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STANISŁAW BRETSZNAJDER (1907–1967)

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The Fourth Stanisław Bretsznajder Nation-wide Seminar with foreign participation took place on the day before the 80th anniversary of his birthday and the 20th anniversary of his death. This unusual man, who continued the best Polish scientific traditions in chemical technology and applied physicochemistry, will always be remembered by those who had the opportunity to become acquainted personally with his strong character, his bróad mind, his profound knowledge, his culture and his personal charm.

Stanisław Bretsznajder was born on 19th July 1907 in Mikolajewo (USSR). In 1926 he graduated from a grammar school in Radom and continued his studies at the Chemical Faculty of the Technical Institute of Warsaw. After four years there, he graduated as a chemical engineer. His postgraduate work was performed in Vienna where, under the world-famous scientist Professor Billiter, he studied technical electrochemistry. He next acquired industrial experience in the firm "Crebs" in Berlin. On returning to Poland, he worked at the Technical Institute of Warsaw as a senior assistant at the Inorganic Technical Chemistry Department run by Professor Zawadzki. Here he carried out research work on problems of the thermal dissociation of solid substances. In 1933 he presented the results of his research work as a doctoral thesis, on the basis of which he was awarded the title of Doctor of Science.

After his doctorate, the 24-year-old scientist spent several months gaining further practice in large factories in Moscice, Szopienice, Trzebinia and Szarlej. Then, at the requrest of Prof. Zawadzki he began studies on obtaining metallic aluminium from Polish clays. In 1936 he presented the results of his studies on this problem before the Chemical Faculty Council of the Technical Institute of Warsaw for purposes of qualification. He submitted his thesis for the title of Assistant Professor, which he was awarded at the age of 29 years.

The outbreak of World War II made it impossible for Bretsznajder to take over the Faculty of Inorganic Technology at the Mathematics-Natural Science

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Department of Warsaw University after the death of Prof. Mieczyslaw Centnerszwer, and it also prevented him from carrying out research work and teaching. In the period 1940–1944 he was technical supervisor at the chemical reagent works "J. Tobis" in Warsaw, and was one of the first to start the fight against the invader in the resistance movement [1].

In spring 1940, on the orders of the Commander of the Fighting Resistance Union (later called the "Home Army"), Col. Stefan Rowecki ("Grot" = Arrowhead), The Revenge Union (ZO) was formed. At the suggestion of Lieut. Col. Franciszek Niepokólczycki ("Teodor"), the Bureau of Sabotage Studies (BBS) and the Bureau of Technical Studied (BBT) were formed. Prof. Józef Zawadzki, the last Rector of the Technical Institute of Warsaw before the war, ran one of the BBS departments, while Asst. Prof. Stanisław Bretsznajder ("Chemik") managed fire sabotage studies in the BBT, which used "chemical" weapons against the enemy. "Chemik" luckily survived the war, but his only sister was brutally murdered by the invader.

Immediately after the war, on 1st February 1945, Bretsznajder started work in the Polish chemical industry, as a technical consultant and a scientific manager in the State Synthesis Works in Dwory near Oświęcim, where he was employed till 1949. Simultaneously, in June 1945 he was appointed Manager of the Industrial Inorganic Technology Department at the Silesian Institute of Technology in Gliwice.

Due to his outstanding abilities, great knowledge and devotion to work, he quickly succeeded in his scientific career. In Octoer 1946 he was appointed Associate Professor, in May 1954 Corresponding Member of the Polish Academy of Science, in 1956 Professor, and in 1961 Full Member of the Polish Academy of Science.

