

# Experimental estimate of relative contribution of homogeneous mechanism in aerosol formation in Western Siberia

A.S. Kozlov, A.N. Ankilov, A.M. Baklanov, A.L. Vlasenko,  
S.I. Eremenko, S.B. Malyshkin, and S.E. Pashchenko

*Institute of Chemical Kinetics and Combustion,  
Siberian Branch of the Russian Academy of Sciences, Novosibirsk*

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Comparison has been made between the amount of a monomer formed in the atmosphere and that of the aerosol nucleation mode under different conditions throughout Siberian region. It was shown that the channel of homogeneous transformation of the newly formed particles is not the case in the atmosphere in both very clean and smog situations. The heterogeneous mechanism seems to be more likely to occur in practice.

## Introduction

As was shown about 50 years ago, ammonium sulfate is one of the principal components of atmospheric aerosol particles with the size below  $1\ \mu\text{m}$ .<sup>1</sup> The increase of anthropogenic emissions of sulfur dioxide (up to 50% of the total content in the atmosphere)<sup>2,3</sup> oxidation of which is the principal source of atmospheric sulfate, as well as a significant effect of secondary (formed in the atmosphere directly) aerosols on the meteorological visual range, acidity of precipitation, human health, and albedo (heat balance) of the Earth over vast areas became a reason for increased attention of scientists to the formation and transformation of sulfate aerosol in the atmosphere (Charlson et al.).

Siberian region, with many big industrial centers and vast rural areas, is a very interesting object for study, however, the research works based on the data of field measurements and dealing with formation of atmospheric aerosol are still rare events.

## Theoretical approach

Physical and chemical atmospheric processes involved in the sulfate cycle are too complicated. There exist different mechanisms of oxidizing sulfur dioxide in the atmosphere. Those can include gas-phase oxidation (with subsequent nucleation), catalytic and non-catalytic oxidation in droplets and on the surface of aerosol particles. Thus, the sulfate formation process is a complicated function of several determining processes. Among those there are diffusion of gases, chemical and photochemical reactions in gas phase, solution in a liquid, chemical reactions in liquid phase, formation of nuclei and catalysis on the surface of particles.

A diagram depicting the physical and chemical processes of  $\text{SO}_2$  transformation into sulfates is shown in Fig. 1. The arrows in the diagram denote a physical or chemical process, and rectangles show the products in different phases.<sup>4</sup>

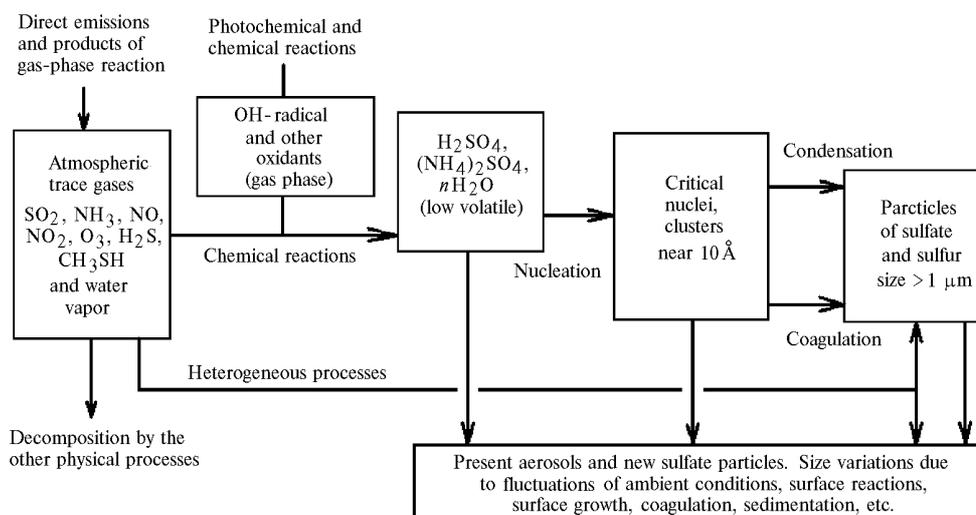


Fig. 1. Diagram of the gas-to-particle transformation (chemical and physical transformations of  $\text{SO}_2$  to sulfate).

The initial raw material for aerosol formation are trace gases such as sulfur dioxide and ammonia. The chemical and photochemical reactions in the atmosphere result in oxidation of sulfur dioxide, and sulfate monomers are formed that contain only few molecules of sulfate and water. The monomers form, in the nucleation process, stable sulfate nuclei with the size up to tens of angströms.

