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Interpretation of fusion and vaporisation entropies for various classes of substances, with a focus on salts

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ABSTRACT

Entropies of fusion and vaporisation of a variety of elements and compounds have been derived from literature data. Fusion entropies range from low values for metals and certain cyclic hydrocarbons (*e.g.,* cyclopentane) through modest values for salts to high values for materials undergoing drastic rearrangement or disentanglement such as aluminium chloride and *n*-alkanes. Entropies of vaporisation for most substances are close to the Trouton's Law value of $\sim 100\,\mathrm{J \cdot deg.^{-1} \cdot mol^{-1}}$, with low values for species which associate on boiling (*e.g.,* acetic acid) and higher values signifying simple dissociation (*e.g.,* nitrogen tetroxide) or total decomposition (*e.g.,* some ionic liquids). The nature of inorganic and semi-organic salts in all 3 phases is discussed.

1. Introduction

Thermodynamic data, available for many varieties of substances, often focus on *enthalpic effects* for the chemical event of interest. This quantity is usually considered superior in characterisation of changes to the chemical potential, for bond making and breaking transformations, or, for transfer of materials across their available phase boundaries. *Entropic effects*, all but completely overlooked, except for high temperature reactions [1], are comparatively more apt in the unmasking of structural and bonding characteristics that accompany changes of the chemical potential (*i.e.,* the Gibbs energy, at constant pressure and temperature) for thermodynamic recordings of phase transition events of pure materials.

Structures of solids are generally available from X-ray analysis and the nature of gases can be determined using various techniques ranging from vapour densities to varieties of mass spectrometry. The liquid state, however, poses more problems; structural units may be identified spectroscopically, but overall arrangements can be difficult to define. Of particular interest are liquid salt ensembles, ranging from high-temperature systems, in which, for example, first co-ordination spheres can be indicated by X-ray spectra and co-ordination tendencies suggested by the electronic spectra of dissolved transition metal ions, to the organic salts, popularised as *ionic liquids*, with some amenable to investigation by NMR spectroscopy and many of the techniques well-used in the study of aqueous solutions.

The following report is presented with a focus on the relationship of structure and bonding with the outcome of a given phase transition, in terms of the entropy accompanying each event. We find that entropies of fusion are naturally less than those of vaporisation, and fall into groups characterised by substance type while entropy of vaporisation values cluster quite closely around the Trouton's Law value of $\sim 100\,\mathrm{J \cdot deg.^{-1} \cdot mol^{-1}}$.

1.1. Classification of materials

A deliberate classification of liquids into types *via* critical constants was offered in 1957 by Moelwyn-Hughes, *viz.* metallic, non-polar and polar [2]. Liquid salts were not discussed, but rather thought of as ionic solutions. Conductivity can act as a distinguishing factor ranging from electronic for metals to ionic for salts and solutions in certain polar solvents, although there may be overlap in values found for the latter two groups. Furthermore, the obvious relation expected (*i.e.,* Walden's viscosity rule) between diffusion of charge and diffusion of matter is not always straightforward, as noted for several liquid organic salts [3].

It may be informative to study liquids *via* their formation from solids and change to gases, noting the much greater free volume available in the vapour. Thus we have collected the phase change enthalpies of a wide variety of elements and compounds for evaluation [4]. We attempt an interpretation of the data in terms of the feasible structures and bonding in the different phases.

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2. Results

2.1. Entropies of fusion

Entropies of fusion ($S_{\text{fus.}}$) that record disordering accompanying the solid-liquid phase transition, have garnered less attention in general, although, some grouping has been noted [2]. Loss of defined bulk structure on melting is obvious but it may or may not be accompanied by a change from libration to free rotation [5]; interesting comparisons between the chlorine and hydrogen molecules and cyclohexane and methyl-cyclohexane molecules were made [5]. In discussing the relative simplicity of molten salts, Førland noted the small values of fusion entropies for the alkali halides [6]. Table 1 contains values for a wide range of substances, together with indications of solid structures and liquid electrical conductivity levels. They are conveniently grouped by type rather than by value.

2.2. Entropies of vaporisation: Trouton's Rule

First noted in 1876 [33], the nearly constant value of $\sim$100 J · deg.$^{-1}$ · mol^{-1} (*i.e.*, $\sim 12R$) for the entropy of vaporisation ($S_{\text{vap.}}$) of many liquids became known as Trouton's Rule or Law [34]. $S_{\text{vap.}}$ can be derived simply from the van der Waals equation of state [34] or from the theory of classical oscillators, where a linear relationship to $\ln(T_c/V_c)$ (subscript c denotes the critical constants) is inferred by Eq. (1) below, in accord with the corresponding proportionalities of T_b and $V_{\text{sup.}}$ with T_c, and V_c, respectively [2]:

$$S_{\text{vap.}}/R = -2.093 + \ln\left[T_b/V_{\text{sup.}}(m \cdot n \cdot S_{\text{sup.}}/R)^{3/2}\right] \tag{1}$$

where m and n are Mie's integers [35], T_b is the liquid boiling temperature, $S_{\text{sup.}}$ is the entropy of vaporisation of the liquid supercooled to 0 K, and $V_{\text{sup.}}$ is the accompanying volume. The ratio of critical constants, T_c/V_c, is appropriate for various reasons, but most importantly, it serves to ensure that substances of interest are in a common corresponding state of existence, devoid of relative, incrementally imposed, thermodynamic state changes that could result from liquid-vapour co-existence at temperatures below the critical temperature.

