SPACE THERMAL DIFFUSION EXPERIMENT IN A MOLTEN AgI–KI MIXTURE
"Theoretical Convection Approach and Relation with in situ Measurement Results"

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ABSTRACT

The first measurement in Space of a Soret effect with an AgI/KI molten mixture is discussed as a new method of evaluating transport properties of molten salts without the perturbations of convection. The possibilities and requirements for this Space experiment are analyzed theoretically and experimentally, and new results are given dealing with wetting, interfacial properties of molten salts, and variations of the thermoelectric power with time. In each case, the comparison is made between the behavior of the molten salt on Earth and in Space, and the conditions for the theoretical convective stability are given. As a conclusion, the authors show that the interdiffusion coefficient in Space is significantly smaller than measured on Earth. This confirms some recent other Space diffusion experiments on liquid metals. It also confirms that the Soret coefficient corresponds to AgI migrating towards the cold end of the cell.

I. INTRODUCTION

The study of the liquid transport properties—electrical conductivity, diffusion, viscosity and thermal diffusion—should improve our understanding of the physical and chemical phenomena from a thermodynamic and dynamic point of view. In the case of ionic molten salts, the problem is simplified because of the absence of the usual dipolar solvent and because of the relative simplicity of these compounds. When a temperature gradient is applied throughout a binary mixture, a diffusion phenomenon appears, which leads to the partial separation of the constituents; this effect is called thermal diffusion or Soret effect. The separation created by the thermal diffusion expressed with a coefficient $D'$ is limited by a back-diffusion with a coefficient $D$. An equilibrium state is reached in the system and is characterized by the Soret coefficient $S_T = D'/D$, which will be considered positive when the "heaviest" component migrates towards the cold side.
The Soret effect was intensely studied for molten salts in the sixties, either by direct analysis or by thermoelectric power measurements, see, for example, references (1) to (8). After 1970, most of these investigators left these studies for two reasons: first, they encountered theoretical difficulties interpreting their results; the problem was complex compared to the theoretical knowledge of the processes involved. Second, a great dispersion in the experimental results was generally obtained and attributed to convective disturbances (3), which could not be controlled and impeded further experimentation. Since this time, numerous computations, for instance molecular dynamics simulations, have been performed, thus offering a renewal of the interpretation possibilities. An important improvement for performing scientific experiments in new conditions has been offered by the multiplication of Space flights. This led to a new development of the transport properties studies in the liquids because the microgravity conditions allow one to assume complete disappearance of convection. However, the flight conditions only diminished quite notably the gravity levels, but did not annul them. It was then necessary to develop new kinds of calculations in order to know the influence of such reduced gravity levels.

In the case of molten salts, it is impossible to measure a Soret effect in normal gravity conditions (9). In a perfectly vertical situation, which should be the best situation, an equilibrium state is reached, which could be destabilized if the parameters of the system exceed the critical values corresponding to the onset of the instabilities. During an Earth experiment, the parameters correspond to the unstable domain where a convective motion is generated, except in the case of top heating with a positive Soret coefficient, which is an unconditionally stable situation. In fact, the perfectly vertical situation is impossible to obtain and small experimental imperfections cannot be avoided. In the case of top heating and a positive $S_T$, small departures from verticality will generate convective motions strongly perturbative if $S_T$ is small. In addition, the thermal boundary conditions can create radial thermal gradients that will also generate convective perturbations. The complete numerical study (9) that we performed has permitted us to explain those problems encountered by experimenters, as mentioned above. Whatever the situation on Earth, the separation created by the thermal diffusion is always reduced, compared to the perfect one mentioned above, which only takes in account diffusive phenomena. This led us to perform our experiment on a molten AgI/KI mixture during the S1-Spacelab flight of October 1985 and also to control the convection effects in such a microgravity environment by simultaneous numerical simulations.
2. DEFINITION OF THE SPATIAL EXPERIMENT

2.1 Important Experimental Parameters

As has been seen above, the main problems encountered when measuring processes related to the diffusion in liquids are those coming from usual convection. However, this is not the only cause, and perturbations can be generated for at least two more reasons:

1. The surfaces, which are necessary because the experimental cell cannot have infinite dimensions, thus, in addition to the volume convection, a surface convection must be considered.

2. The free volumes existing inside the cell create bubbles, which will involve a continuous remixing of the molten mixture since their mobility could be much larger than that of the diffusion species. A supplementary surface effect can be added to the bubbles if they exist (Marangoni effect). The eviction of the free volumes is one of the most difficult problems that we had to solve, but we were helped by the salt expansion upon melting; all the excess volume could be absorbed by a porous material during the melting operation, if the material wetting and interfacial properties are known.

