# CATALYSIS OF CHEMICAL PROCESSES: PARTICULAR TEACHING ASPECTS

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**ABSTRACT**

The paper is devoted to two main issues of catalysis from the viewpoint of teaching and learning activities. The first part deals with positive catalysis which treats the general features of catalytic processes and textbook imperfections. The second part focuses on decelerating or stopping-down chemical processes. It is shown that contrary to the "positive" catalysis, *i.e.* enhancement of the rate of chemical reactions, which is a regular part of chemical education at secondary/high schools and universities, the inhibition of the chemical reactions is frequently missing in educational curricula. The importance of inhibition is explained, its mechanism presented and examples offered. *[African Journal of Chemical Education—AJCE 5(2), July 2015]*

**INTRODUCTION**

The word "catalysis" was introduced into chemistry by the Swedish chemist Jöns Jacob Berzelius in 1835 [1] who realized that there are substances which increase the rate of a reaction without being themselves consumed.
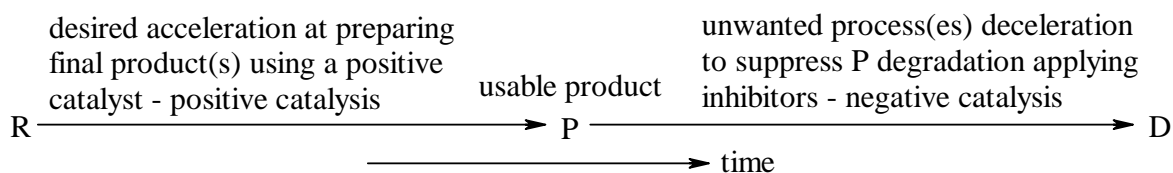
A catalyst which enhances the rate of a reactionby providing an alternative, less energy demanding pathway is called a „positive catalyst"and the process "positive catalysis" or usually simply"catalysis". A substance which retards the rate of a reaction is called a "negative catalyst"or "inhibitor" and the process "negative catalysis" or "inhibition".

It is estimated that more than 90 % of the production of chemical industry is based on catalysis [1] and in living organisms the proportion of enzymes-catalyzed processes is even higher [2-5]. According to a study from The Freedonia Group, a Cleveland-based market research firm, world demand for catalysts will rise 5.8 percent per year to $19.5 billion in 2016 [6]. As a result, the lesson catalysis is frequently included in chemistry education curricula at secondary/high schools and university levels indicating that catalysis is very important. The field of catalysis is included in the majority of textbooks covering, in particular, general chemistry, industrial processes and technologies, biochemistry and biotechnology[7-16].

Catalysis understood as an acceleration of a chemical reaction in approaching the equilibrium state is extremely important at the stage of obtaining the final product. However, once the product is prepared, there is a requirementto preserve its utility properties or, in other words, to suppress any changes leading to the product deterioration[17, 18]. Cosmetics, foodstuffs, beveriges, medicinal drugs, textiles and plastic materials can be used as illustrative examples where such stability is required. To prevent undesirable processes from occurring, substances known as antioxidants, preservers, stabilizers or conserving agents are applied[18-

20]. Their function can be, in a broader sense, described as negative catalysis or inhibition. Suprisingly, the phenomenon of inhibition and its essence is usually not mentioned or correctly, from the viewpoints of kinetics, explained in educational materials and activities. This statement can be exemplified by textbooks [8, 11-14].

The progress of a reaction with time progress starting with reactantsR,continuing to their transformation to final product(s) P and subsequentlyundesired change of P to degradation product(s)D may be illustrated as follows

desired acceleration at preparing final product(s) using a positive catalyst - positive catalysis                usable product                unwanted process(es) deceleration to suppress P degradation applying inhibitors - negative catalysis

R ————————————————————→ P ————————————————————→ D

————————————→ time

This contribution is aimed at

*i)*   introducing catalysis in a general mode;

*ii)*  providing examples of the most common textbook imperfections in this field, and,

*iii)* explaining and exemplifying the importance of decelerating or stoppingdown chemical processes.

