ENERGY BALANCE OF REACTING SYSTEMS

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Summary

This section considers the energy balance in reacting systems. This equation—valid for any system—is written here with reference to systems that are open to the exchange of heat, mass, and work with their ambient environments. If the equation is written with reference to a closed system operating in steady state conditions, it degenerates into the standard formulation of the first law of thermodynamics.

The energy balance is employed in the study of reacting systems, paying attention to all calorimetric aspects. The state function enthalpy is introduced, and the fundamental laws of thermochemistry are also derived. Finally, the implications with regard to mass conservation are presented.

1. Introduction

This section concerns the conservation of energy in reacting systems. The conservation of energy is governed by one of the fundamental laws of our world. This, like all the other fundamental laws of science, cannot be derived using other laws or rules or by any other means known today; otherwise it would not be termed "fundamental." Furthermore, these fundamental laws are valid under all circumstances, and no

exceptions have been found to any of them. They apply to small and large, microscopic and macroscopic systems, and for any time interval, short or long.

Since they cannot be derived, conservation equations can only be written down. Here, the rules for writing them correctly will be reported on with particular reference to the conservation of energy, but these rules also apply to the conservation of other properties of matter, such as mass and charge.

As a first statement, it is important to remark that, because here only chemical reacting systems are considered, neither relativistic effects nor nuclear transformations are present. Thus, energy is a property of the matter well distinguished by mass.

Energy as a physical quantity is somewhat difficult to define. In thermodynamics textbooks worldwide, it is hard to find the statement "definition of energy"! Reading these volumes, it can be found that energy is related to a system's potential for exchanging heat and work with its surroundings (the definition of energy in a pure mechanical framework, at least), and furthermore, that it cannot be defined in terms of absolute value. Only variation in the energy level can be calculated, by the measurement of the state functions defining the physical status of the system and its surroundings. The conservation law applies rigorously only to the total energy of a system. In the cases examined here this is the sum of the three different forms: *internal*, *potential*, and *kinetic*. The first of these is related to the motion of the atoms and molecules constituting the system, the second is related to its position in space, and the third to its velocity. Each of these terms is also directly proportional to the system mass.

If the process occurring in the system does not involve any change in its volume, the transformation from the initial state to the final one leads to a change in the system temperature. In this case, the energy change is due to the flow of heat through the system boundaries. Alternatively, if the transformation occurs in a system where the exchange of heat across boundaries is inhibited, the system temperature change is then coupled to an alteration in its volume: therefore the energy change is due to the exchange of mechanical work with its surroundings. Generally, both exchanges (of heat and work) occur between the system and its surroundings, but special apparatus can be constructed to prevent one, or both, of these. The energy content of a system can be also modified by the exchange of mass with the external ambient environment, and thus the contributions of all the mass fluxes (for example, convective and diffusive) must be introduced into the energy balance equation.

