Thermodynamics of Phase and Chemical Equilibrium of Involved Systems Aluminium Alkyls and Their Derivatives

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This work presents an investigation of liquid-vapor equilibrium and chemical processes in the vapor phase for a system of alkyl compounds and their derivatives over wide temperature and pressure intervals in saturated and unsaturated vapor. The results illustrate the possibility of a static method with zero-manometer to study complicated systems. Thermodynamic properties of evaporation, dimerization process, dissociation in the vapor phase with C_4H_{2n} formation, temperatures of stable existence, decomposition process and its mechanism of alkyl compounds and their derivatives are discussed. Investigation of unsaturated vapor showed that $Al(CH_3)_3$ (100), $Al(C_2H_5)_3$.(60), $Al(n\text{-}C_3H_7)_3$ (~3%), $Al_2O(CH_3)_4$. $Al_2O(C_2H_5)_4$, $AlH(C_2H_5)_2$ form dimers in the vapor phase. We have determined partial pressures and calculated thermodynamic properties. In the lecture we discuss thermodynamic properties of different process and the reactions:

$$AR_3 \leftrightarrow AlHR_2 + 0.5C_2H_{2n}$$
$$R_2Al\text{-}O\text{-}AlR_2 \leftrightarrow RHAl\text{-}O\text{-}AlHR + C_2H_{2n}$$
$$R_2Al(OR_2) \leftrightarrow RHAl(OR_2) + 0.5C_2H_{2n}$$

Thermodynamic properties showed that presence of oxygen bond Al-O-Al in alumoxane brings down of the energy $Al\text{-}C_2H_5\text{-}Al$ dimerization process. The regularities change of thermodynamic properties lead to an idea of (reverse) dative bond Al¬C or A¬C [1] in complex AR_k. In the lecture we bring results of quantum chemical calculations of an electron configuration in complex AR_k and substantiate that it really exists. We discuss specific intermolecular interaction realized in liquid alkyl compounds. This kind of bond formed by essential non-divided $2s^2$(c)-electron pair localized on carbon atom in basic and, on the other hand, on central atom (A) of complex AR_k [2]. Only two electrons of four valence electrons of the carbon atom form four bonds (one C-A and tree C-H) for expanse of the same electrons on three valence AO $2p_x$, $2p_y$, $2p_z$. Using thermodynamic properties we determined energy of specific intermolecular interaction.

[1] A.K.Baev // Russian Journal Coordination Chemistry. 1996. V .22. № 5. P. 399.
[2] A.K.Baev, D.V.Korolkov // Book of Abstract. 14 th International FECHEM Conference. Zurich University. 2003. P. 350.