## POSITIVE CATALYSIS

### *Introduction*

It is worth beginning with catalysis in its usual meaning, *i.e.* a process of acceleration in the rate of a reaction caused by the presence of a substance – catalyst – that does not appear in the chemical equation among the reactants and products, does not change thermodynamics of the overall process, and acts also when being in substoichiometric amount in the reaction system. A catalyst thus does not changethe energetic characteristics of the reactants, products and the

reaction ($\Delta_\mathrm{r}U$,$\Delta_\mathrm{r}H$, $\Delta_\mathrm{r}G$) and the barriers between them($E^{\neq}$,$\Delta H^{\neq}$, $\Delta G^{\neq}$)[7, 15]. It instead finds an alternative reaction pathway (with a faster reaction rate) that bridges reactants and products with lower energy barriers. It implies that in a reversible reaction the catalyst acceleratesthe forward and reverse reaction equally. Therefore, although it shortens the time required to approach the equilibrium,acatalyst does not affect the final position of equilibrium and, consequently,percentage yield of the products[21].

In spite of its involvement in the reaction mechanism, the catalyst is not consumed in the overall reaction process,however, it is a constituent of some intermediates[7, 15, 21].

Contrary to the stoichiometric equation not involving the catalyst, it may be included in the rate lawwith a partial order greater than zero[7]. The rate law for a general reaction of the reactants A and B in a system containing a catalyst C consists of two terms expressing the rate of uncatalyzed and catalyzed reaction *v*and may be written generally in the form [7]

$v = k_\mathrm{uncat}[\mathrm{A}]^\mathrm{a}[\mathrm{B}]^\mathrm{b} + k_\mathrm{cat}[\mathrm{A}]^\mathrm{x}[\mathrm{B}]^\mathrm{y}[\mathrm{C}]^\mathrm{z}$

where*k* are the corresponding rate constants, a, b, x, y, z are the partial orders. When the catalyst is a solid (heterogeneouscatalysis), its concentration is constant and it does not appear as an independent termin the rate law. Its effect is included in the value of $k_\mathrm{cat}$.

The best kind of catalysts are enzymes. They produce rate enhancement (expressed as $k_\mathrm{cat}/k_\mathrm{uncat}$) ranging from $10^7$ to $10^{19}$[21].In addition to their efficiency, enzymes are usually specific (one enzyme catalyses one reaction) and stereospecific.

### *Misinterpretations in teaching and perception of catalysis*

In the area of positive catalysis, three mainkinds of imperfections appearing in textbooks may be identified. A first one lies in the claiming that "the catalyst decreases the activation

energy of the reaction". Reality is that the activation energy of the original reaction is not changed by the catalyst[22, 23]. Suppose, you have a mountain between two valleys so that the only way for people to get from one valley to the other is over the mountain. The tunel (analogy with catalytic pathway) does not change the original mountain pass, it just represents a new route. The effect of catalysts arises from the fact that in their presence a pathway with lower activation energy becomesavailable to the reactants and it does not lower the activation energy of the original reaction [22, 23].

A second imperfection relates to the expression of the activation energy for uncatalyzed and catalyzed process. An effort to be as simple as possible may alter a simplification to an incorrectness. Also in otherwise excellent textbooks [8-11] the potential energy curves for catalyzed and uncatalyzed reactions are depicted with the same number of transition states (usually a single state) without documenting the action of the catalyst and its involvement in the reaction mechanism, *i.e.* without intermediates (Fig. 1a).

The involvement of a catalyst should be illustrated both by a higher number of intermediates and a higher number of transition states (with the activation energy lower than that of uncatalyzed process) [12-16].A very simple and illustrative example (Fig. 1b) is the oxidation of CO to $CO_2$ occurring in the gas phase by oxygen $O_2$. The mechanism of both uncatalyzed reaction and that catalyzed by metal (Pt) surface was proposed by the Nobel-prize winner, Gerhard Ertl [24].

