Laws of Thermodynamics

A remarkable feature of the subject called thermodynamics is the extent to which it is founded on four laws: Zeroeth, First, Second and Third. These laws summarise elegantly the results of experiments. Actually these are not laws in the sense of being laid down by government or by religious doctrine. Rather the laws are axioms. As McGlashan notes [1] each axiom is a ‘rule of the game’. These axioms refer to state variables such as temperature, pressure, energy and entropy. At this level the laws are not of immediate interest to chemists. However chemists have discovered how to ‘tell’ these axioms about chemical substances and chemical reactions.

The First Law invokes the concepts of energy and energy change. The law states that the energy of the universe is constant. In a realistic sense, at least for chemists, the law states that the energy of a chemical laboratory is constant. Then if the energy of system held in a reaction vessel increases, an equivalent amount of energy is lost from the rest of the laboratory. Then

$$\Delta U(\text{system}) + \Delta U(\text{surroundings}) = 0 \quad (a)$$

The Second Law of thermodynamics invokes the concepts of entropy and entropy change. In summary the law states that heat cannot flow spontaneously from low to high temperatures. The elegant studies carried out by James Prescott Joule (1818 -1889) were crucial to the development of thermodynamics [2].

Footnotes
