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CHEMICAL CONSEQUENCES OF NUCLEAR STABILITY

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The matter around us contains chemical elements in the elemental state and in a variety of combinations. Some materials consist of two or more elements joined in chemical compounds, or are mixtures of elements or compounds or both.

Very early, in the opinion of XVIII century chemists all chemical elements should be treated as “eternal”. However, after Becquerel’s discovery of radioactivity of certain atomic nuclei such invariability became problematic and depended only on longevity of a given time scale. A chemical element can consist of different isotopes (stable or radioactive) as was firmly established by J.J. Thompson. In chemistry, atomic binding energies (*i.e.* energies of chemical bonds) are of the order of eV, whereas the level of many MeV is useful in nuclear physics. Electron structure of atom determines its chemical behaviour, and the nucleus binding energy decides about its stability. About 273 different nuclei are stable because they lack enough mass to break up into separate nucleons. The energy equivalent of the missing mass of a nucleus is called the binding energy of the nucleus. The greater its binding energy, the more energy must be supplied

to break up the nucleus. For given nucleus, the binding energy per nucleon is found by dividing the total binding energy of the nucleus by the number of nucleons, A , it contains.

The greater the binding energy per nucleon the more stable the nucleus. The graph (Fig.) illustrating the relationship between binding energy and mass number has its maximum at 8.8 MeV/nucleon when the number of nucleons is 56. The nucleus that has 56 protons and 56 neutrons is ^{56}Fe , the iron main isotope. This is the most stable nucleus, since the highest energy is needed to pull a nucleon away from the iron nucleus. All the larger nuclei are unstable and decay radioactively.

It is an empirical fact that the binding energy per nucleon is roughly the same for all stable nuclei, *i.e. ca.* 8 MeV. As the mass number increases, the binding energy per nucleon gradually decreases. This systematic trend is a consequence of the electrostatic energy repulsion of the protons within the nucleus. The binding energy curve is the key to energy production in the universe, mainly nuclear fusion leading to nucleosynthesis of heavy elements. The graph has a good claim of being the most significant in the whole science. The fact that the binding energy exists in general means that the nuclei more complex than the single proton of hydrogen ($A=1$) can be stable. This stability, in turn, accounts for the existence of the various chemical elements and, consequently, for the existence of the truly enormous amount of chemical compounds and their mixtures we see around us. For example, there are several millions of known and described chemical compounds, and even theoretically about 10^{48} of different proteins.

The semi-empirical mass formula (SEMF) was originally devised by C.F. Weizsacker [1] to represent the known nuclear masses in term of a few (five) adjustable parameters and enable useful estimates to be made of the masses of unknown nuclei. In the SEMF, the total binding energies expressed as a sum of five terms:

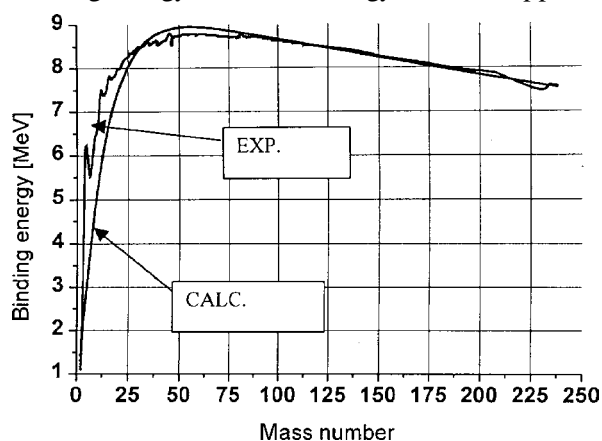


Fig. Binding energy per nucleon plotted against mass number A (experimental and calculated values, respectively).

$$\frac{BE}{A} = A_v \cdot A - A_s \cdot A^{2/3} - A_c \cdot Z^2/A^{1/3} - A_a \cdot (N - Z)^2/A \pm \Delta$$

where: A – mass number, A_v – volume binding term, A_s – surface term, A_c – Coulomb term, A_a – asymmetry term, BE – binding energy, Δ – pairing term, Z – atomic number, N – neutron number.