In the absence of a catalyst, the activation energy is given by bond energy in molecular $O_2$. In the presence of Pt-catalyst, both reactants, CO and $O_2$ are chemisorbed on the metal surface and molecules of $O_2$ dissociate to O atoms. Within these three processes the energy is released ($-259 kJ \cdot mol^{-1}$). In order the adsorbed CO molecules to react with adsorbed O atoms,

the activation energy of 105 $kJ \cdot mol^{-1}$ should be overcome, their conversion to adsorbed $CO_2$ molecules is an energy-releasing ($-45$ $kJ \cdot mol^{-1}$) process. The final step of the process, desorption of $CO_2$ molecules is an energy-consuming process ($21 kJ \cdot mol^{-1}$). The enthalpy change for the both uncatalyzed and catalyzed overall reaction of CO oxidation is, of course, equal ($-283$ $kJ \cdot mol^{-1}$).
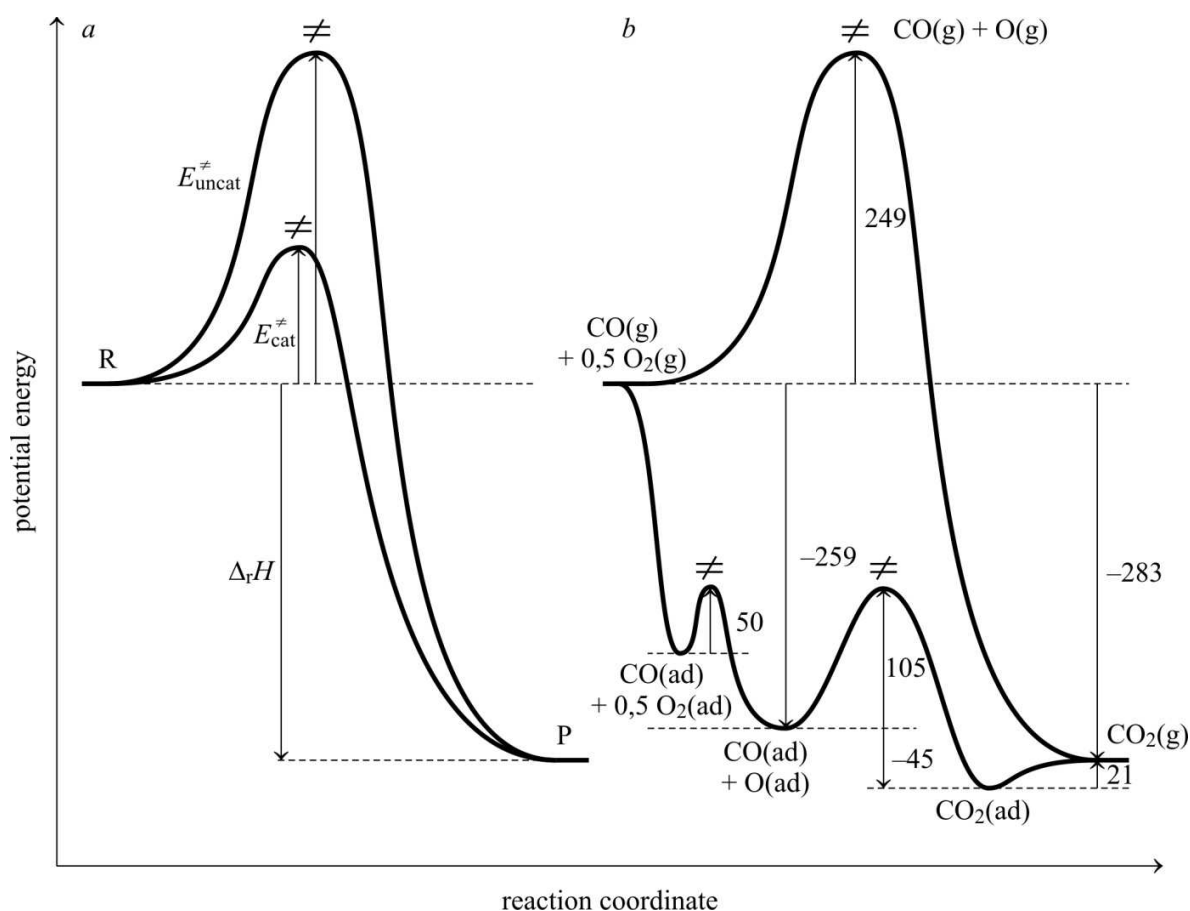


