

*The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professors James O. Wilkes and Mark A. Burns, Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.*

## A SIMPLE HEAT OF CRYSTALLIZATION EXPERIMENT

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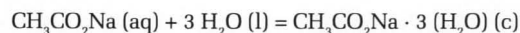
A permanent problem in engineering education is to find simple, portable, low-cost classroom demonstrations of the principles we present to our students. The more we can convince them that the equations in their textbooks describe what actually occurs in nature, the better engineers they are likely to become. For that reason, educators are always looking for opportunities to present experimental confirmation of textbook principles. If possible, we seek to find simple things, available to the public in general, which illustrate engineering principles—and then to show the students how those principles apply to things in their daily lives.

A sportsman's handwarmer is a great comfort on cold days. It is also a simple, portable tool that can be used to show students that textbooks do describe the real world. The "Heat Solution Reusable Heat Pack"<sup>[1]</sup> is available in sporting-goods stores for \$3.00. It is a 3-by-4 inch clear-plastic pouch, containing approximately 100 gm of an approximately 50 wt% solution of sodium acetate (NaAc) in water, plus a

roughly 5/8-inch diameter, thin, stainless steel disc.

This device can be used in a sophomore heat and material balances class by first assigning the following as a homework problem or exam question:

A solution of 50% by weight water and 50% by weight sodium acetate (NaAc), ( $\text{CH}_3\text{CO}_2\text{Na}$ , molecular weight 82), is at 25 °C. This solution now crystallizes adiabatically by the reaction



for which the heat effect is  $\Delta H = -30.74$  kJ/mol of NaAc.

Here assume that the original solution was one mole of NaAc (82 gm) and 82 gm of water. At equilibrium at the final temperature the composition is 56.44 gm of crystalline  $\text{CH}_3\text{CO}_2\text{Na} \cdot 3(\text{H}_2\text{O})$ , and a solution consisting of 59.59 gm of water and 47.97 gm of dissolved NaAc.

The heat capacities are: water,  $C_p = 4.18$  J/gm °C,  $\text{CH}_3\text{CO}_2\text{Na} \cdot 3(\text{H}_2\text{O})(\text{c})$ ,  $C_p = 2.4$  J/gm °C, and dissolved NaAc,  $C_p = 2.58$  J/gm °C.

What is the final temperature of the mixture of NaAc solution and crystals after equilibrium is reached?

### SOLUTION

For an adiabatic, constant-pressure batch process with no work other than expansion against the surroundings, we have

$$\Delta H = 0 = m_{\text{crystallized}} \Delta H_{\text{crystallization}} + \sum m C_p \Delta T$$

$$\Delta T = \frac{-m_{\text{crystallized}} \Delta H_{\text{crystallization}}}{\sum m C_p}$$

$$m_{\text{crystallized}} = \frac{56.44 \text{ gm of trihydrate}}{136 \frac{\text{gm}}{\text{mol of trihydrate}}} = 0.415 \text{ mols}$$



*Noel de Nevers has been a faculty member at the University of Utah since 1963. His principal technical interests are fluid mechanics, thermodynamics, and air pollution. He has also developed a course and edited a book of readings on Technology and Society. In addition to his technical work, he had three of his laws published in the 1982 Murphy's Laws compilation and won the coveted title of "Poet Laureate of Jell-O" at the annual Jell-O Salad Festival in Salt Lake City.*

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$$\Delta T = \frac{-0.415 \text{ mol} \cdot \left(-30,740 \frac{\text{J}}{\text{mol}}\right)}{\left(56.44 \text{ gm} \cdot 2.4 \frac{\text{J}}{\text{gm} \cdot \text{C}} + 59.59 \text{ gm} \cdot 4.18 \frac{\text{J}}{\text{gm} \cdot \text{C}} + 47.97 \text{ gm} \cdot 2.58 \frac{\text{J}}{\text{gm} \cdot \text{C}}\right)} = 25.1 \text{ }^{\circ}\text{C}$$

$$T_{\text{final}} = 25 + 25.1 = 50.1 \text{ }^{\circ}\text{C}$$

Thus one would expect the final temperature to be about 25°C higher than the initial temperature, for this initial temperature.

