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Conference Paper

Study of Recrystallization Mechanism in Disperse Systems*

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An experimental and theoretical study is described of the recrystallization kinetics and mechanisms for some model substances of different solubilities like ammonium-aluminum sulfate, silica gel, and gypsum, under temperature and concentration variations. The assymetry of kinetic parameters for dissolution and recrystallization is due to different influence the solid phase surface exhibits in hindering or favoring hydration/dehydration and incorporation/elimination equilibria. A major obstacle in theoretical interpretation is the lack of a comprehensive theory of concentrated solutions.

Most of natural solids as well as contemporary technology materials are disperse systems. Many of these systems are composed of a large number of crystals. Properties of any polycrystalline system depend on size and homogeneity of crystals. As a rule, crystals of the same system are usually all different in size. The crystalline system composed of crystals in state of equillibrium with saturated solution may involve a thermodynamic way of recrystallization: large crystals may grow at the cost of smaller ones. The recrystallization phenomenon, however, is not observed under isothermal conditions. This is quite understandable for crystals exceeding 10^{-5} cm. size. According to the well-known Thomson equation the solubility of crystals exceeding 10^{-5} cm is not practically size dependent. Hence, neither recondensation (isothermal distillation) should take place. This reasoning is true for isothermal conditions. Indeed, recrystallization is not observed under isothermal conditions when studying different systems composed of saturated solution and crystalline particles of dissimilar dispersity (alumo-ammonium sulphate solution, Seignette salt solution, saccharose, gypsum).

If, however, there are variations (periodical) of the system temperature or that of concentration of the intercrystalline mother solution (dispersion medium), or both, the recrystallization process is observed even in case of rather coarse particles. The question of the disperse phase particle growth at cost of recondensation (in particular case — recrystallization) both in process of structure formation and when using various disperse materials becomes therefore of great theoretical and practical importance.

The recondensation process is known to occur in disperse systems with dissimilar aggregate state of substance of disperse phase and dispersive medium: in case of solidification of mineral astringent substance[1], by hydrothermal

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processing of adsorbents, catalysts[2], and natural disperse minerals[3], by crystallization and coprecipitation of substances from solutions[4], by ripening and ageing of precipitates[5] and photoemulsions[6], in aerosols[7], *etc.*

The recondensation process is usually substantiated by the Ostwald's ripening and isothermal distillation stipulated by the influence of size of disperse phase particles on their solubility (vapour pressure), as well as by the Gibbs-Curie-Wolf effect.

Upon the analysis of relationship established between the heat- and mass-exchange of the crystallizable disperse systems we arrived at conclusion that there should exist a recrystallization mechanism responsible for the growth of macroscopic-size particles, the recrystallization intensity being according to this mechanism of the same order as the intensity of growth and dissolution of the disperse phase particles. It is not a difficult task to confirm experimentally the existence of such a mechanism. Fig. 1 and 2 show quantity- and size variation of the disperse phase particles as a result of recrystallization under the isothermal-isohydric conditions of boiling of the crystallizing disperse system. The experimental installation diagram is shown in Fig. 3. If the experiments are run under constant temperature and pressure (at which no boiling takes place), the recrystallization doesn't happen. Neither duration of