*Fig. 1a: Over-simplified energy profile of a general catalyzed and uncatalyzed reaction not involving the role of catalyst in the reaction mechanism [8, 10, 11].*
*Fig. 1b: Energy profile for the uncatalyzed ($E^{\neq} = 249 kJ \cdot mol^{-1}$) and Pt-catalyzed oxidation of CO by $O_2$. Symbols "ad" and "$\neq$" denote adsorbed molecules and transition states, respectively. All the values are extracted from [24, 25] and expressed in $kJ \cdot mol^{-1}$.*

While the energy profile in Fig. 1a might suffice at high school level where the students do not deal with reaction mechanisms, university students of chemistry having the fair

knowledge of physical chemistry and reaction mechanisms should work only with the profiles as depicted in Fig. 1b.

A third imperfection lies in the confusing use of energy quantities in graphical illustration (energy profile) of both catalytic and uncatalytic route of the transformation of the reactants to the productsand should be corrected at least at university-level education. Frequently the energy profile is shown as a dependence of energy on reaction progress, without specifying what kind of energy (internal energy, potential energy, total energy, Gibbs energy?) is in question, and what is the meaning of "reaction progress". Thermodynamics of the overall reaction is usually expressed as enthalpy change while kinetics as potential energy[11, 26].

In any case, only one quantity should be used. Also, it should be clear that the "reaction progress" does not represent time evolution. It is in fact "reaction coordinate".

It is customary to use activation enthalpy and activation energy interchangeably[13, 26], but there is, in fact, a difference between them from the viewpoint of both physical meaning and value. Activation energy $E^{\neq}$ is an empirical parameter in Arrhenius equation in collision theory of chemical reactions[21].Activation enthalpy $\Delta H^{\neq}$(as well as activation Gibbs energy $\Delta G^{\neq}$ and activation entropy $\Delta S^{\neq}$) are parameters of Eyring relationship[21], originating from transition state theory. As for values, $E^{\neq}$ is lower by a few kJ·mol$^{-1}$ than $\Delta H^{\neq}$[21].As for the quantity used, preferablemight be Gibbs energy (including activation Gibbs energy) due to its direct relation to equilibrium constant or enthalpy due to direct connection tothe heat effect of reaction and the temperature dependence of equilibrium constant. The use of Gibbs energy was correctly documented in [27].

**NEGATIVE CATALYSIS**

The concept of negative catalysis was evaluated in scientific literature back in 1920s[28, 29]. Negative catalysis is useful to slow down or completely stop an unwanted reaction[22, 30]. The student may ask whether any chemical reaction can be inhibited. The answer is "no". Generally speaking, only catalyzed, photochemical and unbranched chain radical processes may be effectively decelerated[22]. In more detail, inhibition can thus be applied in processes involving substances able to chemically transform (poison) the catalyst, to trap or scavenge intermediates in unbranched chain radical reactions, or to deactivate reactive molecules in electronically excited states.A chemical process may be stopped also due to deposition of substances on the catalyst preventing thus its participation in the catalytic process. It is importantto stress within teaching the matter that, contrary to the positive catalyst, the inhibitor does not introduce a new reaction route with a higher activation energy. Due to its action just the reaction continues to occur by the non-catalyzed route.

