Heat Capacities of Liquids: The Quest for a Molecular-Based Description

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Thermodynamics provides a mathematical framework of equations (and a few inequalities) yielding exact interrelations between thermodynamic equilibrium properties of bulk phases. This aspect itself is of the highest value for the practising physicisist, chemist or chemical engineer. Moreover, in conjunction with statistical-mechanical theory, chemical thermodynamics contributes substantially towards a better understanding of molecular interaction and thus leads to improved molecular-based descriptions of macroscopic systems [1].

Undoubtedly, heat capacities are one of the most important thermophysical quantities not only from a practical point of view, but also from a theoretical one. For instance, the molar heat capacity C_V at constant volume contains information of the *type of motion* executed by the molecules. Thus, in this lecture I will focus on

(1) Experimental determination of C_V of pure liquids;

(2) Prediction of C_V from fairly simple equations of state;

(3) Resolution of C_V into contributions depending on the motion of the center of gravity of the molecule, into contributions from internal vibrations, and into contributions due to molecular overall rotation. Using the residual property formalism, the (hindered) rotational behavior of "rigid" molecules in the dense liquid phase may be described quantitatively [2,3].

References

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