

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 that elucidate difficult concepts. Please submit them to Professor H. Scott Fogler, ChE Department, University of Michigan, Ann Arbor, MI 48109.

A WINE PROBLEM

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TOPPER, OUR LABORATORY Assistant, told us an interesting story about a problem he had with a customer in the restaurant where he works on weekends. Topper said that only scientific minds like ours (chemical engineers, after all!) could help him.

Some days ago, a very handsome, elegant gentleman came to the restaurant where Topper tends bar and ordered a very simple drink consisting of a mixture of three rare, expensive wines and some orange peels. The mixture should contain: 500 cc of French Romanée, the rarest of the great wines from Borgoña, according to the gourmet; 200 cc of Italian Falerno, "the wine sung of by Horatio," boasted the customer; 300 cc



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TABLE 1

Topper's experimental data for mixtures containing Romanee (A), Falerno (B), and Vintage Port (C). All data at $T = 295$ K.

Composition Vol. %			V^E			
A	B	C	S^E/R	G^E/RT	U^E/RT (cc/mol)	
50	40	10	0.0251	0.0498	0.0750	-3.0
50	30	20	0.0400	0.0700	0.1101	-5.5
50	25	25	0.0448	0.0751	0.1199	-6.0
50	20	30	0.0402	0.0688	0.1102	-5.5
50	15	35	0.0301	0.0549	0.0848	-4.5

of an authentic Portuguese Vintage Port 1947; and 5 cm² of orange peels. The customer said that all the wines and the pieces of orange peels should be at 22°C and be carefully mixed for 10 seconds . . . not less . . . not more. Then the drink should be served in a mug, hopefully an earthenware mug to keep the temperature constant. Topper took the thermos which he uses to prepare all the drinks, put the wines and peels in it, and mixed them as the customer had indicated. After 10 seconds of mixing, he poured the potion into a mug and brought it to the sophisticated customer. The gentleman then took a high-precision thermometer he carried with him, measured the temperature of the liquor, and or, my God! . . . What a tragedy! The thermometer indicated 24.52°C instead of 22°C as the gourmet expected. He made a big deal out of that little detail, arguing that the flavor, bouquet, and aroma were all destroyed by that slight temperature rise. He also observed that in the mug and thermos the total volume of liquor was less than one liter, as anyone who has had a material balance course should expect when mixing 500 cc, plus 300 cc, plus 200 cc. Topper was fired

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after the scandal.

Our hero, of course, was not happy with the lay-off and was determined to find the root of the problem. He came to the laboratory to perform some experiments. He had heard that thermodynamics has something to do with mixing phenomena and had notions of excess functions, mixing properties, activity coefficients and so on. He thought that there should be a way to find something to convince his boss that he was not responsible for what had happened. He measured, very carefully, the excess volume, excess free energy, excess entropy, and excess internal energy at 22°C for five mixtures. His results are shown in Table 1. Topper's trouble now is that he doesn't know what to do with the experimental data. Let's help him!

- Topper's data for H^E , G^E , and S^E agree with other results published in the literature (J.R. Sot et al., *J. Alcoholism & Drugs*, 81 (4), 348-53, 1980) and can be considered to be accurate and correct. However, the excess volume seems to be inconsistent. Are Topper's data for the excess volume correct?
- Show, quantitatively, that the rise in temperature is natural because of the mixing phenomena. Is the customer's thermometer accurate enough?
- The customer argued that he usually prepared the mix at home, that the temperature never rose more than a half Celsius degree, and that he always got the liter he expected. What could have possibly happened that made Topper's mix hotter? Why didn't Topper get one liter after the mixing?
- Prausnitz, in his book *Molecular Thermodynamics of Fluid-Phase Equilibria* (p. 484), asserts in respect to the Regular Solution

TABLE 2

Pure component data at 22°C for Romanee (A), Falerno (B), and Vintage Port (C). (All the data were taken from the Wine Tester's Handbook by Terry and Chitton).

Property	A	B	C
V^L (cc/mol)	44.0	44.1	43.9
δ (cal/cc) ^{1/2}	9.0	6.5	9.0
ρ (gr/cc)	0.851	0.849	0.850
C_p (cal/mol K)	25.0	20.1	29.9
p_i^{sat} (atm)	0.871	0.870	0.869
Molecular Weight	40.1	39.8	40.2

Theory: "It is therefore surprising that these equations work as well as they do. It is likely that the success of the regular-solution treatment is due to a considerable amount of fortuitous cancellation of those errors which are introduced by the many simplifying assumptions."