These five adjustable parameters were obtained by fitting the formula to the experimentally determined values. There are significant differences between the values of the above five adjustable parameters reported by various authors [2-7], for example, 31% for the surface term and 28% for the asymmetry term.

Instead, in this paper is propose another approximation of binding energy per nucleon, BE , in the form of the difference of two simple exponential functions of mass number, $A-1$ (because BE of the nucleus of the lightest hydrogen isotope is equal to zero, then the ordinate should be shifted by one unit on the mass number scale, A).

$$\frac{BE}{A} = E_{\text{extr}} \cdot (e^{-\lambda \cdot (A-1)} - e^{-((\lambda \cdot C)/\alpha) \cdot (A-1)})$$

where: C – the Euler-Mascheroni constant, α – the Sommerfeld's fine structure constant, E_{extr} – extrapolation constant, e – a base of natural logarithm, λ – exponent of exponential function.

The three applied constants terms (*i.e.* two exponents: λ and $C/\alpha \cdot \lambda$ and proportionality coefficient, A_{extr}) are a simple combination of some mathematical and physical constants, and not need any fitting for observation.

This formula predicts the binding energy per nucleon for the mass number greater than 25 (Fig. – calculated values). For singular isobars the precision is sufficient, and only in the case of an isobaric triad the maximal error is equal to 2.4%.

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RADIOLYTIC DEGRADATION OF HERBICIDE 4-CHLORO-2-METHYLPHENOXYACETIC ACID (MCPA) BY γ -RADIATION FOR ENVIRONMENTAL PROTECTION

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Worldwide application of intensive methods in modern agriculture in the last few decades results in the presence of variety of agrochemicals in the environment. Many pesticides that are commonly used are resistant to natural degradation in the environment, hence, there is a great concern about possible adverse effects for human health and for equilibrium in ecosystems [1-3]. Chlorophenoxy herbicides, which have potential toxicity towards humans and animals [4], and are suspected mutagens and carcinogens, are used worldwide on a large scale as plant growth regulator for agricultural and non-agricultural purposes. Among them, 4-chloro-2-methylphenoxyacetic acid (MCPA) is used in amounts exceeding 2000 tons per year in West European countries [5]. In commercial preparations it is used as dimethylammonium, potassium or sodium-potassium salts, very often in mixtures together with other chlorophenoxy pesticides (2,4-dichlorophenoxyacetic acid – 2,4-D, 3,6-dichlorophenoxyacetic acid – dicamba, 4-(4-chloro-2-methylphenoxy)butyric acid – MCPB), but also with other groups of pesticide compounds. In aqueous solutions, it occurs mainly in anionic form ($pK_a=3.1$), and its reported field half-life time ranges from 6 to 60 days, which is longer than, for instance, reported for 2,4-D or dicamba [6].

In the literature on degradation or removal of MCPA for environmental purposes, mostly photodegradation methods have been reported [7-10]. In electrochemical degradation, oxidation was carried out with hydroxyl radicals produced from Fenton's reaction between Fe(II) and hydrogen peroxide generated in anodic reaction that can be additionally accelerated using a photoperoxy-coagulation treatment under UV irradiation of solutions, providing more hydroxyl radicals [11]. Other methods reported in the literature include ultrasonic decomposition in an argon atmosphere [12], biodegradation using a microcosmic technique [13], and removal of MCPA from aqueous solutions by acid-activated spent bleaching earth, which is a solid waste from edible oil processing industry [14].

The aim of this work was to study chromatographically the effectiveness of degradation and to identify products of degradation of MCPA in synthetic aqueous solutions and industrial wastes from the production of this herbicide. The chromatographic determinations of MCPA and products of its radiolytic decomposition were determined in a reversed-phase high pressure liquid chromatography (RP-HPLC) system using a Shimadzu chromatograph with a diode array UV-VIS detector, using a column C18 Luna ODS2 (5 μ m, 250 \times 4.6 mm) and