

Практикум по общей химической технологии

под редакцией
проф. И. П. Мухленова

Издательство «Высшая школа»
Москва



A Practical Course in Chemical Technology

Edited
by
I. P. Mukhlyonov

Translated from the Russian
by V. Vopyan

Mir Publishers
Moscow

281
241

First published 1982
Revised from the 1979 Russian edition

TO THE READER

Mir Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make.

Our address is:

Mir Publishers

2 Pervy Rizhsky Pereulok

I-110, GSP, Moscow, 129820

USSR

На английском языке

© Издательство «Высшая школа», 1979

© English translation, Mir Publishers, 1982

Contents

Preface	7
Chapter 1. Noncatalytic Processes	9
Laboratory Work 1. Production of Phosphoric Fertilizers by Acid Decomposition of Natural Phosphates	23
Laboratory Work 2. Carbonization of Ammoniacal Brine	38
Laboratory Work 3. Froth-Bed Gas Absorption	47
Laboratory Work 4. Polycondensation of Dichloroethane and Sodium Tetrasulphide (Production of Polysulphide Rubbers or Thiokols)	58
Laboratory Work 5. The Kinetics of Sulphide Ore Roasting	64
Laboratory Work 6. The Kinetics of Dicalcium Silicate Formation	74
Laboratory Work 7. Coal Carbonization	80
Laboratory Work 8. Low-Temperature Carbonization	89
Laboratory Work 9. Pyrolysis of Petroleum Products	96
Laboratory Work 10. Studying the Oxidation Rate of Metals at Elevated Temperatures	106
Laboratory Work 11. Manufacture and Testing of Plastics	116
Chapter 2. Catalytic Processes	126
Laboratory Work 12. Catalytic Cracking of Petroleum Products	134
Laboratory Work 13. Contact Oxidation of Sulphur Dioxide	142
Laboratory Work 14. Oxidation of Ammonia	151
Laboratory Work 15. Dehydrogenation of Ethyl Benzene	159
Laboratory Work 16. Catalytic Dehydrogenation of Alkyl Benzenes	163
Laboratory Work 17. Dehydration and Dehydrogenation of Ethanol in the Production of Butadiene	172
Laboratory Work 18. Copolycondensation of Phenol and Formaldehyde	182
Laboratory Work 19. Catalytic Processes of Formaldehyde Production	194
A. Conversion of Methanol	195
B. Incomplete Oxidation of Methane	198
C. Oxidation of Dimethyl Ether in a Fluidized Catalyst Bed	201
Laboratory Work 20. Esterification of Alcohols with Carboxylic Acids	207
Chapter 3. Automated and Computerized Apparatus	221
Laboratory Work 21. Automated Absorption Plants	224
Laboratory Work 22. Performance Analysis of Liquid-Phase Reactors	255
Laboratory Work 23. Optimization of a Contact Plant of Sulphuric Acid, Operating on a Double Contact-Double Ab- sorption Principle	271
Laboratory Work 24. Analysis of Heterogeneous Catalytic Processes on an Automated Continuous-Circulation Plant	293
Laboratory Work 25. Analysis of Reactor Models	299
A. Continuous Tubular Reactor	299

B. Batch Perfectly Mixed Reactor	304
C. Continuous Perfectly Mixed Reactor and a Cascade of Reactors	306
Chapter 4. Electrochemical Processes	341
Laboratory Work 26. Electrolysis of Sodium Chloride Solution . . .	344
Laboratory Work 27. Electrolysis of Lead Chloride Melt	324
Laboratory Work 28. Chromium Plating of Metals	329
Chapter 5. Preparation of Raw Materials and Material Analysis Techniques	339
Laboratory Work 29. Flotation	340
Laboratory Work 30. Water Treatment	345
Laboratory Work 31. Determination of Dispersity, Density of Solid Loose Materials, Density and Viscosity of Liquids	353
Laboratory Work 32. Analysis of the Porous Structure of Solids . . .	367
A. Analysis of Porous Structure Using an Absorption Vacuum System with a Quartz Spring Balance	369
B. Analysis of Secondary Structure of Porous Solids by Mercury Porometry	375
C. Determination of Specific Surface by the Low-Tem- perature Nitrogen Sorption Method	381
D. Determination of Specific Surface in a Chromatographic System	385
Laboratory Work 33. Analysis of Sorbent and Catalyst Structure by Electron Microscopy	388
Laboratory Work 34. Thermal Analysis	393
Laboratory Work 35. Analysis of Solid Materials by Infrared Spectroscopy A. Location of the Maxima of the Main Absorption Bands in the Spectra of Known Compounds	396
B. Qualitative Analysis of a Mixture of Inorganic Salts by Infrared Spectra	400
C. Determination of the Structure of Inorganic Compounds from Infrared Spectra	401
Laboratory Work 36. Gas Analysis	402
Laboratory Work 37. Chromatographic Analysis of Multicomponent Gas and Liquid Mixtures	403
A. Effect of the Sample Injection Technique on the Accuracy of Analysis Results	416
B. Separation of Methane-Air Mixture	420
C. Qualitative and Quantitative Analysis of a Mixture of Aromatic Hydrocarbons	421
D. Analysis of a Mixture of Alkyl and Alkylene Benzenes	421
E. Separation and Quantitative Analysis of Mixtures Containing O ₂ , N ₂ , CO, CH ₄ , and CO ₂	423
Appendix	425