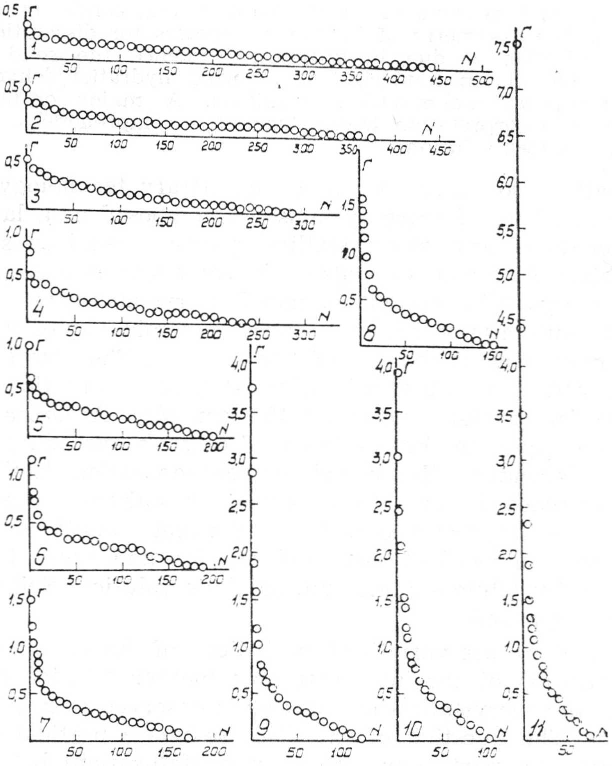


Fig. 1. Plots of the alumo-ammonium sulphate crystal variation series as arranged according to diminishing mass values.

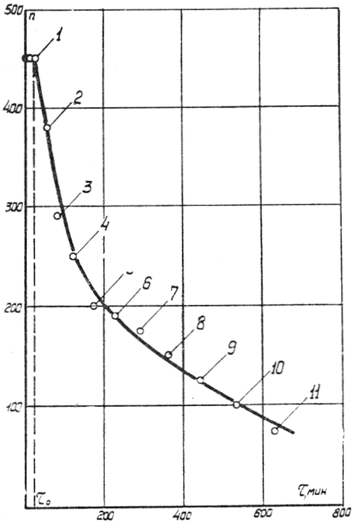


Fig. 2. Variation of the alumo-ammonium sulphate crystal number (the initial size being 5 + 7 mm) in the course of their recrystallization under isothermal-isohydrical conditions of boiling at 70 °C.

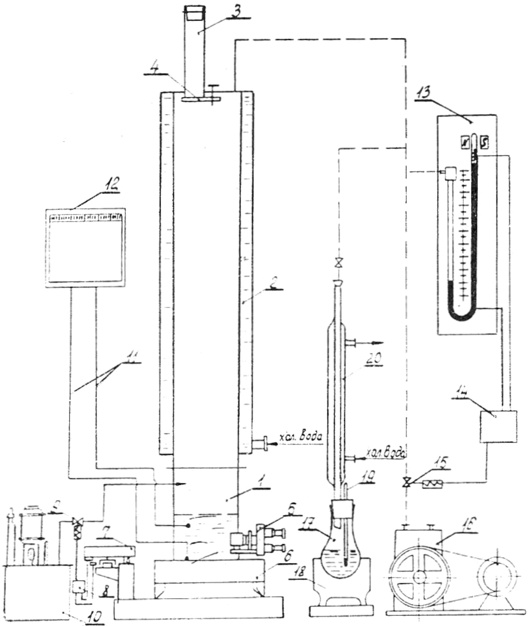


Fig. 3. Scheme of the experimental plant: *1* — vacuum catalyzer; *2* — surface condenser; *3* — crystal receiver; *4* — rotating little bottom; *5* — refractometer; *6* — electric heater; *7* — scales; *8,14* — relays; *9,15* — electromagnetic valve; *10* — thermostat; *11* — thermocouples; *12* — potentiometer; *13* — mercuric electrocontacting manometer; *16* — vacuum pump; *17* — additional crystallizer; *18* — electric heater; *19* — thermometer; *20* — reflux condenser.

the experiment nor mechanical stirring bring about alteration in the size distribution of particles.

If, however, the pressure is lowered and the boiling occurs, a rapid recrystallization begins. (Boiling here involves refluxing; the partially evaporated water losses are compensated by an automatic »injection« of solvent. So, the mass of water and crystals in the system remains constant).

Fig. 1 illustrates variation of quantity and size of the system particles as a function of the experiment duration: *1* — 25 minutes, *2* — 56 min., *3* — 58 min., *4* — 112 min., *5* — 175 min., *6* — 228 min., *7* — 291 min., *8* — 362 min., *9* — 442 min., *10* — 533 min., *11* — 628 min.

