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Abstract: The precipitation characteristics of excess silver and calcium solutes in their respective liquid sodium solutions were studied in the temperature range of 425 to 1500°C and the concentration range of approximately 20.0 to 0.10 weight-percent of solute. The excess solute was observed to precipitate out of the bulk of the respective solution as rapidly as the temperature was reduced. The data obtained best fit the empirical equation

\[ \frac{C_o - C_r}{C_o} = \frac{(\Delta T \times \Delta t)K}{d^2} \]

where \( C_o \) is the initial solute saturation (number of atoms per gram of sodium) and \( C_r \) is the concentration at any subsequent lower temperature. The quantity \( (C_o - C_r)/C_o \) is then the fraction of the total solute that precipitated out of solution; this excess was observed to be directly proportional to the product of the temperature decrement \( \Delta T \) (°C) and corresponding elapsed cooling time \( \Delta t \) (min) and inversely proportional to the square of the interatomic solute distance \( d \) (cm). The factor \( K \) is a proportionality factor assumed to be nearly constant over the concentration and temperature range of the solutions investigated.

INTRODUCTION

This investigation was undertaken as part of a broad program to measure the properties of liquid metals. The main objective of this investigation was to establish any time lag for excess solute precipitation when an initially saturated liquid sodium solution is continuously cooled at a known rate under stirred conditions. Such time-lag information is of value for the prediction of mass transfer and corrosion rates of structural material components in dynamic liquid metal systems. Although silver and calcium have high solubilities in liquid sodium and would not be considered for practical use in heat transfer systems, silver-sodium and calcium-sodium binary systems were expediently chosen for this investigation for the following reasons:

1. Established phase diagrams of both systems indicated only liquidus regions existed over comparable temperature but different solubility ranges. On cooling in these liquidus regions, no solid compound formed; the only solid phase was excess solute material.

2. The solubility of silver at 425°C is approximately 20 weight-percent, while that of calcium at the same temperature is less than 3 weight-percent. The difference in solubilities between the two systems studied afforded an opportunity to investigate the dependence of solute concentration on the precipitation characteristics in addition to the differential solute species effect.

3. Precise and conventional analytical procedures for the determination of both silver and calcium in sodium metal were readily available over the concentration ranges to be encountered.

4. A relationship could be derived between the excess solute precipitation rate parameters of such concentrated solutions that might be reasonably extrapolated to dilute solutions of materials more practical for heat transfer systems, since the dilute solutions lack analytical precision and phase diagram certainties.

APPARATUS AND SAMPLING SYSTEM

The solubility apparatus is diagrammed in Fig. 1. With the exception of the auxiliary glass sampling and inert gas/vacuum port attached to the top of the apparatus through a Kovar metal-to-glass seal, the solubility container was made
of type 347 stainless steel, known to have good corrosion resistance to liquid sodium. The solubilities of stainless steel components in liquid sodium have been established [1] to be in the low parts per million region over the temperature range of this study. The container was assumed to be inert to the liquid sodium in view of the high solubility systems that were studied.

The liquid sodium solutions were sampled using two different techniques. The bucket-dip technique gave mainly a sample of the solution surface, while the gas-flow-pipette technique gave a bulk liquid sample. The results of both sampling techniques were compared and evaluated in the perspective of the objective of this investigation. Both the buckets and pipettes were made of type 347 stainless steel also. The pipette, 3/8 inch in diameter and 12 inches long with a 4-1/2-inch length of 1/8-inch-diameter tubing concentrically welded in place at the tip, is shown in Fig. 1 also. This pipette design was used as a precaution against loss of sample. Sampling with tubing simply constricted at the tip proved unreliable, as the siphoning action necessary to withdraw a 2 to 4 gram sample of solution required only a slightly reduced pressure from atmospheric.

The reaction vessel was heated by a Nichrome heating element. The solution was stirred electromagnetically during the initial temperature equilibrium period, but the stirrer was turned off during the subsequent cooling period. The temperature of the system was determined within ±2°C by a chromel-alumel thermocouple contained in a well and was automatically recorded on a strip chart of a controlling potentiometer.

**PROCEDURE**

Approximately 50 grams of sodium were vacuum distilled from a nickel still into a Pyrex receiver fitted with a sintered glass filter frit. The sodium was heated to just above the melting point and filtered by differential argon pressures into the apparatus that contained the required quantity of solute material necessary to saturate the volume of liquid sodium at the highest temperature of the cooling range. The purity of the silver was 99.999 weight-percent. The calcium was electrolytic grade of nominal 99 weight-percent purity.