Preface

The course in chemical technology taught at chemical colleges and departments consists of three parts: lectures, practical studies, and laboratory works. A combination of these three teaching methods provides students with a sound foundation for studying any discipline of chemical technology.

This course is aimed primarily at presenting the basic laws of chemical technology, applicable to most chemical processes as well as processes of the metallurgical, silicate, pulp-and-paper and fuel processing industries. Studying the basic types of chemical processes—homogeneous and heterogeneous, noncatalytic and catalytic, electrochemical—and the associated reactors is combined with analysis of concrete processes of the greatest importance for the national economy. Particular attention is given to typical processes embodying the major aspects of chemical technology. The lectures and laboratory works also cover the structural materials used in the manufacture of chemical reactors.

In the 3rd Russian edition, emphasis is placed on analysis of automated and computerized reactors, as well as new methods and instruments employed in the investigation of material properties. Thus, students performing a laboratory work better assimilate the facts presented in lectures, acquire skills for controlling industrial processes with the aid of advanced instrumentation and computers, learn analytical procedures, and improve their techniques of processing the experimental results.

In a laboratory, students carry out the first (according to the syllabus) experiment. Each work covers practically all stages of experimental procedures. First of all, students learn about the subject from the textbook in chemical technology, the present practical course, and the literature recommended at the end of each work. Then, they go through the safety rules to be observed in a chemical labo-

ratory (see Appendix, p. 425) and the instructions to the work being carried out. After a briefing by the instructor (colloquium), students are assigned to conduct the experiment. Students then become familiar with the experimental setup, check whether it is assembled correctly, activate individual units, and calibrate some instruments.

The next stage is an experimental study of the effect of some process parameters on the course of the process. Some assignments involve analysis of the effect of temperature, concentrations, time, and other factors within a broad range so as to enable students to plot the process characteristics as a function of a particular variable.

Students make the necessary calculations using the experimental results and write a report including the statement of the problem and purpose of the work, process flow sheet calculations and plots based on the experimental results, and conclusions. An assignment must be stated in such a manner as to enable students to complete the experiment within six hours. Every student must carry out laboratory works from all six chapters, while particular assignments are given depending on his or her specialization.

Most of the works included in the 3rd Russian edition have been presented by the Lensovet Technological Institute in Leningrad. Other contributors include the Kuybyshev Polytechnic Institute (Work 16), Kazan Institute of Chemical Technology (Work 20), and the D. I. Mendeleyev Institute of Chemical Technology in Moscow (Work 25).

The introductions to all works have been written by I. P. Mukhlyonov. Works 1, 2, 5, 10, and 14 have been written by E. S. Tumarina; Works 4, 7, 8, 9, 11, 12, 18, 19, 28, and 36 by A. Ya. Averbukh; Works 17 and 27 by B. A. Kopylev; Works 6, 15, 29, 30, and 31 by E. S. Rumyantseva; Work 33 by N. P. Matveyeva; Work 34 by E. A. Vlasov; and Works 35 and 37 by G. V. Cherepkov.

The authors will be grateful to all those who will send their critical comments and suggestions concerning the practical course.