In 1949 he returned to the Warsaw Institute of Technology and begin to organize the Technological Design Department as its manager. Next followed the most intensive period of his work both as a scientist and as an organizer at posts of responsibility in the Institute and beyond it. For many years he was director of scientific and technical problems in the Main Institute of Industrial Chemistry, and subsequently in the Institute of Physical Chemistry of the Polish Academy of Science, where he additionally ran the Division of Physico-chemical Bases of Technology. He was also a member of the Economic Council in the Bureau of the Cabinet, the Main Council of Chemistry in the Committee for Science and Technology, the Scientific-Technical Council at the Ministry for Chemical Industry, etc. For many years he was on the editorial committees of "Yearbooks of Chemistry", "Applied Chemistry", "Chemical News" and "Chemical Industry". In the last years of life, despite his terminal illness, his creative energy was not diminished. He died on 14th April 1967 and was buried in the Alley for Persons of Merit in the Powazki Cemetery in Warsaw.

Professor Bretsznajder has left an immense scientific output, consisting of 237 published items [2], among others 146 original research papers, 15 individual or joint monographs and 35 patents.

We participants in this Fourth Seminar are particularly attracted by those problems which were the subject of his research at the beginning of his scientific activities and to which he was faithful all his creative life: problems concerning the thermal dissociation of solid substances.

In various research papers, some published together with Prof. Zawadzki, Bretsznajder explained completely new phenomena which occur during the formation of solid phases in thermal dissociation processes and in reversible reactions. The main findings were as follows:

1. The first observation of phenomena of adsorption and chemisorption at high temperatures for gases reacting on the surfaces of crystalline phases; these lead to the occurrence of a "false equilibrium" (Fig. 1) characteristic at that moment of the state of the reacting surfaces of solid phases [3], and connected with the rapid formation of new phase nuclei. In this research work, detailed explanations were given for the reasons for the deviation of the course of the reaction from the phase rule, the occurrence of unstable active forms and their influence on the course of the reaction.

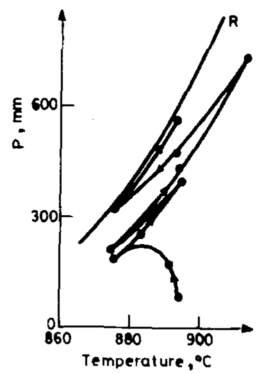

Fig. 1 Course of the process of thermal dissociation of calcium carbonate under pressure much lower than equilibrium pressure

2. The finding of an interesting regularity of importance as concerns the explanation of the mechanism of formation of the solid nucleus in reactions in which products and substrates take part. It was assumed that the new phase nucleus formed always increases to some definite value, and that next, due to the difference in size of the elementary cells of the substrate and the product, there occurs the

separation of a small crystal of a product from the substrate lattice, and the process of creation must then start again. From this, the conclusion was drawn that the observed reaction rate must be directly proportional to the rate (i.e. frequency) of nucleus formation. This conclusion was confirmed by the analysis of kinetic curves of crystal growth and the results of experiments on the reaction rate, which depends on the distance of the reacting surface from the state of equilibrium (Fig. 2). This conclusion resulted in the finding that the logarithm of the number J of crystalline nuclei of a new phase formed in unit time is inversely proportional to the squared logarithm of supersaturation (Fig. 3):

$$\log J = -A\left(\log^2 \frac{p}{p_0}\right)^{-1} \quad (1)$$

where p = the actual concentration

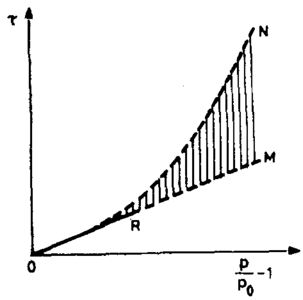

Fig. 2 Relationship between the reaction rate of thermal decomposition r and the deflection of state of equilibrium $\frac{p}{p_0}-1$. The line OM designates relationship of rate of reaction occurring at the border of substrate—product. Area NRM (crossed lines) shows increase of rate due to forming nuclei of a new phase

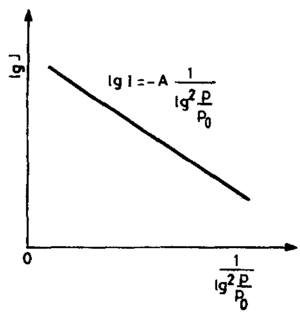

Fig. 3 Dependence of forming rate of nuclei J on state of supersaturation $\frac{p}{p_0}$