These first studies were performed during 1976-78 by Mellon (10), who defined the best conditions necessary for a successful Space experiment. He then calculated theoretically the isotherm surface tension for several molten mixtures with a model which had been successfully applied to binary and ternary metallic systems. In this model, the surface parameters are analogous to those of regular solutions proposed by Guggenheim (11) and by Defay and Prigogine (12) (quasi-structure of the liquid phase with no long distance interaction and separation of the degrees of freedom). Then the volumetric phase is related to the thermodynamic properties and the surface tensions when the physicochemical equilibrium is reached. It is concluded that, in contrast to liquid metals, the simple statistical model is not sufficient to explain the deviation from ideality observed for the surface tension measurements in molten salt mixtures. This study was then followed by calculations of the contact angles and shapes of the equilibrium meniscus as a function of the gravity values. Experimental 1-g determinations of the wetting properties (contact angles and surface tensions) of a molten AgI/KI mixture were also made by Mellon; he concluded that such an equimolar mixture wets imperfectly all materials with various contact angles (40°<θ<90°). The evolution with temperature is slight, but usual. We are now able to state that no fundamental change of these values appears under microgravity conditions.
2.2 Choice of the Experiment

The Space experiment consists of the measurement of the separation coefficient in a molten AgI\textsubscript{0.75}KI\textsubscript{0.25} submitted to a strong temperature gradient. The choice of the type of molten salt has been discussed earlier (13, 14). Let us only mention that this salt has valuable characteristics from the thermal point of view (small thermal diffusivity compared to that of a liquid metal), as well as from the electrical point of view (very good ionic conductor). This led to a theoretical study for which we obtained a decoupling between the mass flux and the heat flux (9), and for which the microgravity will be of great interest, thus permitting the mass transfer created by the temperature gradient. Another reason for using this salt involves the method which can be used for the detection of the diffusion phenomenon in real time: the measurement of thermoelectric power. This type of measurement is greatly facilitated by using a silver salt, which allows the use of silver electrodes without being impeded by Space charge capacitance effects induced by blocking electrodes. The mixture composition (eutectic) has been determined while taking into account the minimum electrical power requirements (melting point 260°) as well as the probable maximum separation effect (related to the interdiffusion coefficient). In Figure 1, we give the most recent AgI/KI phase diagram obtained by Claudy and Letoffe (15), which is slightly different from others given in the literature, especially around the eutectic area.

The choice of the experimental cell takes into account the various problems, which are:
- no free volume (100% cell filling)
- electrically insulated cell with the possibility of measuring the thermopotential with silver electrodes
- chemical inertia and tightness at all temperatures
- maximum temperature gradient obtained by the heat flux inside the furnace
- flight security.

We chose to absorb the salt volume increase when melting occurs (10%) by use of a porous material cylinder (special variety of alumina) surrounding the salt. The choice of porous material was guided by its thermal characteristics, its wetting by the liquid, and its chemical reactivity. Some preliminary experiments helped us in the choice of the porosity (18% volume and 30 μm pore diameter) (16). The cell was made of an impervious alumina tube, this material having the best qualities for solving the problems mentioned above. For flight security, we were obliged to enclose the total cell inside a stainless steel tube. The experimental cell design inside the Space cartridge is given in Figure 2.
2.3 Determination of the Experiment Duration

The furnace used was the Gradient Heating Facility designed by the C.N.E.S. for a great number of users and mounted inside the Spacelab Material Science Double Rack. It is composed of three identical 22 mm diameter cartridges. The heating program has been carefully calculated as well as the thermal and geometric characteristics of the cartridges in order to obtain, in the shortest time, a stable temperature gradient (about 70°C/cm) combined with a minimum electric consumption (Space requirements). Successive trials on Earth combined with calculations gave a good value for the thermal coupling between the cell and diffusers. The thermal kinetics curve is given in Figure 3, which shows that the stable gradient is obtained within less than one hour. It can be maintained with a precision better than two degrees during several hours of experiments. The experiment duration was determined based on a preliminary result of Mellon (10), who measured the self-diffusion coefficients of the silver and potassium ions on Earth. He then calculated the interdiffusion coefficient of AgI/KI as a function of the mole fraction of KI and different temperatures. The curves given by Mellon clearly show that the interdiffusion coefficient is maximum for the eutectic composition (22% KI, according to Claudy and Letoffe). The maximum obtained D value is about $27 \times 10^{-5} \text{ cm}^2/\text{s}$. The evolution of the Soret effect separation with time can be approximated to the first order, by an exponential form. The time constant $\tau$ of this evolution is bound to $L$, length of the experimental cell, and to $D$, interdiffusion coefficient:

$$\tau = \frac{L^2}{\pi^2 D}$$

A quick calculation indicates that $\tau$ approaches one hour when $L = 3 \text{ cm}$.