Chapter 1

Noncatalytic Processes

In general chemical technology, systems and processes are classified in accordance with the phase state of the reacting substances since it determines the selection of processing techniques and design of the reactors. All interacting systems and the corresponding processes are divided into homogeneous and heterogeneous ones. The homogeneous systems are characterized by all interacting substances being in a single phase—gas (G) or liquid (L). The heterogeneous systems comprise at least two phases*. The following may be the types of two-phase systems: gas-liquid (G-L), gas-solid (G-S), two immiscible liquids (L-L), liquid-solid (L-S), and two solid phases (S-S). The systems most commonly used in the industry are L-S, G-L, and G-S. In many cases, industrial processes involve three or four phases, for example, G-L-S, G-S-S, G-L-S-S, and so on. Solid mineral stock almost invariably includes several phases for each mineral is essentially equivalent to an individual phase. In general, however, only the basic minerals are considered as individual phases, while the numerous impurities are disregarded.

In some cases, all solid materials interacting with other portions of a system are considered, for simplicity, as a single solid phase, while the liquid emulsion consisting of two or more phases is regarded as just one liquid phase, and the system is referred to as L-S although it essentially comprises two liquid and several solid phases. The L-L and L-S systems normally include a gas phase stemming from the fact that liquids and many solids undergo some degree of evaporation. However, the resulting gas (vapour) phase is taken into account, provided it plays a significant role in the interaction. As a general rule, only those substances and process parameters are taken into account in the analysis and development of processes, whose influence on the latter is decisive.

The laboratory works presented in this manual cover processes with different combinations of phases in two- and polyphase systems. Some of the processes are initiated in a homogeneous liquid

* A group of substances involved in a physical or chemical interaction is referred to as a system. A phase is the totality of homogeneous portions of a system, having identical composition as well as physical and chemical properties and separated from other portions of the system by a definable boundary.

system which then becomes heterogeneous as a result of emergence of a new liquid (Works 4 and 17), solid (Works 2 and 9), or gas (Works 1 and 26) phase. In the processes of solid fuel pyrolysis and decomposition of limestone (Works 6, 7, and 8), the starting material is solid with a gas phase appearing at the end of the process. In other cases, a process initially involves a two-phase system, then yields a product in the form of a third phase (Work 2). Sometimes, a plurality of products in the form of different phases are yielded (Works 1, 18, and 30).

An *industrial chemical process* comprises the following interrelated unit processes (steps): (1) transfer of the reacting substances into the reaction zone, (2) chemical reactions, and (3) removal of the products from the reaction zone.

The *transfer of the reacting substances* into the reaction zone in homogeneous systems as well as within each liquid or gas phase of a heterogeneous system is by way of molecular diffusion or convection. The heterogeneous systems additionally involve the step of transition of a reacting substance from one phase to another, which occurs through absorption, adsorption or desorption of gases, condensation of vapours or evaporation of liquids, melting of solids or their dissolution in liquids. The phase change is in most cases the slowest step of a process and determines its overall rate. It is essentially a complex diffusion process.

The *chemical reactions* occur between the basic reagents, between the basic reagents and impurities, as well as between impurities. Several consecutive (or, in some cases, simultaneous) reactions may yield the same product. Main and by-products are formed in a process. Since the feed stock always contains various impurities, speaking strictly in chemical terms one may assume that a process involves a great number of reactions. However, in practice, account is taken of only one or several reactions yielding a sizable amount of main and by-products.

The *removal of products* from the reaction zone is also by way of molecular diffusion, convection, and phase change, just as in the case of their transfer into the latter. The product is often removed through condensation or absorption from a gaseous reaction mixture and through precipitation or desorption from a liquid one.

Processes and the associated reactors are also classified according to some of the operating conditions. Such a classification implies, primarily, batch processes and continuous ones conducted in flow reactors. As far as the degree of mixing of the reaction masses is concerned, processes and reactors belong to the following categories in terms of the limiting cases: plug-flow, perfect-mixing, and partial-mixing ones. Classification according to temperature conditions includes isothermal, adiabatic, and polythermal flow reactors and processes conducted in the latter.

According to reaction types, processes are divided into simple (Works, 1, 3, and 13) and complex ones that may involve consecutive and parallel reactions (Works 2, 14 and 18). Processes are also known to be reversible and irreversible, the latter being unidirectional. Depending on the actual conditions, reversible processes may be forward or backward. Irreversible processes are observed in the decomposition of natural phosphates by acids, as well as in polymerization and polycondensation. Typical irreversible processes also include fuel pyrolysis, roasting of raw sulphides, and some others covered in the laboratory works. Reversible processes include causticization of soda solution, the phase changes and reactions involved in the carbonization of ammoniacal brine, oxidation of sulphur dioxide, and others.