Many researchers have carried out laboratory experiments on studying the aerosol formation in the SO<sub>2</sub>-air system.<sup>5-7</sup> Only few of them tried to study the possibility of new particle formation at the presence of "external" aerosol particles.<sup>8,9</sup> The aerosol particles are always present in real atmosphere, and the formed sulfate monomers can sink (condense) on the aerosols that already existed. These aerosol particles can consume the major part of thus formed sulfates and, as a result, suppress possible processes of homogeneous formation of particles. Formation of new particles was observed in Ref. 10 at the heterogeneous surface area about 4 μm<sup>2</sup>/cm<sup>3</sup>. The author of Ref. 11 observed formation of new particles from onboard an airborne laboratory practically everywhere over the Pacific ocean, at almost full absence of primary particles in the air.

Thus, there are two ways of further evolution for the formed sulfate: condensation on the already existing aerosol particles and (or) homogeneous growth resulting in formation of the ultrafine sulfate particles. To address the question on which of these mechanisms dominates, the author of Ref. 12 used, as a criterion, a comparison between the characteristic time of "sink" of the initial particles on the aerosols that already existed and the characteristic time necessary for the homogeneous formation of new particles to occur. He derived a formula describing the change of the number concentration of the initial particles ("monomers"),  $N(t)$ , for the case of heterogeneous condensation:

$$N(t) = R\tau[1 - \exp(-t/\tau)],$$

where  $R$  is the rate of generation of a "monomer,"  $\tau$  is the characteristics time of "sink" of the latter on the existing aerosols.

According to Refs. 12 and 13, the number concentration,  $n$ , of the newly formed particles can be described, taking into account their "sink," as follows:

$$\frac{dn}{dt} = k [\text{SO}_2] - n/\tau, \quad (1)$$

where  $k$  is the gross constant of the rate of sulfur dioxide oxidation in the atmosphere;  $\tau$  is the characteristic time of heterogeneous sink of monomers on aerosols. The equality of the derivative to zero gives the value of the stationary number concentration of the monomer

$$n_s = k [\text{SO}_2] \tau. \quad (2)$$

A solution of Eq. (1) can be written in the form

$$n(t) = k [\text{SO}_2] \tau [1 - \exp(-t/\tau)]. \quad (3)$$

Obviously, we have obtained the formula that is analogous to that proposed in Ref. 12. The number concentration of the initial particles reaches its steady state level during time  $\tau$ . It follows, in particular, that if  $\tau$  is less than the characteristic time of the change in sulfur dioxide concentration, then every time the concentration of the latter changes there will be enough time for the monomer to reach a steady state level of its number concentration.

Here it is necessary to consider the assumptions inherent in the approach which we accept.

First, the time of sink of the formed particles should be significantly less than the characteristic time of the sulfur dioxide concentration variation, in order that one can assume the monomer number concentration to be constant.

Really, if the characteristic time of variation of the SO<sub>2</sub> concentration is estimated from below by its lifetime or the time of diurnal variation (8 hours), and the time of heterogeneous sink by tens of minutes, then one can consider the difference of one order of magnitude as satisfactory.

Second, it is supposed that the initial oxidation of sulfur dioxide occurs in the gas phase, but not in the liquid cover of aerosol particles or droplets.

According to a recent review,<sup>14</sup> the heterogeneous effects of that type can be observed at relative humidity not lower than 75%, that is related to formation of the liquid cover of aerosol particles. In our experiments the mean day-time humidity was 50%. On the other hand, an increase in the sulfate concentration during daytime is, probably, significantly related to photochemical processes, which can occur on the surface or inside aerosol particles. However, following Ref. 15, such processes are observed only in a strongly polluted atmosphere.

### Calculation of the characteristic time of heterogeneous sink

If data on aerosol disperse composition are available, it is easy to calculate the characteristic time of sink of the formed monomers on the aerosol particles already existing in the air. Next, if the size of absorbing aerosol is much larger than the monomer size, it is expedient to use a relatively simple formula for the diffuse flux to a "black" (totally absorbing) sphere of the radius  $R$  proposed by V.I. Smirnov<sup>16</sup>:

$$I = \frac{4\pi R D n_\infty}{1 + \lambda l / R}, \quad (4)$$

where  $D$ ,  $l$ , and  $n_\infty$  are the diffusion coefficient, free path, and concentration of the condensed substance, respectively;  $\lambda$  is the correction factor weakly changing in the limits from 0.8 to 1, so we accept it to be constant and equal to 0.95.