Figure 2 is drawn up on the basis of Fig. 1 data. These Figures show that as recrystallization proceeds the larger crystals of the alumo-ammonium sulphate grow while the smaller ones dissolve and disappear completely, and though the overall quantity of particles is reduced, the total weight of crystals (as well as that of mother solution) remains constant. Similar results were obtained with other substances both organic and inorganic.

Such a significant and intensive growth of particles cannot, certainly, be accounted for by any of the known recondensation mechanisms. And it is the aim of this study to discover the regularities of the recrystallization phenomenon in disperse systems.

Analysis of our results allows a conclusion to be drawn that an indispensable condition of recrystallization should be a periodic variation of temperature and concentration of disperse medium. Under boiling conditions the periodic variation takes place due to the overheating of suspension near the heating surface and the subsequent cooling at the expense of self-evaporation of solvent in boiling up at the liquid-vapour interface, as well as owing to the variation of temperature depression in lower and higher layers of boiling suspension. Periodic variation of the solution concentration (under the effect of temperature or the solvent coming from the reflux condenser) brings about a periodic dissolution and crystallization of particles.

Study of conditions of the collective growth and dissolution of the disperse phase particles has shown that the recrystallization process under the above mentioned conditions is possible in case the relative linear dissolution rate (ratio of the linear dissolution rate of smaller particle to the linear dissolution rate of larger one) — is greater than relative rate of particle growth.

$$(L_1/L_2) > (L_1'/L_2')$$

where L_1 and L_2 are the linear dissolution rates, L_1' and L_2' are those of growth for the smaller and larger particle, respectively. Therefore, the reason for recrystallization is a different effect of the disperse phase particle sizes on the linear rate of growth and dissolution of particles.

If we suggest that the growth (diminution) of any crystal is proportional to its mass, and designate the relative growth (diminution) of particle as:

$$m_j = (g_j - g_{oj})/g_{oj}$$

where g_{oj} and g_j are initial and final masses of the j^{-th} particle, then we find

$$r_j = \sqrt[3]{r_{oj}^3 \pm m_j\, r_j^3} \tag{2}$$

We suppose that m_j is a constant value, then for r_i particle we find:

$$r_{i.\,k} = r_{oj} \sqrt[3]{1 + m_{j.\,k}} \tag{3}$$

$$r_{i.\,p} = r_{oi} \sqrt[3]{1 + m_{j.\,p}} \tag{4}$$

In this case dependence of r_i on r_{oi} should be of linear nature. In many experiments such a linear dependence is observed.

Fig. 4 shows a combined plot of variation of the linear sacharose crystals' dimensions in their collective growing and dissolving. As can be seen from the plot, the linear dependence is kept, in case of not very fine crystals, both in growing and dissolving of them. The smaller are crystals (in size) the more is deviation from linearity. Besides, the $m_{j.k}$ is always much lower than the $m_{j.p}$ value. Hence, the relative growth (diminution) of crystal linear dimensions is not the same for dissolution and crystallization processes. Also this value especially for small crystals is dependent on their size as well.

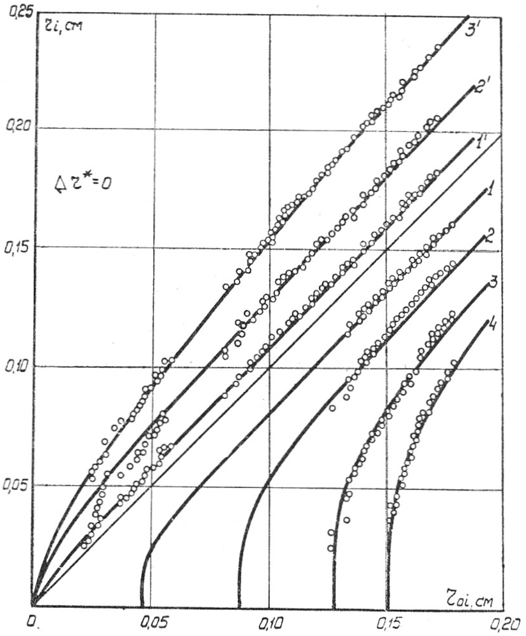
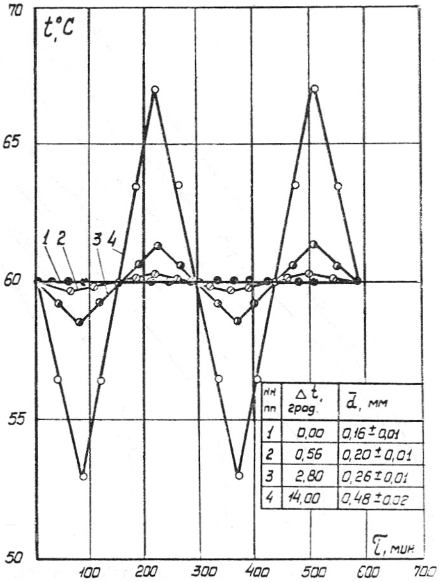