In the next part the mechanism of negative catalysis will be documented and selected examples presented.

*Poisoning a catalyst*

A negative catalysis may be a consequence of irreversibly poisoning the catalyst present in the reaction mixture.For example, the traces of transition metal cations released from the container catalyze decomposition of hydrogen peroxide, $H_2O_2$. But the addition of a complex-forming compound (*e.g.*, derivatives of phosphoric acid, phosphonic acid, various organic acids [31, 32])to solutions of $H_2O_2$would bind the metal cations acting as catalysts into complexes and thus prevent decomposition. Aqueous solutions of $H_2O_2$containing $H_3PO_4$ are called "stabilized".
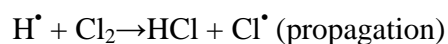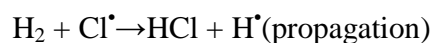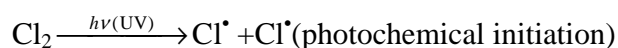
In case of transition metal containing enzymes, hydrogen sulphide and/or sulphide anions act as catalytic poisons forming metal sulphides[33]. A consequence for the involved chemical process is transition from a fast catalytic route to a slow uncatalytic one.

A huge amount of knowledge has been accumulated and rationalized in the field of enzyme catalysis and inhibition. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme[4]. One of the oldest and most widely used commercial enzyme inhibitors is aspirin (acetylsalicylic acid), which selectively inhibits an enzyme involved in the synthesis of molecules that trigger inflammation[34].

*Breaking an unbranched chain reaction*

Unbranched chain reaction is a process in which the number of chain carriers is equal (usually 1) in each propagation step[35].In some cases, negative catalysts are believed to operate by breaking the chain of reactions. For example, the combustion of $H_2$ and $Cl_2$ which is a chain reaction is inhibited by oxygen,$O_2$[36]. The mechanism of the reaction can be expressed by three elementary reactions:

$$Cl_2 \xrightarrow{h\nu(UV)} Cl^\bullet + Cl^\bullet \text{(photochemical initiation)}$$

$$H_2 + Cl^\bullet \rightarrow HCl + H^\bullet \text{(propagation)}$$

$$H^\bullet + Cl_2 \rightarrow HCl + Cl^\bullet \text{ (propagation)}$$

$O_2$ breaks the chain of reactions (decreases their rate)interacting with atom$H^\bullet$ forming the unreactive radical $HO_2^\bullet$

$$O_2 + H^\bullet \rightarrow HO_2^\bullet$$
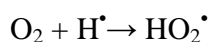
It should be pointed out that branched chain reactions (chain reactions in which the number of chain carriers increases in each propagation step,*e.g*., explosions) cannot be effectively inhibited by this mode[35].


### *Deactivating excited states*

The absorption of ultraviolet (UV), visible or near-infrared radiation by a compound may be a cause of its destruction[17]. Undesirable photochemical processes may be inhibited via deactivation of excited molecules. The substances playing the role of inhibitors are called photostabilizers. The mode of their actions depends on the nature and properties of the excited molecules[17].

One of the deactivating modes is energy transfer, applied, *e.g.* in transforming (quenching) reactive excited singlet oxygen $^1O_2$to unreactive ground-state triplet oxygen$^3O_2$. The process can be examplified by the quenching of singlet oxygen with the photostabilizer bis(*N*-phenyldithiocarbamato)nickel(II), abbreviated as [Ni(PDC)$_2$]  in its ground singlet state[37, 38]

$$^1O_2 + {}^1[Ni(PDC)_2] \rightarrow {}^3O_2 + {}^3[Ni(PDC)_2]$$
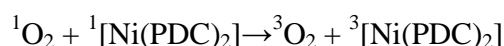
The rate constant of the reaction is $1.1 \times 10^{10}$ L·mol$^{-1}$·s$^{-1}$. In general, photostabilizers must comply with at least two conditions: the rate constant of their reactions with excited molecules must be as high as possible, and the excited reaction product (in the above example $^3$[Ni(PDC)$_2$] in its excited triplet state) must be deactivated solely by a photophysical mode and its excitation energy converted to heat[17].