After the problem has been discussed in class, the instructor measures the temperature of the uncrystallized pouch; this is most easily accomplished by using a small portable LCD thermocouple gauge (Kiethley Model 870 Digital Thermometer or equivalent). The instructor (or a student) lays the pouch on a piece of any kind of insulating plastic foam with the thermocouple between the pouch and the plastic. The gauge quickly shows the temperature, which should be practically room temperature.

Then the instructor initiates crystallization by flexing the stainless steel disc inside the pouch, which presumably causes a small oxide particle to flake off, which in turn starts the crystallization. The entire crystallization takes place in three to five seconds, with a visible, white, opaque crystallization front moving across the pouch from the initiation point. The instructor (or the students) then measures the temperature as described above, finding that it does increase by very close to 25°C. The instructor then hands the pouch around to the students so they can feel that it is quite warm.

This is probably as much as the instructor would want to do with the demonstration and/or the calculations in a typical sophomore heat and material balances class. But there are even more possibilities for instruction in this simple device.

The instructor can use the experiment for demonstrating supersaturation and nucleation. The device can be regenerated and reused by placing it in boiling water for a few minutes and then allowing it to cool. The published melting point of the pure trihydrate is 58°C, so at room temperature it is about 35°C supercooled. It can be supercooled to freezer temperature (-13°C) without initiating solidification.

The homework or examination problem can be made more complex by not specifying the final masses of crystals, water, and dissolved NaAc, but rather by specifying the initial state and giving the final condition that the uncrystallized solution has 0.805 gm dissolved NaAc per gm of water (which corresponds

to equilibrium at 49°C) in the final state. In that case the student may solve for the values of the final masses shown in the problem by writing three material balances. If  $x$  represents the grams of crystalline trihydrate,  $y$  the grams of water, and  $z$  the grams of dissolved NaAc, then

$$x + y + z = 164 \text{ gm}$$

$$z = 0.805 y$$

$$y = (164 - 82) - x \cdot (54 \text{ gm water of hydration} / 136 \text{ gm trihydrate})$$

These may be solved together to find the values in the problem statement.

The problem can again be made more complex by using a heat capacity equation for the crystalline trihydrate instead of using the average values shown above. The data in reference (2) are reasonable well represented by

$$C_p = 1.44 \text{ J/gm }^{\circ}\text{C} + (0.028 \text{ J/gm }^{\circ}\text{C}^2) T$$

The average  $C_p$  value used in the problem corresponds to  $T = 34.3^{\circ}\text{C}$  in this formula, which is about half-way between room temperature and the final temperature of the crystallized system.

The final temperature of the hand warmer is surprisingly insensitive to the initial temperature because the solubility of sodium acetate in water increases rapidly in the range from about 45°C to the melting point of the trihydrate at 58°C.<sup>[3]</sup> Using the above equations and working backwards from assumed final temperatures, one computes that

Assumed Final Temperature, °C	NaAc Solubility gm/gm Water	Computed Starting Temperature °C
48	0.78	20.4
50	0.83	27.5
52	0.90	37.7

Thus, for initial temperatures between 20.4 and 37.7°C the computed final temperatures change only from 48 to 52°C. Experimentally, the independence of final temperature on starting temperature seems even stronger than this calculation suggests, but the experimental temperature measurements are not very precise. For an initial temperature of -13°C (freezer temperature) the observed  $\Delta T$  was 46°C, and the resulting crystalline mass at 33°C was quite firm. For an initial temperature of 41°C the final temperature was 51°C ( $\Delta T = 10^{\circ}\text{C}$ ) and the resulting crystalline mass was quite mushy.

