Boiling of the Chemical Elements

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Abstract

The molar boiling entropy, ΔS_{boil}**,** has been assumed in the literature to be approximately the same for one-component systems, which is known as the rule of Pictet-Trouton. Using experimental data on $\Delta S_{boil}$of the chemical elements, however, this rule must be questioned. Instead, the increase of the molar entropy upon boiling is estimated from the expansion of the melt to the volume of the vapour under atmospheric pressure. This yields the right order of magnitude for ΔS_{boil}.

The molar boiling entropy depends on the number of electrons in the outermost electron shell of the free atoms of the chemical elements. Thus, the electronic system stores some entropy needed for boiling and seems to cause the phase transition liquid/vapour. This is supported by the correlation between the electron configuration and the molar specific heat capacities in the liquid and the vapour state near the boiling temperature. Accordingly, boiling is induced by electronic transitions into anti-bonding states at a rate sufficient to increase the partial pressure of the vapour within a melt. This is in contrast to the traditional explanation of boiling by breaking pair bonds between the atomic constituents of a melt which neglects the effect of transitions of the bonding electrons.