As a result, it was shown that in a very complicated process the same simple laws must hold as are responsible, for example, for the formation of nuclei(the small drops during the condensation of saturated steam). In this simple phenomenon, the reason why the nucleus is formed is known; this is the fact that accidental density fluctuations exist. From this, the new and important conclusion can be drawn that in thermal dissociation reactions accidental fluctuations must decide the formation of new phase nuclei. These fluctuations result in the accumulation of a sufficient quantity of elements at some sites of the substrate solid phase, and from this quantity of elements a new crystalline nucleus of a product. On the basis of certain known analogies, it can be accepted that the nucleus can arise when enough lattice micro-defects with the product composition can accumulate at certain sites on the substrate surface. Because of the thermal vibrations of the ions or atoms at the lattice points, the micro-elements are active, especially in the thermal dissociation area, and easily change their position in the lattice, so that fluctuations of the micro-defects are also possible. Such a mechanism seems to be confirmed by the research conducted recently by Maciejewski and Oswald and presented during the Third Seminar [5].

3. The finding of a relationship between the apparent activation energy and the temperature of the thermal dissociation process carried out under various pressures of a gaseous reaction product.

The original results of this research are shown in Fig. 4.

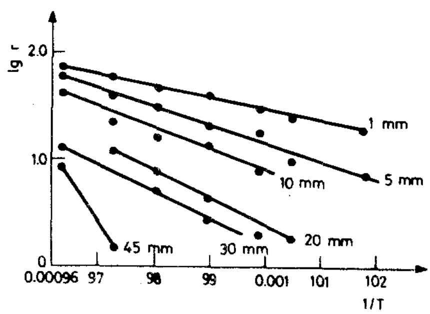

Fig. 4 Relationship between decomposition reaction rate of calcium carbonate and temperature and pressure of carbon dioxide over the system

This relationship is known in the literature as the Zawadzki–Bretsznajder relationship [6]. Its consequences are the existence of an isokinetic temperature and a compensation effect [7].

4. The application to dissociation reactions of the theory of similarity of phenomena formulated by Diakonow [8] for reactions in the kinetic area.

Bretsznajder tested [9] the general Diakonow criterion formula:

$$\frac{1}{K_0} = 1 - R_a \tag{2}$$

where $K_0 = \frac{r_1}{r}$ is the rated number of contacts defining the ratio of the time for the reagents to be in the reaction area to the time needed by the substrates to react ($r = r_1 - r_2$) and $R_a = \frac{r_2}{r_1}$ is the rated number of system discrepancies from the state of equilibrium, defining the rate of restoration of the state of thermodynamic equilibrium.

He examined whether the above formula is identical with the kinetic formula of thermal dissociation

$$A_{(\text{solid substance})} = B_{(\text{solid substance})} + C_{(\text{gas})} \tag{3}$$

if the kinetic formula of reaction (3) describes the kinetics of elementary transformations.

The school of Bretsznajder subsequently extended this research to reactions occurring under conditions of irreversibility [10].

These four groups of problems, selected as examples, not only present theoretical aspects, i.e. explain the mechanism and kinetics of processes, but also contributed significantly to the recognition of some new phenomena in technological processes. The relevant research related to the production of active catalysts, the dissolution of raw materials containing aluminium, the leaching of sulphur from Polish ore, the precipitation of pure aluminium compounds, the decomposition of basic aluminium sulphate salts, catalysis in solution, the separation and utilization of residual hydrogen sulphide, and many other problems. The characteristic feature of all Bretsznajder's research work was its close relation to the national economy.

Bretsznajder is a scientist who created his own school. During about twenty years, 150 masters of science, 10 doctors of science and 3 associate professors graduated from this school. The Scientific and Organizing Committee of the Stanisław Bretsznajder Seminars would like to express the wish that these Seminars might be a modest, but specific continuation of the work of the school.

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