Fig. 4. Combined plot of the sucrose crystal (linear) dimension variation by their collective growth (1′, 2′, 3′) and dissolution (1, 2, 3, 4).

Hence, some conclusions may be drawn:

For instance, if the amplitude of temperature and concentration variations of disperse phase is equal to zero, then the periodical growth and dissolution of the disperse phase particles is absent. Therefore, a different effect of size on the linear rate of growth and dissolution of particles does not manifest itself and the recrystallization process will not occur. As the variation amplitude increases (up to a certain extent) the intensity of recrystallization should increase too, because in this case the growth and dissolution stages take a more profound course and the effect of size of particles on their growth and dissolution rate shows itself more distinctly. The higher is frequency of variations the greater number of elementary recrystallization actions per the same time and, hence, the recrystallization intensity should increase.

All these consequences were confirmed by experimental facts. It has been found that the intensity of recrystallization grows with amplitude and frequency of temperature- and concentration variation of disperse medium, the solubility of the disperse phase substance in disperse medium, the dispersiveness of the disperse phase particles, and the temperature elevation. Fig. 5 shows the variation of average sizes of crystals with amplitude of temperature variations, the duration of the experiment being 600 minutes. With the amplitude of temperature variations changing from 0 to 14 °C and average size of crystals grows by a factor of three.



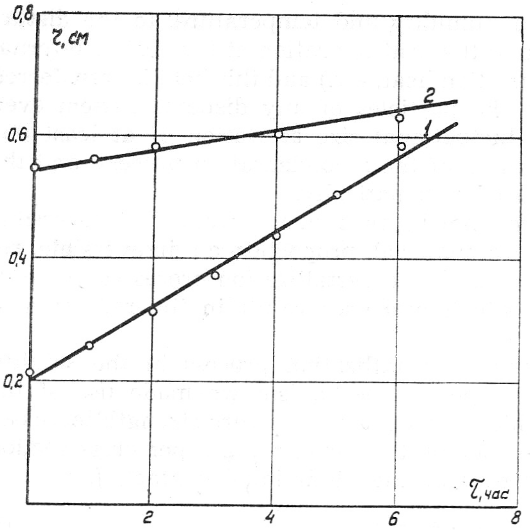
НН пп	Δt, град.	$\bar{d}$, мм
1	0,00	0,16 ± 0,01
2	0,56	0,20 ± 0,01
3	2,80	0,26 ± 0,01
4	14,00	0,48 ± 0,02

Fig. 5. Effect of the amplitude of temperature variation on the recrystallization intensity.

Fig. 6 illustrates dependence of average sizes of the alumo-ammonium sulphate particles upon the frequency of temperature variations at constant amplitude.

Fig. 7 shows the effect of the dispersiveness on the intensity of recrystallization. The growth kinetics of a large »crystal-leader« in presence of minute ones: 1 — 1 + 2 mm, 2 — 5 + 7 mm. The minute crystals, as we see, affect the rate of large crystal growth. The large one grows faster in presence of the minute crystals.