The solubility apparatus was sealed off from the filter and the internal pressure adjusted with purified argon such that the system was at atmospheric pressure at the sampling temperature. The apparatus was transferred to the controlled furnace assembly and gradually heated to the maximum temperature of the run. The liquid sodium was allowed to equilibrate with the metallic solute material for at least 48 hours under stirred conditions. The solution was then checked for initial solute concentration by both sampling techniques. All sampling was against a backflow of purified argon.
argon with the electromagnetic stirrer off. The argon flow was introduced to the apparatus through the side arm connected to the auxiliary vacuum/inert gas system and exited into the room atmosphere through the vertical sampling port. After the power to the furnace was turned off, the solution was allowed to cool by ambient room air conditions. Almost-simultaneous sampling by both techniques was done at various points along the cooling range. To avoid atmospheric contamination of the solution the pipettes were highly evacuated and purged with purified argon before insertion in the sampling port, and the buckets were simply purged with a fine jet of purified argon. Both the buckets and pipettes were allowed to remain just above the solution surface for variable time periods of at least 3 minutes before dipping, depending on the sampling frequency, for preheating to as near temperature equilibrium with the solution as possible. During sampling, the pipette was inserted to a predetermined solution depth with purified argon flowing out the tip. The argon flow was then stopped and the gas volume of the auxiliary pipette sampling system cracked into a partially evacuated calibrated volume such that a 2 to 4 gram sample of solution was siphoned from the predetermined depth. The pipette was then removed from the bulk solution and allowed to cool in the upper region of the glass sampling port. The pipette, containing the sample, was then removed from the apparatus, and the sampling sequence was repeated at a different temperature with a new pipette. The above-described sampling procedure maintained a bright shiny surface on the solution after continual sampling of at least 3 hours as evidenced by the visual appearance of the bucket samples; the bright shiny surface indicated minimal atmospheric contamination of the liquid.

The solute concentrations of the nonequilibrium temperature samples were compared with known equilibrium solubility values at the same temperature, and differences in concentration were the criteria used for investigation of supersaturated or colloidal solutions. The excess solute precipitation rate was determined by comparison of the solute concentrations of the nonequilibrium temperature samples with the initial solute concentration of the liquid sodium at zero time. The stability of general solution conditions and/or the excess solute precipitation rate are important considerations that require qualification in $\Delta T$ liquid sodium systems and were the phenomena of principal interest under investigation in this study.

RESULTS

Samples, removed by the bucket technique, of a continuously cooled (425 to 157°C) sodium solution of silver were dissolved and analyzed for sodium content by simple acid-base titration and for silver content by the chloride gravimetric method. These preliminary results are plotted in Fig. 2. The curves produced were typically S-shaped and indicated apparent colloidal suspensions and/or supersaturated solution conditions over most of the cooling range when compared to the equilibrium solubility curve fitted to the observed solution cooling rate data.

\[ \text{TEMPERATURE (°C)} \]

\[ \text{SILVER CONTENT (wt.%)} \]

\[ \text{TIME (MIN)} \]

Fig. 2 — The apparent colloidal suspension of silver in liquid sodium as determined from bucket-dip samples

Samples, removed by the same bucket technique, of a continuously cooled (425 to 158°C) sodium solution of calcium were analyzed for calcium volumetrically by an EDTA titration method (2). The results are plotted in Fig. 3 in the same manner as described for the silver-sodium solution. The curve produced is likewise S-shaped—however with a much greater degree of apparent supersaturation and/or colloidal suspension evident than in the former case, especially over the initial part of the cooling
curve. The high peak region of the curve was reproducible and was further investigated in light of both surface-active phenomena and localized thermal effects of the cooled solution. The surface tension values of calcium and sodium are reported (3,4) to be relatively close. Contaminants such as oxygen in the solution, combined as CaO (CaO is thermodynamically more stable than Na2O), would tend to lower (5) the surface tension of the calcium.

When the solute has a lower surface tension than the solvent, excess solute is deposited in a film at the surface as the temperature of the solution is decreased. It was reasonable to assume that conditional requirements for surface-active phenomena were closely approximated. Localized thermal effects, especially in the solution surface as cooling occurred, due to the geometry of the experimental setup were also believed to have contributed to the observed anomaly. In order to circumvent any deleterious surface effects inherent in the sampling technique used, two procedural changes were made. The method of sampling the solution was changed primarily to more accurately reflect the precipitation behavior of the true solute specie in the bulk of the liquid. The new method (which was shown in Fig. 1) was a gas-bubbling-pipette technique which broke up the surface film and enabled a bulk sample of the solution to be taken. The second change entailed sample removal from near the thermocouple well tip, which gave a more accurate sampling temperature and also obviated any localized thermal effects in the surface of the cooled solution.