The *equilibrium in processes* corresponds to equality of the rates of the forward and backward processes, which results in the system component ratio remaining invariable until changes occur in the process conditions. Changes in such process parameters as temperature, pressure, and concentration of the reacting substances upset the equilibrium of a system, thereby bringing about spontaneous chemical reactions and diffusion processes in the system with the result that its equilibrium is restored. The effect of the basic process parameters on equilibrium is determined by Le Chatelier's principle stating that if a system in an equilibrium state is disturbed, it will readjust itself so as to minimize the disturbance and restore the equilibrium.

A quantitative measure of mobile equilibrium is the chemical reaction equilibrium constant for all homogeneous and heterogeneous processes occurring in the kinetic region. For example, in the case of processes in which the percentage conversion is determined by the equilibrium of the reaction



the equilibrium constant K is determined from the following equation:

$$K = \frac{[D^*]^p}{[A^*]^m [B^*]^n} \quad (1.1)$$

where $[D^*]$, $[A^*]$ and $[B^*]$ are the equilibrium concentrations of the reacting substances. In chemical-engineering studies Eq. (1.1) is often simplified.

The equilibrium of heterogeneous processes in the diffusion region is qualitatively defined by the Le Chatelier principle, whereas in quantitative terms it is defined by the distribution law establishing a constant ratio between the equilibrium concentrations of a component in different phases of a system at constant temperature and pressure. When applied to G-L systems, the distribution law is re-

ferred to as Henry's law:

$$p = \psi C_1^* \quad (1.2)$$

where p is the equilibrium partial pressure of the component absorbed in the gas, ψ is the Henry's law constant having the dimension of pressure, and C_1^* is the mole fraction of the component absorbed in the solution.

The phase equilibrium in two- and polyphase systems is governed by the phase rule

$$F = 2 + C - P, \quad (1.3)$$

where F is the number of degrees of freedom, or variance, of a system, C is the number of individual chemical components in the system, P is the number of phases, and 2 is the number of external factors affecting the phase equilibrium. As a rule, the external factors include temperature and pressure. In some cases, pressure is ignored and instead of 2 we have 1 (e.g. when the effect of pressure variations is insignificant).

Experimental or calculation data are used to plot, on the basis of the phase rule, phase diagrams in which a particular property of a system, such as melting or boiling point, is determined as a function of composition.

The *process rate* is the resultant of the rates of the forward, back, and side reactions plus those of the convection and diffusion of the starting substances into the reaction zone and of products from the latter. If the reaction rate is less than that of the diffusion processes involved in the introduction of the reacting substances and removal of the products, then the process is said to occur in the kinetic region, and, in order to speed it up, one must raise the temperature, increase the reagent concentration, and use catalysts. The kinetic region is where most homogeneous processes take place. If the reaction rate exceeds by far the rate of the diffusion processes, the overall rate is determined by diffusion (the process occurs in the diffusion region). Such a process can be accelerated primarily by mixing the reacting substances and controlling pressure. The use of a catalyst does not make the diffusion faster. Many heterogeneous processes are associated with the diffusion region. If the rates of the reactions and diffusion processes are commensurate and the process is observed in a region intermediate between the kinetic and diffusion ones, one should first of all resort to the factors that speed up both the reactions and the diffusion at a time, that is increase the temperature and concentrations.

The rate of a process is calculated on the basis of the product yield within a time interval or the process rate constant (coefficient).

The first kinetic characteristic of a process, which is calculated from experimental data, is the product yield. The product yield x

is defined as the ratio of the actual amount of the obtained product (G_a) to the maximum amount that could be obtained from the starting substances (G_{\max}):

$$x = G_a/G_{\max}. \quad (1.4)$$

The maximum product amount G_{\max} is calculated for chemical reactions, at a stoichiometric ratio of the starting substances (e.g. in ammonia synthesis), as a sum of the amounts of the starting substances that could enter into the reaction (in accordance with the reaction equation). For example, in the case of the reaction