It was noted early that Trouton's Law does not hold for liquids which associate in the vapour, such as acetic acid [2]. We present vaporisation entropies of a wide range of liquids in table 2 below. Liquid polarities, as characterised by respective static relative dielectric permittivities, have been included, but apparently play no obvious role in the magnitudes of $S_{\text{vap.}}$ observed, regardless of the molecular or ionic nature of the substance.

3. Discussion

3.1. Fusion

Entropies of fusion span a wide range although classification by molecular type is possible, with geometry, symmetry, and molecular volume providing a large and guiding contribution to the magnitude of the values observed. Additional short and long range interactions, affected by induced polarisations, resultant from through space charge separation brought to bear by ions, endow salts with a somewhat more complex nature.

Values for organic materials tend to increase proportionally with V_m (molecular volume) except for cyclopentane and cyclohexane. Large differences are also observed between cyclohexane and methyl-cyclohexane, more so than one might expect based on variation of V_m alone. This is due to structural effects where the latter is entangled in the solid, just like *n*-hexane, and is free to rotate in the liquid (with accompanying "pseudo-rotational" contributions dictated by varieties of internal ring conformations) while the more symmetric cyclic is just free to translate on melting, like metals [53].

Simple salts, particularly the alkali and alkaline earth halides, merely change from fixed to relaxed ionic lattices with addition of significant electrical conductivity (crystals conduct only *via* defects); their fusion entropies are in the 20–30 J · deg.$^{-1}$ · mol^{-1} range. Their entropies do not distinguish between single and multi-step ionisation of MX_n type systems. In comparison, values for pure metals, with identical particles, are relatively lower because only their atoms need be set in motion, as distinct from salts, with oppositely charged ions. Fusion entropies recorded for the family of *N,N*-dialkylimidazolium based C_n-sulfonate *low melting temperature* liquid salts ($n = 1 - 4$), and for the family of *high melting temperature* Group I metal bis{(trifluoromethane)sulfonyl}imide liquid salts, fall within range of other *high melting temperature* liquid salts, such as $BiCl_3$. Considering the magnitude of the volume differences, it could be said that the much smaller bismuth salt would yield drastically reduced relative entropy values, in the absence of its superior ionicity.

Further complexity may arise for salts comprised of ions of molecular proportions where various intermediate phases between the solid and the liquid, at temperatures far below that of fusion, become apparent. *n*-Alkyl ammonium chlorides exhibit rotator phases prior to melting for $n \geqslant 2$, characterised by $S_{\text{fus.}}$ - $\leqslant$ 20 J · deg.$^{-1}$ · mol^{-1}. These phases are similar in nature to plastic crystals but exhibit relatively dimensionally restricted motion; cations in the plastics give rise to both translations, and rotations, in 3*D*, while those of the rotators are restricted to 1*D* and 2*D*, rotations and translations, respectively [54]. In the case of $n = 2$, the rotator phase is destroyed upon replacement of Cl^- with planar asymmetric $[NO_3]^-$, where increases in thermal energy are taken up as structure breaking motion with a relative lowering of the fusion temperature resulting as a function of hydrogen bond disruption [55]. Different lines of approach to the fusion event therefore also contribute to the recorded entropic outcome, beyond what is dictated by the various complexities of crystal structures at hand.

In the liquid state of salts, the presence of even small fractions of "ion-pairs", characterised by large dipole moments ($\geqslant$ 18–20 D) in the dielectric relaxation spectroscopy (DRS) experiment, would serve to minimise liquid state entropies already at the onset of melting, considering the magnitude of molarities available with the pure liquids are typically on the order of [4–30] M. In any case, it is unlikely these configurations contribute to any large extent to the liquid landscape, in terms of their entropics, since such species have not yet been observed within the time frame of the DRS experiment (*i.e.*, to an upper limit of picoseconds) for varieties of liquid salts [56]. While the lack of ion-pairing inconveniently contravenes notions of "missing" ion-transport, put forth by highly idealised models (*e.g.*, Walden's viscosity rule), their absence provides a satisfactory basis to rationalise the extremely low saturated vapour pressures many liquid salts are known for.

3.2. Vaporisation

A $S_{\text{vap.}}$ of $\sim$100 J · deg.$^{-1}$ · mol^{-1} appears to signify the disorder concomitant with increased degrees of freedom as molecules escape the liquid and form the gas. Molecular polymerisation, to any extent, imparts order to the gas, thus reducing entropy changes, whereas decomposition of molecules present in the liquid increases disorder, and thus the entropy. The extent of decomposition can be estimated from the value of the entropy change: numbers in the hundreds of J · deg.$^{-1}$ · mol^{-1} suggest total rearrangements or decomposition rather than simple dissociations.