

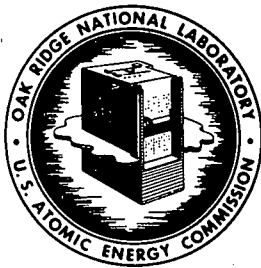
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SUBJECT: Proposal for an Experimental Study of Thermal Gradient
Mass Transfer in a Thermal Convection Loop

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PROPOSAL FOR AN EXPERIMENTAL STUDY OF THERMAL GRADIENT MASS
TRANSFER IN A THERMAL CONVECTION LOOP

Introduction

The present state of knowledge regarding thermal gradient mass transfer must be considered highly unsatisfactory. Several theories^{2,3} have been advanced to explain the phenomenon, but agreement between them and experimental results has been marginal at best. Various factors have made it impossible to give any theoretical explanation a fair test; among them are a lack of accurate physical properties data on the systems of interest and a lack of definition in the mass transfer experiments which have been performed to date.

Previous experiments on thermal gradient mass transfer have been designed and operated solely to obtain engineering information on the expected lives of given systems. They provide data only on the overall amount of material transported over a long time interval, and the regions in which solution and deposition occur are poorly defined and extend over a wide temperature range for a given run. Under such conditions it is impossible to estimate how the actual rates of mass transfer vary with time and position in the system.

As part of an attempt to improve understanding of thermal gradient mass transfer, it is proposed to design, construct, and operate a thermal convection mass transfer loop which will provide data on rates of solution and deposition as functions of time for systems of interest. Furthermore the hot (solution) zone will be operated under controlled isothermal conditions. It is felt that data obtained from such a loop will be of real value in assessing the validity of presently proposed mechanisms for thermal gradient mass transfer, or in devising new ones. It appears to the writers that any rational attempt to alleviate the problem of thermal gradient mass transfer must be preceded by an understanding of the process.

Theory

Thermal gradient mass transfer occurs in closed loop, nonisothermal flow systems in which the container material shows a temperature dependent solubility in the circulating fluid. Quantities of the container material may be dissolved from the hot parts of the system and deposited in the colder regions. The basic driving force for the process is the difference which exists at any point in the

system between the concentration^x of dissolved container material in the circulating fluid and its equilibrium solubility at the fluid temperature at that point. The tendency is for solution to occur when the fluid composition is below the equilibrium value (the hot zone), and for deposition to occur when the composition is above the equilibrium value (the cold zone). This driving force is modified somewhat in systems where solid diffusion in the container plays a significant role in the overall mass transfer process, as may occur with containers made of certain alloys.

A thermal gradient mass transfer process is said to be hot zone controlled if the circulating fluid leaving the cold zone is saturated with solute at the temperature existing over the bulk of the cold zone; and if the fluid leaving the hot zone is unsaturated at the hot zone temperature. Factors influencing the overall mass transfer rate in such a process could be liquid diffusion and convection, kinetics of the solution process at the solid-liquid interface, and solid diffusion in the container where the container is not a pure material.

A process is said to be cold zone controlled if the fluid leaving the hot zone is essentially saturated at the temperature existing over the bulk of the hot zone, and if the fluid leaving the cold zone is supersaturated at the cold zone temperature. The overall mass transfer rate in such a system could be affected by the rates of nucleation and growth of solid crystals in the cold zone. The growth rate of the crystals would be, in turn, affected by the same factors influencing hot zone controlled mass transfer. Also of importance would be whether the crystals adhered to the wall of the container or were swept along and redissolved in the hot zone.

A situation in which the fluid leaving the hot zone is unsaturated at the hot zone temperature, and that leaving the cold zone is supersaturated at the cold zone temperature would imply that both hot and cold zone processes affected the overall rate of mass transfer. If such a system operates at steady state, however, the rate of solution in the hot zone must equal the rate of deposition in the cold zone. This fact is based on the law of conservation of mass, and must hold for any system, whatever the rate controlling steps, so long as concentrations and flows remain steady with time.