Photodegradation of polymers is decelerated also by using UV absorbers which are compounds absorbing UV radiation with a very high molar absorption coefficient

($\varepsilon_{UV}>10^4$L·mol$^{-1}$·cm$^{-1}$) and thus preventing the absorption of UV radiation by the polymer or its components[17, 39].

### *Scavenging reactive radicals*

To inhibit undesirable radical decomposition reactions from occurring, radical scavengers are used. Among the radicals initiated such processes, hydroxyl radical $^{\bullet}$OH may be mentioned[40, 41]. Radical scavengers are added,*e.g*., to foodstuff, beveriges, polymers, textiles etc.Many of them form integral part of living organisms and inhibit reactions of radicals by reacting with them. Well-known example represents enzymes superoxide dismutases, SOD, inhibiting redox processes of the radical $O_2^{-\bullet}$ through its dismutation into dioxygen and hydrogen peroxide molecules (the mechanism is not so simple)

$$2\ O_2^{-\bullet}+ 2\ H^+ \xrightarrow{\text{SOD}} H_2O_2 + O_2$$
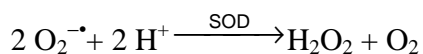
Sorbic acid,benzoic acid and their derivatives are foodstuff and beverages preservatives inhibiting usually redox processes of reactive oxygen species such as$^{\bullet}$OH, $O_2^{-\bullet}$, $RO_2^{-\bullet}$by their bonding to a double bond or their reduction[20,41]. In polymer chemistry highly effective radical scavengers are 2,2,6,6-tetramethyl piperidine derivatives, known as hindered amine light stabilizers (HALS)[39]. Itis worth pointing out that scavengers are consumed in the processwithout their regeneration, and do notreturn chemically unchanged to the system.In spite of this fact, they are very useful in protecting and preserving original, required properties of products.

### *Depositing substances on the catalyst surface*

When a liquid or solid substanceis deposited, or a gas adsorbed on the solid catalyst, itprevents contant of reacting species with the catalyst and the process becomes slower[42]. Such

a situation may happen in the heterogeneous catalysis in which at least one of the reactants or products is a highly viscous or solid substance. As example, residue hydrocraking process of naphta pitch using the catalyst composed of activated alumina, Ni and Mo is inhibited by deactivation of the catalyst due to deposition of coke and high-molecular hydrocarbons (so called coking or fouling effect) on its surface[40].

In heterogeneous gas-phase catalysis one of the reactants may be adsorbed (chemisorbed) on the solid catalyst surfacein such an extent that it prevents contact of the catalyst with another gas reactantreducing or destroying thus the catalyst's efficiency. Together with economical factors, this is whythe course of such reactions is governed in a definite pressure and temperature range, *e.g*. ammonia is industrially synthesized at 400-450 °C and 200 bar.


**CONCLUSIONS**

Catalysis of one of the most important issues in chemical education, industry and life-relating processes. This is why the correct teaching at all levels of chemical education should result in correct understanding the matter. The most frequently misinterpretationsappearing in textbooks and scientific literature are presented and modes of their correction suggested.  In   the literature and education curricula the issues of catalytic acceleration and deceleration of chemical processes is not sufficiently balanced. Inhibition of chemical processes understood as their deceleration or even totally bring to a stop is of importance equivalent to that of positive catalysis. It deserves a due attention at secondary/high school and university levels. Its significance should be demonstrated by examples from real industrial, environmental and biological systems. When dealing with catalysis, the teacher and textbooks should be careful not to oversimplify the matter.

