CONCENTRATES

Science

Preliminary testing of the Texas Tokamak has begun, following seven years of development and construction work on the device for generating thermonuclear reactions. One of six such machines in the nation, the Texas Tokamak differs from others in that it has a method for turbulent heating built in with the Tokamak confinement scheme. With this combination the University of Texas development group, headed by Dr. William Drummond, hopes to achieve thermonuclear temperatures.

Heavy metals in drinking water may affect cardiovascular-renal (kidney) diseases. The possible relationship is being studied by Dr. Ray E. Ferrell, Jr., a geochemist at Louisiana State University. In certain regions, the diseases occur more frequently—likelihood of death for the general population is about 10% greater. Heavy metals to be covered in the study, considered preliminary, are cadmium, arsenic, copper, lead, silver, and zinc. Naturally present in aquifers used as municipal water sources for Baton Rouge, La., they were chosen because some are essential to good health, and others are toxic even at low concentrations.

Education

The smallest fall enrollment increase in 28 years for U.S. schools and colleges is predicted by HEW's Office of Education. Total enrollment in elementary and secondary schools, and colleges and universities will rise to a record 60.4 million people, but the increase will occur mostly at the higher education level. Enrollment in colleges and universities will increase 6% from last year, compared to a rise of only 0.5% in enrollment at all educational institutions.

Two new Sea Grant Colleges have been named—the University of Wisconsin and the University of Hawaii. Receiving the designation from the Department of Commerce, the universities are part of the National Sea Grant Program conducted by the National Oceanic and Atmospheric Administration. They join the University of Washington, the University of Rhode Island, Oregon State University, and Texas A&M University, all named Sea Grant Colleges in 1971.

Students Against Fires (SAF) is the project for 1972–73. It is the new international student engineering project for the current academic year sponsored by Student Competitions on Relevant Engineering, Inc. (SCORE), the organization that sponsored the just-concluded Urban Vehicle Design Competition (C&EN, Aug. 28, page 18). The new competition emphasizes quality and practicality of student-initiated solutions to problems currently encountered in fighting and controlling fires.

Technology

A huge pilot plant will produce formed coke for blast furnace tests. A four-company group of steel and coal producers—Bethlehem Steel, National Steel, Republic Steel, and Consolidation Coal—has let a contract to Dravo Corp. and Lurgi Mineralöltechnik Co. of West Germany for engineering and construction of the 500 ton-per-day coke pellet plant. The $25 to $30 million program will test the Consol-BNR process, a fully enclosed process that yields strong coke pellets by direct hot pelletizing, followed by calcining, of a single high-volatile coal. Construction of the plant at Bethlehem's Sparrows Point, Md., complex should be completed by 1974, with blast furnace tests scheduled for 1975.

A single-step isoprene synthesis developed by Takeda Chemical Industries has an economic edge over all synthetic routes to the monomer now in commercial use, according to the Japanese firm's analysis of pilot trials. A unique catalyst system permits direct conversion of isobutene and formaldehyde to isoprene. Cost of a 60,000 metric-ton-a-year plant in Japan is put at $10.7 million. Polyisoprene made from Takeda-process monomer, the firm says, has cis content as high as that via the two-step Institut Francais des Pétroles route from the same raw materials or the three-step Goodyear/Scientific Design route from propylene.

Silicon carbide will be produced from waste rice hulls and iron oxide in a process developed at the University of Utah and exclusively licensed to Hulco, a new Utah corporation formed by Utah and Louisiana businessmen. Silicon carbide is currently made from coke and sand, and the process requires heating for several days at about 4500° F. The new process, developed by Dr. Ivan B. Cutler and coworkers in the university's department of material science, operates at lower temperatures.

Aflatoxin may be inactivated in cottonseed and peanut meals by an ammonia treatment method developed by USDA's Southern Regional Research Laboratory, New Orleans. Scientists there find that contaminated meals treated with ammonia at up to 50 p.s.i. for 30 minutes show a reduction in the mold-produced toxin (which causes cancer in susceptible test animals) to 7 or less p.p.b. of meal, well below FDA guidelines. If feeding tests prove the method's safety, contaminated meals could be salvaged for animal rations.

