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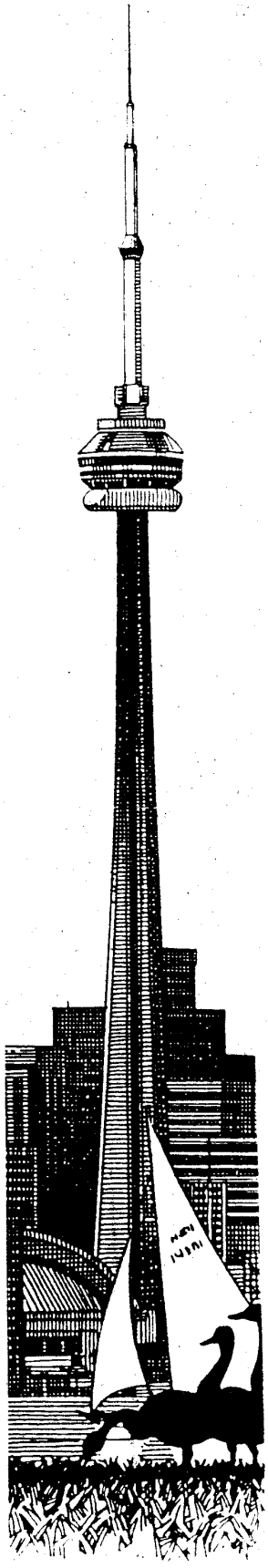
PROCEEDINGS



42nd Canadian Chemical Engineering Conference
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Calculation Method for Determination of Thermodynamic Properties of Chlatrate Hydrates of Water-soluble Gases

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Gas hydrates are widely used compounds in practice. E.g., chlorine hydrate may be used for water disinfection, condensation of chlor, high pressure chlorination, and for electrolites of high energy density batteries. Hydrates of other poisoning or reactive gases, as a chlor, sulphur dioxide, hydrogen sulphide, etc., also can be used for safe storage and shipping of these gases [4].

The chlorine hydrate is the oldest known gas hydrate discovered, by Davy in 1811 [1], but the composition (relative amounts of free chlor in hydrate)-formation condition relationships are not clear.

The accurate knowledge of thermodynamic properties are ultimately necessary in determining the circumstances and conditions of formation and decomposition of these compounds, and in determining their gas-content.

The simplest method for determination of composition and the thermodynamic properties of the gas hydrates are the calculation from easily measurable value of vapour pressures of hydrates by using Clausius-Clapeyron equation.

In the case of water-soluble gases, however, must not be neglected the real properties and the significant solubility of hydrate-former gases in water, and generally for any gases the fact must be considered that the composition of the hydrate always changes belonging to each p,T-values.

We are working out a simple in situ method for preparation of chlorine hydrate with reaction between a water-soluble hypochlorite and a hydrochloric acid solutions in low temperatures. We also present the phase diagram of chlorine - water system in interval of chlorine hydrate formation [2].

In order to eliminate such inadequacy in this report we calculated the heat of reaction of the following decomposition process:

$$Cl_2.nH_2O_{(s)} = Cl_{2(g)} + nH_2O_{(s)} \quad (1)$$

The solubility of chlor in solid ice, and the vapour pressure of ice in this low temperatures are negligible. The changes of composition between the three following measured points with low temperature difference are negligible, so fitting the simple applicable function curve, as a second-order polinom for **1**={1,2,3}, **2**={2,3,4}, **3**={3,4,5}....**N-2**={n-2,n-1,n} measured points, we can write the Clausius-Clapeyron equation by using a fugacity of chlor. From this equation we have calculated the heat of formation of chlorine hydrate from ice and gaseous chlorine. From fugacity values we have calculated the equilibrium constant of

dissociation, considering the fact, that the activity of ice and solid hydrate can be united. From the value of K_p can be calculated the standard free enthalpy and the entropy of chlorine hydrate at the individual p,T-points belonging the equilibrium curve.

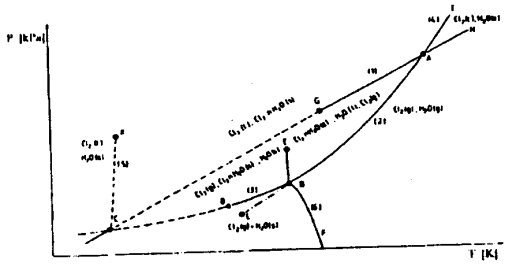

Fig.1. The p,T phase diagram of chlorine-water system in existence interval of chlorine hydrate

The experimental vapour pressure data for chlorine hydrate for the calculation was obtained from [3], because in this articles are exact data for composition of studied hydrate at 0 °C.

We also calculated the value of ΔH for reaction

$$Cl_2.nH_2O_{(s)} = Cl_{2(g)} \text{ and } nH_2O_{(l)} \quad (2)$$

at 0 °C , considering the solubility and real properties of chlor.

Because the reversible equilibrium is standing ((1) and (2) reaction) at -0.24 °C (see the phase diagram in *Fig.1*), we can calculate the composition of chlorine hydrate in this temperature (we neglected the difference between ΔH values at 0 and -0.24 °C) from the two reaction heat, considering the fact, that the difference in the two reaction heat is equal to the heat of melting the n mole water. By using a second-order polinom from this calculation we resulted the n=8.35 value, while the Roozeboom gave the value n=8.34 for hydrate, from which dissociation pressures data we had for calculation.

The synthetic method and the approximation for calculation of thermodynamic data can spread over the chlorine for other water-soluble gases.

[1] Davy, H.: Phil. Trans., 1811, 101(1), 1-35
[2] Kótai, L., Bódi, F., Sebestyén, A. and Harfouch, S.: Hung. J. Ind. Chem., 1991, 19(1), 63-68
[3] Roozeboom, H. W. B.: Rec. Trav. Chim. Pays-Bas, 1885, 4(1), 65-73
[4] Berecz, E., Balla-Achs, M.: Gas hydrates, Akadémiai Kiadó, Budapest, 1980.