**REFERENCES**

[1] J. Haber: Catalysis – where science and industry meet, Pure Appl. Chem. 66 (1994)1594-1629

[2] D. Voet and J.G. Voet: Biochemistry, 4th. Ed., Wiley, Hoboken (2000) 469-556,ISBN 13 978-0470-57095-1

[3] E. Ramsden: Chemistry, 2nd. Ed., Stanley Thornes Ltd., Cheltenham (2001), 276-277, ISBN 0 7487 6242 6

[4] R.A. Copeland: Enzymes, 2nd. Ed., Wiley-VCH, New York (2000) ISBN 0-471-35929-7

[5] D.L. Purich: Enzyme Kinetics, Academic Press, London(2010)1-6, ISBN 978-0-12-380924-7

[6] The Freedonia Group, Study No. 2989: World Catalysts to 2016 - Demand and Sales Forecasts, Market Share, Market Size, Market Leaders (2013) http://www.freedoniagroup.com/World-Catalysts.html

[7] L.Arnaut, S. Formosinho, and H. Burrows: Chemical Kinetics – From Molecular Structure to Chemical Reactivity, Elsevier, Amsterdam (2007), ISBN 978-0-444-52186-6

[8] S. S. Zumdahl and S. A. Zumdahl: Chemistry, (7th. Ed.), Houghton Mifflin Company, Boston, (2007) 557-563, ISBN 978-0-618-52844-8

[9] P. Atkins and L. Jones: Chemical Principles: The Quest for Insight(3rd. Ed.), Freeman, New York (2005), 517-522, ISBN: 0-7167-5701-X

[10] S. L. Seager and M. R. Slabaugh: Chemistry for Today (8th. Ed.), Brooks/Cole, Belmond USA (2014), 262-264, DOI: 978-1-133-60227-9

[11] J. G. Smith: Principles of General, Organic and Biological Chemistry, McGraw-Hill, New York (2012), p. 155, ISBN 978-0-07-351115-3

[12] J. C. Kotz, P. M. Treichel, and J. M. Towsand: Chemistry and Chemical Reactivity (8th Ed.), Brooks/Cole, Belmond USA(2012)695-697, ISBN 978-0-8400-4828-8

[13] M. Silbergerg and P. Amateis: Chemistry: The Molecular Nature of Matter and Change (7th. Ed.), McGraw-Hill, New York (2015) 712-716, ISBN 978-0-07-351117-7

[14] K. W. Whitten, R. V. David, M. L. PecK, and G. G. Stanley: Chemistry (10th. Ed.), Brooks/Cole, Belmond, USA (2014) 647-653, ISBN 978-1-133-61066-3

[15] W. L. Masterton and C. L. Hurley: Chemistry – Principles and Reactions, (6th. Ed.), Crooks/Cole, Belmont USA (2009) 305-307,  ISBN 978-0-495-12671-3

[16] J. Orsay: Chemistry (7th. Ed.), Osote, New Jersey (2007) 34-36, ISBN 978-1-893858-49-7

[17] J. Šima and J. Sýkora: Photochemistry of Coordination Compounds, Coord. Chem. Rev. 107 (1990) 1-225

[18] A. K. Mukhopadhyay: Antioxidants – Natural and Synthetic, Amani Int. Publ., Kiel, (2006) 1-10, ISBN 978-3-938054-05-5

[19] S-Z. Kang: Stabilizers of antioxidants and stabilizer-added antioxidant antioxidant formulations and products, Patent WO2002098411 A1 (2002) http://www.google.com/patents/WO2002098411A1?cl=en

[20] M. S. Rahman: Handbook of Food Preservation, 2nd. Ed., (2007), CRC Press, Boca Raton, ISBN 978-1-57444-606-7

[21] P. Atkins and J. de Paula: Physical Chemistry for the Life Sciences, Freemen, New York (2006) 165, ISBN 0-7167-8628-1

[22] J. Šima and R. Šípoš: Inorganic Reaction Mechanisms, STU Press, Bratislava (2012), ISBN 9788022737821 (in Slovak)