^x In these discussions, radial concentration and temperature variations in the fluid are neglected, and concentrations and temperatures imply bulk (mixed mean) values at a given flow cross section.

It is also possible to have a system in which saturation is attained in both the hot and cold zones. For this case, the mass transfer rate depends only on the flow rate and the differences in solubility of the container material at the hot and cold zone temperatures. Figure 1 illustrates hypothetical concentration profiles which might exist in the systems described above.

The material balance equation describing mass transfer between a tube wall and a flowing liquid is found to be

$$R = \frac{w}{\pi D} \frac{\partial x}{\partial z} + \frac{D \rho}{4} \frac{\partial x}{\partial t} \quad (1)$$

where R = rate of mass transfer between wall and fluid
mass/(area)(time)

w = mass fluid flow rate, mass/time

D = tube inside diameter

ρ = fluid density, mass/volume

x = bulk fluid composition, solute weight fraction

z = longitudinal distance along tube

t = time

If one could determine the solute concentration as a function of distance and time, it would be a simple matter to compute the rate of mass transfer at any point in the system. However, for the systems of interest in thermal gradient mass transfer, viz. molten salts and metals at high temperatures, problems of sampling and analysis are formidable. In fact, it appears that in most situations, the best available analytical techniques are unable to detect the changes in composition that occur along a given loop. It will be noted from Figure 1, that although the differences between high and low temperature solubilities may be large, the difference in concentrations between the parts of a hot or cold zone controlled system may be quite small. Presently available data appear to substantiate this concept. It appears then that the only information that can be obtained by chemical analysis on the system is whether the hot zone, cold zone, neither, or both are controlling the rate of mass transfer for a given system.

As an alternative to chemical analysis of the flowing fluid, there is the possibility of constructing a flow loop out of some insoluble material and inserting in the hot zone a small sample of soluble container material to be tested. If the weight of this sample could then be obtained as a function of time, it would be possible to compute the average rate of hot zone mass transfer over the length of the sample, also as a function of time. The sample could be

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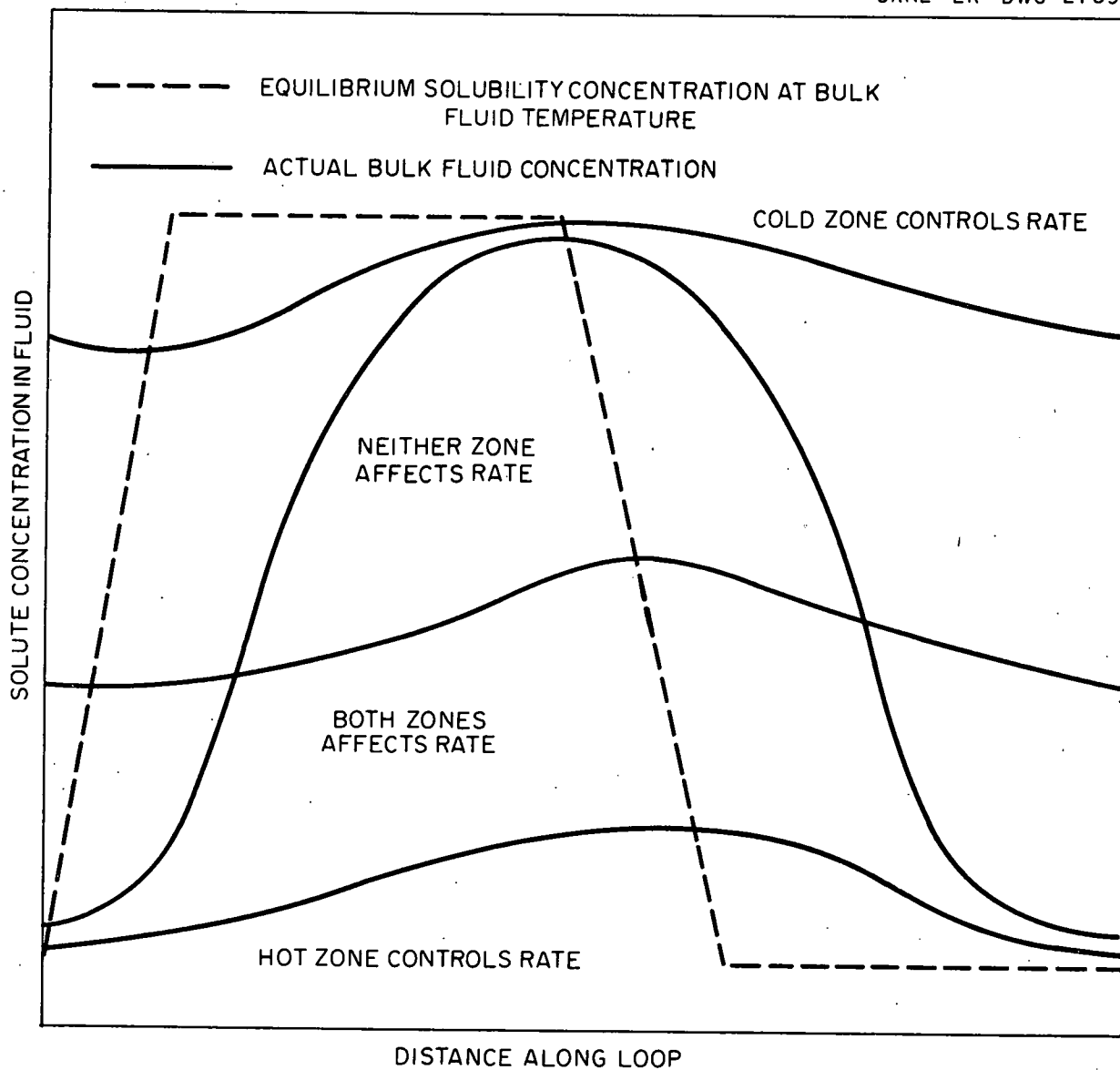


