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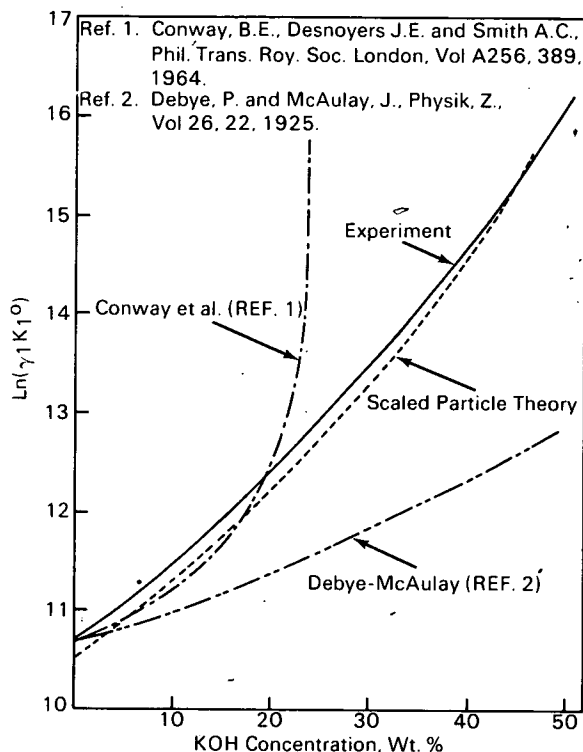
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NASA TECH BRIEF



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Solubility of Non-Polar Gases in Electrolyte Solutions



Theoretical and Experimental Activity Coefficients of Oxygen at 25°C.

A general theory has been developed which permits accurate prediction of the solubility of non-polar gases in concentrated potassium hydroxide (KOH) electrolyte solutions. It will be even more useful when extended to other electrolytes. The theoretical treatment is superior to previous attempts in its description of the effects of both concentration and temperature on the solute activity coefficients (which express the

deviation from ideal solution behavior). Because of this, it predicts very well the salting-out effect, the sharp decrease in solubility of non-polar gases with increased electrolyte concentration, and can be used to calculate heats of solution, entropies, and partial molal volumes of dissolved gases.

The theoretical approach is based on the scaled particle theory, in contrast to various electrostatic theories previously used to explain observed properties of electrolyte solutions. The latter theories are at best only applicable in very dilute solutions, and cannot be used at electrolyte concentrations of interest in fuel cell and battery applications. In the case of salting-out of gases, these theories do not explain the observed behavior even in dilute solutions.

At the present stage of development, various statistical mechanical theories (based on the radial distribution function) have difficulty in explaining the properties of even simple fluids such as liquid argon, and such a treatment for electrolytes is extremely difficult. There does exist, however, a satisfactory approach for hypothetical mixtures in which the molecules behave as hard spheres. The gas solubility problem in concentrated electrolytes was treated by extending a theory of this type (the so-called scaled particle theory). This approach has the advantage that the expression for solute chemical potential is derived from the equations of statistical mechanics by a series of well defined approximations. It provides very good agreement with experiment for the solubility of seven non-polar gases in KOH solutions, and was at least an order of magnitude better than any existing electrostatic theory. This is illustrated for oxygen in the figure. The experimental data are reported as the activity coefficient γ_1 , an inverse function of solubility. $\ln \gamma_1 K_1^0$ is plotted against

(continued overleaf)

weight percent KOH, where K_1° is the Henry constant for the gas in pure water. A comparison of the experimental results with the predictions of two electrostatic theories and the scaled particle theory is shown. The latter is obviously superior in its ability to reproduce the effect of KOH concentrations on the activity coefficient for oxygen in the solution. This corresponds to a decrease in solubility with increasing concentration.

The new theory works well at high electrolyte concentrations, and the parameters necessary for its use are readily available.

Notes:

1. It may be possible to extend the theory to explain the effects of vapor pressure. At present, no suitable theory exists for this important property.
2. The theory is useful in electrolytic, ecologic, oceanographic, and fuel cell studies. It will enable one to predict with confidence solubility data in electrolytes which are at high temperatures (above 100°C), high pressures, and high concentrations.

3. A more detailed description is available: S. K. Shoor and K. E. Gubbins, "Solubility of Non-Polar Gases in Concentrated Electrolyte Solutions," J. Phy. Chem., Vol. 73, March 1969, No. 3, pg. 498-505.

4. No additional documentation is available. Specific questions, however, may be directed to:

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Patent status:

No patent action is contemplated by NASA.

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