A nationwide plan for hazardous waste disposal will be developed by Battelle-Northwest, Richland, Wash., under contract from the Environmental Protection Agency. The laboratory will plan a system of national sites for storage, treatment, recovery, or disposal of organic and inorganic wastes, radioactive materials, and chemical-biological warfare agents. Battelle will supplement data from other EPA contractors and draft a comprehensive report.

Tank-car volumes of chloropicrin may detonate under certain conditions, Dow Chemical Co. says. Tank-car shipments of the compound—used as a soil fumigant and as a warning agent with other fumigants—are allowed by current regulations, the firm notes. However, tests have indicated that there is a "critical volume" above which sufficient shock may cause detonation. Thus, Dow will now ship chloropicrin only in 1500-pound pressurized cylinders and special 400-pound drums. Dow has notified federal agencies and the Manufacturing Chemists Association of its findings.

Long-term monitoring of ocean water quality may become routine with General Dynamics' XERB program. Tests of XERB-1, an unattended buoy anchored 100 miles off Cape Hatteras, N.C., were described by G. T. Barlow and M. B. Folkert at the 8th Annual Conference of the Marine Technology Society in Washington, D.C. The monitoring system pumps water samples into a test chamber, records pollutant levels, and flushes the chamber periodically. Data are telemetered to shore stations for interpretation.

Chemical composition of ocean sediments could be determined in situ, according to a proposal at the marine technology meeting by L. D. Maus and Dr. V. C. Rose of the University of Rhode Island. The proposal includes specification of a new type of gage employing a radioisotope source of gamma rays and a detector for the gamma photons scattered by the sediments. Objective is to prospect for mineral-rich sediments.

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Phthalate effect on health still not clear

"An etiology in search of a disease" is way FDA sums up current findings of research into health hazards of phthalates

Do phthalic acid esters, widely used as plasticizers and also appearing as nonplasticizing components of pesticides and cosmetics, present a human health hazard or a danger to the environment? With increasing frequency this question has been asked in recent years following detection of the esters in human tissues, in water, air, and fish, in human blood stored in plastic bags, and elsewhere. Unfortunately, the extent of any biohazard is still largely conjectural, despite much research. Nor is it clear yet that a switch to other, presumably safer, compounds is justified.

Much of the research on phthalic acid esters (PAE's) was brought into focus and perspective added, however, at a two-day meeting held at Pinehurst, N.C., earlier this month and sponsored by the National Institute of Environmental Health Sciences. Summing up the findings and conclusions of 21 papers, Dr. Lloyd B. Tepper, associate commissioner for science for the Food and Drug Administration, observed that the PAE problem was still "an etiology in search of a disease" and that the U.S. "cannot afford to be stampeded into substitutes." Nevertheless, he indicated that the research findings are a cause for concern and pointed up the need for further work.

At stake could be a health problem affecting significant numbers of Americans as well as the fate of a multimillion-dollar chemical technology. Roughly 90% of the 7 million or so pints of blood transfused every year in the U.S. are stored in plasticized polyvinyl chloride bags, chosen over glass for their convenience and less chance of breakage. Other PAE uses with possible health implications are in food wraps and medical tubing, applications estimated to consume 18 million pounds and 15 million pounds, respectively, of phthalates in 1972, according to Monsanto, a major producer of the compounds.

Nonplasticizer uses of PAE's where the compounds, not bound to a resin matrix, would appear to have a more direct route to the environment, should total about 50 million pounds this year. All told, about 1 billion pounds of some 20 different PAE's will be produced this year. Total sales of PAE plasticizers were nearly $119 million in 1971, according to preliminary statistics just released by the U.S. Tariff Commission.