Solubility of the alumo-ammonium sulphate in the aqueous-alcoholic mixture depends on the alcohol concentration. So, the intensity of the alum recrystallization in this mixture should also be dependent on the concentration of the latter. In Fig. 8 the average size of alumo-ammonium sulphate crystals is plotted along the Y-axis, and along the X-axis — the solubility of this alum in the mixture. It's clear that with the increase of solubility of alum the recrystallization of the latter grows (the temperature variation amplitude



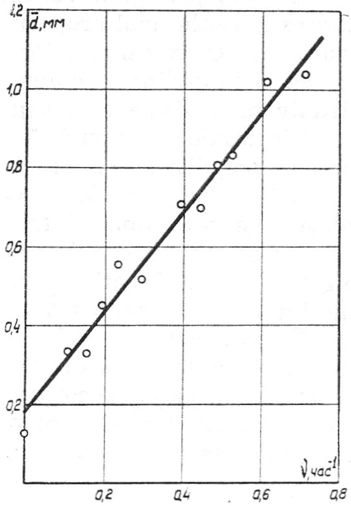


Fig. 6. Effect of the frequency of temperature variation on the recrystallization intensity.

Fig. 7. Effect of dispersiveness on the recrystallization intensity: kinetics of the leader--crystal growth under recrystallization together with crystals: 1 — 1 + 2 mm; 2 — 5 + 7 mm.

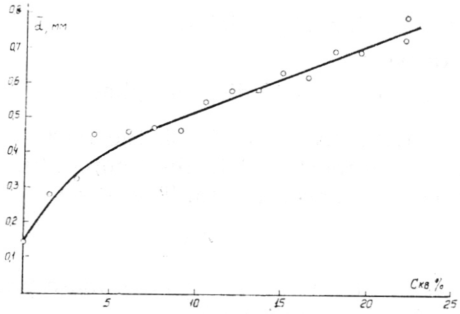


Fig. 8. Effect of the alumo-ammonium sulphate solubility in the water-alcoholic mixture on the recrystallization intensity.

— 5.6 °C, the variation frequency — 0.22 hr^{-1}, initial average crystal size — 0.14 mm, duration of experiment — 10 hr).

On the basis of principal analogy of properties of disperse systems with different aggregate state of the substance disperse phase and disperse medium substance we may conclude that the recondensation mechanism in question may take place in various disperse systems provided the following conditions are met:

1. A limited solubility of the disperse phase substance in disperse medium.
2. Periodic variation of temperature and concentration of the disperse medium.
3. Polydispersity of the disperse phase particles.

Practically, these conditions are met always: there are no absolutely insoluble substances; under natural conditions various disperse systems are subjected to freezing and thawing, wetting and desiccation, to daily, seasonal, annual, and perennial variations of humidity and temperature, to the disturbances of isothermal properties due to the heat liberation at the cost of internal source (the chemical reaction heat, friction heat, *etc.*) and this heat is transferred to the surrounding medium; were the particles of any disperse system even strictly monodisperse, a slightest fluctuational size alteration of at least one particle would be enough for beginning of the recondensation process, and the further polydispersity will be ensured automatically.

Rehbinder and Segalova have shown, that apart from the reversible adsorptive reduction of the disperse material properties an irreversible reduction of properties takes place due to the recrystallization processes proceeding in the solidification structure which processes result in the reduction of the intergrowth contact quantity.

To verify the possibility of the recrystallization process in the solidification structure according to the suggested mechanism we made use of the Rehbinder equation according to which the disperse structure strength increases with number of contact of particles per unit volume, n_1, and per cross section unit, $n_1^{2/3}$, as well as with the increase of each individual contact, f.

$$P_m = \gamma_1 \cdot f \cdot n_1^{2/3} \tag{5}$$

Number of particles forming the space lattice per unit volume is:

$$n_1 = C_1/100\, \varrho_1\, \delta^3, \tag{6}$$

where δ — effective diameter of particles,
ϱ_1 — particle density
C_1 — weight concentration of disperse phase.

