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EXPERIMENTAL STUDY OF SOME THERMODYNAMIC PROPERTIES OF COMPLEX SOLUTIONS AT LOW TEMPERATURES (TO − 196°C)

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The experimental method and results of a study of some thermodynamic properties of complex technical HNO_3–N_2O_4–H_2O solutions are reported. A phase diagram has been plotted in the p-t coordinate system on the basis of the experimental data obtained.

Solutions A and B of the following composition were taken for the study (%): 75.96 and 70.96 HNO_3; 20.67 and 27.85 N_2O_4; 2.4 and 1.3 H_2O; 0.97 and 0.16 impurities, respectively.

Conducting the experiments with a varied content of nitric acid and nitrogen tetroxide made it possible to determine the effect of the relative content of the components on the thermodynamic properties being studied.

The results of the investigation enabled us to plot a p-t phase diagram for technical HNO_3–N_2O_4–H_2O solutions of the above composition (Fig. 1).

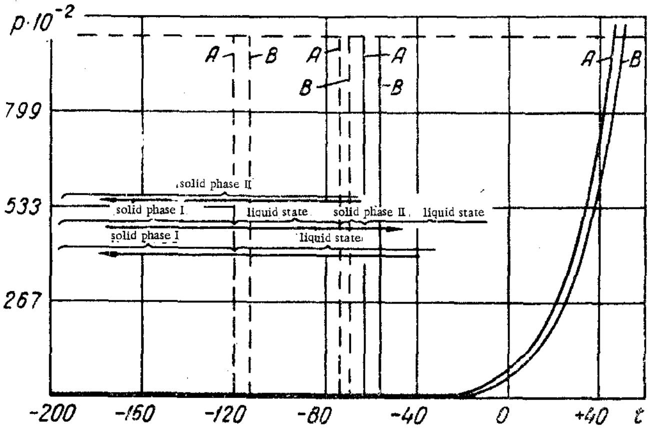

Fig. 1. Phase diagram in the p–t coordinate system for solutions A and B.

Interesting facts were observed in the course of the experiments: for example, the existence of two types of solid phase for these solutions (provisionally designated solid phase I, solid phase II) and of a stable supercooled state, and the change in the nature of the function $\lg p_s = f(1/T)$ over certain low-temperature ranges. All of this is characteristic for precisely the technical HNO_3–N_2O_4–H_2O solutions investigated and was not observed in comparative experiments on the individual components (N_2O_4, 70% nitric acid, water, ethanol).

The phenomena observed are represented graphically in Fig. 1, where the limits of existence of the different phases are shown on the phase diagram and possible changes of the solid and liquid phases are indicated by arrows. The qualitative picture of these phenomena was checked repeatedly. Reliable values of the temperature limits of the phase transitions were determined in the experiments described below.

We have previously determined the total saturated vapor pressure of the solutions down to a temperature of −100°C [2] with satisfactory accuracy. Therefore, in the present experiments only the temperatures were measured. This simplification made it possible to exclude entirely the possibility of an irreversible composition change in the liquid or vapor phases of the solutions in the course of temperature changes in different directions.

The experimental setup for studying the above phenomena is shown schematically in Fig. 2.

A copper-constantan thermocouple was sealed inside the vessel by a special technique. It was protected from the corrosive solutions by a thin glass shell (about 0.1 mm thick), which tightly enclosed the thermocouple bead. The thermocouple was calibrated over the whole working temperature range after being placed in the vessel.

The vessel was carefully evacuated to a pressure of 1.3–0.13 newton/m^2 using a pump, a trap, and a gas-air flame to heat the vessel walls. Then it was sealed off from the system at point I. The experimental liquid was introduced through the capillary. When the liquid level in the vessel reached the base of the capillary, the latter was resealed at the constriction II.

To avoid the possibility of a change in liquid composition during filling of the vessel, the HNO_3–N_2O_4–H_2O solution was precooled and held at a temperature of −21° to −30° C.