The change of the "monomer" number concentration at its condensation on particles, which have the size distribution  $f(R)$  and the number concentration  $N$  is described by the following formula:

$$\frac{dn}{dt} = - \int dR \frac{4\pi R f(R) DN n}{1 + \lambda l / R}, \quad (5)$$

the solution of which is  $\exp(-At)$ ,  $A$  is the reciprocal characteristic time of the process:

$$\tau = \left( 4\pi DN \int dR \frac{R f(R)}{1 + \lambda l / R} \right)^{-1}. \quad (6)$$

In computing the integral is transformed into a simple discrete sum to calculate it easier.

## Review of experimental data

As follows from the title, the principal goal of the paper is to determine the contribution of homogeneous mechanism to the aerosol formation using the maximum possible quantity of experimental data. All the results presented here were obtained by means of a mobile laboratory of ICKC SB RAS.<sup>17</sup>

A significant bulk of data have been obtained in the experiments. A detailed description of these would hardly suit the goal of this paper, so in this section we present only most important results, brief description, and peculiarities of the experimental sites in chronological order. The general problem that unites these data is the study of atmospheric aerosol and trace gases under conditions of relatively clean air far from big sources of anthropogenic emissions.

### Chik

The village Chik is situated 30 km to the West of Novosibirsk, and the measurement site was 4 km to the north of it. The place is characterized by a relatively large distance from the populated areas (Chik is the nearest one) and, hence, by low influence of anthropogenic emissions. Measurements were carried out in February 1996.

Diurnal behavior of the number concentration of ultra-fine aerosols was observed during the arctic air mass passage,<sup>17</sup> at a low area of heterogeneous surface of aerosol particles being on the order  $5 \mu\text{m}^2/\text{cm}^3$ . This manifested itself in a marked difference between the day- and nighttime spectra of submicron particles (Fig. 2). The number concentration of the smallest detectable aerosol (2–4 nm) served as an indicator of the process of homogeneous formation of new particles from the gas phase.<sup>17</sup> Taking into account the daytime increase in the mass content of sulfate in aerosol and comparing it with the amount of the formed fine disperse particles, one can suppose the presence of a significant sulfate amount in the latter (Fig. 3).

### Plotnikovo

The village Plotnikovo is situated in Tomsk Region 220 km directly to the north of Novosibirsk.

There are about 150 to 200 private houses that are situated on both sides of the local asphalt-covered road. The intensity of traffic here does not exceed 1–2 cars during 10 min in the daytime and practically is equal to zero in the nighttime. The mobile laboratory was operated in the village at about 1-km distance from the road in its northern part. The north-east sector was free of the local aerosol sources.

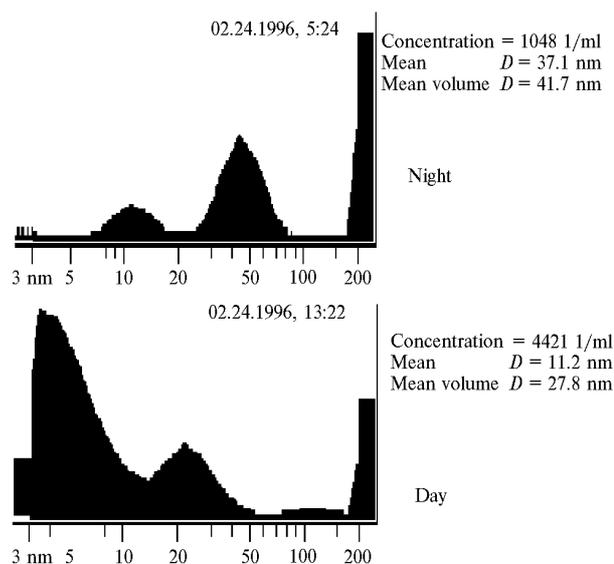


Fig. 2. Particle size-distribution functions in the daytime and nighttime.