One of the important problems of Space experiments is the experiment duration, for two reasons. The first comes from the economics of a Space flight, which encourages completing the maximum number of experiments. The second comes from the energy, which is necessary for an experiment to be undertaken. Both the flight organizers, as well as the experimenters, have to take into account these problems. According to these requirements, it has not been possible for us to maintain isothermal conditions during a sufficient time for equilibrium or to use the total cartridge volume in order to complete two different experiments in each of the three cartridges. Other problems come from the fact that, because the maximum number of experiments must be performed in a minimum volume, some perturbations can be induced by other experiments working at the same time. These perturbations can come from the vacuum system, which is common to several racks, as well as from movements (astronauts or experiments) inducing residual accelerations, as well as from astronauts.
themselves who have to undertake considerable work, sometimes when being space-sick, or more simply missing some experiments despite their long training on Earth before the flight.

We thus fixed our experiment duration to five hours, with stable gradient, assuming that the stationary state is obtained. This adds up to about six hours with the furnace working, and seven hours when taking into account the checking of the cartridges and the heating program, plus the time necessary to obtain a sufficient vacuum. We must add that the total experiment was automatic after the astronauts had closed the furnace door (the heating program had been prepared on memories, which could not be modified when running, except for the total break off of the experiments).

3. RESULTS

3.1 Thermoelectric Potential Evolution

This first Soret-effect Space experiment on a molten salt was fully successful. We were able to measure a thermoelectric emf in the three closed impervious cells containing the molten salt. In addition, it was decided during the flight itself that another run with three cartridges could be performed at the end of the mission, when all other experiments had been made. This supplementary experiment was made with the Space cartridges, which had been loaded on board the Spacelab. This second run further confirmed, with three new cartridges, the possibility of measuring thermoelectric power under good conditions in Space. In fact, these two runs were performed under quite different conditions: during the first run, there were continuous activations-deactivations coming from other experiments, thus creating vacuum problems involving temperature variations. On the other hand, the second run was made during very quiet conditions, with no resulting temperature problems. In each experiment, we used two sizes of porous tubes:

- small salt diameter; inside 3 mm, outside 7 mm (2 mm thickness)
- large salt diameter; inside 5 mm, outside 7 mm (1 mm thickness)

These two different geometries should permit us to vary the convective stability conditions.

Figure 4-a gives the thermoelectric signal obtained on Earth (vertical cell), and Figure 4-b the signal obtained in Space with large diameter cells, together with the chromel-alumel thermocouple indication of the temperature difference. We see that the Earth signal, which started quite smoothly, shows perturbations after three hours of experiments. These perturbations are probably due to contact problems or oxidation on the top electrode.
Figure 10 gives the x-ray photographs of these last cells: (a) before salt melting, (b) after melting on Earth, (c) after melting in Space. It should be noted that all the x-ray photographs given in this paper have been made after complete cooling down to ambient temperature. In these three photographs, the porous tube is almost invisible, which tends to prove that the salt did not penetrate inside the porous material. The remainder of the cell-free volume before melting was sufficient for the expansion. The problems appearing during the Earth experiment are not visible on the 10-b photograph.

Figure 5 gives the thermoelectric signal and temperature difference signal obtained on Earth, with two other cells maintained vertical (small diameter cells). Note that the thermoelectric signal 5-a is perturbed, with no contact at the beginning of the experiment. This signal then starts with a lower value and maintains a low value all during the experiment. Oppositely, curve 5-b looks quite normal. Figure 11 shows the corresponding x-ray photograph. One can see the great differences between these three photographs. The second photograph shows the liquid level after a shrinkage, which is due to a large liquid absorption by the porous alumina tube, clearly visible here. On the third photograph, no problem occurred, the liquid absorption being very slight. This shows that the contact concerning Figure 5-a appeared after the salt had been absorbed by the porous material toward the top electrode. The small potential value can be explained by the temperature difference, which is smaller than expected in the diffusion zone of the molten salt.

As a conclusion for these thermoelectric measurements, one can say that measurement is possible in Space with a completely filled cell and with a reproducibility of 100% over six cells. Second, the porosity combined with the interfacial salt properties never resulted in the salt absorption being under the sole influence of capillarity. However, some supplementary absorption is obtained on Earth under the influence of the salt weight. In space, one always obtains a thermoelectric potential, which corresponds to complete cell filling.