In reacting systems, the energy balance is particularly useful when calculating the amount of work or heat that can be obtained (in an algebraic sense) from a chemical reaction. Examples of this include the mechanical work obtained in a internal combustion engine, the electrical work furnished by a reaction in a electrochemical pile or fuel cell, and more generally, the amount of heat released by a combustion reaction or needed to perform an endothermic reaction. Finally, the interchange of heat and work stated by the first two *principles of thermodynamics* allows the system's energy change during the transformation considered to be obtained in the form of either work or heat, depending on the apparatus (in other words, the system) employed. Examples of these systems are illustrated in Figure 1.
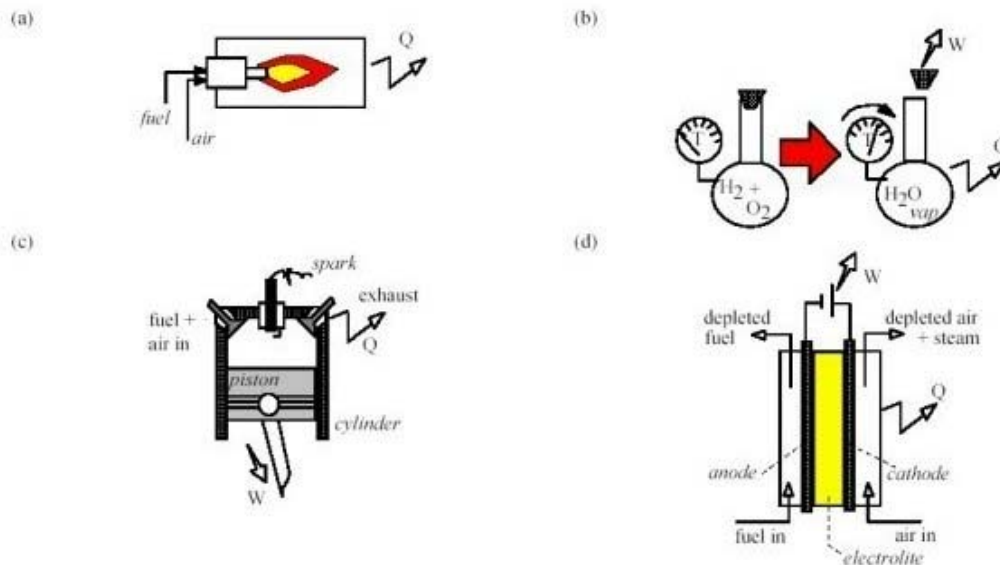
Figure 1. Examples of reacting systems exchanging heat and work with the external surroundings: (a) industrial burner involving exchange of heat; (b) chemical reaction involving exchange of heat and work; (c) internal combustion engine involving exchange of heat and mechanical work; (d) fuel cell involving exchange of heat and electrical work.

2. Historical Perspectives

The experimental observation forming the basis of any energy balance formulation is the fact that heat and work are both expressions of an exchange of energy. This observation was only first expressed at the end of the eighteenth century. Since that time, and mainly during the nineteenth century, a new definition of the energy conservation law has been developed, including the contribution of heat in addition to the traditional terms (in other words, potential and kinetic) used in any consideration of the conservation of mechanical energy.

The first quantitative experiments were performed by Benjamin Thompson, who evaluated the *mechanical equivalence of heat* during the drilling of cannon barrels(1798). This idea was strongly objected to by the "caloric" sustainers, whose theory was dominant at that time. Humphry Davy, who observed the melting of ice by friction under vacuum conditions, provided additional confirmation of the validity of Thompson's work (1799). The mechanical theory of heat started to be accepted after the fundamental work of John Dalton on the atomic theory of matter; which lead to an understanding of heat in terms of molecular motion. By 1840 the energy conservation equation was accepted for purely mechanical systems, but the contribution of heat was still not considered universally. In 1842 Julius Robert Mayer published his fundamental work on the mechanical equivalence of heat, thus becoming the philosophical father of the first law of thermodynamics. An almost-exact value for the equivalence factor was determined by the various measurements of the thermal effect of electric current

performed by James Prescott Joule, starting in 1840 and discussed at the Royal Society in 1849. Thus Mayer's philosophical presentation and Joule's experimental work led to the general acceptance of the principle of energy conservation, whose mathematical formulation was finally defined by Herman von Helmholtz in 1847.

Thermochemistry began to be developed before the formulation of the mechanical equivalence of heat by Germain Henry Hess (1840), who studied the thermal effects associated with the aqueous dilution of mineral acids. The terminology concerning endothermic and exothermic reactions was proposed by Marcellin Berthelot, while the change in the heat of a reaction, with temperature as a function of the heat capacities of reactants and products, was formulated by Gustav Kirchoff in 1858. (See *History of Chemistry*.)

Figure 2. Scientists whose work contributed to the development of concepts inherent to the energy balance and thermochemistry

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Biographical Sketch

Maurizio Masi (born 1960) is Professor in Applied Physical Chemistry at the Department of Chimica, Materiali e Ingegneria Chimica of Politecnico di Milano. His research activity is centered on reaction kinetics and chemical reaction engineering; on the study of production processes for advanced inorganic materials for microelectronics, optics, and opto-electronics; and on the simulation of chemical, physico-chemical, and separation processes generally. In 1992 he was Visiting Scientist at Massachusetts Institute of Technology. He has co-authored about 100 scientific papers on these topics.