# THERMAL ENERGY AND CHEMISTRY: FROM HUMAN EXPERIENCE TO FUTURE APPLICATIONS OVER 40 YEARS TEACHING.

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In early times, the reaction enthalpy of oxygen with organic molecules of vegetal origins has been an extremely important source of energy for mankind, allowing the primitive nearly hairless human body to withstand over centuries to sometimes extremely hard, wet and cold environmental conditions. But far beyond this daily experience of heat as an essential condition for survival, fire and heat excited continuously the curiosity of mankind since the most ancient times of prehistory: although heat could easily be felt by the skin, fire remained a mysterious phenomenon, something immaterial like a link between God and Mankind. But it required an extremely long period of time for mankind to discover by the end of the 18$^{th}$ century, the power of heat and the use of steam in thermal engines. Time went on and research activities developed more and more scientific knowledge from calorimetric devices the accuracy of which could be continuously improved by the development of new manufacturing technologies. By the end of the 20$^{th}$ century, more and more sensitive and accurate thermo-analytical devices became commercially available letting thermal analyses and calorimetry become nearly routine techniques for material identification and characterization, quantitative determinations and more recently safety assessment applications.

But although the available techniques had been drastically improved, the fundamental nature of heat still kept hidden its own part of mystery. In the field of thermal measurements, the only measurable magnitude is the temperature, which is a potential. All other thermal measurements are derived from local temperature measurements. No *direct* entropy-meter neither heat nor heat-flow-meter do exist. All other thermal measurements than temperature require reliable supplementary information concerning device or sample related data and properties (such as thermal conductivity, the mass, the number of moles, the volume etc …). However, by the end of the twentieth century, calorimetric measurements had reached an extremely high level of quality due to the simultaneous progress in manufacturing technology, in signal detection and in signal processing. So far the question ***how*** heat interacts with matter had been rather satisfactorily answered. However some fundamental questions about ***why*** it is so are still open.

To answer such questions requires a much broader scientific culture than just a thermal one. Heat is an energy the amount of which can be expressed in Joules exactly like all other forms of energy. This observation leads to a main conclusion which could be expressed as follows: heat, motion, electricity, chemical energy, gravity, light and matter are all made of a unique substance. The exact nature of the substance giving all forms of energy an additive character is not yet clearly defined, but goes on being studied in order to solve some extremely practical problems concerning as well technical than societal aspects. Such kind of questions require often just a clear re-formulation of the question to be solved in order to open the way to new answers and better understanding of aspects which remained previously hidden by lack of semantics.

In the early $70^{th}$ of the last century, some chemical accidents lead to the development of chemical safety research, which has been initially more especially induced and promoted by the Swiss chemical industry. Although many teams all around the world struggled hard to fight against all sources of runaway situations, some accidents went on occurring. Some of them were extremely difficult to clear and required nearly 10 years to be completely understood [1].

On hand of some examples like unexpected segregation phenomena in metallic phases, or the limited reaction conversion of alcohols with alkali metals, the question of the true nature of chemical bonds rose in some chemists' minds [2]. On the other hand, entropy reducing phenomena can *release* important amounts of heat although no actual heat *production* takes place during such a transformation. Such an entropy driven transformation leads to an exothermic behaviour which is characterized by an increasing temperature under adiabatic conditions *although no heat* is actually *produced* thereby. To the opposite, during many chemical reactions, heat can be stored by a simultaneous entropy increasing process which is characterized by an endothermic contribution to the total thermicity of the ongoing reaction. Generally, as a consequence of the endothermic contribution, such a phenomenon does not draw the attention of the chemists to its hidden dangerous character. However, it can become potentially *extremely* dangerous because it stores more energy in a constant amount of chemical matter, the stability of which it decreases by increasing its *total* potential. Solvent evaporation from alkali alcoxide solutions or other organo-metallic compounds can result therefore in extremely explosive end-products. Further, some minor impurities can induce huge entropic effects on reaction enthalpies: for instance, increasing by more than 250 kJ/mol exothermic reaction enthalpies can be observed by the introduction of less than 0,1% water (by weight) into dry organic reagents intended to yield alcoxides from metals.

Moreover, safety investigations in dangerous systems led often to take into account much more than just three main system steering variables. But in more than tree dimensional systems, the orientability is lost. That means that two contradictory answers to a unique question can be simultaneously right. Such aspects are extremely important to discuss for safety teams when fast decision taking is required. Therefore, despite all progress made in thermal studies since the early times of mankind until nowadays, many fields remain still open for further investigation and will provide scientists huge fields of interest for the future. Some possible alternative descriptions of chemical bonds and atoms will also be presented here in order to give a small insight into what to-morrow thermal research could look like and which kind of a new paradigm could provide new ways for understanding the origins of the chaotic behaviour of some complex unstable systems.

[1] WALTER S., HADJ MEBAREK A., COGNEVILLE C : Etude des causes de l'accident survenu au CEA-Cadarache en avril 1994 (2001), document confidentiel de 170 pages.

[2] WALTER S., Contribution à l'étude d'alliages binaires entre sodium et traces d'autre métal alcalin. Elaboration d'un nouveau procédé de purification. Compléments sur la réaction métal alcalin-alcool. Thèse d'Etat, U.H.A. n° 06811664, Mulhouse (19/12/1987)