Predicting the behaviour of nuclear materials

by P. Bull, J.D. Navratil, F.L. Oetting, and P.A.G. O'Hare*

The technical tasks which confront those responsible for developing any technology are: to make it work; to make it work reliably; and to make it work safely. Nuclear technology involves the use of a very wide range of materials and operating conditions. The most common materials used or under study at one time or another for the various types of nuclear reactor are shown in the box. In addition, one has to consider the products of nuclear processes: the fission products, activation products, and actinide elements.

Many of these materials only became available in significant quantities for the first time in the 1950s so that little was then known of their physical and chemical properties, and even less of their behaviour and possible interactions at the temperatures of interest for nuclear reactors. Nonetheless, it is possible to conceive of a great many processes of physical and chemical interaction amongst this diverse group of materials and many of these interactions could be detrimental. For example, we can consider the fuel cladding which forms the first barrier retaining the nuclear fuel and fission products. It is essential to know the answers to questions such as: will the cladding material interact with the fuel, the fission products, or the coolant? If so, will this involve phase changes? How will it affect the retention properties of the cladding (strength, creep resistance, corrosion resistance, etc.)? In the event of abnormal conditions (excursions or accidents) will the cladding fail, and what will be the subsequent form and behaviour of the radioactive fission products? If we can answer these questions we are in a better position to choose combinations of materials and conditions so as to avoid the undesirable interactions or at least to control them within acceptable limits.

Materials commonly used or studied for use in reactors

Solid fuels	Uranium metal and alloys High-melting compounds: UO_2, UC, UN, US, UP Pu enrichment ~2% for thermal reactors ~20% for fast reactors
Fuel cladding	Mg, Al, Be, Zr alloys, stainless steels
Fuel coating	C, SiC, Al_2O_3
Dispersed fuels	Cermets UO_2 in steels, UO_2 in W, etc. UC_2 in C, UO_2 in BeO, UC in SiC
Coolant	H_2O, D_2O, CO_2, He, Na, Na-K, Pb
Fertile materials	ThO_2, ThC_2 – often in solid solutions
Liquid fuels	Uranium in bismuth UF_4 in LiF-BeF_2 (ThF_4 in LiF-BeF_2 as fertile material) $PuCl_3$ in NaCl-KCl
Control materials	Boron alloys and B_4C, cadmium alloys, rare earth alloys and oxides
Structural materials	Austenitic and ferritic steels, graphite, special alloys
Moderators:	Graphite, BeO, H_2O, D_2O

To carry out those tasks mentioned in the first sentence of this article, we need a mechanism by which we can decide, out of all the conceivable processes of interaction, which processes are feasible and, for the feasible processes, to what extent they will proceed under any given conditions, i.e. to quantify the process. The branch of science concerned with answering these questions is known as thermodynamics. In order to apply thermodynamics it is necessary to have a great

* Mr Bull is in the Industrial Applications and Chemistry Section of the Agency's Division of Research and Laboratories. Messrs Navratil and Oetting are former IAEA staff members, now with Rockwell International, Rocky Flats Plant, Golden, Colorado, USA. Mr O'Hare is also a former IAEA staff member, now with the Argonne National Laboratory, Illinois, USA.

deal of accurate data on such properties of the materials as the heat of formation and standard entropy at 25°C, the temperature and heat of high-temperature transitions, and the variation of the heat capacity with temperature for all the phases of interest. For over twenty years the International Atomic Energy Agency has played a major role in producing and assembling these data by furthering the exchange of information on the thermodynamics of nuclear materials between scientists all over the world. The main activities of the IAEA in this area are summarized in Table 1.

Table 1. IAEA activities in thermodynamics

International symposia on thermodynamics of nuclear materials	IAEA-sponsored symposia held in 1962, 1965, 1967, 1974 and 1979
Thermodynamic data compilation	IAEA published monographs edited by O. Kabaschewski, No.1 Pu (1966), No.2 Nb (1968), No.3 Ta (1972), No.4 Be (1973), No.5 Th (1975), No.6 Zr (1976), No.7 Mo (1980), Hf and Ti to come
	Chemical thermodynamics of actinides: IAEA-convened consultants' compilation and critical assessment of available data, 14 volumes commencing 1976 (see Table 2)
Co-ordinated research programme	7 Member States are co-operating in a study of thermodynamic and transport properties of nuclear materials

Bringing scientists and engineers together

In recent years, co-operation has been growing between nuclear engineers who require thermodynamic data and the scientists who provide such data. Because practical experience of reactor accidents is almost totally lacking, nuclear engineers have to place considerable reliance on the accuracy and reliability of thermodynamic information. Workers in the field of thermodynamics of nuclear materials need to know those areas of reactor science and engineering in which their particular research can be of most value. The cost of thermodynamic research in terms of materials, equipment, time, and manpower is very high, and thus the choice of those experiments or studies that will provide the optimum data is crucial. Through international meetings at which thermodynamicists and engineers meet to discuss data and to seek ways of obtaining information that is lacking, unnecessary duplication of effort is avoided.

