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CONSEQUENCES OF SOLVATION PHENOMENA ON THERMAL MEASUREMENTS AND CHEMICAL SAFETY

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While chemical reactions go on, the reacting species as well as the formed products interact with each other, each present species playing more or less the role of a solvent for the other ones. Following their respective properties, the corresponding developed solvation effects can be very different.

While the reaction goes on, some species are formed, and their solvation energies resulting from their interactions with other species present in the reacting mixture become free. Other species which are consumed must be extracted from the solvates they have already formed, and this desolvation process requires some energy.

As far as solvation and desolvation processes are of the same order of magnitude, their effects nearly compensate each other, so that the global enthalpy of solvation is often small.

Sometimes however, it may occur that the solvation of the consumed species is quite different from the solvation of the formed ones. Thus, the balance between solvation and desolvation no longer can be zero. The total enthalpy of the reaction going on is then the sum of both the enthalpy of the reaction itself and the enthalpy of solvation.

However, the enthalpy of the reaction itself just depend on the amount of transformed matter, independently on the stoichiometric conditions. To the opposite, since solvation effects are concentration dependent, their effects will vary within a large range as a function of the reaction rate and the stoichiometric conditions. Addition of an inert solvent can drastically modify this contribution.

Under such conditions, the apparent heat of the reaction of A with an excess of B may become quite different from the heat of B reacting with an excess of A. If the solvating reagent is not present in excess, the solvation phenomena are hindered. The higher the excess, the more complete the solvation.

Thus, the apparent enthalpy measurements for a reaction includes the contribution of the associated solvation processes. These are dependent on the stoichiometric conditions used for the reaction. Since they can be as important as the enthalpies of the main reaction itself, just measuring the heat evolved by a reaction without any consideration concerning the variations induced by modifications of the stoichiometric ratio of the reagents can result in completely wrong values assumed to characterise the reaction enthalpy.

Moreover, when the solvating species is added progressively to a semi-batch reactor, since it will never reach excess conditions, will not release the corresponding heat of solvation. Locally, however, at the introduction point of the reagent, the contact with the soon reacted mixture will result in temporary, local dilution effects. This will result in local release of the heat of solvation, enabling hot spots formation. Thermally unstable reaction mixtures can so be brought up to runaway situations arising from locally induced thermal decomposition as a consequence of the release of the accumulated potential heat of solvation in the reactor. Such a behaviour is described on hand of an organo metallic reaction.