Nitrogen Gas Solubility in Molten Sodium Nitrate-Potassium Nitrate Mixture

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The nitrogen gas solubility over the entire concentration range of molten sodium nitrate-potassium nitrate mixture has been measured by an elution method at 543, 593, and 643 K. The obtained values of solubility, K_p , are found to be in the range from 1.5×10^{-7} to 3.4×10^{-7} mol cm⁻³ atm⁻¹. The enthalpy change for solution of nitrogen gas in this mixture shows the positive value, indicating the endothermic reaction. By comparing the calculated value of K_p with the experimental value, the concentration dependence of K_p could be explained.

1 Introduction

Many data have been reported on gas solubilities in pure molten salt but only a few data on gas solubilities in a limited range of molten salt mixture, *i.e.*, an eutectic mixture, and few experiments have been carried out in the entire range of molten salt mixture¹⁾. Generally, the gases dissolving in molten salt are divided into two classes²⁾; a) non-polar gas such as He, Ne, Ar and perhaps N₂, O₂, Cl₂, and CO₂, b) polar gas such as HF, DF, H₂O, BF₃, and NH₃. According to another classification the gases belong to one of the following two classes; a) inert gas such as He, Ne, Ar, and N₂, b) reactive gas such as halogens, CO₂, SO₂, HF, HCl, TiCl₄, and NbCl₅.

In addition to that there is no published data on the nitrogen gas solubilities over the entire range of sodium nitrate-potassium nitrate mixture, another motivation for investigating this system arises from the hope in examining how the solubilities of non-polar or inert gas such as nitrogen vary with the concentration of one component in mixture. Comparing the experimentally obtained nitrogen solubility with the calculated one in molten sodium nitrate-potassium

nitrate mixture, one can make it possible to elucidate the behaviour of dissolved nitrogen gas molecule in molten salt.

2 Experimental

Experimental techniques can be categorized into following three classes²⁾; a) absorption method, where the solubility is determined by means of observing the volumetric or manometric change in the solute or the gravimetric change in the solvent, b) elution method, where the solubility is determined from the quantity of gas stripped from a saturated solution, c) cryometric method, where the solubility is determined from the freezing point depression of the solvent. In this paper, elution technique was used for the determination of nitrogen gas solubility.

Materials; Reagent grade sodium nitrate and potassium nitrate were mixed and dried in an oven at 423 K for a week. Then the dried salts were transferred to the experimental cell and desiccated under vacuum just below the melting point for a half or one day. Nitrogen and helium gases were obtained in cylinders and nominal purities of both nitrogen and helium gases were 99.9989% and 99.998%, respectively.

Apparatus; The apparatus used in this work was almost identical with that developed by Grimes³⁾ as shown in Fig. 1. It consists of gas saturating and elution vessels which are connected in series with a 0.8 cm *i.d.* tube. All the vessel are made of 304 stainless steel. The sizes of both cylindrical saturating and elution vessels were 12.6 cm in diameter and 40.1 cm in length.

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Fig. 1 Schematic diagram of apparatus for determination of nitrogen gas solubility in molten sodium nitrate-potassium nitrate mixture

- 1: Electric furnace, 6: He gas purifier
 2: Saturation vessel, 7: Manometer
 3: Elution vessel, 8: Vacuum pump
 4: He gas supply, 9: P₂O₅ desiccant
 5: N₂ gas supply, 10: Gas chromatography

The vessels are located in large resistance furnace and the lid of vessel is provided with gas inlet tube, gas outlet tube, and thermocouple well.

Procedure; A 6 kg charge of salt was placed in the saturating vessel. Bubbling of nitrogen gas in saturation vessel was achieved by heating the salt at the desired temperature and was carried out for 4 h. Thereafter, the saturated

molten alkali nitrate was transferred to the elution vessel through the connecting tube by heating the frozen seal of salt and helium gas was bubbled through the melt in elution vessel in order to remove the dissolved nitrogen gas in melt. The stripped nitrogen gas was analyzed quantitatively by means of gas chromatography.

