Calculation method for determination of thermodynamic properties of chlatrate hydrates of water-soluble gases

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Klórhidrát

Introduction

The gas-hydrates belong to the group of the non-stoichiometric chlatrate compounds of water. The oldest known gas hydrate is a chlorine hydrate, discovered by Davy in 1811. It has gained wide spread application in numerous fields in practice, e.g.:

- for safe storage of chlorine gas
- for high-pressure chlorination
- for small-scale preparation of liquid chlorine
- for electrode in high-energy density batteries
- for leaching of low-raw zinc ores
- as a desinfectants for water and air, etc.

The accurate knowledge of composition (relative amount of free chlorine in hydrate) and the thermodynamic properties are very important and necessary for determining of optional parameters of production, storage and utilisation of chlorine hydrate.

Synthesis of chlorine hydrate

For synthesis of chlorine hydrate a reaction of free chlorine gas and a chloride-containing metal salt solution was generally applied for avoid of hydrolysis of chlorine:

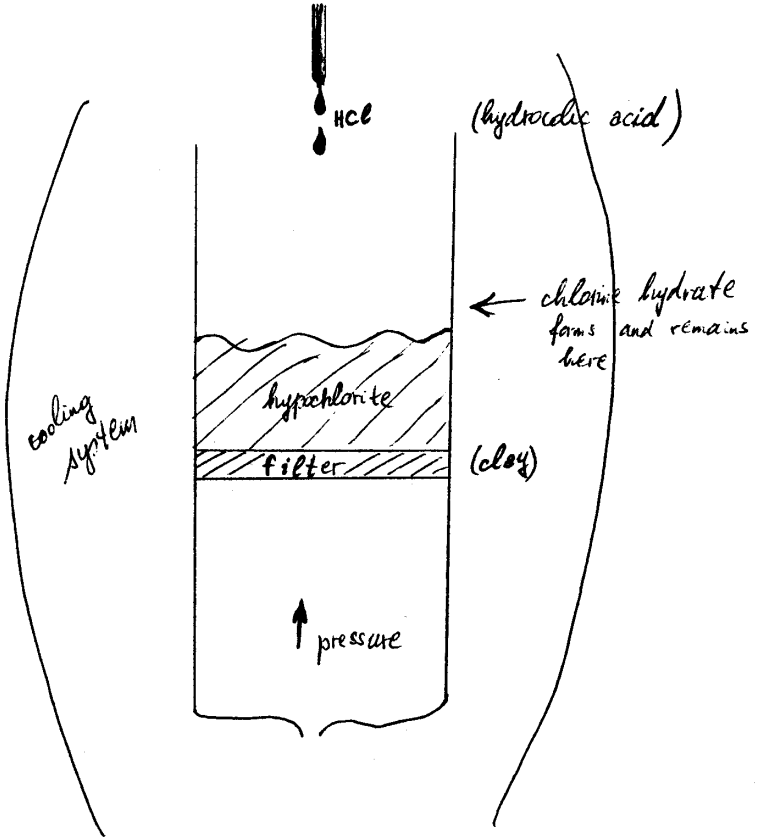
$$Cl_2 + H_2O = H^+ + Cl^- + HOCl$$

In the present work the reaction between a cold metal hypochlorite (sodium or calcium hypochlorite) and a cold hydrochloric acid solution was applied:

$$NaOCl + HCl = Na^+ + Cl^- + HOCl$$
$$HOCl + HCl = H_2O + Cl_2$$
$$Cl_2 + nH_2O = Cl_2.nH_2O$$

The advantages of this method are as follows:

- We did not worked with gaseous chlorine
- The hydrolysis could be avoided (chloride and hydrogen ions are present in high excess)



- The concentration interval is wide for production of chlorine hydrate (even the 25% aqueous solution of hypochlorous acid is stable).

- Using calcium chloride and calcium hypochlorite solutions the temperature of hydrate formation can be decreased to -50 °C

- The procedure of synthesis is very simple

-The yield of hydrate and the utilisation of active chlorine content of hypochlorous salts are very high

-The separation of hydrate and the mother-liquor is a simple pressure filtration if the synthesis was carried out in a thermostationary reaction vessel furnished with filter
(see Figure 1)

- At appropriate cold conditions the chlorine gas does not leave the solution

Determination of the composition

The composition of chlorine hydrate is not clear from the literature data. In the present work for determination of real composition of each hydrates of chlorine a new method was introduced.

The advantages are as follows:

- Indirectly, the errors originating from decomposition of hydrate do not occure
- The errors in the composition due to the inclusion of mother-liquor does not occure

- The conditions of formation - and determination of the composition (temperature, pressure, salt, acid and ion concentrations) are well-controlled

The method based on a reaction of synthesis with excess of hydrochloric acid in the following:

Knowing the initial concentrations of sodium, chloride and hypochlorite ions (or sodium hydroxide concentrations) the amount of the necessary hydrochloric acid and of the released chlorine is known .

From the solution after the filtration of hydrate suspension a sample was taken and concentrations of hydrochloric acid and chlorine were determined. Knowing the excess of the hydrochloric acid the volume and the weight as well as the mole number of the free (not involved in the hydrate) water can be calculated.

