negative (-)? Explain how you know.
- Will the entropy, S°, for the system (the ocean) increase or decrease for this process? Explain how you know.
- 3. Based on your answers above, will the enthalpy change,  $\Delta H^{\circ}$ , for this process be positive (+) or negative (-)? Write an equation to support your answer.
- 4. In the story, the author makes no mention of any temperature change that occurs when the entire ocean "froze" to ice-nine. Based on your answers above, is it necessary that the temperature of the ocean and its surroundings change as the liquid water is converted to ice-nine? Explain.
- 5. Given that the melting point of ice-nine is much higher than that of regular ice, will the  $\Delta H^{\circ}$  for the conversion of water to ice-nine be more positive or more negative than the  $\Delta H^{\circ}$  for the conversion of water to regular ice? Does ice-nine have stronger or weaker intermolecular attractions than regular ice? Explain.

### Part B

- 6. The melting point of ice-nine is given as 114.4 °F. What is the melting point of ice-nine in Celsius degrees?
- 7. If 1.00 mol of water at 0 °C were converted to ice-nine, what is the minimum quantity of heat that would be released? (The enthalpy of fusion for regular ice is 6.01 kJ/mol.)
- 8. Imagine 1.00 mol of water being converted to ice-nine in an insulated container. Liquid water has a heat capacity of 4.184 J/(g °C). Since liquids generally have a higher heat capacity that their corresponding solids we can make the assumption that the heat capacity for icenine would not be more than 4.184 J/(g °C). Given the minimum quantity of heat released when 1.00 mol water is converted to ice-nine (step 7 above) and our assumption about the maximum heat capacity of ice-nine, calculate the temperature change that would have to result from the conversion of 1.00 mol liquid water at 0 °C to ice-nine in an insulated container. Is this possible?
- 9. If we imagine that ice-nine really existed, is it possible that the ocean could be "instantly" converted into icenine as described by the author? What other changes might need to take place?

# Discussion

After the students have had an opportunity to think about the questions in Part A and discuss them in small groups, we come together as a class to defend our answers. From the information given, most students are able to determine that the formation of ice-nine is a spontaneous process (in the story) and that the  $\Delta G^{\circ}$  for the process must be negative. From previous discussions on entropy changes associated with changes of state, most students remember that in going from a liquid to a solid, the entropy of a system decreases, and  $\Delta S^{\circ}$  for the formation of ice-nine from liquid water (in the ocean) would be negative since solids are inherently more ordered than liquids. Given that the process is spontaneous and that the entropy change is negative, students can then reason that the  $\Delta H^{\circ}$  must be negative as well. This is easily shown from the Gibbs function,  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ . If  $\Delta S^{\circ}$  is negative, the only way for  $\Delta G^{\circ}$  to be negative is if  $\Delta H^{\circ}$  is negative as well. This idea can be reinforced in the discussion with the saturated sodium acetate demonstration. A stoppered flask containing newly solidified sodium acetate, made by dropping a seed crystal into a flask of supersaturated sodium acetate (5), is passed around so that the students can feel for themselves that this related process is exothermic. A commercial hot pack could suffice here as well.<sup>2</sup>

Once the formation of ice-nine is shown to be exothermic, it should follow that the process must be accompanied by an increase in temperature since this is how we define an exothermic process. This is not necessarily obvious to the students since many of them associate the formation of ice with getting colder. Indeed, room temperature water, when placed in a freezer, gets colder and freezes but the freezing process is exothermic and will not occur unless the freezer removes the heat.

The discussion is also used to review intermolecular interactions. Since ice-nine is a solid at room temperature and has a higher melting point than regular ice, it can be deduced that the intermolecular interactions that hold the water molecules to each other in ice-nine must be stronger than the intermolecular interactions holding water molecules together in regular ice. This would also mean that the enthalpy of fusion for ice-nine must be greater than the enthalpy of fusion for regular ice since the enthalpy of fusion results from these intermolecular interactions.

After discussing the qualitative aspects of the change in Part A, the students then consider a few calculations for the process in Part B. We begin with a simple temperature conversion problem by converting the reported melting point of ice-nine from 114.4 °F to 45.78 °C.