Fig.1. Hypothetical Concentration - Distance Curves in an Idealized Thermal Gradient Mass Transfer Process.

maintained under controlled isothermal conditions, and the crystals deposited in the cold zone could be collected and weighed at intervals to provide average cold zone deposition rates. The experimental problems involved are difficult, but apparently less so than those of obtaining accurate fluid concentration profiles. The data, in terms of rates, would be far more significant than the overall long-time weights of material transported, which are at present all that are available. In addition, data on average loop concentration as a function of time would give an indication as to which, if either, zone had a controlling effect on the mass transfer rates.

Description of Experiment

General

Of the many possible experimental arrangements for studying thermal gradient mass transfer, two types of closed flow loops appear to be best capable of yielding significant results. The first of these is the thermal convection loop in which the fluid flow is induced by density differences between hot and cold portions of the system. The second is the forced convection loop which employs a pump to circulate the fluid. The forced, convection loop has the advantage of allowing independent control of flow rates and operating temperatures, and also of permitting much higher flow rates to be attained. However, it is planned to employ a thermal convection loop in the present study for simplicity and to avoid the higher pressures obtained in forced convection loops. Quartz and pyrex are to be used as inert tubing materials, and these would be unsafe at the higher pressures. It is felt that the flow rate limitations will not be significant in this initial study.

Systems to be Studied

It is planned to confine this investigation to systems in which a pure solid metal is dissolved in a pure liquid metal. Several specific systems have been chosen for study based on the following criteria:

1. The liquid metal (solvent) must be inert to the material of construction of the loops (pyrex for low temperature work, quartz for higher temperatures).
2. The rates of mass transfer must be sufficiently high that significant quantities of material will be transported in a reasonable length of time.

3. Analytical methods must be available for determination of concentrations of dissolved solid metal (solute) in liquid metal (solvent). These methods should be convenient and accurate.

The liquid metals used will be mercury, lead, and bismuth. The solid samples will consist of nickel, iron, and chromium. These provide nine possible systems of widely varying properties for study. The results obtained should provide some insight as to the effect of solid and liquid metal properties on the mass transfer process.

