three contributions to the isothermal reversible work, W_c, required to transfer a gas molecule to the interior of a liquid phase

$$W_c = Y_1 + Y_2 + Y_3 \qquad (17)$$

Y_1 is the molecular cavity creation work which may be roughly approximated as

$$Y_1 \simeq 4\pi\gamma r^2 + 4\pi P r^3/3 \qquad (18)$$

(where r is the radius of the created hole) if the microscopic surface tension, γ, can be considered curvature independent. Y_2 is a complicated term for the energy of interaction, involving pair correlation functions acting in the molten salt between solute molecules and ions, and neglecting polarization forces. It is predominantly exothermic. The term Y_3 is the exothermic polarization energy involving the solute molecule of polarizability α and the mean-square electric field, $\langle E^2 \rangle$, it experiences.

$$Y_3 = -(^1/_2)\,\alpha\langle E^2 \rangle \qquad (19)$$

Blander, Grimes, Smith, and Watson[9] ignored the exothermic Y_2 and Y_3 terms in comparison to the large Y_1 work necessary to accommodate a gas molecule against the high surface tensions of their fluoride melts. They also neglected the second term in Y_1, since the pressures, P, that they used were small, and they tacitly assumed γ to be curvature independent, as well as to be approximately the same as the macroscopic surface tension. Thus, eq 5 was conceived.

In the present work with Ar, it is apparent that the Y_2 and Y_3 exoenergetic terms are not insignificant in comparison to Y_1, as was found also in the N_2 solubility work.[2] Thus, choosing as an example from Table II a pressure of 395 atm and a temperature of 714°K, the Y_1 term results as approximately 7.65 kcal mol^{-1}. From the observed heat of solution of Ar of -1.84 kcal mol^{-1}, we conclude that the $Y_2 + Y_3$ exothermic sum

should exceed Y_1 in magnitude by about 1.84 kcal mol^{-1}. Of the Y_2 and Y_3 terms, it is apparent from eq 19 that the Y_3 polarization energy should be larger the greater the α of a solute molecule in the given solvent presenting a fixed $\langle E^2 \rangle$. Thus, at least Y_3 correlates with the observed greater exothermic heat of solution for the more polarizable N_2 molecule in fused $NaNO_3$ than for the less polarizable Ar molecule in the same solvent. Again, the endothermic Y_1 term should be nearly the same for both molecules in this system. At this point, it is still impossible to draw any quantitative conclusions as to the relative contributions of the extremely complex Y_2 interaction term applied to these two solutes.

As in the N_2 work, the $\Delta S_c°$ value for solution of -4.97 eu for Ar indicates an unusual environment and set of interactions for the Ar molecule in $NaNO_3$. This is not quite so pronounced as the -6.78 eu for N_2 in the system. However, as mentioned earlier,[2] rotational degrees of freedom exist for N_2, and these may be affected in solution, whereas such cannot be the case for atomic Ar. While the value -4.97 eu for Ar is certainly unusually large in magnitude for such a gas, it is not without precedent, since Watson, Evans, Grimes, and Smith[13] did observe an unusual standard solution entropy of -4.2 eu for both Ar and Ne in a 64–36 mol % LiF–BeF_2 molten solvent. Helium and Xe in the same solvent gave rise to values of -3.4 and -3.1 eu, respectively.