In accordance with data given in Fig. 6, the recrystallization intensity in the first approximation is proportional to the temperature variation frequency and to the disperse medium concentration. Therefore,

$$\delta_i = \delta_o + a\nu \tag{7}$$

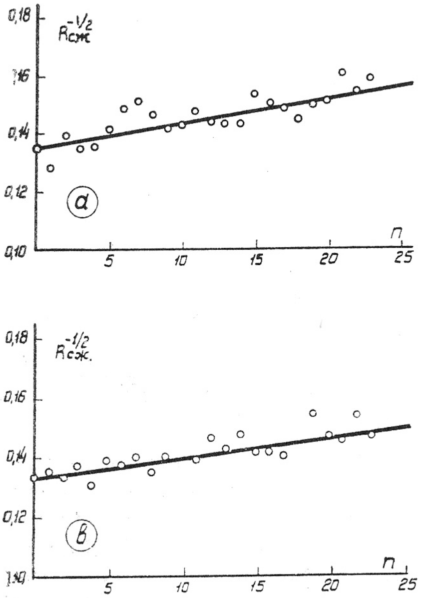
where δ_0 — initial average diameter of disperse phase particles, ν — variation frequency, a — proportionality coefficient.

Taking into account (7) and using (6) we may convert equation (5) into:

$$\gamma P_m^{-1/2} = \gamma P_{m.\,o}^{-1/2} + a\nu \tag{8}$$

To check this equation we run experiments on strength variation of gypsum samples in case of constant relative humidity (saturated steam) under periodic variations of temperature, as well as under freezing, and melting. The ultimate strength (R_c) of these gypsum samples was decreasing as a number of temperature variations (cycles) grew. Fig. 9, where these runs are illustrated, shows the experimental data to fall along straight lines of the equation (8) co-ordinates. A close agreement with equation (8) is also obtained in treating experimental data of Segalova, Izmailova, and Solovieva on strength variation of gypsum samples and the tricalcium hydroaluminate under repeated wetting and drying (Fig. 10).

Numerous studies carried out by Kiselev, Neumark, Strazhesko *et al.* have established that by hydrothermal treatment and elevated temperature steam attack a recondensation process proceeds in adsorbents and catalysts,



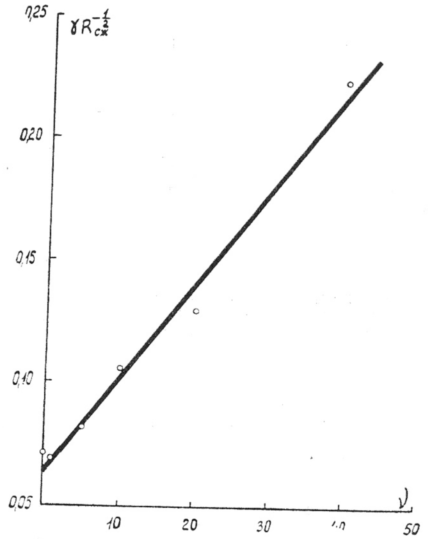


Fig. 9. Dependence of the compressive strength, R_{cs} (kg/cm²), of gypsum samples (2 × 2 × 2 cm, water/gypsum = — 0.6) under humid conditions, on number of cycles (n) of periodic temperature variation: *a* — + 21.4 : + 40 °C; *b* — — 9.4 : + 21.5 °C.

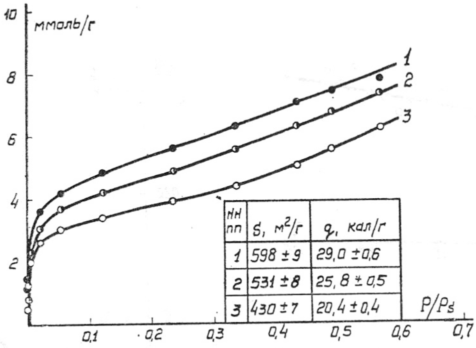
Fig. 10. Dependence of the compression strength, R_{cs} (kg/cm²), of gypsum samples (2 × 2 × 2 cm, water/gypsum = 0.6) on number of repeated wettings and desiccations (E. E. Segalova and V. N. Izmailova).

which manifests itself in growth of larger particles at the cost of smaller ones to result in the reduction of specific surface and change of other structural-mechanical, adsorptive, and catalytic properties.