Once it is shown that the  $\Delta H^{\circ}$  for the conversion of liquid water to ice-nine is more negative than  $\Delta H^{\circ}$  for the conversion of liquid water to regular ice, a lower limit on the quantity of heat released in the process can be estimated. The enthalpy of fusion for water is 6.01 kJ/mol so the conversion of 1.00 mol of liquid water to ice-nine will release at least 6.01 kJ. For simplicity, the students are asked to consider what would happen if 1.00 mol water were converted to ice-nine in an insulated container. We can calculate a lower limit on the temperature increase that this process would need to produce if we make the assumption that the specific heat capacity for ice-nine would not be greater than that for liquid water, 4.184 J  $^{\circ}C^{-1}$  g<sup>-1</sup>. This assumption is, by necessity, pure speculation but not unreasonable since liquids tend to have higher heat capacities than their corresponding solids (6). Given this assumption and the lower limit to the  $\Delta H^{\circ}$ for the process, we can calculate that the conversion of 1.00

mol (18.0 g) liquid water to ice-nine in the insulated container would need to be accompanied by a temperature increase of at least 79.8 °C!<sup>3</sup> Even if the temperature of the water started out at 0 °C, this would put the temperature in the container above the melting point of ice-nine.<sup>4</sup> Clearly, the complete conversion of liquid water to ice-nine could not occur unless a large quantity of heat was transferred to the surroundings. If the ocean were to be converted to ice-nine, the atmosphere would certainly need to warm considerably.<sup>5</sup>

It may be helpful, particularly for the more advanced students, to discuss the reasonableness of this estimation of the temperature increase. First, the physical changes discussed above are for substances that are not in their standard states and the phase transitions do not occur at constant temperature and pressure. As we are making generalizations and estimations, this should not affect our conclusions. Since the enthalpy for the conversion of liquid water to ice-nine is likely to be more negative than the enthalpy for the conversion of liquid water to regular ice and the heat capacity of ice-nine is likely to be less that that for liquid water, as discussed above, our estimated temperature increase is merely a lower limit on what might be expected for such a process. A higher enthalpy or a lower specific heat capacity would each result in a larger estimated temperature increase. Our estimation ignores the fact that heat capacities generally increase with temperature although the change is usually small for a narrow temperature range (6). Taking an increased heat capacity at higher temperature into account would bring our estimated value down slightly.

In considering whether or not the author's description of the formation of ice-nine is reasonable from a thermodynamic point of view, we could make a few conclusions. Since the author makes a visual description of the surface of the ocean being converted to ice-nine we can deduce that either the entire ocean was converted to ice-nine or that only the surface of the ocean was converted to ice-nine, which would then require that ice-nine be less dense than liquid water. It could be pointed out that the majority of solids are more dense than their corresponding liquids (regular ice is an exception) so that if ice-nine were to float it would be unusual in that respect. Also, if ice-nine were less dense than liquid water, the transition from liquid water to ice-nine would require an increase in volume. The author gives no indication of any shock waves or earthquakes that accompany the transition indicating that there were no significant changes in the volume of the ocean. There is the mention of the tornadoes formed that would indicate that a tremendous quantity of energy was somehow transferred to the atmosphere. It is certainly reasonable that rapidly heating the atmosphere could cause tornadoes. As stated above, the formation of ice-nine from room temperature water is not possible without a large quantity of heat being transferred to the surroundings. A great deal of the heat released could also be transferred into the ocean floor. If only the surface of the ocean were converted to ice-nine, much less heat would be released and the liquid water underneath could absorb a great deal of it. In any case the conversion of liquid water to ice-nine will release a great deal of heat that will eventually be transferred to the environment.

### Conclusion

I have used this example in both my regular second semester introductory course as well as in my accelerated general chemistry courses. I cover the qualitative aspects of the discussion (Part A) with all my students and I am able to have a much deeper discussion (Part B) with groups of stronger students. The exercise requires from 15 to 30 minutes depending on student interest. In general, the students come up with reasonable answers but occasionally need a bit of guidance. I have found this discussion to be well received and some students are particularly enthusiastic about the discussion. It is quite rewarding when a student says, "I want to go read this book" or "this is the example that made thermodynamics stick in my head".

