

ON THE ENTROPY OF MELTING OF ELEMENTS AND SOME
SIMPLE COMPOUNDS

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The correlations of the enthalpy of melting ΔH_m with the melting temperature T_m at normal pressure for the elements and some simple compounds are considered. The well known constant entropy of melting S_m for metals, which is defined as $S_m = \Delta H_m / T_m$, is around 2 e.u. and the straight line in $\Delta H_m - T_m$ diagram passes through the origin. The halogen elements and nonmetals with semiconductor elements are described by two approximately parallel lines, which do not pass through the origin (Fig.1). This suggests that the entropy of melting could be described by two terms in the following way:

$$S_m = S_{eq} + S_{corr}$$

where S_{eq} is a constant called here as equivalent entropy of melting, and S_{corr} is a correction term defined by $S_{corr} = \Delta H_0 / T_m$. ΔH_0 is the energy obtained by the intercept of extrapolated experimental line with ΔH_m axis. For halogens $\Delta H_0 = -0.2$ kcal mol⁻¹ and $S_{eq} = 10.1$ e.u., but for nonmetals $\Delta H_0 = -2.4$ kcal mol⁻¹ and $S_{eq} = 9.1$ e.u. (Note: for substances with solid-solid transitions with entropy S_c , final $S_{eq} = S_m - S_{corr} + S_c$). Simple ionic crystals of alkali halide type and molecular crystals show similar behaviour (Fig.2), for which S_{eq} is equal to 9.0 and 11.3 e.u. and corresponding ΔH_0 are -3.0 and -0.5 kcal mol⁻¹, respectively.

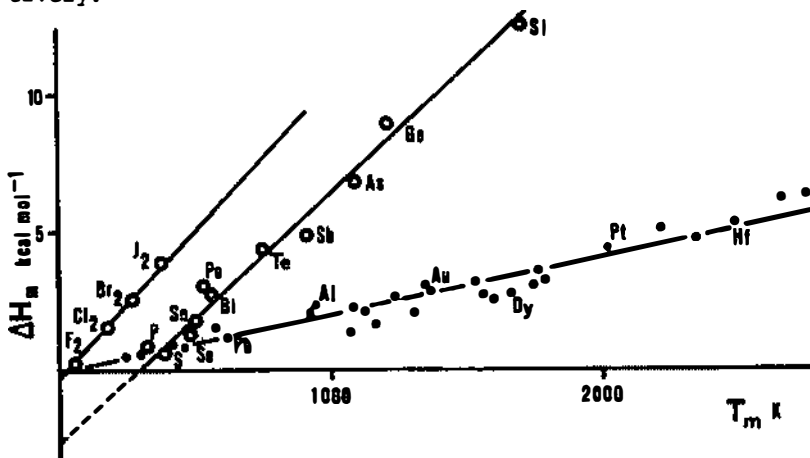


Fig.1 Correlation of enthalpy of melting ΔH_m with temperature of melting T_m , for elements

Some other ionic compounds as MX_2 type, (M=metal, X=halogen) and alkali nitrates, sulphates and also simple organic compounds show similar behaviour. For the chain molecules as normal parafins, in the calculations of S_{eg} , the conformational entropy has to be taken into account. This has a consequence of positive ΔH_0 .

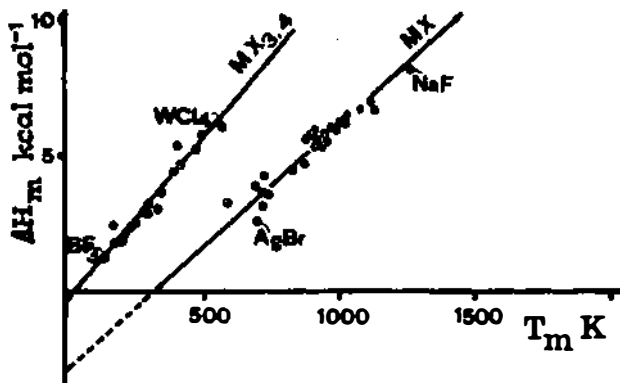


Fig.2 Correlation of enthalpy of melting ΔH_m with the temperature of melting T_m , for some molecular and ionic compounds

S_{eg} has a physical meaning of the maximal entropy of simple positional and orientational disorder of molecules in transition from solid to liquid state and S_{corr} includes the change of the geometry of molecules during the melting. For van der Waals substances S_{corr} is small, because the molecules are very little changed at melting, but for ionic substances S_{corr} is much larger, because the interionic distances cation-anion are considerably changed going from the solid to the liquid. For the chain molecules, S_{corr} is still larger and positive as a consequence of the conformational changes at melting.

In conclusion, we may generalize the Richards' rule, which states that the entropy of metals is a constant. This generalization is: for monoatomic substances the entropy of melting is around 2 e.u. and for polyatomic substances the equivalent entropy of melting is around 12 e.u. (Deviations of this rule cannot be treated here). It follows that the simple substances with different chemical binding between molecules and various shapes of molecules have the same equivalent entropy of transition from solid to liquid state.

Note: the experimental data are taken from American Institute of Physics Handbook, McGraw-Hill, New York, 1972.