

COMPARISON OF EXPERIMENTAL K_H AND ΔH VALUES WITH THOSE PREDICTED BY BLANDER'S THEORY

Blander² has used a theory originally proposed by Uhlig³⁶ to estimate the solubilities and heats of solution of inert gases in fluoride melts. The dissolution process is considered in three stages: (i) the gas is expanded from concentration C_g to concentration C_d . The free energy change is $\Delta G_1 = RT \ln (C_d/C_g)$. (ii) The gas molecules are contracted to points and mixed with the liquid. The free energy change is ΔG_2 . (iii) The gas molecules are expanded to their proper size. The work required to create the cavities in the melt to accommodate the molecules is $\Delta G_3 = 4\pi r^2 N \gamma$, where r is the radius of the gas molecule and γ is the surface tension of the melt, here considered as a continuum.

Since the gas is in equilibrium with the liquid, the sum of these free energy changes is zero. If no chemical interaction occurs between the gas molecules and the ions in the melt, ΔG_2 may be neglected and

$$RT \ln (C_d/C_g) = -4\pi r^2 N \gamma. \quad (4)$$

Eqn (4) may be used to calculate the solubility of the gas at different temperatures, using experimental values of the surface tension. The heat of solution can be calculated from the temperature dependence of the solubility. This has been done for the systems studied here, and the results are included in table 1. The radii used in the calculations were^{2, 11} (in units of 10^{-10} m): He, 1.22; Ar, 1.92; N₂, 2.00. This simple model predicts the solubilities to within an order of magnitude, and gives the heats of solution to within a factor of 2. The agreement is about as good as that obtained by Blander *et al.*,² and confirms the general validity of the model for inert gas solutions. The observed trends in our results are correctly predicted, i.e., (i) for a given gas and melt, the solubility increases with temperature. (ii) For a given melt and temperature, the solubilities of a series of gases follow the inverse sequence of the molecular diameters. (iii) For a given gas dissolving in a series of melts, the solubilities increase with decreasing surface tension. This is exemplified by the series Ar+AgNO₃, Ar+NaNO₃, Ar+LiNO₃, Ar+RbNO₃ (see table 1).

A feature of the results is that $K_H(\text{expt.})/K_H(\text{calc.})$ is about 0.1 for He+NaNO₃ and for He+LiNO₃. Blander² obtained a similarly low value for this ratio for He+NaF/ZrF₄. As he suggests, this may reflect thermal motion of the gas atom in its cavity, so that the cavity radius is larger than the radius of the gas atom deduced from gas phase studies.

The broad agreement between theory and experiment increases the confidence with which the theory may be used to estimate gas solubilities in systems which have not been studied experimentally. Conversely, if experimental results differ greatly from the predicted values (e.g., if the solubility is more than a decade higher than predicted, or if ΔH is negative), this may be taken as an indication that the free energy term ΔG_2 is not negligible.

STANDARD ENTROPIES OF SOLUTION

Entropies of solution have been calculated from the experimental results for those systems which have been studied over a temperature range, and are listed in table 1. ΔS° is negative, and takes values between -8 and $-24 \text{ J K}^{-1} \text{ mol}^{-1}$. These are more negative than the corresponding entropy changes for inert gases dissolving in NaF/ZrF₄¹ ($\Delta S^\circ = 0$ to $-6 \text{ J K}^{-1} \text{ mol}^{-1}$), for CO₂ in alkali halide melts⁵ ($\Delta S^\circ = -2.5$ to $-5 \text{ J K}^{-1} \text{ mol}^{-1}$), or for inert gases in benzene ($\Delta S^\circ = -4$ to $-7 \text{ J K}^{-1} \text{ mol}^{-1}$),

but less negative than for inert gases in water ³⁸ ($\Delta S^\circ = -54 \text{ J K}^{-1} \text{ mol}^{-1}$ for He, and $-82 \text{ J K}^{-1} \text{ mol}^{-1}$ for argon, at 25°C). The large, negative values for aqueous solutions are generally attributed to structuring of the water surrounding the gas molecule, to give an ice-like cage. For nitrate melts, the fact that ΔS° is more negative than it is for halide solvents may possibly be due to some restriction of the rotational movement of the nitrate ions near the gas molecules.

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