

Solubility of Argon in Molten Nitrates Mixtures

Y. Wang, Y. Sasaki, K. Kashiwaya,
and
K. Ishii

Division of Materials Science
and Engineering, Fac. of Engineering,
Hokkaido University, Sapporo, 060 Japan

ABSTRACT

To measure the solubility of Ar in molten salts, a modified gas probe has been developed which consists of injection of He into molten salts through a nozzle, collection of ascending bubbles of He-Ar gas mixture, determination of concentration of Ar in the He-Ar gas mixture using a high sensitive mass spectrometer.

The solubilities of Ar in molten LiNO_3 - NaNO_3 - KNO_3 ternary system have been determined as a function of composition and over the temperature range from 463 to 513K. From the temperature dependency of Ar solubility in ternary eutectic point, the enthalpy of solution of about 1 Kcal/mole and the standard entropy of solution of -15 cal/deg was obtained. The present results are discussed in the light of hole model.

1. INTRODUCTION

Many important metallurgical processes involve metals and molten salts (slags). The equilibria between metals and salts (slags) have been discussed in detail for many years. To understand these equilibrium, It is useful to consider the limit of low concentration of the non-ionic component in the molten salts and deal with the solubility of gases in molten salts.

The noble gases presumably dissolve in molten salts as neutral atoms. If so, the polarization of the dissolved atoms by the fluctuating field of the solvent should be the only source of attractive

interactions. Measurement of the solubilities of noble gases in molten salts might afford a convenient method of evaluating the thermodynamics and the structures of molten salt mixtures.

However, It is not so easy to measure the solubility of noble gas in molten salts, because of its very low solubility. Therefore, the measurements of the solubilities of noble gases are quite sparse.^{1) - 3)}

The solubility of gases in molten materials usually measured by Sieverts method. In case of noble gases, it is not applicable due to their very small amounts of solubilities. In this study, the devised method was developed for determining the low solubility of Ar in molten salts by using a mass spectrometer. In the present work attention was focused on the temperature and composition variation of the solubility of argon in molten nitrates mixtures.

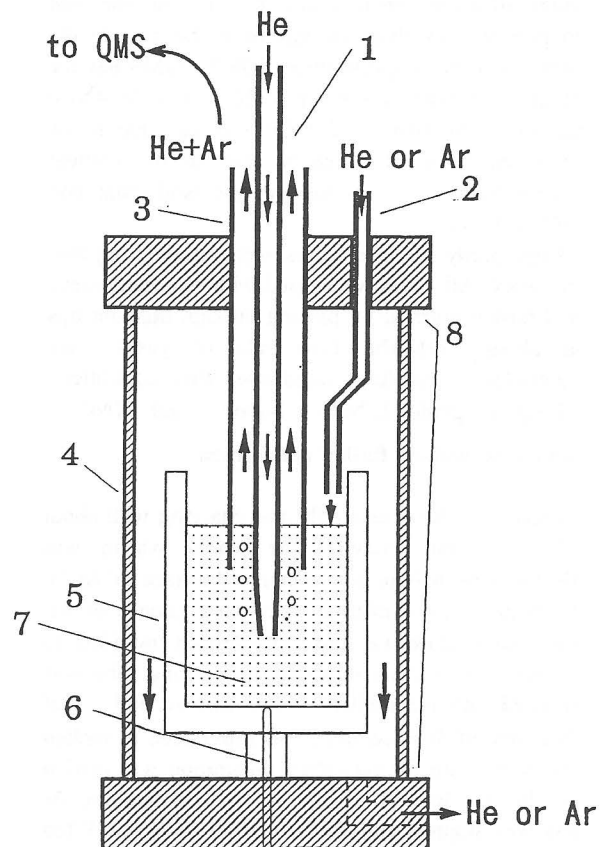


Fig.1 Experimental arrangement for the Ar solubility studies.

