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GAS HYDRATES IN CAPILLARIES

CRYSTALLOGRAPHY

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Abstract

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GAS HYDRATES IN CAPILLARIES

(Presented by Academician A. V. Shubnikov, 18 IV 1968)

In 1961 L. Pauling proposed his molecular theory of general anesthesia ^(1,2). This theory is based on the assumption that, under the action of an anesthetizing gas, gas hydrates are formed in nerve capillaries, preventing the propagation of the excitation wave along the nerve. Pauling showed that the minimum gas pressures required to achieve anesthesia are proportional to the pressures of these same gases at which gas hydrates arise. It should be noted that in the case of anesthesia the temperatures are much higher, and the gas pressures three orders of magnitude lower, than in the classical cases of gas-hydrate formation. In this connection it is of interest to consider the question of the possibility of stabilizing gas hydrates in capillaries by means of an equivalent pressure of surface forces under certain special conditions.

Let us consider, for example, the possibility of obtaining chlorine gas hydrate in well-dehydrated capillaries. If a vessel with water is connected to an evacuated system, then dissolved gases, in particular chlorine, will begin to be vigorously evolved together with the vapors. In this case, as follows from the experiments of M. Faraday ⁽³⁾, interpreted by B. A. Nikitin ⁽⁴⁾, there is a high probability of the formation of chlorine gas hydrate in the vapors. The failure to satisfy the classical conditions for the formation of (crystalline) gas hydrate should not be surprising: as is known, many compounds can exist in the gas phase under conditions under which their existence in the condensed phase is impossible ⁽⁵⁾.

On entering a capillary, chlorine gas hydrate will be adsorbed by the walls under the action of uncompensated surface charges. The hydrate molecules at the capillary walls will then be subjected to an attraction which, at distances of 10-12 Å from the wall, corresponds to a pressure of about 10 atm. ⁽⁶⁾. Such pressure is more than sufficient at a temperature of 20° to preserve the stability of chlorine gas hydrate in the condensed phase. (According to M. Stackelberg, chlorine gas hydrate can form in the solid phase up to 28.7°; at this temperature a pressure of 6 atm. is sufficient for the formation of gas hydrate. ⁽⁷⁾.) Several monolayers of the gas hydrate that have formed, with a sufficient rate of supply of condensate from the vapors, will make it highly probable, owing to the cooperativity of the system, that a three-dimensional phase will form. The stability of the latter may be ensured by stabilization of the gas hydrate along the phase boundaries

(⁸), in the present case at the capillary walls.

That the condensate obtained in this way will be chlorine gas hydrate can be checked, for example, by its density. The density of chlorine gas hydrate is known to be 1.37 g/cm³ (⁷). An additional confirmation that this is precisely chlorine gas hydrate may be provided by the possibility of distilling it from one capillary into another up to a temperature of the section of the tube connecting the capillaries equal to the temperature at which molecular chlorine begins to dissociate (400°). (Disruption of hydration on passing through a zone of elevated temperatures below 400° is of no significance, since on leaving the zone the hydration is restored.)

The mechanism considered applies, of course, not only to chlorine gas hydrate, but also to the possibility of the formation of other dodecahedral gas hydrates in capillaries. It cannot be a model, in the strict sense of the word, for processes in the capillaries of the nervous system, but it apparently makes it possible to explain qualitatively certain aspects of the phenomenon. On the other hand, the considerations set forth may possibly have some bearing on the fundamental work of B. V. Deryagin and his school on the study of water with special properties, formed under certain conditions in capillaries (⁹).

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Note: Figure translations are in progress. See original paper for figures.

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