The IAEA has sponsored five international symposia on the thermodynamics of nuclear materials. The themes of these symposia reflected the state of knowledge of the thermodynamics of nuclear materials as well as the major areas of technological interest at the time. The first meeting in 1962 was an opportunity for experts to review the very limited thermodynamic information on nuclear materials then available. Since few measurements were availabe, much effort was devoted to establishing correlations – between the properties of classes of materials, and between different physical properties of particular materials – so that useful estimates of unknown thermodynamic quantities could be made by extrapolation from known properties of the material or from the known properties of similar materials. Nuclear technology at the time was concerned with the development of homogeneous reactors and high-temperature reactors so the nuclear materials of interest at this symposium were generally relevant to these concepts. The use of solutions or suspensions of uranium compounds in liquid bismuth as reactor fuel and coolant received considerable attention as did carbide fuels and graphite moderator. The symposium helped to answer such questions as: will uranium in bismuth solution attack moderator graphite? will a dispersion of thorium carbide in bismuth react to form thorium bismuthide? are certain proposed fission-product removal processes feasible with liquid bismuth? is steel suitable for liquid bismuth reactor circuits?

The second symposium, in 1965, recognized that more direct measurement of thermodynamic data and experimental information were needed so that scientists could evaluate the precision and reliability of the data being published. The symposium therefore concentrated mainly on recent developments in experimental methods and procedures with particular emphasis on diffusion and e.m.f. (electrode potential) methods. The third symposium, in 1967, showed the fruits of these earlier meetings in that a wealth of new experimental data was presented, many discrepancies in older estimates were either explained or eliminated, and fresh insights were given into the theoretical aspects. In line with the continuing interest in solution systems for reactors the materials considered were generally alloys, semi-metal compounds, transition metal and actinide carbides, solid solutions, and molten-salt systems.

The next stage in development of the nuclear industry saw greater demands being made for assurances of safety of nuclear operations. This was reflected in the technological theme of the fourth symposium, in 1974, which was the application of thermodynamics to the understanding of the chemistry of irradiated nuclear fuels and to safety assessment for hypothetical accident conditions in reactors. Sessions were also held on more basic thermodynamics, phase diagrams, and the thermodynamic properties of a wide range of nuclear materials. This meeting continued the work of the earlier conferences and gave evidence of the growing interaction between thermodynamicists and engineers.

Many studies were described to obtain data that the engineers lacked.

The symposium in 1979 was aimed at applied thermodynamics and at those basic studies of direct relevance to nuclear engineering. Systems and materials discussed included those relevant to fast breeder reactors, environmental and waste management concerns, and fusion reactor systems. The very positive response engendered within the international scientific community showed the value of supporting such co-operation between science and technology. A significant portion of the symposium programme was devoted to oxide fuels, particular reference being made to fast breeder reactor applications. Oxygen diffusion and its effect on fuel/cladding interactions were discussed, while the behaviour of fission products, especially caesium, were considered in detail. Binary, ternary, and even some quaternary phase diagrams were presented for fuel/fission-product systems, these studies being based on both experimental and theoretical work. Studies were also reported on diffusion of elements in glass matrices intended for fixing high-level radioactive waste. The stability of such vitreous storage media and the resistance of the glasses to leaching can be improved by considering the thermodynamic properties of the major components. A new feature, and one that will be of growing importance as moves are made towards setting up the first international fusion experiment (Intor) was the presentation of work on the thermodynamics of materials in fusion reactors – liquid lithium, solid lithium alloys, and lithium-containing ceramics.