1. He injection tube, 2. Ar saturating tube,
3. Gas collector tube, 4. Quartz tube, 5. Crucible,
6. Thermocouple, 7. Molten salt,
8. Water-cooled cap

2. EXPERIMENTS

Apparatus. The experimental arrangement is shown approximately in Fig.1. Nitrate mixture (about 25 g) was melted in the alumina crucible (ID=26mm, and height is 70mm) with resistance furnace. Temperature measurement was by means of a noble metal thermocouple which was held in a silica protection tube outside the crucible. Ar gas probe consists of an injection nozzle and a gas collector. The gas collector alumina tube (ID=17mm) was inserted into the bath. The He bubbling gas was delivered through the gas injection alumina nozzle of 0.8mm internal diameter held coaxially about 10 mm below the surface of the molten bath. Saturating Ar gas was introduced into the molten bath by the another narrow alumina tube. An appropriate system of O-ring sealed end caps was used to allow argon to be passed between the outer silica reaction tube and the alumina tube, and to pass the dissolved Ar gas from the bath to the quadrupole mass spectrometer (QMS). QMS has the ability to measure the order of 20 ppb Ar in Ar-He mixture with 1000V of MCP voltage. Due to its high sensitivity, it is easily affected by ambient temperature, so it was kept in the isothermal box held at 313K.

High purity cylinder gases were used throughout the work. All gases were dried with molecular sieve and further purified by passing through titanium tips at about 973K. The flow rate of gases were controlled by carefully tuned mass flow controller.

Reagent grade LiNO_3 , NaNO_3 and KNO_3 were used without further purification.

Procedure. After assembly and charging with about 25g of nitrate mixture, the whole system was flushed with helium and examine the trace of Ar by QMS and after confirmation of no existence of Ar, then temperature was raised to desired one (463 to 513K). After melt down, the saturating tube was inserted into the molten nitrate mixture and Ar of flow rate of 300 (cc/min.) was introduced to molten nitrate mixture for saturating. Saturation was carried out for a 2 to 6-hr period. After the saturation, Ar gas was stopped and the saturating tube was lifted up, then the coaxially held alumina gas collector tubes and gas injection nozzle were inserted into the molten bath, immediately He carrier gas of flow rate of 140 (cc/min.) was introduced to the molten bath through a narrow gas injection alumina tube and produce the small bubbles. Dissolved Ar was liberated into the He bubbles. The He bubbles with

Ar ascend to the gas collector alumina tube inside and carried away to QMS and analyzed. During the measurement, the intensities of He and Ar were recorded in every 4 seconds.

3. RESULTS and DISCUSSION

To determine the Ar concentration in gas mixture, the intensity ratio of Ar/He was converted to the concentration ratio of Ar/He from the predetermined relation between the intensity ratio of Ar/He and the concentration ratio of Ar/He. This relation is shown in Fig.2. There is a good linear dependency and the Ar intensity was easily converted to the Ar concentration. The typical example of the variation of intensity ratio of Ar/He with time is shown in Fig.3. The amount of released Ar was calculated from the area of Ar peak. The solubility can be calculated from the total amount of Ar in the molten salts and its weight.

Results of the study to determine the times necessary for equilibration are depicted in Fig.4. From this result, It can be concluded that saturation is completed after 2hrs. At another compositions and temperatures, it is found that the equilibrium were established within 2hrs. Most of saturation works were carried out for 3 hrs.

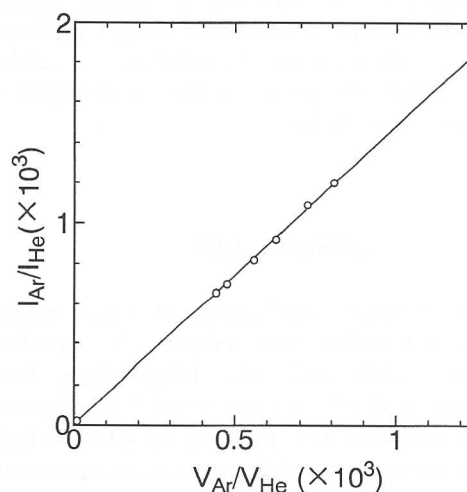


Fig.2 The relation between the Ar/He intensity ratio and Ar/He flow rate ratio. Sensitivity is about 10-12 A/V and measurement was carried out at 2×10^{-6} Torr.