Thanks to the sealing process described, a hermetically sealed solution and its pure vapors remained in the vessel. The ratio of the volumes of the liquid and vapor phases was 1:1 (the same as during determination of the total saturated vapor pressure). The uniformity of the solution composition immediately before and after its introduction into the apparatus was checked several times and confirmed by careful chemical analyses of the quantitative composition of the liquid. Then the vessel was placed in a cryostat and observations were carried out. At the same time, another vessel, similar to the first and filled with a solution of the same composition, was immersed in the cryostat. However, the second vessel was unsealed and closed with a glass stopper. It was used to study phase transitions and the temperature limits of the solid and liquid phases of the test solution at atmospheric pressure.

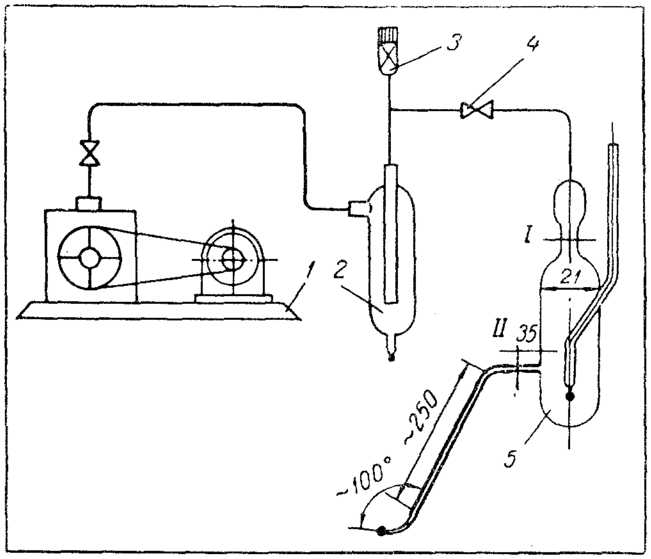

Fig. 2. Schematic of experimental setup for studying thermodynamic properties of solutions A and B: 1) mechanical vacuum pump; 2) glass trap, liquid nitrogen-cooled; 3) manometric vacuum gauge; 4) glass stopcocks; 5) experimental vessel with thermocouple and capillary.

From Fig. 1 it is seen that during cooling of solutions A and B from the normal liquid state (i.e., at $t > t_{\text{triple pt}}$), regardless of the cooling rate and liquid pressure ($p_{\text{satd vapor-liq}} \leq p_{\text{liq}} \leq p_{\text{atm}}$), a stable supercooled state (bottom arrow Fig. 1) is formed. The following experimental facts indicate its stability: the cooling process from −55° to −118° C for solution A and to −110° C for solution B was carried out purposely over a period of 6–7 hr; the solutions were held at the latter temperatures for not less than 1 hr; the liquid in the vessels was shaken periodically. All this, however, did not lead to formation of a crystalline phase during the experiment (up to 8 hr). At these temperatures the solutions remained perfectly pure and clear. No demixing in the form of precipitating crystals or other formations were observed in the course of the experiment.

At temperatures below −120° C for solution A and −113° C for solution B the liquid goes over into solid phase I, which at any lower temperatures remains stable for a considerable interval of time (the duration of the experiment). Phase I is monolithic, fairly clear, and light, having various hues that evidently depend on the impurities. For example, solution A has a pale light-green tint, solution B a light-green tint. This phase is formed by gradual freezing of the whole volume of liquid beginning from the walls and surface. Eventually, the monolith thus formed cracks because of thermal strains.

With temperature increase (middle arrow, Fig. 1) it melts at the same temperatures (−120° to −113° C), forming a supercooled, transparent, uniformly colored liquid. The melting process proceeds at nearly constant temperature. On further heating the liquid crystallizes, at temperatures of −73° C for solution A and −70° C for solution B, forming a solid phase of new structure, phase II. It is dense, opaque, snowy, colored green for solution A, and colored light green with a brown tint for solution B. The formation of this phase began with the formation in the liquid mass of separate crystal fibers (in A) or globules (in B), which grew rapidly filling the whole volume of the liquid. During formation of the "ice" the temperature of the solution stayed nearly constant.

