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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# ON A METHOD FOR INVESTIGATING SYSTEMS ON MASSIVE SPECIMENS OF VARIABLE COMPOSITION

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The study of "composition—property" diagrams is one of the most important physicochemical problems. Usually, in order to study systems it is necessary to carry out tens and hundreds of melts of individual compositions differing by successive substitution of components. From each melt, specimens are prepared for investigating physical properties, and from the results the "composition—property" curves are constructed. In this connection, the investigation of systems is a lengthy and labor-consuming process, and attempts to accelerate it by choosing a sparser grid of compositions involve the danger of missing the most important regions. In work (1), an accelerated method was proposed for studying "composition—property" diagrams on specimens of variable composition in the form of films, which were prepared by simultaneous evaporation in vacuum of the components of a given system with subsequent condensation on a substrate. However, in the case of certain systems whose components are oxides or more complex compounds (for example, silicates, glasses, etc.), the realization of this method encounters great difficulties associated with decomposition of the components during melting, as well as with the different vapor pressures of the evaporated substances and decomposition products.

**Fig. 1.** Schematic diagram of the production of massive specimens of variable composition

In this connection, we developed a new method for producing massive specimens of variable composition.

The method is based on preparing a powder-like mixture of variable composition with a specified change in the concentration of the components, followed by zone melting, as a result of which the powder-like mixture of variable composition is transformed into a solid specimen of variable composition. With sufficiently fine powders and good mixing of the components, with continuous variation of their concentrations, and also with correctly chosen dimensions and rate of displacement of the molten zone, a continuous specimen of variable composition is formed, homogeneous in cross section normal to the concentration gradient.

Depending on the design of the dispenser for the powder-like mixture and of the furnace for zone melting, massive specimens of variable composition may be obtained in the form of plates and bars with a one-dimensional or two-dimensional concentration gradient.

The basic scheme for preparing a "one-dimensional" specimen of variable composition is shown in Fig. 1. With the aid of a multicomponent continuous dispenser 1, a moving refractory or fire-resistant boat 2 is filled with a mixture of powder-like components of the system under investigation in such a way that, along the length of the boat, a layer of a mixture of variable composition is formed, in which one (or several) components are replaced by another—

(or by other means). The mixture of variable composition is subjected to zone melting in circuit 3, followed by relief of thermal stresses in furnace 4. Thus, in the boat one obtains a sample of variable composition, in the form of a bar of the required dimensions.

The preparation of a multicomponent powder mixture of variable composition can be carried out by various devices. Fig. 2 shows a schematic of a dispenser for studying two- and three-component systems, as well as three-component sections of multicomponent systems on "one-dimensional" samples of variable composition, which are a materialized linear section of the corresponding system. The operation of the dispenser is based on the proportionality of the amounts of components entering from hoppers 1 to the areas of their outlet openings, covered by shutters 2 and 3. It is easy to show that, for any position of the shutters, the relation for a three-component system is satisfied:

$$A + B + C = 1.$$

The composition $P_{\mathrm{ABC}}$ at a given point of the system is determined as

$$P_{\mathrm{ABC}} = (1-\alpha)(1-\beta)P_{\mathrm{A}} +$$

$$+\alpha(1-\beta)P_{\mathrm{B}} + \beta P_{\mathrm{C}},$$

Fig. 2. Schematic of a dispenser for making a three-component mixture of variable composition

where $P_{\mathrm{A}} = \sum a_i x_i$; $P_{\mathrm{B}} = \sum b_i x_i$; $P_{\mathrm{C}} = \sum c_i x_i$ are the compositions of the initial components in weight or mole percent, and $\alpha = x/a$ and $\beta = y/a$ are

Fig. 2. Schematic of a dispenser for making a three-component mixture of variable composition

Figure 2: Fig. 2. Schematic of a dispenser for making a three-component mixture of variable composition

the relative openings of the shutters (*a* is the side of the square opening of the hopper; see Fig. 2).

With uniform motion of shutter 2, a linear replacement of component A by B occurs at a specified content of component C, which is equivalent to movement of the figurative point parallel to side AB of the concentration triangle ABC. Movement of shutter 3 with shutter 2 stationary moves the figurative point along lines of equal ratio of components A and B, and when both shutters move the figurative point can traverse any prescribed path inside the concentration triangle; moreover, the gradient of concentration change along the sample of variable composition is determined by the speed of motion of the shutters (at constant dispenser output).

Depending on the properties of the materials under study, various methods of obtaining samples of variable composition are used: pouring the powder into a vertical boat, hot pressing before melting, and also stirring the molten zone. With a properly chosen zone-melting regime, the concentration gradient along the length of the sample does not change, except at the ends, whose length corresponds to the molten zone ([2]). The deviation of the composition at the ends of the sample does not exceed 2% of the initial concentration of the powder mixture.