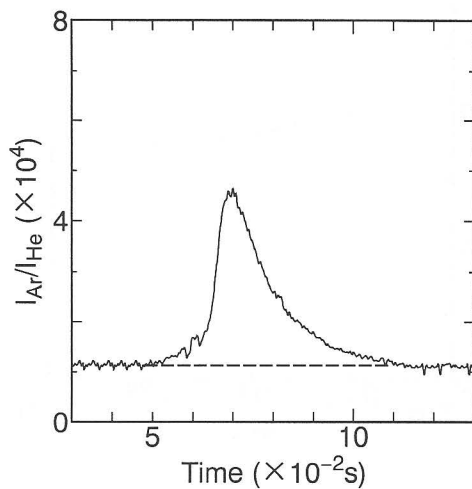


Fig.3 The variation of Ar/He intensity ratio with time for LiNO_3 75wt%- KNO_3 mixture at 523K.

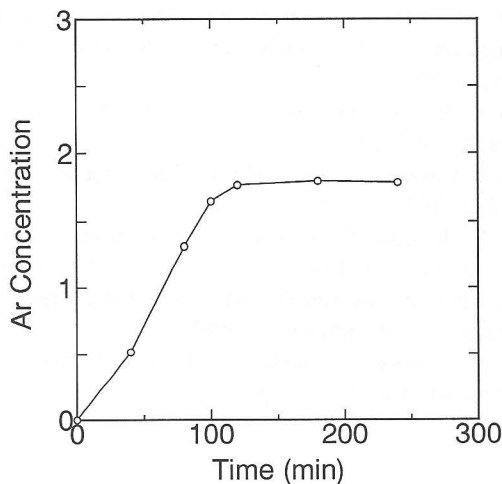


Fig.4 Results of an experiment to determine the time needed to saturate molten salt (ternary eutectic composition) at 523K. Flow rate of Ar is about 300 cc/min..

Solubilities in molten salts are usually sufficiently low for Henry's law to be followed, and it is also permissible to apply ideal gas laws to the

equilibrium gas phase. The solubility was usually expressed in terms of the equilibrium constant, K , related to Henry's law, is taken as

$$K_p = C_d/P \quad (\text{mol of gas})/(\text{cm}^{-3} \text{ of melt})(\text{atm}) \quad \text{---(1)}$$

The distribution coefficient, K_c (of theoretical interest), is defined as the ratio of the concentration of solute to that in the gas phase

$$K_c = C_d/C_g = CRT \quad (\text{unitless}) \quad \text{---(2)}$$

In keeping with common practice, an enthalpy of solution was calculated from the relationship

$$d \ln K_p / d(1/T) = - \Delta H/R \quad \text{---(3)}$$

This equation gives rise to a linear function

$$\ln K_p = - (\Delta H/R)(1/T) + \Delta S_p/R \quad \text{---(4)}$$

in which ΔS_p is a standard entropy corresponding to a standard state of gas at 1atm both inside and outside the melt. The thermodynamics quantities of solution for Ar can be evaluated from the slope and intercept of the fitted curves as indicated by eq.4.

The temperature dependence of the solubility, K_p , at the eutectic composition of ternary system was shown in Fig.5 as $\log K_p$ vs. $1/T$. The endothermic heats of solution, about 1 Kcal/mol and entropy of solution, ΔS_p , around -28 cal/deg mol was found. A more satisfactory form of the standard entropy of solution corresponds to a standard state of gas at 1 mol/cc in bot phase, ΔS_c , is obtained by using $\ln K_c$ rather than $\ln K_p$ in eq.4 and is about 15 cal/deg mol.

The solubility of Ar in LiNO_3 - KNO_3 binary system at 523K is shown in Fig.6. The solubility slightly decrease with KNO_3 content.