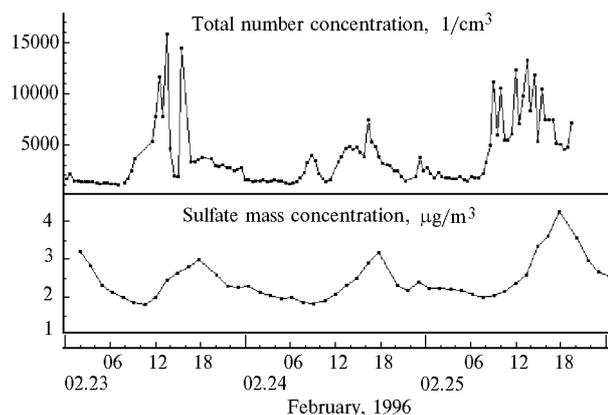


Fig. 3. Diurnal variations of the sulfate and aerosol concentrations.

Monitoring measurements were carried out from the 11 until 19 of August 1996.

The total number concentration and the scattering coefficient showed characteristic peaks in the morning and in the evening. This is related to the regime of using stoves in the village houses. As our experience and the experience of foreign researchers showed, it was very difficult to find a site for experiment, with an

access to power supply, where the effect of local anthropogenic sources could be neglected. Such a situation has periodically been observed even at the Antarctic stations when the research instrumentation recorded the emissions from the stations themselves. One can avoid this in long-term observations, which could allow one to analyze the data for eliminating local components<sup>18</sup> and taking into account wind direction.

Preliminary analysis has shown that the integral background scattering coefficient (inverse to local meteorological visual range) in the Plotnikovo was  $3 \cdot 10^{-5} \text{ m}^{-1}$ , that undoubtedly characterizes low aerosol content in the air over this locality.

The concentration of  $\text{SO}_2$  was at its background level of 0.3 ppb during practically all time, however, it increased by 0.5 ppb before the sunrise and sunset.

The number concentration of ultra-fine aerosol has well pronounced anthropogenic maxima in the morning and in the evening and well correlates with the nephelometric data and the data of the photoelectric particle counter. The background level is within the limits from 1 to 3 thousand particles of the size larger than 3 nm per  $1 \text{ cm}^3$ . The mean size of the background aerosol particles is too large, up to 120–150 nm, that is not usually observed and, probably, is related to high humidity of air during the work.

As seen from the data presented, the concentration of admixtures was extremely low in the vicinity of Plotnikovo. Nevertheless, we did not observe the daytime increase of the number concentration of ultra-fine particles (diurnal behavior). The latter allows us to suppose that the contribution of the process of homogeneous formation of new particles from gas phase was small in this case.

### Artybash

Gorno-Altai region is characterized by a low density of the sources of anthropogenic emissions. It is, along with Lake Baikal, a unique geographic site for studying of natural concentrations of aerosol and trace gases as well as their natural interconnections. At the same time, atmospheric aerosol of Altai highlands has been much poorer studied as compared with other regions.

One of the goals of our field mission was to study the aerosol disperse composition and the concentration of trace gases in the near-ground layer of the atmosphere, while neglecting, when possible, the effect of anthropogenic sources. To achieve this task, we have chosen a place near village Artybash.

The village Artybash is situated 150 km to the south-east of Gorno-Altai. The mobile ecological laboratory was situated in the area of Altai National Park on the shore of Teletskoe lake (May 23 till June 2, 1997). The place is far from the nearest population area and, hence, there are only few sources of anthropogenic emissions.

The background (minimum) number concentration of ultra-fine particles there was 400 particles per  $1 \text{ cm}^3$ . The inverse, relative to the typical continental one, diurnal behavior of the number concentration was observed in this region (up to  $5000 \text{ cm}^{-3}$ ).

The background value of the total scattering coefficient was  $3 \cdot 10^{-5} \text{ m}^{-1}$ . Regular increase up to  $6 \cdot 10^{-5}$  was recorded on nights. It should be noted that the minimum values of the scattering coefficient in Arctic air mass measured in Chik<sup>17</sup> were  $7 \cdot 10^{-5} \text{ m}^{-1}$ .

### Mondy

Measurements of the atmospheric characteristics at the Sayany Solar Observatory were carried out since 13 until 19 August, 1997. The measurement site is situated at the height of 2000 m over the sea level and is far enough from big sources of anthropogenic emissions.<sup>20</sup> The nearest populated area is situated 5 km to the south of Mondy and 700 m lower than the observatory.

