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THE LAWS OF THERMOCHEMISTRY

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In this paper we give the Laws of Thermochemistry, the van der Waals Thermochemical Equation and the Relativistic Energy in Quantum Chemistry.

The Laws of Thermodynamics and Chemistry do not apply to thermochemical systems in general. In a thermochemical system in conditions of small variations of energy and entropy the molecular variations of energy and entropy can be considered all equal for most of the molecules, however in a thermochemical system in conditions of large variations of energy and entropy the molecular variations of energy and entropy depend on the global energy and entropy, and so on the molecule.

First Law of Thermochemistry. An isolated thermochemical system evolves irreversibly to the state of thermochemical equilibrium.

$$dU \to 0 \text{ as } t \to \infty$$

in which U is the molecular energy of the isolated thermochemical system at time t.

Second Law of Thermochemistry. In a thermochemical system the energy is conserved.

$$\frac{dU}{U} = \frac{dQ+dW+dE+c^2dm+d\gamma A}{Q+W+E+mc^2+\gamma A}$$

in which U is the energy, Q, the thermic energy, W, the mechanical energy, E, the electromagnetic energy, mc^2, the relativistic energy and γA, the surface tension of the thermochemical system.

Third Law of Thermochemistry. In a thermochemical system the sum of the variations of the molecular thermomechanical energy and the molecular kinetic energy is the sum of the variations of the molecular thermic energy and the molecular surface tension.

$$\frac{VdP+PdV+dK}{PV+K} = \frac{dQ+d\gamma A}{Q+\gamma A}$$

in which PV is the thermomechanical energy, K, the chemical kinetic energy, Q, the thermic energy and γA, the surface tension of the thermochemical system.

Fourth Law of Thermochemistry. In a thermochemical system the molecular kinetic energy tends to half the Planck's constant times the characteristic frequency of the molecular normal mode as the molecular temperature tends to zero.

$$K \to \tfrac{1}{2}\hbar\nu \text{ as } T \to 0$$

in which K is the molecular kinetic energy, $\hbar$, the Planck's constant, ν, the characteristic frequency of the molecular normal mode and T, the molecular temperature of the thermochemical system.

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Fifth Law of Thermochemistry. In a thermochemical system the variation of the molecular entropy is the variation of the molecular thermic energy minus the flow of molecular relativistic energy per molecular temperature.

$$\frac{dS}{S} = \frac{dQ - \sum a_{ik}\mu_{ik}d\xi_k}{(T_m/T)(Q - mc^2)}$$

in which S is the entropy, Q, the thermic energy, T, the global temperature, T_m, the molecular temperature, mc^2, the relativistic energy and a_{ik} and μ_{ik}, the stoichiometric coefficients and chemical potentials of the i chemical reactants and products in the k irreversible and reversible matter and energy exchanges and irreversible chemical reactions with extent of reaction ξ_k of the thermochemical system.

Sixth Law of Thermochemistry. In a thermochemical system the variation of the molecular entropy due to irreversible variations of the molecular thermomechanical energy and the molecular kinetic energy and irreversible chemical reactions is always positive.

$$dS_i \geq 0$$

in which S_i is the molecular entropy of the thermochemical system due to irreversible thermochemical processes.

Seventh Law of Thermochemistry. In a thermochemical system the molecular entropy tends to zero as the molecular temperature tends to zero.

$$S \to 0 \text{ as } T \to 0$$

in which S is the molecular entropy and T, the molecular temperature of the thermochemical system.

The van der Waals Thermochemical Equation

A differential behaviour of the van der Waals Equation on pressure in solids and liquids arises, as large variations on pressure give small variations of volume, and so, small variations of the intermolecular forces of collision, which shows that the van der Waals Thermochemical Equation for solids and liquids is

$$Pe^{aN^2/V^2}(V - Nb) + K = Q + \gamma A$$

in which PV is the thermomechanical energy, K, the chemical kinetic energy, Q, the thermic energy, γA, the surface tension, N, the molecular number and a and b, the van der Waals coefficients of the thermochemical system.

The Earth Thermochemical Equations

Now we give the Earth Thermochemical Equations.

By the Third Law of Thermochemistry, since the atmosphere is a thermochemical system with no varying heat capacity within a spherical ring volume with a radius H for which small variations of temperature occur within large variations of pressure, small variations of radius and small variations of chemical kinetic energy, its thermochemical differential equation is

$$\frac{H_0 dP + PdH + dK}{H_0 P + K_0} = \frac{dT}{T_0}$$

and so,

$$(H_0P + K_0)e^{(HP+K)/(H_0P+K_0)} = (H_0P_0 + K_0)e^{T/T_0}$$

in which K is the chemical kinetic energy, P, the pressure, T, the temperature, and H, the radius of the atmosphere, and K_0, the chemical kinetic energy, P_0, the pressure, T_0, the temperature and H_0, the radius of the atmosphere at sea level.

By the Third Law of Thermochemistry, since the Earth is a thermochemical system with no varying heat capacity in which small variations of temperature and no variations of surface tension occur within large variations of pressure, large variations of radius and small variations of chemical kinetic energy, its thermochemical differential equation is

$$\frac{HdP+PdH+dK}{HP+K_0} = \frac{dT}{T_0+\gamma A_0}$$

and so,

$$(HP + K_0)e^{K/(HP+K_0)+T_0/(T_0+\gamma A_0)} = (H_0P_0 + K_0)e^{T/(T_0+\gamma A_0)+K_0/(HP+K_0)}$$

in which K is the chemical kinetic energy, P, the pressure, T, the temperature and H, the radius of the Earth, and K_0, the chemical kinetic energy, P_0, the pressure, T_0, the temperature, H_0, the radius and γA_0, the surface tension of the Earth at sea level.

By the Third Law of Thermochemistry, since the nucleus of Earth is a thermochemical system with varying heat capacity in which large variations of thermic energy and surface tension occur within large variations of pressure, small variations of radius and large variations of chemical kinetic energy, its thermochemical differential equation is

$$\frac{\frac{4}{3}\pi H_0^3 dP+4\pi H^2 PdH+dK}{\frac{4}{3}\pi H_0^3 P+K} = \frac{dQ+d\gamma A}{Q+\gamma A}$$

and so,

$$(Q_0 + \gamma A_0)(\tfrac{4}{3}\pi H_0^3 P + K)e^{\frac{4}{3}\pi H^3 P/(\frac{4}{3}\pi H_0^3 P+K)} = (\tfrac{4}{3}\pi H_0^3 P_0 + K_0)(Q + \gamma A)e^{\frac{4}{3}\pi H_0^3 P/(\frac{4}{3}\pi H_0^3 P+K)}$$

in which K is the chemical kinetic energy, Q, the thermic energy, P, the pressure, H, the radius and γA, the surface tension of the magmatic core and K_0, the chemical kinetic energy, Q_0, the thermic energy, P_0, the pressure, H_0, the radius and γA_0, the surface tension of the magmatic core surface.

In Quantum Thermochemistry

In Quantum Thermochemistry, the relativistic energy of a quantum thermochemical system is the thermomechanical energy plus the chemical kinetic energy.

$$mc^2 = PV + \tfrac{1}{2}\hbar\nu + \frac{\hbar\nu}{e^{\hbar\nu/kT}-1}$$

in which mc^2 is the relativistic energy, PV, the thermomechanical energy, $\hbar$, the Planck's constant, ν, the chacteristic frequency of the normal mode, k, the Boltzmann's constant and T, the temperature of the quantum thermochemical system.

This paper is dedicated to my father Dr Daniel Cordero Hernández