Obtaining sufficiently massive samples of variable composition makes it possible to use industrial equipment for studying their physicochemical properties, equipped with appropriate attachments for measuring properties in small regions of the samples. As an illustration, Fig. 3 shows changes in dielectric loss $\mathrm{tg}\,\delta$, dielectric permittivity $\varepsilon$, refractive index $n$, microhardness $H$, and

also of chemical composition when replacing $Na_2O$ by $K_2O$ in a glass of composition 20% $Na_2O$, 10% CaO, 70% $SiO_2$, measured on one variable-composition specimen of size $200 \times 10 \times 2$ $\mathrm{mm}^3$, a photograph of which is given in Fig. 4.

Fine powders of glasses 20 $Na_2O$, 10 CaO, 70 $SiO_2$, and 20 $K_2O$, 10 CaO, 70 $SiO_2$ (wt. %) were used as components A and B, respectively; moreover, in order to monitor the composition gradient along the specimen, 0.1% CoO was introduced into component B.

**Fig. 3.** Changes in physical properties and chemical composition along the length of variable-composition glass specimens. Changes in properties when $Na_2O$ is replaced by $K_2O$ in glass 20 $Na_2O$, 10 CaO, 70 $SiO_2$, wt. % (a–d—on one specimen). a—dielectric losses; b—dielectric constant; c—refractive index; d—microhardness; e—change in $K_2O$ content along the specimen: solid

Fig. 3. Changes in physical properties and chemical composition along the length of variable-composition glass specimens. Changes in properties when $Na_2O$ is replaced by $K_2O$ in glass 20 $Na_2O$, 10 CaO, 70 $SiO_2$, wt. % (a-d—on one specimen). a—dielectric losses; b—dielectric constant; c—refractive index; d—microhardness; e—change in $K_2O$ content along the specimen: solid line—specified concentration, circles—analysis results; f—change in optical density upon introduction of cobalt oxide into glass 20 $Na_2O$, 10 CaO, 70 $SiO_2$ ($\lambda = 582$ m$\mu$).

Figure 3: Fig. 3. Changes in physical properties and chemical composition along the length of variable-composition glass specimens. Changes in properties when $Na_2O$ is replaced by $K_2O$ in glass 20 $Na_2O$, 10 CaO, 70 $SiO_2$, wt. % (a-d—on one specimen). a—dielectric losses; b—dielectric constant; c—refractive index; d—microhardness; e—change in $K_2O$ content along the specimen: solid line—specified concentration, circles—analysis results; f—change in optical density upon introduction of cobalt oxide into glass 20 $Na_2O$, 10 CaO, 70 $SiO_2$ ($\lambda = 582$ m$\mu$).

line—specified concentration, circles—analysis results; f—change in optical density upon introduction of cobalt oxide into glass 20 $Na_2O$, 10 CaO, 70 $SiO_2$ ($\lambda = 582$ m$\mu$).

In order to check the prescribed linear change in concentration without destroying the specimen, specimens were prepared in which only the CoO content was varied; for this purpose glass A with an addition of 0.1% CoO was used as component B.

Measurements of physical properties (without destroying the specimen) were carried out with the aid of simple attachments on the following instruments: tg $\delta$—on a measur-

loss meter IP-ZA, $\varepsilon$—on the PIMED instrument, $n$—on the RLU refractometer, $D$—on the FM-58 photometer, $H$—on the PMT-3 instrument. The points on the graphs correspond to the mean value of the given property in a small region (5-8 mm) of the specimen, determined by the dimensions of the measuring probe of the corresponding instrument.

It should be noted that, when special instruments are developed, the dimensions of the measured regions can be reduced considerably; at the same time it is not difficult to ensure continuous measurements along a specimen of variable composition. Taking into account that the intensity of the coloration of glass by cobalt oxide is proportional to its concentration ($^{3,4}$), the change in optical density (Fig. 3e) can serve as evidence of a linear change in composition concentration along the specimen; this was confirmed by direct analysis of the $K_2O$ content in small pieces of glass taken from different places of the specimen of variable composition (Fig. 3d). Determination of the $K_2O$ content (with destruction of the specimen) by the method of flame photometry was carried

Fig. 4. Glass specimen of variable composition (for scale, a 1-kopeck coin is placed beside it)

Figure 4: Fig. 4. Glass specimen of variable composition (for scale, a 1-kopeck coin is placed beside it)

out after the physical properties had been measured on this specimen.

**Fig. 4.** Glass specimen of variable composition (for scale, a 1-kopeck coin is placed beside it)

In Fig. 3a the "neutralization effect" ($^5$) is clearly visible; as a result of it, the presence of two alkali oxides lowers the dielectric losses in the glass as compared with the same content of a single alkali oxide. This confirms that the specimen is indeed a glass of variable composition, and not a mechanical mixture of two initial glasses.

The values of the physical quantities determined on specimens of variable composition agree with analogous measurements on specimens of constant composition obtained under the same conditions. The method of obtaining massive specimens of variable composition can also be applied to the accelerated investigation of a number of metallic systems.

Thus, the preparation of massive specimens of variable composition by zone melting of powder mixtures of variable composition with a specified concentration gradient can considerably broaden the possibilities for investigating a wide range of systems.

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