Relatively inert, PAE's generally have a low order of chronic toxicity in animal studies. In fact, the most widely used PAE, di-(2-ethylhexyl) phthalate (DEHP), is safer than ethanol in terms of oral LD_{50} (a dose lethal to half of the animals tested) data, according to L. G. Krauskopf of Union Carbide, a major supplier of the chemical. Commenting on a literature survey, Mr. Krauskopf also noted that there have been three adult human ingestions of DEHP cited in journals with resulting nausea and vertigo in one case from intake of 10 cc. of the compound—equivalent to 144 mg. per kg. of body weight for a 70-kg. individual.

Aside from chronic toxicity determinations, the biomedical literature on PAE's is very meager. "Surprisingly few sophisticated toxicological studies have been done considering the ubiquitous nature of these compounds," remarked one official of the National Institutes of Health.

Much of the current concern over PAE's dates back nearly two years when Dr. Robert J. Rubin, associate professor of environmental medicine at Johns Hopkins University, and Dr. Rudolph J. Jaeger, then a graduate student and now at Harvard's school of public health, discovered that the plasticizers were leached out of PVC tubing used in rat liver experiments. Further analysis showed levels of 5 to 7 mg. of DEHP in human blood stored up to 21 days (the expiration period) in PVC blood bags (which contain up to 40% DEHP or other plasticizers to give flexibility). "Significant quantities" of the plasticizer were found in the spleen, lung, liver, and abdominal fat of patients transfused with blood from the plastic bags. Dr. Jaeger has also detected a phthalic acid-containing substance in the urine of three normal adult males as well as in a transfused patient, suggesting a dietary or inhalation source of phthalates.

Research by others has confirmed these results on stored blood as well as the absence of PAE's, as determined by gas chromatography-mass spectrometry, in the blood of normal volunteers who have not undergone transfusion. The findings have prompted the blood bag industry to launch a study by Stanford Research Institute aimed at helping resolve the safety question. Recent research, however, by Dr. C. Robert Valeri at the Naval Blood Research Laboratory, Chelsea, Mass., shows that 98% of DEHP accumulated in liquid-stored whole blood can be washed out with continuous-flow centrifugation.

Meanwhile, PAE's have been detected elsewhere. For example, Dr. Eugene F. Corcoran of the University of Miami has found 0.6 p.p.m. of PAE's, primarily DEHP, in samples of Mississippi River water. One third of this concentration, he notes, if found throughout the total flow of the Mississippi, would account for the total production of DEHP in 1970 of 350 million pounds. Smaller concentrations of PAE's have also been found in the

Phthalates find wide use despite safety questions

End use	Millions of pounds[a]
CONSTRUCTION	
Wire and cable	185
Flooring	150
Swimming pool liners	20
Weatherstripping	13
Window splines	10
Other	9
HOME FURNISHINGS	
Furniture upholstery	90
Wall coverings	38
Housewares	30
Garden hose	15
Appliances	10
Other	20
TRANSPORTATION	
Upholstery and seat covers	80
Auto mats	15
Auto tops	12
Other	10
APPAREL	
Footwear	45
Outerwear	20
Baby pants	7
FOOD AND MEDICAL	
Food wrap film	18
Closures	7
Medical tubing	15
Intravenous bags	6
NONPLASTICIZERS (Pesticide carriers, cosmetics, fragrances, munitions, industrial oils, insect repellent)	50

[a] Estimate of sales in 1972. Source: Monsanto

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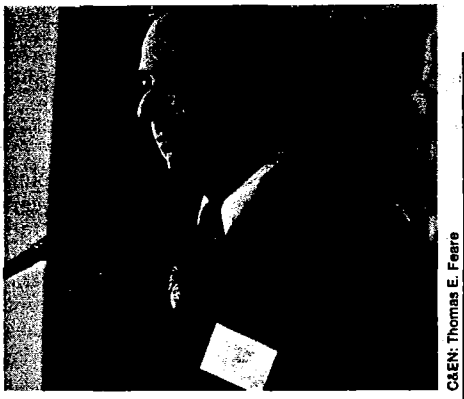
Rubin: problem in stored blood



C&EN: Thomas E. Feare

Graham: car window fogging

Charles River—0.9 to 1.9 p.p.b. (total phthalate concentration) depending upon sampling location—by Dr. Ronald A. Hites, assistant professor of chemical engineering at Massachusetts Institute of Technology, employing high-pressure liquid-solid chromatography.