Show that such a cancellation of errors occurs here in some cases, while in others it doesn't.

- The gourmet bragged about his tasting abilities claiming that by only smelling the mix he could detect the various wines and in what proportion they were present in the mixture. He actually did it with the mixture prepared

Then the drink should be served in a mug, hopefully an earthenware mug to keep the temperature constant. Topper took the thermos which he uses to prepare all the drinks, put the wine and peels in it, and mixed them as the customer had indicated.

by Topper, announcing: "I smell 48% of Romanée, 27% of Falerno, and 25% of Vintage Port (in volume %)." Then he said that the quantities established by the recipe (500 cc of A, 200 cc of B, and 300 cc of C) were correct, but not the temperature, nor the volume! Do you agree with the client's assertions?

SOLUTION

- From thermodynamics courses

$$PV^E = H^E - U^E \quad (1)$$

$$H^E = G^E + TS^E \quad (2)$$

$$PV^E = (G^E + TS^E - U^E)$$

or

$$\left(\frac{PV^E}{RT}\right) = \left(\frac{G^E}{RT} + \frac{S^E}{R} - \frac{U^E}{RT}\right) \quad (3)$$

For all compositions shown in Table 1 we get $V^E \cong 0$, which indicates that Topper's data for the excess volume are wrong.

- We know from our thermodynamics courses that

$$\Delta H^M = H_{\text{mix}} - \sum_i x_i H_i^0$$

and

$$H^E = H_{\text{mix}} - H_{\text{ideal mix}}$$

Since

$$H_{\text{ideal mix}} = \sum_i x_i H_i^\circ$$

We have that

$$\Delta H^M = H^E \quad (4)$$

The heat developed by the mixing process, that is, ΔH^M , is entirely used to increase the temperature of the mixture. (Remember that Topper prepared the drink in a thermos, that is, an adiabatic reservoir). Therefore, from an energy balance, we have

$$\Delta H^M = H^E = \bar{C}_p \Delta T$$

with

$$\bar{C}_p = \sum_i x_i C_{p,i}$$

and

$$H^E = G^E + TS^E$$

we have

$$\Delta T = (G^E + TS^E) / \sum_i x_i C_{p,i} \quad (5)$$

For the mixture under consideration ($X_A = 0.5$, $X_B = 0.2$, $X_C = 0.3$), we obtain from Table 1 $G^E/RT = 0.0751$, $S^E/R = 0.0448$; and from Table 2

$$\begin{aligned} \bar{C}_p &= 0.5 (25.0) + 0.2 (20.1) + 0.3 (29.9) \\ &= 25.49 \text{ (cal/mol K)} \end{aligned}$$

Note that since the densities and molecular weights of all wines are approximately the same, the volume percent is equal to the mole percent.

Introducing values into Eq. (5), we obtain

$$\Delta T = \frac{(0.1101)(1.987 \cdot 295)}{25.49}$$

$$\Delta T = 2.53^\circ\text{C}$$

It can be seen that the temperature rise comes from the mixing process itself (carried out adiabatically). The customer's thermometer can be considered accurate enough for the objectives of the measure.

- c) Probably the customer prepared the drink in a good mixer (like the good gourmet he was!), but perhaps it was not an adiabatic one. Therefore, the heat released by the mixing process was absorbed by the surroundings. In respect to the volume, there is no doubt that Topper drank a sip and then cheated with the values to justify the reduction of volume.

- d) From our studies on Regular Solution Theory for multicomponent mixtures, we know that

$$G^E = \sum_i X_i V_i^L (\delta_i - \bar{\delta})^2 \quad (6)$$

$$\bar{\delta} = \frac{\sum_i X_i V_i^L \delta_i}{\sum_i X_i V_i^L} \quad (7)$$

If the volumes V_i^L are equal, as in this case (from Table 2, $V_i^L \cong 44$ for all i)