The magnitude of the solubility of the inert gases and of the positive ΔH involved can be explained in terms of the energy required to produce a hole in the melt, of the size required to accommodate the gas molecule.⁴⁾ This quantity is given by

$$\Delta H = 4 \pi r_g^2 N \sigma \quad \text{---(5)}$$

where r_g is the radius of the gas molecule (if spherical, otherwise $4 \pi r_g^2$ is its effective surface) and σ the surface tension of the salt (the macroscopic value assumed to apply also to the microscopic hole). This ΔH should apply to the

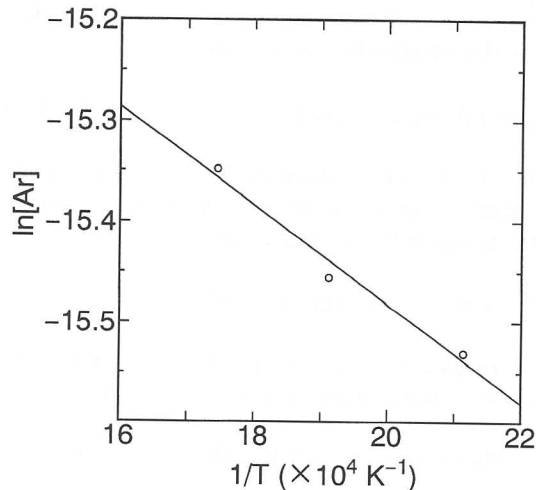


Fig.5 Temperature dependence of the solubility constant K_p for Ar dissolution for the eutectic composition of ternary system.

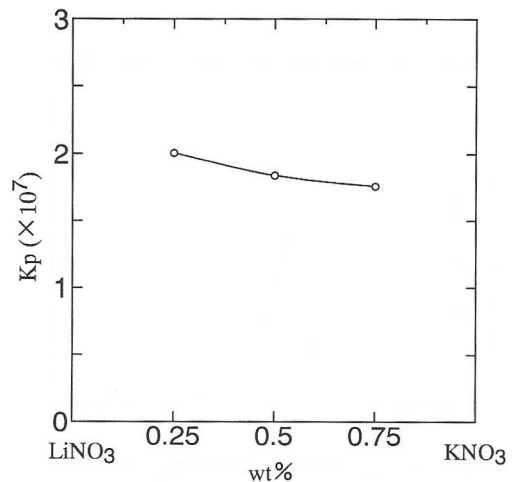


Fig.6 The solubility of Ar for LiNO_3 - KNO_3 binary system at 523K as a function of composition.

transfer of the gas molecule from the gas to melt phase at constant concentration, the entropy effect of this step being negligible. For the dissolution process at unit pressure, the (ideal) gas is first compressed isothermally to its pressure at the concentration equaling that in the melt. The enthalpy effect for this step is zero, the entropy effect $\Delta S_p = R \ln RT K_p$. The value of gas solubility arising from these consideration is

$$K_p = (RT)^{-1} \exp(-4\pi r_g^2 N \sigma / kT) \quad \text{---(6)}$$

Namely, the solubility can be estimated from the surface tension of the molten salt. The surface tension of LiNO_3 and KNO_3 is roughly equal and that of LiNO_3 - KNO_3 mixtures is also almost constant with compositions. Therefore, the solubilities in LiNO_3 - KNO_3 mixture could be constant. Unfortunately, there are no experimental results for the surface tension of nitrate mixture at 523K, the surface tension of LiNO_3 - KNO_3 mixture at 523K was extrapolated from the reported values and is about 120 dyne/cm.^{5, 6)} Shown in Fig.6, the weak dependency of solubility on compositions support the model qualitatively. The calculated K_p is almost 0.1×10^{-7} and there are some difference between the experimental and calculated solubilities. The relative small ΔH and large ΔS_c in the molten mixture suggests that Ar molecules not only create their own hole, but may occupy the existing free volume in the mixtures.

Reference

- 1) Y. Marucus, Introduction to liquid State Chemistry, John Wiley & Sons Ltd., 1977, pp.255-300
- 2) P. E. Field and W. J. Green, J. Phys. Chem., vol.75, 1971, p821
- 3) B. Cleaver and D. E. Mather, Trans. Farady Soc., vol.66, 1970, p2469
- 4) M. Blander, W. R. Grimes, N. V. Smith, and G. M. Watson, J. Phys. Chem., vol.63, 1959, p1164
- 5) NIST Molten Salt Database, National Institute of Standards and Technology, 1987
- 6) T. Tanaka, K. Hack, T. Iida, and S. Hara, Z. Metallkd., vol.87, 1996, p380