Adequate sewage treatment might remove these contaminants from water. Experiments by Monsanto indicate biodegradabilities of 91% for DEHP and 99% for butyl benzyl phthalate compared to 99+% for linear alkylbenzene sulfonate, a detergent component, in semicontinuous activated sludge.

During the course of studies to detect polychlorinated biphenyls, Dr. Gordon H. Thomas of the Ontario Research Foundation found nanogram quantities of PAE in air samples taken in the vicinity of incinerators in Hamilton, Ont. At the Interior Department's fish-pesticide research laboratory, Columbia, Mo., Dr. David L. Stalling and associates have detected DEHP residue levels from 0.2 to 10.0 micrograms per gram (whole fish basis) in fish from various locations, with the higher levels associated with industrialized areas. And PAE's have been a contaminant plaguing unmanned space experiments of the National Aeronautics and Space Administration. Although there is no conclusive evidence of a mission failure due to PAE's, NASA chemist Frederick C. Gross notes that the plasticizers can compromise optical experiments in the ultraviolet spectral region.

Car window "fogging" by PAE release from upholstery and seat covers has also been shown in several industrial labs. Tests by Monsanto indicate that di-undecyl phthalate or trialkyl trimellitate are much less volatile plasticizers in this application than is DEHP, according to the firm's Paul Graham. And an analysis of "new car odor" turned up at least 60 organic compounds, principally hydrocarbons, with PAE's amounting to 0 to 6% of the total.

Naturally occurring sources of the phthalate moiety have also been found, Mr. Graham adds. Among such sources noted in the scientific literature are cigar smoke, tobacco leaves, grapes, cranberries, poppies, oxidized corn oil, soil, and crude oil. (In analyzing for PAE sources, there is the possibility of contamination of analytical equipment from the plasticizers in plastics in the laboratory.)

Determination of the toxicological significance of these natural and man-made phthalate sources is now under way in a number of laboratories. But the efforts are hampered by the relatively large doses of PAE's that must be administered to animals to produce detectable effects (also, DEHP is an oily, viscous liquid sparingly soluble in water). There is also the difficulty of extrapolating results to man.

Embryo-fetal toxicity was observed in rats given intraperitoneal doses of one tenth, one fifth, and one third the LD_{50} dose for the six least toxic PAE compounds and 10 ml. per kg. body weight for dimethyl and dimethoxyethyl phthalate by Dr. E. O. Dillingham and Dr. J. Autian of the University of Tennessee Medical Units, Memphis. Fetal malformations found included absence of tail and twisted hind legs. Significantly, DEHP was among phthalates having the least adverse effect on embryo-fetal development. Similar intraperitoneal doses of PAE's were given male mice prior to mating, with the result that some degree of infertility and mutation was induced.

Experiments at Michigan State University on rat reproduction following intraperitoneal injections of DEHP, dimethyl phthalate (DMP), or dibutyl phthalate (DBP) at levels up to 4 grams per kg. resulted in smaller litter sizes in some cases and excessive hemorrhaging during birth for animals treated with DEHP and, to some extent, DMP and DBP. This hemorrhaging is of major significance from the standpoint of human health, Dr. J. W. Peters contends. So-called "subtle" toxicological effects of DEHP involving behavior changes in rats and changes in platelet aggregation in dog blood have also been demonstrated by Dr. Rubin and Dr. Jaeger.

Clearly, the significance for man of these toxicological results is still largely unknown, although the consensus of most scientists at the meeting was that means for avoiding any PAE residue in man should be found. The plasticizer industry is certainly on the alert to substitute materials, judging from the many corporate officials at Pinehurst. New materials for blood storage bags will get FDA's "special scrutiny," Dr. Tepper observes, but then existing materials, he says, "should not be sacrificed for unknown polymers."