The calculated results are quite sensitive to the assumed initial water content. Again, using the above assumptions we may calculate

Assumed Final Temperature, °C	Assumed Initial NaAc wt. Fraction in Solution	Computed Starting Temperature °C
50	0.49	32.8
50	0.50	27.5
50	0.51	22.1

In making up the problem, the value of 50 wt% NaAc was chosen because the resulting calculations gave the best match to the experimental tests. (By phone a Prism staff member said the concentration was between 50 and 55 wt%, but declined to say exactly what the value was.)

The heat of crystallization was computed from the data in reference 3.

## REFERENCES

1. Prism Technologies, 3111 N. Knox, Chicago, IL 60641 (312-685-0999)
2. *International Critical Tables*, E. W. Washburn, ed., Vol. 5, pg 100, McGraw-Hill, NY (1929)
3. *Gmelins Handbuch der anorganischen Chemie* 8. Auflage, System Nummer 21, Natrium, Verlag Chemie, GmbH, Berlin, pg. 822 (1928)
4. Rossini, F.D., et al., "Selected Values of Chemical Thermodynamic Properties," *NBS Circular 500*, pg. 470 (1952) □

## ChE book review

### PROCESS CONTROL: STRUCTURES AND APPLICATIONS

by Jens Balchen and Kenneth Mummé

Van Nostrand Reinhold, 115 Fifth Ave., New York, NY 10003; \$59.95 (1987)

Reviewed by

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This book aims to "bridge the long-standing gap between process and control." Toward this end, the second chapter reviews most control theory and control system design methods. Chapter 3 gives a mainly qualitative description of many important chemical and physical processes, ranging in complexity from valves to crystallization and reaction processes. Chapters 4 and 5 present alternate control structures for the processes described in Chapter 3. These structures are combinations of PID, ratio, feedforward, and cascade controllers, along with arithmetic and logic blocks which are standard in most distrib-

uted control systems. The book concludes by presenting the control structures for several integrated process systems such as a paper machine and an ammonia plant. The discussion is mostly qualitative.

The authors have undertaken to present an immense amount of material to an extremely wide audience; indeed, too much material to too wide an audience. Chapter 2, by necessity, gives only the most cursory overview of the topics covered. In some places the need to be concise has led to inaccurate and/or misleading statements as, for example, on page thirteen where it is stated that in order for a feedback controller to be effective, the loop transfer function  $h_0(s)$  must satisfy  $|h_0(s)| \gg 1$ . The discussion on multivariable decoupling and predictive control completely omits treatment of control effort constraints. Such an omission is unforgivable in a text that claims to bridge gaps.

Later chapters suffer from very uneven coverage of subject matter. While most discussions describe various pieces of equipment and how they work, every so often the discussion gets very detailed. In the discussion of compressors, for example, it is pointed out that "it is important that the pressure and temperature be such that the gas does not reach the critical point." This somewhat imprecise statement is then illustrated by PVT diagrams (page 103) for water and carbon dioxide, with no explanation of how to use the diagrams. In the discussion of chemical reactors, the reader is presented with a partial differential equation model for the reaction  $A \rightarrow B$  in a plug flow tubular reactor (pages 238-239). These equations are then followed immediately by the statement that if the heat transfer coefficient can be used as a control variable, it can be expressed in terms of a new variable which is the relative change in heat transfer coefficient with respect to the steady-state heat transfer coefficient. No justification is given for the equation which follows nor is it clear why the change of variable was even mentioned since the subject is immediately dropped. This reviewer remains confused as to why we would even wish to use variations in heat transfer coefficient as a control variable for tubular reactors.

In summary, it is difficult to know to whom to recommend this book. It assumes too much chemical engineering background for the average control engineer and too much control background for the average chemical engineer. Perhaps, my academic colleagues will find useful some of the detailed process descriptions and P&I diagrams. □