This example provides an opportunity to review thermodynamic concepts and apply them to a new situation. By using minimal information and consistently applying the theory, one could conclude that if ice-nine were to spontaneously form as described in the story, its formation must be accompanied by a very large increase in the temperature of the ocean and its surroundings. This example demonstrates the universality and the tremendous predictive power of thermodynamics. In addition, the discussion allows the students to see chemistry in relation to other disciplines such as literature.

### **Acknowledgments**

The author wishes to thank Cornell College for its support in developing this exercise. Truman Jordan was helpful in the preparation and critical reading of the manuscript.

## <sup>w</sup>Supplemental Material

The student assignment is available in this issue of *JCE Online*.

### Notes

1. The scientist in this story is the fictitious inventor of the atomic bomb and is portrayed as rather cold and impersonal, showing no regard for the lives destroyed by his inventions. The writings of Vonnegut, referenced below, reflect common stereotypes of scientists and shed important insight on the relationship of science and society. The discussions of the thermodynamic example above might also be used as a lead-in to the discussion of these other important topics, which are often ignored in science courses.

2. This is the basis of a commercial hot pack in which a supersaturated solution of sodium acetate is seeded to produce the heat. The pack can be reused by placing it in boiling water and heating it until supersaturation is reestablished. More information can be obtained on *http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA3/MAIN/ACETATE/PAGE1.HTM* (accessed Jan 2004).

3. A standard equation for heat capacity  $q = mc_s \Delta T$  (where q is the heat transferred, m is the mass,  $c_s$  is the specific heat, and T is temperature) can be rearranged to  $\Delta T = q/(mc_s)$ . Taking 1.00 mol of water with a mass, m = 18.0 g, 6.01 kJ for q, and a specific heat of 4.184 J °C<sup>-1</sup> g<sup>-1</sup> we can calculate a  $\Delta T$  of 79.8 °C for the complete conversion of the water to ice-nine.

4. Alternately, we could calculate the amount of the sample in the insulated cup that would freeze if all of the heat released went into heating the contents of the container from 0 °C to the melting point of ice-nine, at which point the freezing process would cease. Warming the sample from 0 °C to 45.78 °C would require 18.0 g × 45.78 °C × 4.184 J °C<sup>-1</sup> g<sup>-1</sup> = 3448 J. This is the quantity of heat that would be released when 3448 J × 1 mol/(6010 J) = 0.5736 mol water (10.32 g) had been converted to ice-nine. Since, as discussed above,  $4.184 \text{ J} °C^{-1} \text{ g}^{-1}$ , the heat capacity of liquid water, is the upper limit on the heat capacity of ice-nine and 6010 J is a lower limit on the enthalpy of fusion, this estimate is an upper limit on the amount of the 1.00 mol sample that could be converted to ice-nine without the presence of some form of a heat sink to remove the tremendous quantity of heat released by this process.

5. If all of the heat released from the conversion of liquid water to ice-nine were transferred to the atmosphere, an even more dramatic temperature increase would occur. The following estimate was suggested by a reviewer: If the ocean contains 35 million cubic miles of water =  $1.4 \times 10^{23}$  mL water =  $8.1 \times 10^{21}$  mol, the water would lose ( $8.1 \times 10^{21}$  mol)(6010 J/mol) =  $4.9 \times 10^{25}$  J heat. If the troposphere were 9 miles deep and had a volume of  $1.8 \times 10^{10}$ mi<sup>3</sup> =  $7.5 \times 10^{22}$  L, there would be  $4.6 \times 10^{21}$  mol of gas (assuming a uniform pressure of 1 atm and a uniform temperature of 200 K). Assuming a heat capacity of 29 J/(mol K) (heat capacity of nitrogen gas) would give a temperature increase of 370 °C. This estimation is offered as a dramatic example of the tremendous quantity of heat involved in the conversion of liquid water to ice-nine. Since heat flows from higher temperature to lower temperature, the newly formed ice-nine would not be able to heat the atmosphere to a higher temperature than the ice-nine itself reaches.

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