the maximum amount of the product D is

$$G_{\max} = G_A + G_B. \quad (1.5)$$

In practice, the starting substances usually are not in a stoichiometric ratio. Then, the yield is calculated from the main (most valuable) starting substance. For instance, when the atmospheric oxygen is used to oxidize sulphur dioxide to sulphur trioxide, ammonia to nitrogen oxide, methanol to formaldehyde, or ethylene to ethylene oxide, the yield is calculated without taking oxygen into account, that is G_{\max} is determined with respect to the end product amount that would be derived as a result of complete conversion of SO_2 , CH_3OH , and $\text{CH}_2 = \text{CH}_2$, respectively. For example, in the case of oxidation of SO_2 to SO_3 , G_{\max} in the final mixture at the reactor exit will be

$$G_{\max} = G_{\text{SO}_3} + G_{\text{SO}_2}. \quad (1.6)$$

Similarly, the amount of water spent in hydration, hydrolysis, and other such processes is not taken into account either.

In Eq. (1.5), the amounts G of the substances can be substituted by their concentrations C_f in the final mixture having a definite (measured) volume v in view of the fact that $G = Cv$. For example, the yield of the sulphur trioxide resulting from oxidation of sulphur dioxide is determined from the equation

$$x = C_{\text{fSO}_3}/(C_{\text{fSO}_3} + C_{\text{fSO}_2}). \quad (1.7)$$

If the maximum amount of the product of a chemical reaction is assumed to equal the amount that would be obtained in accordance with the equation of the reaction (disregarding the equilibrium conditions), the yield is referred to as percentage conversion. The percentage conversion of the main starting substance can be determined from the equation

$$x = (G_1 - G_f)/G_1 = (C_1 - C_f\beta)/C_1, \quad (1.8)$$

where G_i and G_f are the initial and final amounts of the main starting substance, C_i and C_f are its initial and final concentrations, and β is a factor of conversion of the final concentration with respect to the initial one, the factor β takes into account changes in volume as a result of the reaction (synthesis or decomposition) as well as temperature and pressure fluctuations.

In mass-transfer processes, the yield defined by Eqs. (1.4) and (1.8) is called the degree of phase-to-phase transfer or, more specifically, the degree of absorption, desorption, and so on. In this case, the maximum amount of the product is assumed to be that present in the donating phase such as gas during absorption. The percentage conversion of irreversible processes tends to unity in the course of time while that of reversible processes is always less than unity.

As far as reversible processes are concerned, two more definitions are associated with the product yield. The theoretical or equilibrium yield (x_{eq}) is the ratio of the amount of the product at equilibrium (G_{eq}) to the maximum possible amount that is

$$x_{eq} = G_{eq}/G_{max}. \quad (1.9)$$

The yield as percentage of the theory (x_a) is the ratio of the actually derived amount of the product to that expected at equilibrium, that is

$$x_a = G_a/G_{eq} = G_a/G_{max}x_{eq}. \quad (1.10)$$

In Eqs. (1.9) and (1.10) just as in Eq. (1.4) G_{max} can be expressed as the sum of the amounts of the starting substances G_A and G_B . In the case of homogeneous media, the amounts of substances can be substituted by their final concentrations (cf. Eqs. (1.7) and (1.8)). The product yield x may be dependent on many parameters and even in the case of hydrodynamic similarity it is expressed a complex function which can be written, for the reaction



as follows:

$$x = f(\tau, t, P, C_A, C_B). \quad (1.11)$$

Proceeding from expression (1.11), the dependence of the product yield on any parameter, such as temperature t , in all laboratory works must be determined with all the other process parameters included in this expression being constant, that is measurements should be taken and analyses made at different temperatures but after the same time interval τ has elapsed from the onset of the reaction, at the same starting substance concentrations, and at a constant pressure P . In addition, to maintain the hydrodynamic conditions constant, all experiments should be carried out using the same experimental setup (or geometrically similar setups), at

constant flow rates of the reaction masses, at a constant ratio between the volumes of the interacting phases ($S : L = \text{const}$, $S : G = \text{const}$, $L : G = \text{const}$, etc.), and under constant mixing conditions. Should one of these conditions not be met, then, in comparing the experimental results, for example, in plotting the yield-versus-temperature curve, one must introduce correction factors derived from other experiments or calculations.