On being heated solid phase II melts at −63.8° C for solution A and −57.2° C for solution B, and the normal liquid phase is formed. Melting proceeded at a slightly increasing temperature. The temperatures at which solid phase II began to melt were taken as the triple points. They agree closely with the values of the temperature of incipient crystallization at atmospheric pressure interpolated for our compositions from the data of [1].

If solid phase II is not melted, but cooled again (upper arrow Fig. 1), it stays stable at any low temperature down to −196°C.

Entirely analogous phenomena were observed in the vessel containing solution at atmospheric pressure. Thus, the phenomena we studied occupy the whole region from the saturation line to atmospheric pressure on the phase diagram.

During solidification of the solutions to the solid phases and during melting, stratification of the liquid phase was not observed visually. Phase transitions were accomplished without progressive precipitation of the components. The solution as a whole behaved as a homogeneous liquid during the mutual transitions of the solid and liquid phases. Special experiments were set up to verify this fact.

A certain solution (A or B) was introduced into the left compartment of the vessel shown in Fig. 3. The vessel was prepared and carefully evacuated as for the scheme of Fig. 2, after which it was sealed at point I. Introduction of the liquid and hermetic sealing were carried out by the method of [2]. About $100.0028 \cdot 10^{-6} \text{m}^3$ of solution was introduced.

The liquid in the left compartment was frozen with formation of solid phase I. Then the "ice" began to melt. When approximately half of the solid phase was melted, the liquid formed was decanted into the right compartment by tilting the whole vessel. After this both compartments were sealed at points II and III. The same solution was introduced into a new vessel and solid phase II was treated in the same way. This was done for solutions of both compositions (A and B).

The substances sealed in the two compartments were subjected to chemical analysis. It was found that the divided solid phases I and II and the liquids formed during their partial fusion have exactly the same quantitative composition for a given solution (A or B). This confirms what was said above and indicates that the $HNO_3-N_2O_4-H_2O$ system is not simply a mechanical mixture of the components.

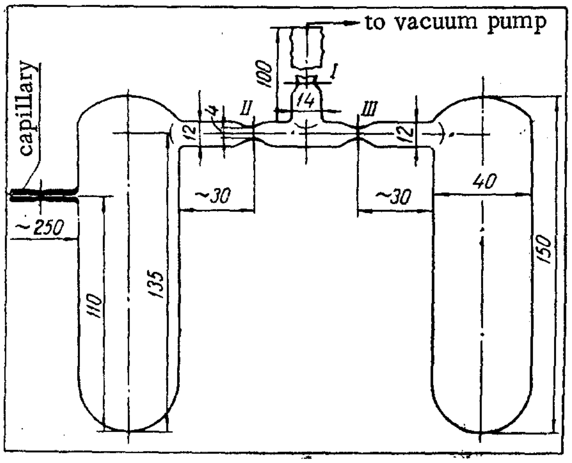

Fig. 3. Experimental vessel.

The existence of two forms of "ice" and a transition state between them in the technical solutions studied is an anomaly and is obviously conditioned by the possibility and nature of the change in the structural arrangement of the molecule in the liquid and solid phases associated with variation of the viscosity of the solutions with change in temperature.

This hypothesis is confirmed by the fact that both solid phase I and solid phase II develop only from the liquid state when the molecules may still have sufficient mobility for reorganization. Phase I develops from a heavily thickened liquid and probably represents an amorphous unstable state of the solid phase. However, in the course of experiments last 2–3 days direct transition from solid phase I to solid phase II (in the solid phase) did not occur. This is explained by the fact that in the solid state the mobility of the molecules is sharply curtailed and they are not able to change their position in order to assume the structure corresponding to minimum energy at a given temperature.

Thus, it is not possible for phase I to go over directly into phase II or phase II into phase I.

The change in the nature of the function $\lg p_s = f(1/T)$ in certain ranges of negative temperature is also attributable to anomalies and, obviously, results from molecular structure changes in the liquid phase. It has a direct relationship with the supercooled state, since the breaks in the lines $\lg p_s = f(1/T)$ are situated close to the region of triple points.

Investigations of the phenomena described are being continued with the $HNO_3-N_2O_4-H_2O$ solutions.

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