It was revealed after preliminary measurements that the aerosol under study has unusually low, for the continental-type aerosol, number concentration and quite a specific disperse composition. The behavior of the total number concentration has the following peculiarities. First, the maximum values are reached in the nighttime (~1–3 a.m. of local time), and the minimum ones are observed at the daytime, that is not typical for the continental aerosol at sunny weather. Second, the variation amplitude is small. The total number concentration of particles was of the order of  $400\text{--}700 \text{ cm}^{-3}$  in the daytime, and  $1100\text{--}1500 \text{ cm}^{-3}$  in the nighttime.

The disperse composition of aerosol keeps practically unchanged independently of the prehistory of air mass and time of a day. The absence of the particle fraction from 3 to 20 nm is an evidence of the fact that the gas-phase reactions that lead to the homogeneous formation of aerosol were suppressed in the region during the measurement period, and aerosol was generated long before the moment of sampling. Episodic appearance of particles in this range is related to the activity of people at the station. The total scattering coefficient was extremely low, only  $\sim 0.5\text{--}1.5 \cdot 10^{-5} \text{ m}^{-1}$ .

The results obtained in this mission are presented in Table 1, as well as the data of measurements in the center of Novosibirsk carried out in 1994–95 and during the strong smog in October 1997,<sup>21</sup> namely number concentration and heterogeneous surface area of coarse particles of the size greater than  $0.7 \mu\text{m}$  (AZ); number concentration and mean size of the ultra-fine particles of the size greater than 2 nm (DSA); sulfur dioxide concentration; mass concentration of sulfate, total aerosol scattering coefficient (Scatt), ozone and nitrogen dioxide concentrations, and the calculated time of heterogeneous sink ( $\tau$ ). The letter *v* (variation) designate the value of the diurnal variations of one or another component, the asterisk marks the inverse (nighttime) diurnal behavior of the component.

Table 1

Parameter	Measurement site					
	Chik	Plotnikovo	Artybash	Mondy	Smog'97	City
N(AZ), 1/cm <sup>3</sup>	3–10	8–14	–	0.4–0.7	250	40–200
S(AZ), μm <sup>2</sup> /cm <sup>3</sup>	4–17	–	–	1–3	280	30–150
N(DSA), 1/cm <sup>3</sup>	1000	800–5000	500	400–600	24·10 <sup>3</sup>	6–20·10 <sup>3</sup>
v(DSA)	15·10 <sup>3</sup>	–	2000*	1500*	–	60·10 <sup>3</sup>
D <sub>Ng</sub> (DSA)	12–40	40–60	60–100	70–110	130–150	30–60
SO <sub>2</sub> , ppb	0.8	0–1	0–0.3	0–3	3	0
v(SO <sub>2</sub> )	1.5	–	1.5	–	–	13
SO <sub>4</sub> , μg/m <sup>3</sup>	1.8	0.5–1.5	0–1	0.05–0.35	–	–
v(SO <sub>4</sub> )	3	–	2.4	–	–	–
Scatt, m <sup>-1</sup>	7·10 <sup>-5</sup>	3–6·10 <sup>-5</sup>	2·10 <sup>-5</sup>	0.5–2·10 <sup>-5</sup>	150·10 <sup>-5</sup>	–
v(Scatt)	–	–	0.6–0.8*	–	–	–
O <sub>3</sub> , ppb	24	5	7	24–45	22	0–20
v(O <sub>3</sub> )	30	24	18	–	–	–
NO <sub>2</sub> , ppb	≈ 5	–	–	–	–	4–8, v30
τ, heter, sec	900	600	900	3500	2	30

Table 2. Calculation of homogeneous contribution and the data on size spectra

Parameter	Measurement site				
	Chik	Plotnikovo	Artybash	Mondy	Smog'97
K, %/hour	0.5	0.5	0.5	0.5	5
SO <sub>2</sub> , ppb	1.2	0.3	0.5	0.3	3
τ, s	900	600	900	3500	2
n <sub>s</sub> , 1/cm <sup>3</sup>	4.5·10 <sup>7</sup>	0.75·10 <sup>7</sup>	1.8·10 <sup>7</sup>	4.5·10 <sup>7</sup>	2.5·10 <sup>6</sup>
N <sub>nucl</sub> , 1/cm <sup>3</sup>	560	50	30	200	0
D <sub>nucl</sub> , nm	7.9	8	10	5	–
n <sub>nucl</sub> , 1/cm <sup>3</sup>	1.4·10 <sup>7</sup>	1.3·10 <sup>6</sup>	1.5·10 <sup>6</sup>	1.3·10 <sup>6</sup>	0
N <sub>uf</sub> , 1/cm <sup>3</sup>	20	6	3	3	375
n <sub>uf</sub> , 1/cm <sup>3</sup>	1.6·10 <sup>4</sup>	4800	2400	2400	1.5·10 <sup>5</sup>
Homogeneous contribution, %	30	16	8	3	0

