LETTER TO THE EDITOR

REMARKS ON THE ARTICLE BY N. M. KUZNETSOV AND V. N. OLEINIK

Applications of the Thermodynamic Similarity Theory to the Generalization of Experimental Data on Heat Transfer of Boiling Organic Heat-Transfer Agents.

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It is known that the law of corresponding states does not have general significance. It is valid within the limits of certain groups of thermodynamically similar substances. Until recently the conditions of membership in a particular thermodynamically similar group had not been formulated.

Starting from the theory of the molecular structure of liquids, we have attempted to classify all the high-temperature heat transfer agents in thermodynamically similar groups (see A. V. Chechetkin: "High-Temperature Heat Transfer Agents," GEI, 1962). We have shown the following:

1. The thermophysical properties of substances depend on their molecular structure in the liquid state and the nature of the interatomic or intermolecular bond.

2. In the region of pressures and temperatures in which high-temperature heat transfer agents are used in practice, their molecular structure in the liquid state is related to that which they have in the solid state.

3. Although, with rare exceptions, substances have several types of bonds, their thermophysical properties are determined by the weakest ones.

This gave us grounds for basing our classification of high-temperature heat transfer agents in thermodynamically similar groups on the following principle: high-temperature heat transfer agents belong to the same thermodynamically similar group if they have the same molecular structure in the solid state, the same type of interatomic or intermolecular bond, and the same critical coefficients $k = RT_K/p_K v_K$. In accordance with this principle we have classified all high-temperature heat transfer agents into three main thermodynamically similar groups: liquid-metal (basic bond metallic), ionic (basic bond ionic), and organic (basic bond residual).

With a few exceptions, heat transfer agents simultaneously have several types of bonds, but the crystal lattices of substances with the same types of bonds are different. Therefore, each of the above-mentioned three groups has been divided into subgroups according to the relationship between the basic bond and the rest and according to type of crystal lattice. Thus, for example, high-temperature organic heat transfer agents are divided into three subgroups: a) with symmetric molecules (glycerin, glycol, etc.) which, apart from a residual bond, have a stronger polar intermolecular bond; b) with long molecules (paraffins characterized by the presence of a nonpolar intermolecular bond); c) with flat molecules (aromatic hydrocarbons) with a characteristic aromatic intermolecular bond. In accordance with this classification diphenyl mixture (DPM) and monoisopropyldiphenyl (MIPD) belong to the same subgroup, that with flat molecules. This accounts for the fact that (as may be seen from Fig. 1 of the article in question) the experimental data on DPM and MIPD are well approximated by one logarithmic curve and the data on water and the standard by another. Obviously, Eq. (8) is valid for organic heat transfer agents with flat molecules. Thus, the work of Kuznetsov and Oleinik confirms our condition for membership in a particular thermodynamically similar group of heat transfer agents.

In the light of the above, certain assertions of Kuznetsov and Oleinik give cause for surprise. Thus, on page 42* they write: "We represent the function f in (4) as a power monomial and remember the following facts c) for liquids having with indentical molecular structures and the same type of interatomic bonds the effect of C_{V0}/R may be neglected" and later on the same page: "In fact, there is no reason to consider water, alcohols, alkanes and polyphenyls thermally similar. Even the critical coefficients, quite apart from the structure of the molecules and the interatomic bonds, are quite different." These quotations imply identification of the structure of the molecules with the molecular structure of the substance! Actually, these are quite different concepts, and we cannot imagine how one could introduce into the principle of membership of substances in the same thermodynamically similar groups a requirement that the structures of the molecules be the same. This may cause the reader some perplexity.

It follows from Kuznetsov and Oleinik's article that the authors, while essentially making use of the principle we propose, have distorted its significance and have also prevented the reader from working things out for himself, since the article even omits a reference to the primary source.

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*English page numbers.