Equipment

The thermal convection loop is to be constructed of quartz or pyrex tubing with all joints of fused construction. Pyrex loops will be used with liquid mercury, and quartz with lead and bismuth. A schematic drawing of the loop is presented in Figure 2. This design permits an isothermal hot zone region about the sample undergoing solution. A small sump above the cooling leg permits collection of crystals of deposited solute which may not adhere to the walls. Degassing, filling and emptying of liquid metal can be accomplished by application of hydrogen pressure and vacuum to the filling and vent chambers. Temperatures are regulated by control of the power input to the electric heater, and are monitored by four thermocouples mounted in small wells.

Experimental Procedure

The loop will be filled with the fluid to be tested and the sample introduced. The heaters will be turned on and adjusted until steady temperatures at the desired levels are indicated by the thermocouples. Operation will be continued until sufficient crystals collect to form a solid plug and block the flow. This "plugging" is indicated by a rapid rise in hot zone temperature and possible boiling over of the fluid into the vent chamber. The flow rate will be monitored throughout the run by making heat balances on the heated section. After plugging, the loop will be emptied of test fluid. Any crystals adhering to the walls or collected in the cold zone sump will be weighed. The hot zone sample will be removed and weighed, and the average fluid composition determined.

The loop will again be placed in operation, with great care being exercised to maintain the experimental conditions the same as before. Operation will be discontinued before plugging occurs, presumably at some convenient fraction of