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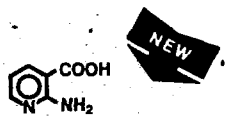
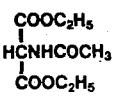


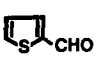
2-Aminonicotinic acid



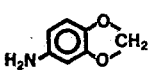
Acetylaminomalonic acid diethylester



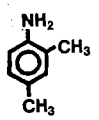
m-Chlorobenzoic acid



Thiophene-2-carboxaldehyde



3,4-Methylenedioxyaniline



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Technique predicts phase equilibria

A new technique for predicting complex reactions and phase equilibria has been devised by John H. Dluzniewski and Stanley B. Adler of M. W. Kellogg Co. According to the originators, for the first time it is possible to predict equilibria among two or more phases including any combination of solids, vapors, and liquids with or without chemical reactions. There are no fundamental restrictions to the number of components, simultaneous reactions, or phases that can be handled. The only physical restrictions are those of the computer that does the calculations.

Details of the new method were presented last week in London at a meeting of the U.K.'s Institute of Chemical Engineers. The method has a considerable advantage over previous techniques in that they have either been restricted to vapor-phase reaction systems or failed to account for nonidealities in the liquid phases.

The new technique employs the method of minimizing free energy of the system for a given set of constraints. For this reason, provided the thermodynamic data are available and the components of the system have been identified, the technique is thermodynamically rigorous. There is no need to consider mechanisms, independent equations for chemical reactions, or simplifying assumptions. In addition to predicting equilibria, the technique also can be used to analyze experimental equilibrium data.

With free energies and components defined, either by measurement or by valid prediction, mass balance constraints for the system may be established. The set of equations that determines the constraints is essentially a set of elemental material balances. It is manipulation of these equations that constitutes the heart of the new technique.

If a component which does not react in a real system is considered to be inert, a fictitious element is simply assigned to its makeup. Since the fictitious element does not appear in another compound in the closed system, the inert compound can neither react nor be formed. By extending this artifice, the entire system may be made nonreacting and only phase equilibria will be calculated.

The basic steps in applying the technique are:

- Calculate the free energy of the feed system.
- Estimate the free energy of the equilibrium mixture (of unknown composition) by using the quadratic form of the Taylor Series.
- Minimize the free energy of the estimated equilibrium system, subject to the mass balance constraints, using the technique of Lagrange multipliers.
- Solve the resulting system of simultaneous equations to obtain improved equilibrium approximations.
- Repeat the first four steps until the equilibrium approximation is adequate for the use intended.

The method is essentially trial and error estimation that can be made to converge to some equilibrium values. By changing the constraints, the optimal configuration of any system may be chosen within thermodynamic restrictions.

The computing power required for application of the method is, according to the originators, within the capability of the normal computing facility. Mr. Adler says that within the Kellogg organization the method is now routinely used for design work, and it is often employed to reduce the amount of experimentation necessary for a new project.

Kellogg's Adler (left) and Dluzniewski



Du Pont has low-cost ESCA spectrometer

For most analytical techniques, instruments tend to be quite expensive when a technique is first introduced. As the technique becomes accepted, continuing instrument development shoves the price range down. Electron spectroscopy for chemical analysis (ESCA)—one of the newer techniques—is no exception.

Now Du Pont's instrument products division has designed a compact electron spectrometer that brings the price down to $39,500. The unit, Model 650, is compact, measuring 52 inches high with a 31-inch-square base. It weighs but 500 pounds. And its performance, Du Pont says, "compares favorably" with that of available instruments of twice the cost.

Du Pont was able to cut cost and size through development of a nondispersive electron energy analyzer. The design does away with conventional slit focusing systems.

In operation, electrons emitted from the sample (from bombardment with x-rays) pass through a retarding field into a broad cutoff prefilter. The resulting beam then passes through a low-pass filter which removes electrons with excess energy. The beam is reflected to the opposite end of the chamber and

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