The experiments were repeated on both the silver and calcium solutions, incorporating the above-described changes. Although the silver-sodium solution was not concerned with surface-active phenomena due to the relatively high surface tension of silver, the localized thermal effects phenomena, however, required qualification. In the interest of further reproduction of the preliminary data, the bucket sampling technique was also employed, almost simultaneously with the gas-flow-pipette technique, during cooling of the respective solutions.

In Fig. 4 are shown the usual comparative plots of solute concentration versus temperature, in terms of elapsed cooling time, with equilibrium solubility values at corresponding temperatures for the silver solution using both sampling techniques. The bucket-sampled data reproduced the preliminary results, while the pipette data correspond with equilibrium solubility values, which indicated that the excess solute precipitated and settled out of the bulk solution as rapidly as the temperature was reduced.

The results of the calcium-sodium nonequilibrium temperature experiment compared with equilibrium solubility values at corresponding temperatures using both sampling techniques
are shown in Fig. 5. The same general conclusions were drawn as in the case of the silver-sodium repeat experiment. The results of the pipette samples likewise indicated no measurable time lag for excess solute precipitation at the solution cooling rate and solute concentration levels encountered.

**DISCUSSION**

As the exact nature of the surface effects phenomena uncovered by the bucket sampling technique was indeterminate, the further treatment of the results, in the perspective of the aforementioned objective of this study, will reflect...
only the pipette-sampled data, which were con-
considered to be most characteristic of the bulk of
the solution. In order to correlate the most
significant system parameters concerned with
the excess solute precipitation rate of a liquid
sodium solution, a simple skeletal model of the
solute matrix was constructed. A cubic lattice
geometrical cell configuration was assumed,
one side of which is shown in Fig. 6. The inter-
atomic solute spacing \( d \) was calculated at a par-
ticular temperature from solubility data. From
a knowledge of the solute concentration per
unit cube of solution, the number of solute atoms
on a side of unit length was readily calculated,
and assuming a homogeneous distribution of
solute atoms in the liquid the distance between
the solute atoms was determined.

![Skeletal model of the solute matrix.](image)

The broken circle in the model diagram desig-
nates an excess solute atom lying in an adjacent
plane. When the temperature of the solution is
decreased, the excess solute atoms are no longer
bound to the sodium but become mutually at-
tractive instead. A physical attraction or col-
losion between the excess solute atoms is necessary
for precipitation to occur. From a purely statistical
point of view, the probability that a collision will
occur between two excess solute atoms lying in
parallel planes can be expressed as approximately
equal to the ratio of the cross sectional area of
a solute atom to the planar area \( d^2 \). Thus the
precipitation rate is expected to vary inversely
as the square of the interatomic distance \((1/d^2)\).

If \( C_0 \) is the number of solute atoms per gram of
sodium at a given saturation temperature, and \( C_r \)
the number at any subsequent temperature
which is lower by an amount \( \Delta T \), then the quantity
\( (C_0 - C_r)/C_0 \) connotes the excess solute fraction
available for precipitation as the solution is cooled.
The precipitation rate, namely, the excess fraction
that precipitates out of solution per increment
of cooling and per increment of time, is then
\[
\frac{C_0 - C_r}{C_0} \times \frac{1}{\Delta T \times \Delta t}
\]
where \( \Delta t \) is the elapsed cooling time (minutes)
corresponding to \( \Delta T \) (°C). If the precipitation
rate is inversely proportional to \( d^2 \), the final
empirical equation is
\[
\frac{C_0 - C_r}{C_0} \times \frac{1}{\Delta T \times \Delta t} = K \times d^2
\]
where \( K \) is a factor characteristic of the liquid
sodium solution including expressions for the
ucleation and growth of crystallites from cooled
mells. A fit of the observed data of the conti-
uously cooled sodium solutions of both calcium
and silver to the above equation is shown in Fig. 7.
For both solutions studied, the same fairly smooth
curve can be drawn through the points. It is
interesting to note that only the second power of
the \( d \) term in the equation was successful in
normalizing the precipitation rate data of both
solutions.

If the extension of the empirical equation de-
veloped is made to include highly dilute solutions
such as would be experienced in practical liquid
sodium heat transfer systems, the \( d^2 \) term would
be much larger. As the dilute solution is cooled,
the \( \Delta t \) term of the equation will have to be com-
mensurately greater for the equation to apply,
which would indicate that long periods of time
would be required for the excess solute to pre-
cipitate out completely. The prospect of super-
saturated conditions in continuously cooled
dilute sodium solutions is not unreasonable in
view of extrapolation of the measured parameters
of the concentrated solutions studied.