[23] A. Haim: Catalysis: New reaction pathways not just a lowering of the activation energy. J. Chem. Educ., 66 (1989) 935, DOI: 10.1021/ed066p935

[24] G. Ertl: Kinetics of chemical processes on well-defined surfaces, in J. R. Anderson and M. Boudard (Eds.), Catalysis: Science and Technology, Vol. 4 Springer, Heidelberg (1983) 209-282

[25] H. Steininger, S. Lehwald, and H. Ibach: Adsorption of oxygen on Pt(111), Surface Science, 123 (1982) 1–17, DOI:10.1016/0039-6028(82)90124-8

[26] M.E. Davis and R.J. Davis: Fundamentals of Chemical Reaction Engineering, McGraw Hill, New York (2003), ISBN 0-07-245007-X

[27] I.N. de Castro and J.F. Alonzo: Energy Diagrams for Enzyme Catalyzed Reactions: a Confusing point in the Textbooks, Biochemical Education 25 (1977) 87-89

[28] H. S. Taylor: The Problem of Negative Catalysis, J. Phys. Chem., 27 (1923) 322-341, DOI: 10.1021/j150229a002

[29] J. A. Christiansen:J. Phys. Chem., 28 (1924) 145–148, DOI: 10.1021/j150236a004

[30] C. H. Bartholomew: Mechanisms of catalyst deactivation, Appl. Catal. A, 212 (2001) 17-60

[31] P. Wegner: Hydrogen peroxide Stabilizer and resulting product and application, US Patent US20030151024 A1 (2002)

[32] Y. Jung, J. Y. Park, S. O. Ko, and Y. H. Kim: Stabilization of hydrogen peroxide using phthalic acids in the Fenton and Fenton-like oxidation, Chemosphere 90 (2013) 812-819, DOI: 10.1016/j.chemosphere.2012.09.089

[33] J. M. Stellman: Encyclopaedia of Occupational Health and Safety, Vol. 4, 4th Ed., Inter. Labour office, Geneva (1998) 401-402, ISBN 92-2-109203-8

[34] J. J. Nawarskas and S. A. Spinler: Update on the Interaction between Aspirin and Angiotensin-Converting Enzyme Inhibitors, Pharmacotherapy 20 (2000) 698-710, DOI10.1592/phco.20.7.698.35168

[35] J.W.Moore and R.G. Pearson: Kinetics and Mechanism, A Study of Homogeneous Chemical Raections, 3rd Ed., Wiley, New York (1981) 408-411, ISBN 0-471-03558-0

[36] A. L. Marshal: Mechanism of the Photochemical Reaction between Hydrogen and Chlorine, J. Phys. Chem., 29 (1925) 842-852, DOI:10.1021/j150253a008

[37] M. C. deRosa and R. J. Crutchley: Photosensitized Singlet Oxygen and its Application, Coord. Chem. Rev., 233-243 (2002) 351-371,

[38] C.A. Grapperhaus andM. Y. Darensbourg: Oxygen capture by sulfur in nickel thiolates, Acc.Chem.Res. 31 (1998) 451-459

[39] B. S. Butola, M. Joshi: Photostability of HDPE Filaments Stabilized with UVAbsorbers (UVA) and Light Stabilizers (HALS), Journal of Engineered Fibers and Fabrics8 (2013) 61-68

[40] L. M. Dorfman: Recativity of the Hydroxyl Radical in Aqueous Solutions, National Standard Reference Data Systems, National Bureau of Standards, Washington, (1973) 1-59

[41] B. Lipinski: Hydroxyl Radical and Its Scavengers in Healts and Desease, Oxidative Medicine and Cellular Longevity, (2011), Article ID 809696, 9 pages, DOI:10.1155/2011/809696

[42] I. Chorkendorff and J.W. Niemantsverdriet: Concepts of Modern Catalysis and Kinetics, 2nd. Ed., Wiley-VCH, New York (2017), ISBN 978-3-527-31672-4

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