It should be noted that there is certain similarity in the degree of aerosol pollution of the above measurement sites, excluding city and smog situation. The total aerosol scattering coefficient (Scatt) which is an indicator of the degree of aerosol pollution, is 0.5 to 7 m<sup>-1</sup> in remote regions and up to 150 m<sup>-1</sup> in smog. The time of heterogeneous sink is only 2 sec in smog and of the order of some tens minutes in clean places. In general, taking into account the number concentration and particle size distribution, the conditions of regional measurements (except for city and smog) can be evaluated as "remote continental," according to the definition proposed in Ref. 14.

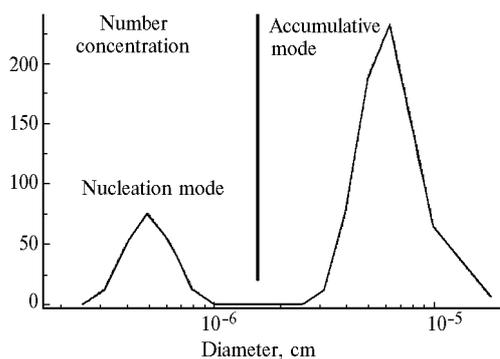
However, the regular daytime increase of the number concentration of ultra-fine aerosol that is an evidence of the appearance of new particles, was observed only once in Chik village (see Table 1, v(DSA)). The inverse (nighttime) dynamics of the aerosol number concentration was principally observed in other sites, that is possibly related to the economic activities there.

### Estimation of homogeneous and heterogeneous contribution into the formation of sulfate particles

To perform calculations and estimates based on the experimental data, we had to develop a criterion for the presence and power of the process of homogeneous formation of nuclei.

According to our previous papers,<sup>17</sup> the presence of ultra-fine aerosols can serve as an indicator of the process of homogeneous formation of new particles from the gas phase. To measure the number concentration of fine particles, our laboratory uses a diffuse aerosol spectrometer (DSA). It is possible to reconstruct the particle size distribution starting from 3 nm, the real threshold of recording is 2 nm (50%). So the mean number concentration of particles of the size of 2 or 3 nm was the indicator of a homogeneous process (Table 2, N<sub>uf</sub>) to occur.

It is known that the characteristic size distribution of small particles ( $d < 300$  nm) has a bimodal shape. It is conventional to call the particle mode with the least mean size (3–30 nm) the nucleation mode, and the larger one (60–130 nm) the – accumulative mode. We propose in this paper to set a conventional boundary of separating the processes between the accumulative and nucleation modes of submicron aerosol (Fig. 4), namely, if the particles formed from the gas phase, interacting between each other, have formed the nucleation mode, the process is homogeneous, while the process involving larger particles is heterogeneous.



**Fig. 4.** Characteristic shape of the particle size-distribution. The line marks the boundary between nucleation and accumulative modes of the distribution dividing the homogeneous and heterogeneous processes.

Taking into account the aforementioned, it is logical to suppose that knowing the size of the initial monomers formed from the gas phase, number concentration, and mean size of the nucleation aerosol mode, one can calculate the number of the initial monomers forming the nucleation aerosol mode based on the ratio of amount of particles in these modes.

Then using the data on the gross constant of  $\text{SO}_2$  oxidation, calculating the time of heterogeneous sink, and using the theory stated above, one can estimate the steady-state number concentration of monomers and, hence, the contribution of the process of homogeneous formation of new particles from the gas phase.

The initial data and estimates obtained, as well as the characteristics of different modes of aerosol particle size-distributions are presented in Table 2.

The following designations are accepted in Table 2:  $n_s$  is the steady-state number concentration of monomers calculated by the formula

$$n_s = k [\text{SO}_2] \tau ,$$

where  $k$  is the gross constant of  $\text{SO}_2$  oxidation,  $\tau$  is the time of sink,  $n_{\text{nucl}}$  is the number of monomers contributed to formation of the nucleation mode:

$$n_{\text{nucl}} = N_{\text{nucl}} (D_{\text{nucl}}/D_{\text{mono}})^3 ,$$

$D_{\text{nucl}}$  is the mean size of the nucleation mode;  $N_{\text{nucl}}$  is the number concentration of particles in the nucleation mode;  $D_{\text{mono}}$  is the monomer size (2.7 angström in our paper).