Typical curves showing the dependence of the product yield on the basic process parameters with all the other experimental conditions

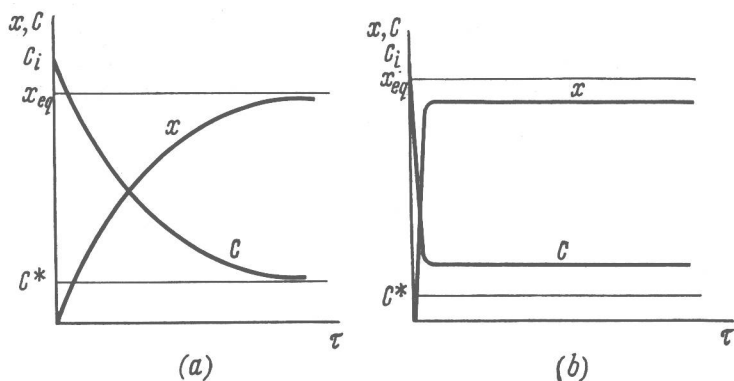


Fig. 1. Product yield x and main starting substance concentration C versus reagent residence time τ :

a —in plug-flow reactor; b —in perfectly mixed reactor

being invariable are presented in Figs. 1 through 5; whatever departures from these curves arise while the experimental data are processed in the laboratory works should be explained in the reports (the factors causing these departures must be mentioned). Fig. 1 represents the kinetics of a chemical process (a) in batch (non-flow) reactors and plug-flow reactors in which the starting reagents are not mixed with the reaction products and (b) in continuous reactors with perfect mixing of the reagents with the reaction products.

In batch and plug-flow processes, the equilibrium (C^* and x_{eq}) is attained sooner than in processes involving mixing, however, processes with mixing under isothermal conditions lead to an increase in x_{eq} and a decrease in the equilibrium concentration C^* of the starting substance, as compared to the adiabatic conditions typical of plug-flow reactors. The plug-flow and perfect-mixing conditions are extreme. The x and C curves for real processes occupy an intermediate position between the plug-flow and mixing curves (Fig. 1a, b,).

The closest one can get to the plug-flow conditions is in apparatus for homogeneous processes involving gases, packed towers, and reactors with a solid filter bed, particularly shaft furnaces and converters. The perfect-mixing conditions are best attained in stirred liquid reactors, bubble columns and froth apparatus, as well as fluidized-bed reactors.

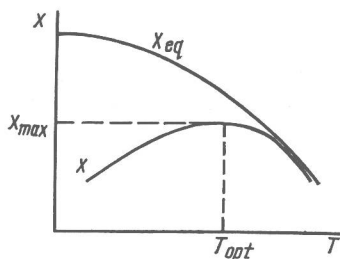


Fig. 2. Effect of temperature on conversion x and equilibrium yield x_{eq} in isothermal reversible reactions

Raising the temperature of an exothermic process brings the system to equilibrium much sooner but the equilibrium shifts toward the starting substances. As a result, the product yield increases with temperature at a point far from the state of equilibrium, reaches the maximum at an optimal temperature, then decreases as the temperature continues to rise (Fig. 2).

When the temperature of an endothermic process is raised, the product yield increases monotonically to a certain limit depending on the nature of the reacting substances (Fig. 3).

Increasing pressure (Fig. 4) in gas reactions accompanied by a reduction of the gas mixture volume and in absorption or conden-

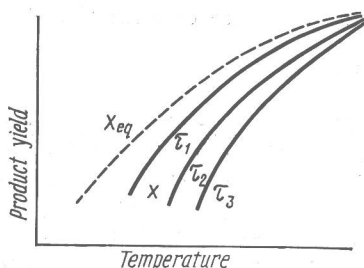


Fig. 3. Effect of temperature on equilibrium (x_{eq}) and actual (x) yields in endothermic reversible reactions at different reagent residence times: $\tau_1 > \tau_2 > \tau_3$

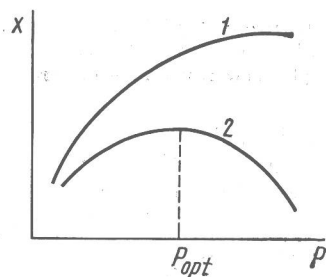


Fig. 4. Product yield versus pressure:

1—in processes with [decreasing volume $\Delta n < 0$; 2—in processes with increasing volume $\Delta n > 0$

sation of gases and vapours leads to a continuous but gradually slowing increase in the product yield. When the volume of the gas mixture in such reactions expands, increasing pressure speeds up the process but the equilibrium shifts toward the starting substances (Le Chatelier's principle). In the latter case, the yield curve 2 passes