3 Results and Discussion

The pressure dependence of the solubility in the limit of low solubility is given by the Henry's law constant k_H ,

$$P_g = k_H X_d \quad (1)$$

where X_d is the mole fraction of the solute gas in melt and P_g is the gas pressure expressed in atm. When Henry's law is experimentally verified, the pressure dependence of the solubility has typically given by the following modified form,

$$K_p = C_d / P_g \quad (2)$$

where C_d , expressed in mol cm⁻³ salt, is the concentration of gas in molten salt and K_p is related to k_H on the approximation that the partial volume of the molten salt, $\bar{V}$ expressed in cm³ mol⁻¹ gas, is constant over the pressure range for which Henry's law is obeyed¹¹.

$$K_p = 1 / (k_H \bar{V}) \quad (3)$$

Since the majority of solubilities have been found to obey Henry's law, the equilibrium constant or pressure independent solubility, K_p expressed in mol cm⁻³ atm⁻¹, is the most commonly reported quantity¹¹.

Table 1 Nitrogen gas solubilities in molten sodium nitrate-potassium nitrate mixtures

KNO ₃ concentration mol per cent	Temperature K	$K_p \times 10^7$ mol cm ⁻³ atm ⁻¹	ΔH kcal mol ⁻¹	$K_{pcyl} \times 10^7$ mol cm ⁻³ atm ⁻¹	$K_{psph} \times 10^7$ mol cm ⁻³ atm ⁻¹
0	593	2.5 ± 0.20	4.7 ± 2.0	0.77	0.11
	643	3.4 ± 0.30	(2.74 ± 0.83)	1.26	0.23
			(3.96 ± 2.2)		
25	593	2.0 ± 0.12	4.0 ± 1.8	0.84	0.13
	643	2.6 ± 0.20		1.36	0.26
50	543	1.8 ± 0.12	2.0 ± 0.6	0.49	0.06
	593	2.1 ± 0.12	(4.07 ± 0.23)	0.90	0.14
	643	2.4 ± 0.12		1.48	0.28
66	593	1.5 ± 0.12		0.92	0.15
75	593	1.7 ± 0.10	2.5 ± 1.0	0.94	0.15
	643	2.0 ± 0.10		1.56	0.30
(100)	(670)	(2.93)	(1.72 ± 0.78)	1.61	0.32

Values in parenthesis were taken from the solubility data reported in ref. 4, 2, 5 and 1

The values of K_p of nitrogen gas over the entire range of sodium nitrate-potassium nitrate mixture at various temperatures are summarized in Table 1. The accuracies indicated are based on the assumption that three sources of error, *i.e.*, the uncertainties in peak area of integrated gas chromatogram, the determination of volume for molten alkali nitrate mixture, and temperature reading, are involved. These errors lead to an average uncertainty 6-10% in the calculated values of K_p .

Although experimental errors are sizable, some tenuous comparisons and conclusions could be still made. The concentration dependencies of K_p are shown in Fig. 2 over the entire range

Fig. 2 Variations of K_p with KNO_3 concentration at 543, 593, and 643 K
 □ 670 K taken from ref. 1), ■ 640 K taken from ref. 2), ▲ 640 K taken from ref. 4), ▼ 640 K taken from ref. 5)

of composition for potassium nitrate, together with the other published data^{1,2,4,5}. It seems that some values of K_p obtained by other workers, *i.e.*, a value of K_p for pure sodium nitrate and a value of K_p for eutectic mixture, are different from those in this work. At first sight of present work in Fig. 2, however, K_p decreases with increasing potassium nitrate until the concentration of potassium nitrate is reached to about 60 mol % and then increases with increasing potassium nitrate.

The enthalpy of solution of gas in molten salt, ΔH expressed in kcal mol⁻¹, is calculated from the relationship;

$$\frac{d \ln K_p}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R} \quad (4)$$

where R is an usual gas constant. The obtained values of ΔH listed in Table 1 with positive values²⁾ show an endothermic enthalpy change for solution. The values for ΔH obtained from other workers^{1,2,4,5} are also included in parenthesis in Table 1 for the purpose of comparison with our data. The agreement between them is good within an experimental error except that for 50 mol % eutectic mixture⁵. Apart from the value of ΔH obtained by Panizza and Zamboni⁵, it seems that the values of ΔH decrease with increasing potassium nitrate concentration^{*1}.

