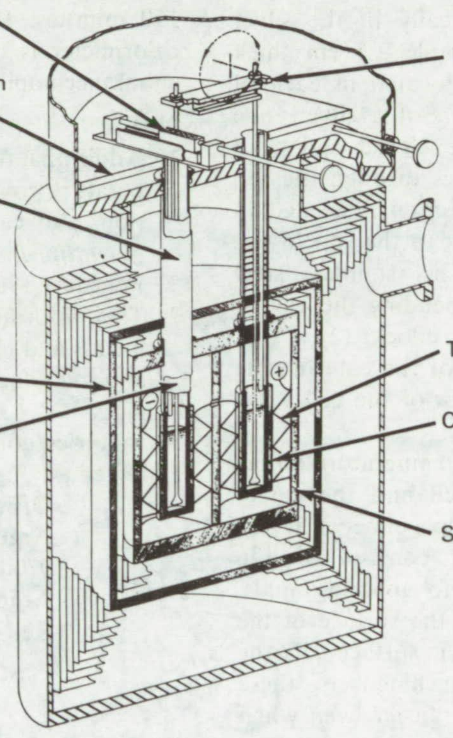
AEC-NASA TECH BRIEF

AEC-NASA Tech Briefs describe innovations resulting from the research and development program of the U.S. AEC or from AEC-NASA interagency efforts. They are issued to encourage commercial application. Tech Briefs are published by NASA and may be purchased, at 15 cents each, from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151.

Twin Solution Calorimeter Determines Heats of Formation of Alloys at High Temperatures



The problem:

To develop a calorimeter capable of determining the heats of formation of transition metal alloys at high temperatures. Calorimeters with single reaction cells have proved very successful in determining heats of formation of alloys when the reaction period is short and when moderate heat effects are observed. Errors increase substantially, however, when the metals or alloys dissolve slowly in a chosen solvent; the transition metals dissolve very slowly at temperatures suitable for precision calorimetry.

The solution:

A Calvet-type, high temperature, twin liquid metal solution calorimeter, particularly suited for determining the heats of formation of alloys containing transition elements. This twin differential calorimeter precisely measures the small heat effects generated over extended periods of time. It has a maximum

(continued overleaf)

operating temperature of 1073°K, and is equipped with an automatic data recording system. The performance of the calorimeter has been checked by measuring the heats of solution of pure noble metals in tin at 685°K. The results agree with existing published data.

How it's done:

The twin solution calorimeter consists basically of two calorimetric cells contained within two symmetrically located cavities in a single metal block thermostat, two thermopiles, a resistance furnace, a reciprocating head to which stirrers are attached, a specimen storage and dispensing device, a movable platform, and inner and outer stainless steel tubes.

The thermostat consists of a cylinder of pure silver 25.4 cm in diameter and 25.4 cm high. Silver is used because of its high thermal conductivity and resistance to atmospheric corrosion. Two cylindrical wells 10 cm in diameter are located symmetrically in the silver block and are covered by removable 2.5 cm thick silver lids. A calorimetric cell is located in each of the enclosed wells. The cell consists of a silver tube which is precisely fitted over the closed end of a stainless steel tube. The latter passes through the top lid of the block, to which it is securely fastened in good thermal contact, and extends to the top of the water-cooled vacuum chamber. This stainless steel tube provides: (1) a means of suspending the calorimetric cell within the cavity of the block, (2) a gas-tight environment for the interior of the calorimetric cell, and (3) an access to the interior of the cell without disassembling the apparatus.

Two thermopiles, which detect a temperature differential between the calorimetric cell and the cavity wall, are located in the annular space between the cells and the cavity walls. Each consists of 176 junctions, which are spot welded to gold terminals. Half the terminals are attached to the surface of the cells, the other half to the inner surface of the surrounding silver block. The attachment of these junctions provides adequate heat transfer even when the apparatus operates under vacuum. Mica washers or strips, approximately 0.05 mm thick, provide electrical insulation.

The two thermopiles are connected in a differential arrangement such that temperature drifts in the silver block produce emf's that exactly cancel. Thus the emf signal is essentially independent of temperature fluctuations in the block. The signal may be amplified and recorded as a function of time. This emf signal is proportional to the rate of heat transfer, and the total area under the emf–time curve is then a measure of the heat of reaction.

The temperature of the calorimeter is measured by a platinum/platinum–10% rhodium thermocouple. The temperatures within the calorimetric cells and the silver block are identical when thermal equilibrium is attained.

The procedure used in determining the heats of solution of several pure metals in liquid tin is as follows: The solvent, about four moles of tin, is contained in recrystallized alumina crucibles which fit snugly inside the removable stainless steel tubes. Solid specimens, of a mass to yield an intended heat effect of approximately 50 cal, are placed in the specimen storage device. The top chamber is evacuated to 1×10^{-6} mm Hg and the inner tubes are lowered into the calorimeter. After the tin melts, the stirrers are turned on and the chamber is filled with 99.999% pure argon gas at a slight positive pressure with respect to atmospheric pressure. Thermal equilibrium is attained in about 18 hours, after which the temperature drift does not exceed 0.1°K per day.

Each calorimetric experiment lasts approximately 150 minutes. In this period the heat pulse in the calorimeter is dissipated and the emf of the differential thermopile returns to the original value.

Notes:

1. Additional details describing furnace, shields, temperature controls, auxiliary features, instrumentation, and calibration are contained in *Review of Scientific Instruments,* vol. 37, no. 2, p. 164–167, February 1966.
2. This information should be of interest to the metals and chemical industry, testing laboratories, and manufacturers of calorimeters and related devices.
3. Inquiries concerning this innovation may be directed to:

   Office of Industrial Cooperation
   Argonne National Laboratory
   9700 South Cass Avenue
   Argonne, Illinois 60439
   Reference: B68-10083

Source: J. B. Darby, Jr.,
Metallurgy Division
and R. Kleb,
Solid State Sciences Division
Argonne National Laboratory
and O. J. Kleppa
University of Chicago
(ARG-10114)

Patent status:

Inquiries about obtaining rights for the commercial use of this innovation may be made to:

Mr. George H. Lee, Chief
Chicago Patent Group
U.S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439