Thermodynamic data compilations

It is not sufficient to encourage the determination and publication of heaps of thermodynamic data. If it was left at this stage then the designer, engineer, or environmental scientist who wished to apply thermodynamics would first have to carry out a thorough literature search to find published data. He would then be confronted with a range of data of varying quality and reliability and, in the worst case, with inconsistent data. There is therefore a need critically to evaluate all published data and produce authoritative compilations of those data which meet defined standards for reliability or, where data of that standard is lacking, to include data of lower quality with an expert assessment of the limitations on its use. Such compilations have been assembled from time to time by experts in the field. In the late 1940s, L. Brewer and colleagues produced a pioneering series of papers dealing with the thermodynamic properties of nuclear materials. This was followed in 1963 by *The thermochemical properties of uranium compounds* by M.H. Rand and O. Kabaschewski. The Agency's decision to publish compilations of physico-chemical data of substances important to reactor technology resulted in a series of monographs edited by O. Kabaschewski. These have appeared as special issues of *Atomic Energy Review.* So far, the following have been published: Special Issue No.1 (plutonium) 1966; No.2 (niobium) 1968; No.3 (tantalum) 1972; No.4 (beryllium) 1973; No.5 (thorium) 1975; No.6 (zirconium) 1976; and No.7 (molybdenum) 1980. Two more monographs in this series are planned, one on hafnium and the other on titanium.

Other surveys of the thermodynamic properties of certain actinide materials have appeared since 1967, but they are either of limited scope or have not been critically evaluated and, taken as a whole, they are not in a format suitable for either science or technology. Moreover, considerable experimental thermodynamic data on the actinide elements and their compounds have been reported in the past decade. It therefore became apparent several years ago that there was an urgent need for a reliable, self-consistent, up-to-date compilation of critically evaluated thermodynamic values for the actinide elements and compounds.

To respond to this need, the IAEA set up a programme of compilation on an international level. To co-ordinate this effort, the Agency established an Advisory Board consisting of F.L. Oetting (Rockwell International, Colorado, USA), V. Medvedev (Institute for High Temperatures, Moscow, USSR), M.H. Rand (Atomic Energy Research Establishment, Harwell, UK) and E.F. Westrum, Jr. (University of Michigan, Ann Arbor, Michigan, USA) to provide editiorial direction and review for the entire project and ensure compatibility

Table 2. The chemical thermodynamics of actinide elements and compounds

Part	Title	Publication date
1	Actinide elements	1976
2	Actinide aqueous ions	1976
3	Miscellaneous actinide compounds	1978
4	Actinide chalcogenides	1981
5	Actinide alloys	1981
6	Actinide carbides	1982
7	Actinide pnictides	1982
8	Actinide halides	1982
9	Actinide hydrides	1982
10	Actinide oxides	1983
11	Selected ternary systems	1983
12	Actinide complex aqueous ions	1983
13	Actinide gaseous ions	1983
14	Aqueous actinide organic complexes	1983

with current major thermodynamic compilations, standards, reference states, etc.

Fourteen groups of authors, from widely separated institutions and laboratories, but with a common aim and high qualifications for the task, are preparing critical analyses of available thermodynamic experimental data and extending and estimating thermodynamic data where experimental values are not available. The compilation is in fourteen parts, and as far as possible each part will contain tables of thermodynamic functions pertaining to the crystal, liquid, and gas phase of each compound or element. An extended temperature range will be covered so that the work will be of maximum benefit to the nuclear engineer and nuclear scientist. The titles and authors of the various parts are shown in Table 2.

Thermodynamics and transport research

Another avenue which the Agency uses to encourage and support international collaboration and exchange of information on specific projects is known as a co-ordinated research programme. Three years ago, the Agency initiated a co-ordinated research programme on thermodynamic and transport properties of nuclear materials. Presently, the following Member States are participating: Bulgaria, Federal Republic of Germany, Japan, India, Netherlands, Poland, and Yugoslavia. The programme includes research dealing with transport properties and thermodynamic equilibria in such diverse problems as the reactions between fission-product caesium and uranium-oxide fuel, oxygen transport mechanisms from fuel to cladding materials, high-temperature stability of zirconia, and oxidation/reduction reactions of polyvalent ions in glass melts. The results will be of particular value in reactor safety analyses.

The future

Priorities inevitably change and it appears likely that work on chemical thermodynamics will in future have lower priority in the Agency's programme. This does not however mean that the job is completed. The history of thermodynamics of nuclear materials has shown that, as the nuclear industry has grown, the demand for a greater quantity and quality of thermodynamic data has grown with it. There is every indication that this process will continue. It is to be hoped that the international co-operation established in this field by the Agency's earlier efforts, will continue and thereby contribute to the provision of safe and reliable nuclear energy for the needs of the world.