The nature of the precipitation process of the
excess solute is expected to be a menomolecular
reaction. The solute atoms are bound to the
solvent atoms in a finite ratio at a particular
temperature consistent with solubility consid-
erations. As the temperature of the solution is con-
tinuously decreased, a smaller solute-to-solvent
atom ratio results. This process is continuous
until at the freezing point of the solution, the
total quantity of solute atoms initially present is
excessive. The precipitation process is considered
to be analogous to the decomposition of a com-

solute-to-solvent atom ratio and excess solute as the solution is cooled to a lower temperature.

Monomolecular reactions are known to follow the exponential rate law \( N/N_0 = e^{-kt} \) and can be derived for the excess solute precipitation process. The rate of change of specific number of solute atoms as the solution is cooled to a lower temperature is set proportional to the number of solute atoms initially present:

\[
-\frac{dN}{dt} = kN,
\]

which can be expressed as

\[
\int \frac{dN}{N} = -k \int dt
\]

or

\[
\ln N = -kt + a.
\]

The integration constant \( a \) is evaluated from the limit \( N = N_0 \) when \( t = 0 \), which gives \( a = \ln N_0 \). Thus Eq. (3) becomes

\[
\ln \frac{N}{N_0} = -kt
\]

or

\[
N = N_0 e^{-kt}.
\]

The constant \( k \) is then the precipitation rate constant for the excess solute specie. If the logarithm of the specific number of solute atoms in solution is plotted versus the elapsed cooling time, and if the reaction rate is first order, the numerical value of \( k \) can be determined from the slope of the resulting straight line. Such plots of the data observed for the continuously cooled sodium solutions of both calcium and silver are shown in Fig. 8. The calcium data fit the exponential rate law quite well over the entire temperature range studied. The calculated slope of the straight line produced gave a value of 0.0173 reciprocal minutes for \( k \). However, the fit of the silver data did not appear to apply over the entire temperature range but only after an initial transient temperature range of 425 to 350°C, after which the slope of the line corresponded to that observed for the calcium data.

Two different rate constants are clearly discernible in the log-Ag-concentration-versus-time plot. The composite curve was resolved into its component parts by back extrapolation of the tail portion to zero time and subtraction of the extrapolated straight line from the original curve. The \( k \) value for the initial transient component was calculated to be 0.0577 reciprocal minutes or a factor of 3.3 times greater than that of the second component. The phenomena ascribed to the dual precipitation rate behavior of excess silver solute are not readily determinable.

**SUMMARY**

Initially saturated sodium solutions of both silver and calcium were continuously cooled and continually examined for general conditions of supersaturation and/or colloidal suspension. Continual sampling of the bulk of the solutions...
and analysis for the respective solute species did not indicate a measurable time lag for excess solute to be removed from the liquid. The precipitation of the excess calcium solute was observed to follow the exponential rate law over the entire cooling range studied. The precipitation of the excess silver solute showed a deviation from the exponential rate law, and two different rate constants were indicated. The excess fraction of total solute of either specie studied that precipitated out of solution at any point along the cooling curve was observed to be a direct function of the temperature decrement and elapsed time and an inverse function of the square of the calculated interatomic solute distance. Extrapolation of the above-mentioned parameters to more dilute continuously cooled sodium solutions tend to indicate that the equivalent of supersaturated and/or colloidal conditions are possible. This would be a desirable effect in a dynamic system such as a practical heat transfer system. The excess solute entrained in the liquid sodium stream would be returned to the heat source and redissolved, in lieu of continuous corrosion of container or structural materials in the hot zone and precipitation with subsequent settling in the cold zone of the loop.

REFERENCES

2. Padhye, V.P., Analyst 82:634-8 (1957)
KINETICS OF EXCESS SOLUTE PRECIPITATION: IN LIQUID SODIUM SOLUTIONS

The precipitation characteristics of excess silver and calcium solutes in their respective liquid sodium solutions were studied in the temperature range of 425 to 150°C and the concentration range of approximately 20.0 to 0.10 weight-percent of solute. The excess solute was observed to precipitate out of the bulk of the respective solution as rapidly as the temperature was reduced. The data obtained best fit the empirical equation

\[
\frac{C_0 - C_T}{C_0} = \left(1 - x \right)^{\frac{1}{2}} K \frac{C_0}{d^2} \Delta T \Delta t
\]

where \(C_0\) is the initial solute saturation (number of atoms per gram of sodium) and \(C_T\) is the concentration at any subsequent lower temperature. The quantity \((C_0 - C_T)/C_0\) is then the fraction of the total solute that precipitated out of solution; this excess was observed to be directly proportional to the product of the temperature decrement \(\Delta T\) (min) and inversely proportional to the square of the interatomic solute distance \(d\) (cm). The factor \(K\) is a proportionality factor assumed to be nearly constant over the concentration and temperature range of the solutions investigated.


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