That recondensation is possible by hydrothermal treatment of adsorbents, catalysts, and other disperse materials is confirmed by other facts. For instance, all factors (pH of medium, temperature, various admixtures *etc.*) affecting solubility of disperse phase affect the recondensation intensity in the same sense: the higher is dispersity of particles, the more intensive recondensation, etc .

For experimental verification of possibility of the recondensation we have run three experiments on fine-porous silica gel hydrothermal treatment. During the first experiment the silica gel was kept under hydrothermal conditions in water-thermostat at constant temperature, 100 ± 0.1 °C. In the second run the hydrothermal treatment of silica gel was carried out under periodic variations of temperature from 95 to 100 °C with frequency 1.75 hr^{-1}. And in the third run the silica gel sample of the same kind was exposed to boiling at 100 °C.

The result of these experiments (see Fig. 11) turned out to be surprizing from the point of view of the isothermal distillation mechanism, but are in a complete agreement with the suggested recondensation mechanism. The isotherm of methanol vapour adsorption by the silica gel sample hydrothermally treated under constant temperature (according to the first experiment conditions) falls higher than other isotherms. Below it goes the adsorption isotherm corresponding to the silica gel sample hydrothermally treated under periodic variations of temperature although the average temperature of the experiment



NN пп	S, м²/г	q, кал/г
1	598 ± 9	29,0 ± 0,6
2	531 ± 8	25,8 ± 0,5
3	430 ± 7	20,4 ± 0,4

Fig. 11. Isotherms of the methanol vapour adsorption by silicagel samples upon the 12-hour hydrothermal treatment of the former: *1* — at constant temperature, 100 °C; *2* — at periodic temperature, 100 °C; *2* — at periodic temperature variations from 100 to 95 °C (ν = 1.75 hr⁻¹); *3* — at boiling (100 °C).

was lower than in the first one. And still below falls the adsorption isotherm taken with the silica gel sample subjected to the hydrothermal processing under boiling conditions. This all is indicative of the fact that, as our previous studies have shown, the recondensation process proceeds under boiling conditions still more intensively since in this case the boiling mass was subjected to more frequent temperature variations due to the overheating near the surface of heating and cooling on account of self-evaporation at the liquid-vapour interface. The specific surface of the three silica gel samples as calculated on the basis of the BET adsorption measurements changed, of course, in passing from one experiment to another, in the same sense. The independently made wetting heat measurements of these same samples are in accordance with the sorption data. (For the first sample — 29.0, the second — 25.8, the third — 20.4 cal/g).

So, this study made it possible to establish that the recrystallization of disperse systems results from different effect of the disperse phase particle size on the linear rate of growth and dissolution of the particles under periodic variation of temperature and concentration of the disperse medium. The rate of recrystallization is of the same order as that of growth and dissolution of the disperse phase particles. Development of the detailed recrystallization theory of disperse systems is hindered for lack of the theory of solutions, especially of concentrated ones. It seems that of great importance for the explanation of the asymmetry of dissolution and crystallization processes under the discussed conditions are dehydration processes of particles in their transition into the crystal lattice as well as the inverse hydration process in dissolving crystals.

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IZVOD

Proučavanje rekristalizacionih mehanizama u disperznim sistemima

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Kinetika i mehanizam rekristalizacionih procesa opisani su za neke disperzne tvari različitih topljivosti. Navedeni su primjeri eksperimentalnih i teorijskih rezultata dobivenih za rekristalizaciju amonijevog aluminijevog sulfata, silika gela i gipsa, pod uvjetima temperaturne i koncentracione varijacije. Asimetrija kinetičkih parametara za otapanje i rekristalizaciju posljedica je različitog utjecaja površine čvrste faze na hidrataciono-dehidratacione i ugradbeno-eliminacione ravnoteže. Glavnim nedostatkom u pokušajima teorijske interpretacije rezultata pokazuje se manjak sveobuhvatne teorije koncentriranih otopina.

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