Kirchhoff's Law of Thermochemistry: new century – new challenge

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Kirchhoff showed in 1858 that the variation of the heat of a chemical reaction is given by equation $d\Delta H / dT = \Delta C_p$. The same equation is also applied for the temperature adjustment of the phase transitions liquid-gas, solid-gas, and solid-liquid. Thus, a heat effect at any temperature of request can be obtained by using the Kirchhoff´s Law, provided that heat capacity values C_p are available. Nowadays the DSC is broadly used for reliable measurements of heat capacity values for liquids and solids. Experimental measurements of the gas phase heat capacities is a challenging task and it is possible only for small volatile molecules by using, e.g. flow calorimetry. Fortunately, the recent developments of the quantum-chemical methods render the assessment of $C_p(g)$ possible. Thus, it seems to be that all prerequisites for successful application of Kirchhoff´s Law for practical and theoretical questions are fullfield. However this optimism is deceivable. Indeed, appearance of neoteric non-volatile materials like ionic liquids, deep eutectic solvents, fullerenes, nanotubes, etc. require experimental studies of their properties at elevated temperatures significantly different from ambient conditions. Thermal stability of new materials is one of the important features for their practical application. The latter feature is directly connected to the measurable vapor pressure referred to the temperature range of application. To date, there are only a few experimental studies of vapour pressures and vaporization enthalpies of extremely low-volatile compounds, and rapid progress to address this paucity of data is hardly to be expected, due to the time-consuming nature of these experiments. Last decade we have deliberately developed in our lab a set of complementary techniques for reliable determination of volatility and vaporization/sublimation enthalpies of extremely low-volatile compounds. They are: quartz-crystal microbalance, static method, thermogravimetry and transpiration method. Using combination of all available techniques we are able to localise the optimal experimental conditions where measurements are performed still without possible thermal decomposition. As a rule, the average experimental temperatures T_{av} of our studies are of 100-250 K above the common reference 298 K. In order to adjust vaporization enthalpies from T_{av} to 298 K, the Kirchhoff´s Law have to be applied. However, there are a number of issues which aggravate this application. First of all, according to the textbook the Kirchhoff Law can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. The second issue is that the $C_p(g)$-values for such materials are not measurable at all. In addition, the quantum-chemical methods suitable for calculations of $C_p(g)$ of conventional molecules failed to predict reasonable value due to the large size and the complexity of the conformational composition. We have been able to overcome these complications and we have developed few empirical, half-empirical or theoretical procedures to estimate ΔC_p–values based either on the experimental measurements or based on the volumetric properties. Using ΔC_p–values estimated from these procedures, the experimental vaporization/sublimation enthalpies have been adjusted to the reference temperature. Thus, new procedures to assess ΔC_p–values open a broad window for application of the Kirchhoff´s Law of Thermochemistry to studies of extremely low-volatile neoteric materials.