3.2 Theoretical Stability Conditions

We undertook numerical simulation of the convection for long, differentially heated cylinders corresponding to our experimental cells. We were mainly concerned with microgravity situations characterized by a gravity (g), which is reduced by a factor $10^3$ to $10^4$ with regard to the Earth gravity ($g_0$), but with an unknown orientation. The equations, the dimensionless parameters, and the numerical method are given in previous papers (9, 17). This study has been performed for various values of the parameters. Various temperature differences and gravity levels were taken into account with the use of the Grashof number $Gr_H$ ($0.01 < Gr_H < 10$).
consider all the possible cell orientations with regard to gravity ($\gamma$, angle between the gravity and the cell axis, $0^\circ < \gamma < 180^\circ$). The Soret coefficient appears in the separation parameter $S$ (-0.75 < $S$ < 1). Finally, the physical properties of the molten salts are used to determine the Prandtl and Schmidt numbers ($Pr = 0.6$, $Sc = 60$). For such a system, the convective motion corresponds to a single regular roll, which has no influence on the isotherm contours (small $Pr$ value). On the contrary, the deformation of the isomass fraction contours can be important, particularly when $Gr_H$ increases (Figure 6). The influence of the motion on the separation, an important result for the experimenters, is given by the variable $X_{bot}$, mean mass fraction at the end of the cylinder, normalized to one for the perfect Soret separation (purely diffusive without convective motion). For different $S$ values, we present the variation of $X_{bot}$ as a function of $Gr_H$ (for $\gamma = 90$, Figure 7) and as a function of $\gamma$ (Figure 8): the separation is almost perfect for small $Gr_H$ values or for certain vertical situations, but decreases quite strongly outside this domain. These curves will allow the experimenters to estimate the degree of perturbation of their experiment. Another interesting result is that the diminution of cell radius, which decreases the perturbations induced by convection, can be used to improve the experimental conditions. These theoretical results applied to the acceleration values measured during the flight have permitted us to ensure that our experiment was not perturbed by convection.

4. CONCLUSION

In conclusion, our first Soret-effect experiment in Space has shown the possibility of measuring thermoelectric power under low convective conditions. The evolution with time of this thermoelectric power measured in Space is given in Figure 9 and compared with the corresponding Earth variation.

The observed variation seems characteristic of a diffusion process, but the phenomenon is much slower than expected; after five hours, the stationary state had not been reached. This corresponds to a smaller diffusion coefficient in Space than measured on Earth. This fact has also been noticed by other authors using liquid metals (18), with a factor of four between Earth and Space coefficients. The Soret coefficient cannot be calculated because the stationary state is too far from being obtained, but the variation indicates that the Soret coefficient is positive, corresponding to the migration of AgI towards the cold side of the cell. The Earth variation given in Figure 9 is at least two times smaller than the Space variation; it then confirms the impossibility of a correct measurement on Earth, although the system is theoretically stable, the hot side of the vertical cell being up.
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Figure 1: AgI/KI phase-diagram from Claudey and Letolle (Ref. 15)

Figure 2: Experiment cell inside the Space cartridge
A-Pydrol 49D cartridge, B-Thermodiffusion cell, C and D-Piece of copper to hold the cell, E-Thermal coupling copper piece, F-Expansible copper cone, G-Stainless steel screw for expansion, H-Carbon fiber for compensation of thermal expansion.

Figure 3: Temperature-time curve obtained in the cell
Figure 4:
Thermoelectric signal on Earth (a) and in Space (b) (large cell)

Figure 5:
Thermoelectric signal on Earth with two small cells
Figure 6:
Iso-mass fraction contours
a) $G_r H = 0.1$, $X_{bot} = 0.999$

b) $G_r H = 0.5$, $X_{bot} = 0.915$

c) $G_r H = 1$, $X_{bot} = 0.733$

d) $G_r H = 3$, $X_{bot} = 0.308$

e) $G_r H = 5$, $X_{bot} = 0.196$

Figure 7:
$X_{bot}$ versus $G_r H$ for different $S$
$AZ = 6$

Figure 8:
$X_{bot}$ versus $\gamma$ for different $S$ at $AZ = 6$, $Pr = 0.6$, $Sc = 60$, $G_r H = 1$

Figure 9:
Comparison of the thermoelectric power in Space and on Earth as function of time
Figure 10:
X-ray photographs of large diameter cells:
a) Before melting
b) After melting on Earth (Cell C1-Earth)
c) After melting in Space (Cell C2-Z)

Figure 11:
X-ray photographs of small diameter cells:
a) Before melting
b) After melting on Earth (Cell C3)
c) After melting on Earth (Cell C2)