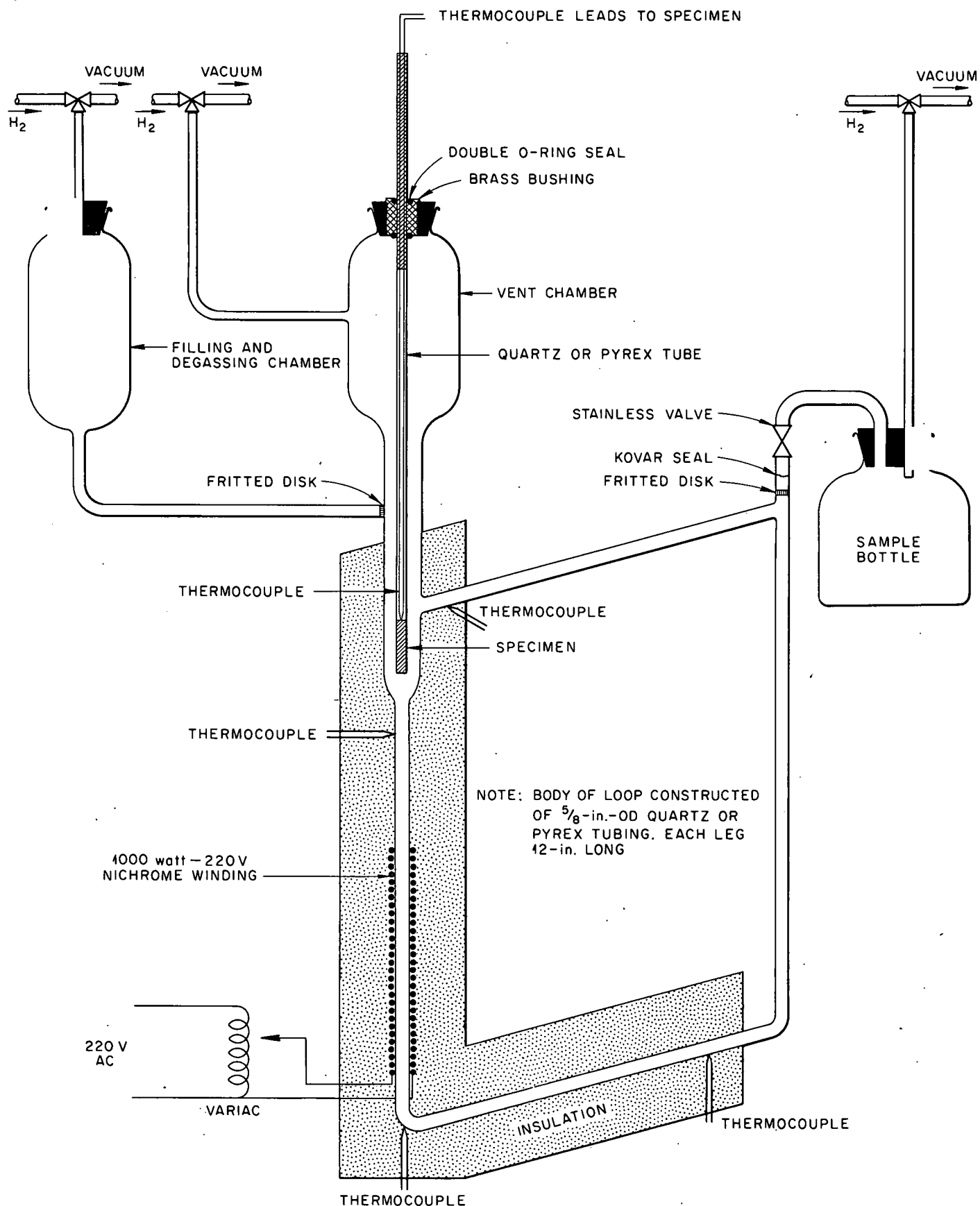


Fig. 2. Schematic Drawing of the Convection Loop.

time required to plug. (Cathcart and Manly¹ found that the plugging time is highly reproducible for a given system of this nature as long as operating conditions remain fixed). The flow rate will again be monitored throughout the run; measurements will be made of weight of crystals collected, weight loss of hot zone sample, and average fluid composition.

Approximately five such runs will be made at successively decreasing operating times for a given system and set of temperatures. Additional runs may be required depending on the scatter of the weight vs time data. For each run the data obtained will be:

1. Operating time
2. Operating temperatures
3. Heat input as a function of time
4. Initial and final weights of hot zone sample
5. Weight of crystals collected
6. Average fluid composition

Analysis of Data

From a series of sample weight measurements at a given set of experimental conditions a curve of weight vs time may be drawn for the sample. The average rate of mass transfer over the length of the sample may then be computed from the relation

$$\bar{R}_s = \frac{1}{A_s} \cdot \frac{dW_s}{dt} \quad (2)$$

where \bar{R}_s = average rate of solution of sample, mass/(area)(time)

A_s = surface area of sample exposed to liquid metal

Numerical differentiation of the smoothed curve of W_s vs t will yield the slope, $\frac{dW_s}{dt}$, as a function of time.

A similar method can be used to obtain information on the rate of crystal deposition in the cold zone. The weight of crystals collected, W_c , as a function of time can be used to evaluate the derivative $\frac{dW_c}{dt}$, and the rate of deposition, R_c is then given by:

$$\bar{R}_c A_c = \frac{dW_c}{dt} \quad (3)$$

Where A_c = surface area of the zone in which crystals are being deposited. Due to the irregularity of the crystal deposits, it is impossible to determine the exact area on which deposition takes place. Hence one can only determine the product ($A_c \bar{R}_c$) from these measurements.

A material balance check between hot and cold zone mass transfer rates can be made about the loop using data on the average fluid composition as a function of time. The following equation must be satisfied:

$$\bar{R}_s A_s - \bar{R}_c A_c = V \frac{d\bar{x}}{dt} \quad (4)$$

where V = total liquid volume in loop

\bar{x} = average liquid composition in loop

Of course, $\frac{d\bar{x}}{dt}$ will vanish as steady state is approached.

The prime results obtained from these experiments will be a series of values of solution and deposition rates as a function of system, temperatures, and flow rates. It is planned to test these results against existing theories of thermal gradient mass transfer and if it appears advisable, to use them as a basis for new or modified theoretical approaches to the problem. Anticipated future studies on liquid and solid diffusivities, solution rates, and equilibrium solubilities for systems of interest will greatly facilitate this task.

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