The basic calculating method for expressing the gas solubility in molten salt has been derived by Blander *et al.*³, who modified the Uhlig model⁷⁾ on gas solubility in non-ionic solvent. According to this model, the gas solubility in molten salt can be calculated from the surface free energy of formation of the cavity created by the solute molecule²⁾. The equation is expressed in terms of K_p ;

$$-\ln(K_p \cdot RT) = \frac{A\gamma}{kT} \quad (5)$$

where k is the usual Boltzmann constant, A is the surface area of the cavity taken as equal to the surface area of the solute molecule, and γ is the "microscopic" surface tension of molten

*1 Although the entropy change for solution, ΔS , is also calculable, we want to have no further discussion on ΔS because the uncertainty in ΔS comes from the limited number of experiment and sizable experimental error of K_p produces some ambiguity.

salt assumed to be equal to the "macroscopic" surface tension. In the case of linear polyatomic molecule such as N_2 , two alternative values of A are possible²⁾. When the molecule is assumed to be freely rotating, the cavity surface area is equal to the spherical region swept out by the radius. When the molecule is assumed to be nonrotating, the cavity surface area would be equal to that of cylinder having hemispherical ends. The values of A for rotating and nonrotating nitrogen molecules are $51.8 \text{ \AA}^2$ and $3816 \text{ \AA}^2$, respectively²⁾.

The calculated values of K_p are also listed in Table 1. It is shown from this table that the calculated values of $K_{p_{cyl}}$ for nonrotating molecules are larger than the calculated values of $K_{p_{sph}}$ for rotating molecules. Qualitatively it is apparent that the calculated values of $K_{p_{cyl}}$ are more agreeable with the experimental K_p values than the values of $K_{p_{sph}}$. However, one possible explanation for the curve of concentration dependence of nitrogen gas solubility with a minimum value is that the nitrogen molecules may be regarded as nonrotating molecules in molten salt in excess of sodium nitrate or potassium nitrate and, on the other hand, as rotating molecules in eutectic or nearly eutectic mixture

at 543, 593, and 643 K. This is not surprising when one takes notice of the higher melting point of alkali nitrate in excess of sodium nitrate or potassium nitrate than that of eutectic or nearly eutectic mixture. At present, no further information can be gleaned from the present results.

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応用電気化学の文献紹介 (5)

Investigation of Laser-Enhanced Electroplating Mechanisms, J. Cl. Puipe, *et al.*, *J. Electrochem. Soc.* **128**, 2539 (1981).

電析においてレーザーを電極に照射したとき析出速度が大幅に上昇する現象の機構と応用について検討した。レーザーの波長を溶液の吸収がない領域に選定してやるとレーザーのエネルギーは金属・溶液界面のみ吸収されて局所的な温度上昇を引き起こす。その結果、部分的に電荷移動過程が促進されることと同時に生じる熱対流により物質移動過程が促進されるという2つの理由により反応速度の上昇を説明している。また温度上昇に伴う自然電位の局所の変動により局部電池が形成されるために照射部分に無電解メッキをすることができるとを示している。このような方法により微細なメッキ加工を行なえることからエレクトロニクス

工業への応用が期待できる。

Electrodeposition of Silicon from Solutions of Silicon Halides in Aprotic Solvents, A.K. Agrawal and A.E. Austin, *J. Electrochem. Soc.* **128**, 2292 (1981).

太陽電池の実用化に伴ってアモルファスシリコン薄膜の製造コストダウンが重要な問題になっているが、ここでは従来の気相成長法に替るものとして液相中電気化学的にシリコンを析出させる方法を試みている。プロピレンカーボネートに良く溶ける SiHCl_3 を用いて導電率を上げるために 0.1 M のテトラブチルアンモニウムクロライドを支持塩として加えた浴を使用している。析出したシリコン中には水素が少量含まれていたが、これは浴の組成を変えることによりコントロールできる。

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