letters

A Possible Explosion Danger

To the Editor:

The recent article, "A Simple and Impressive Laboratory Exercise in Ion-Exchange," by S. Renganathan and B. J. Mehta (J. CHEM. EDUC., 53, 347(1976)) is indeed simple and impressive and should undoubtedly find widespread use in undergraduate laboratories, especially in view of the prevalence of silver chloride wastes and the currently high prices for silver. Therefore, it is extremely important that both student and instructor be made aware of the danger inherent in solutions containing silver ion and aqueous ammonia. On standing, such solutions are known to result in the formation of supersensitive and violently explosive "silver fulminate." Students should accordingly be warned to discard such solutions as soon as possible by washing them down the drain with plenty of water. Under no conditions should such solutions be allowed to stand for several hours either alone or on the resin column.

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Clock Signals in Calculators

To The Editor:

Salama, et al. recently reported observation of an "unadvertised digital clock" set into operation by a special sequence of button pushing on a Hewlett-Packard HP-45 calculator (J. CHEM. EDUC., 53, 385 [1976]). The Princeton University and Naval Research Laboratory scientists calibrated their relatively sophisticated, "scientific," calculator, showing that its clock interval was equivalent to 0.8847 of real time. We would like to report that one of us (R.W.L., age 6 years) has made a similar observation in operation of a General Instruments (of Canada) EZ 2000 calculator. (A count increasing from 0 to 99 with a 0.85 real time equivalent was noted.) He and coworkers (L.I.L., age 8 years, and L.A.L., age 8 years) demonstrated a further manipulation (rapid flipping of the off-on switch) which may activate decreasing counts at as many as two different intervals (~9 and 90 sec) on the same calculator. The latter effect is unpredictable, being noted on about every third

Several other pertinent points should be noted. The initial clock activating sequence for this calculator is division of a negative number displayed in its single register by zero, an operation that might not be attempted by older, more inhibited "investigators." Furthermore, our discovery demonstrates that the phenomenon described by Salama, et al. is not restricted to sophisticated instruments; the EZ 2000 is a simple, four function calculator which retailed for less than \$20 over a year ago.

It is noteworthy that the most basic functions of calculators are dependent on an internal, rapidly pulsing clock mechanism; see "The Small Electronic Calculator" by E. W. McWhorter [Scientific American, 234, 88 (1976)]. What is remarkable in our's and the earlier observations of "unadvertised clocks" is the visible manifestation of pulsed sequential counts appearing at relatively long intervals, activated by peculiar accessing sequences.

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Starch Solubility

To the Editor:

The authors of "Which Starch Fraction Is Water Soluble, Amylose or Amylopectin?" [Green, Mark M., Blankenhorn, Glenn, and Hart, Harold, J. CHEM. EDUC., 53, 729 (1975)] did a service to the scientific community to point out the difficulties of the complex problem of amylose "solubility." However, to state categorically that amylose is insoluble in water will leave many puzzled. It is important to qualify any discussion of the solubility of amylose and amylopectin. Most workers will find amylose in the starch granule easily dispersible in warm water. The dispersed material will gel on cooling and then slowly crystallize and become insoluble. The rate at which this above transformation¹ takes place is dependent upon amylose concentration. In dilute dispersions, the rate is very rapid.

It is when amylose² is dispersed or gelled in water that it is technically interesting and has economic importance to the food industry—not when it becomes insoluble.

I believe a better statement on amylose dispersibility would be something like this:

"Amylose appearing in natural starch is in the disorganized metastable state and as such is easily dispersed in warm water. On the other hand amylose which has been removed from starch and dried is in a organized stable crystalline state which can no longer be dispersed³ in warm water."

Now a few words about the "solubility" 4 (dispersibility) of amylopectin in water. In the starch granule, the amylopectin makes up the continuous network of the granule in which the amylose is dispersed as solid solution (solid in solid). The amylopectin in the granule is so well organized that it takes considerable physical manipulation before this material can be dispersed in water. With gentle manipulation in warm water, a high percentage of the amylose can be leached (dispersed) to the colloidal state ("made soluble"), while the amylopectin remains behind as a hydrated granule which can easily be separated from the "soluble" amylose by centrifugation. Under these conditions, amylopectin can be considered the insoluble fraction. On sharp mixing, however, the amylopectin is dispersed to colloidal dimensions (goes into "solution"). When such dispersions of amylopectin are dried and ground, more or less amorphous powders are formed which swell in water and which can easily be dispersed to colloidal dimensions (put into "solution").

Clearly the amylopectin, after dispersing in water and being dried, is a material that is much more hydrophilic than amyloge

Ostwald's "World Of Neglected Dimensions" plays an important role in understanding the "solubility behavior" of these starch fractions. The solubility of small molecules, as the organic and physical chemist sees them, is much different from the dispersibility of large molecules.

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¹ The term "retrogradation" has unfortunately been applied to the above process. Needless to say, this makes for confusion with hydrolysis at the glycosidic link.

² For a short discussion of the dispersion of amylose and its importance to the technology of starch, see Mitchell, W. A., in "Symposium On Foods—Carbohydrates and Their Roles," (Editors: Schulz, Cain & Wrolstad) Avi Publishing Co. Inc., Westport, CT, 1969, Pages 436–440.

³ Amylose can again be dispersed in water if the temperature is raised to above about 140–150°C, on cooling to room temperatures the dispersion will first gel then slowly crystallize further.

⁴ The term "solubility" is usually reserved for molecular dispersions of small molecules. On dealing with large molecules, when molecular aggregates can also be involved the general term "dispersion" is a better choice.