The percentage of relative contribution of the homogeneous mechanism was calculated as follows:

$$\text{homog} = (n_{\text{nucl}}/n_s) 100\% .$$

All values with the index "uf" (ultra fine) are related to the particles of the smallest measurable size (2–3 nm).

The gross constant of  $\text{SO}_2$  oxidation was selected according to most recent literature data<sup>14</sup> for remote sites – 0.5%/h and for smog events 5%/h. Both constants refer to the midlatitude summer.

The initial monomer size was selected based on the fact that, according to Ref. 22, 99% of sulfate molecules contain one or more molecules of water, and the molecules having only one associated molecule form the principal part (66.46%) at relative humidity of 50%. At such a ratio the sulfur acid is 82% of mass, and the mass content corresponds to the critical nucleus of the size 2.7 Å,<sup>23</sup> which contains one molecule of sulfate and one molecule of water. So this value (2.7 Å) was taken for calculations.

Discussing the data presented in Table 2, one should note once again that homogeneous formation of new particles was observed at only one of the considered sites – Chik village. It was accompanied by a significant daytime increase of the fine particles' number concentration (see Table 1) and a significant daytime number concentration of ultra-fine particles, which, as it was mentioned above, is the indicator of the process of homogeneous formation of new particles from the gas phase. The minimum estimate of the contribution of the homogeneous mechanism for this site is 30% that is at least 2 times greater than for other measurement sites. Obviously, the contribution of homogeneous mechanism is practically equal to zero in smog events.

Let us also note that there is some similarity between the extremely clear and smog situations in absence of homogeneous processes. However, in the first case it is caused by the small value of the constants of  $\text{SO}_2$  oxidation and small content of  $\text{SO}_2$  itself (lack of raw material), and in the second case it is due to very powerful sink of the formed particles during a few seconds.

Of course, one cannot say about the continuous prevalence of the heterogeneous mechanism in the formation of sulfate aerosol only on the basis of the estimates, however, according to the calculations, it dominates.

The location of the measurement sites in the formation-sink coordinates (Fig. 5) is also of interest. Obviously, all effects of aerosol formation are not seen when approaching the origin of coordinates because of low variations that can hardly be noticed. As the sink rate increases, the contribution of homogeneous formation of new particles decreases. It is also obvious that the area, on the diagram, where formation of new particles is explicitly fixed should be sufficiently far from the origin of coordinates, that is determined by the used instrumentation. Hence, the ratio of sink to

formation should be less than 1. We have the only such point in Chik village.

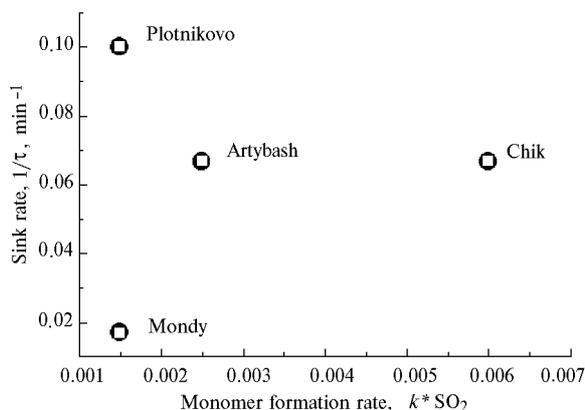


Fig. 5. Diagram of the formation and sink of particles.

## Results

1. Field investigations of atmospheric aerosol and trace gases have been carried out in Siberian region.

2. The characteristic times of heterogeneous "sink" and the particles formed from the gas phase have been calculated based on real particle size distributions in the range of 3 to 10 nm.

3. The method is proposed for quantitative estimation of the contribution of homogeneous formation of nuclei into the formation of the sulfate component of atmospheric aerosol.

4. The estimate is performed of the relative contribution of homogeneous and heterogeneous mechanisms of transformation of particles formed from the gas phase in the real atmosphere.

5. It is shown that the homogeneous way of transformation of new particles is practically absent both in very clear areas and in smog situations.

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