$$\bar{\delta} = \sum_i X_i \delta_i$$

Introducing values

$$\bar{\delta} = 0.5 \cdot 9.0 + 0.2 \cdot 6.5 + 0.3 \cdot 9$$

$$\bar{\delta} = 8.5 \text{ (cal/mol K)}^{1/2}$$

$$G^E \cong 44 [0.5 (9.0 - 8.5)^2 + 0.2 (6.5 - 8.5)^2 + 0.3 (9.0 - 8.5)^2]$$

$$G^E = 44 \text{ (cal/mol K)}$$

From Table 1, for $X_A = 0.5$, $X_B = 0.2$, and $X_C = 0.3$

$$G^E/RT = 0.0751$$

$$G^E = 44.02 \text{ (cal/mol K)}$$

For the mixture under consideration, the RST applies for the calculation of G^E . But, be careful! Remember that RST also considered that $G^E = U^E$ and $S^E = V^E = 0$. Of these, only $V^E = 0$ is fulfilled here. The coincidence has to be considered as a fortuitous case. Also, for other compositions, G^E predicted by RST doesn't agree with Topper's experimental data.

- e) At low pressures the gas phase can be considered ideal. Therefore, the basic relation

$$y_i \bar{\phi}_i P = X_i \gamma_i f_i^\circ \quad (8)$$

becomes

$$y_i P = X_i \gamma_i P_i^{\text{sat}} \quad (9)$$

Let's assume valid the RST for the mixture under consideration, that is

$$\ln \gamma_i = \frac{V_i^L}{RT} (\delta_i - \bar{\delta})^2 \quad (10)$$

$$\gamma_A = \gamma_C = 1.0178$$

$$\gamma_B = 1.3225$$

From Eq. (9)

$$X_i = \frac{y_i P}{\gamma_i P_i^{\text{sat}}}$$

$$X_A = 0.508$$

$$X_B = 0.253$$

$$X_C = 0.239$$

The customer's assertion is correct ($\pm 5\%$ deviation considered acceptable). \square

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ChE book reviews

PRINCIPLES OF POLYMERIZATION ENGINEERING

by J. A. Biesenberger and D. H. Sebastian
John Wiley & Sons, New York, 1983: \$54.50

Reviewed by Donald G. Baird
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Chemical engineers are slowly being exposed to more polymer courses in their education. General courses in polymer science are most commonly available, but courses in polymer processing, materials, and chemistry are also being offered. One area of polymer engineering which should also be studied by chemical engineers and chemists is that of polymerization engineering. Some of the significant problems faced by scientists and engineers in the polymer industry are how to scale up reactors from the bench size, and how to design optimum and efficient polymerization processes. As we update the traditional engineering curriculum, it is important that a course in polymerization engineering be included. Of course, offering a course of this nature requires the availability of a textbook. In this article we review the text *Principles of Polymerization Engineering* by J. A. Biesenberger and D. H. Sebastian.

We first look at the goals of this book and its specific contents. This will be followed by a discussion of whether the authors reached their objectives. We will also discuss briefly the level of student for which the book is intended and

critically evaluate it in terms of its pedagogical and scientific value.

The goal of the book, as stated by the authors, is to formulate generalizations that will be useful in the design, scaling, and modification of polymerization processes. To accomplish their goal, the authors start in Chapter One by defining the important concepts and terms needed in the remainder of the book. For example, the basic types of reactors and polymerization processes, along with the important variables, are discussed. The mathematical description of the reaction mechanisms and other pertinent relations are presented. In Chapter Two the kinetic variables (besides the monomer and initiator consumed) which affect the properties such as the degree of polymerization, the degree of polymerization distribution, degree of branching and its distribution, and copolymer composition and its distribution, are discussed. The main goal of this chapter is to mathematically incorporate the factors which affect the variables just mentioned, into the reaction kinetics.

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ChE letters

ANECDOTES ANYONE?

Dear Editor:

I should be pleased and grateful if you would kindly print this invitation . . . in an early issue of *CEE*. Many of your readers probably know of gems of chemical humor; I'd welcome your help and theirs in finding some.

For possible inclusion in an anthology, "Science with a Smile," I should welcome contributions of humor in the sciences: physics, chemistry, astronomy, mathematics, earth sciences, life sciences and computer science—historic and contemporary. Appropriate would be anecdotes, biographical notes, cartoons, parodies, verse, examples of self-deception, and hoaxes. I especially seek pieces which, while humorous, also have value in the history of science, providing insight into changing attitudes or illuminating personalities.

So far, chemistry is least well represented of the sciences in the manuscript for this anthology. I'd welcome evidence that chemists are not lacking in humor.

Please identify fully the sources of all contributions.

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