Similarly, the amounts of the free and chlatrated chlorine can be calculated from the content of chlorine. These data are useful in determination of the real (without intercalated mother-liquor) composition.

In the knowledge of the initial mole numbers of water and chlorine at well-defined temperature and pressure (until the freezing point of the solutions) inside a wide range of concentration of initial salt, acid and ion content the molar ratio of water and chlorine in the hydrate can be calculated.

This method is also applicable for composition determination of other water-soluble gases.

Calculation methods

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

In the case of water-soluble gases, e.g. chlorine the following factors must not be neglected:

-the real properties of chlorine
-the solubility of the chlorine in the formed water
-the fact, that the composition of the hydrate always changes belonging to each p,T-values

In order to eliminate such inadequacy in this work we calculated the heat of reaction of the

$$Cl_2.nH_2O = Cl_2(g) + nH_2O(s)$$

process, because the solubility of chlorine in solid ice and the vapour pressure of ice in this low temperatures are negligible.

Calculation of the heat of formation

The equation is:

$$\frac{d \ln p}{d\,(1/T)} = \frac{-\Delta H_r}{R}$$

when ΔH_r is the heat of decomposition reaction, and $-\Delta H_r = \Delta H_f$, where ΔH_f is the heat of formation.

From the composition measuring we deduce, that the changes of composition are negligible between three consecutive measured points, where the temperature difference is small.

We have measuring points $T_0 < T_1 < T_2 \ldots T_{N+1}$

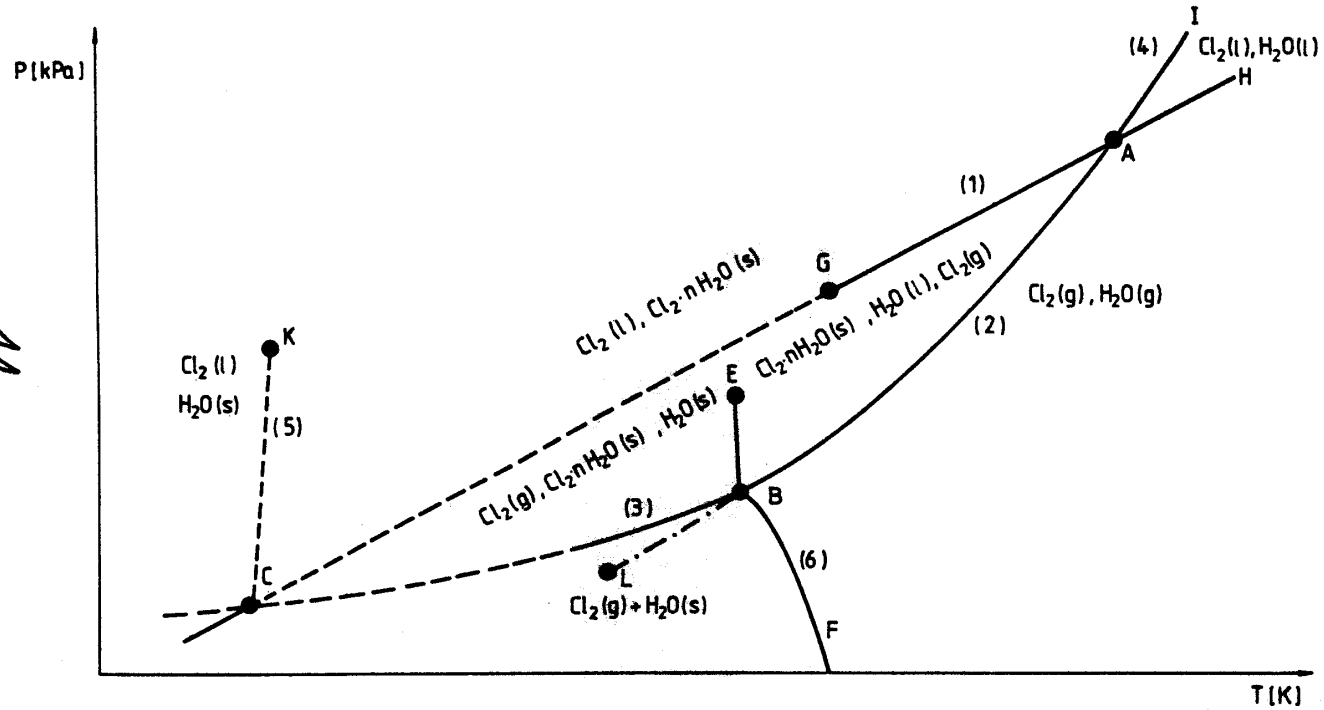
For the composite C_i for fixed i we use the interval (T_{i-1}, T_{i+1}) $(1 < i < N)$.

Fit a second-order polinomial P_i to the measured points at T_{i-1}, T_i, T_{i+1}. This gives the approximating values $P_i(T_0)$, $P_i(T_1)$.....,$P_i(T_N)$ for the composite C_i ($i<N$ is fixed).

Now use these values to solve the Clausius-Clapeyron equality for approximating the values of ΔH_r for the composite C_i.

Apply this method for all composites $C_1, C_2, \ldots C_N$ for approximating their appropriate values of ΔH_r.

Fig. 1: The phase diagram of the chlorine-water-chlorine hydrate system



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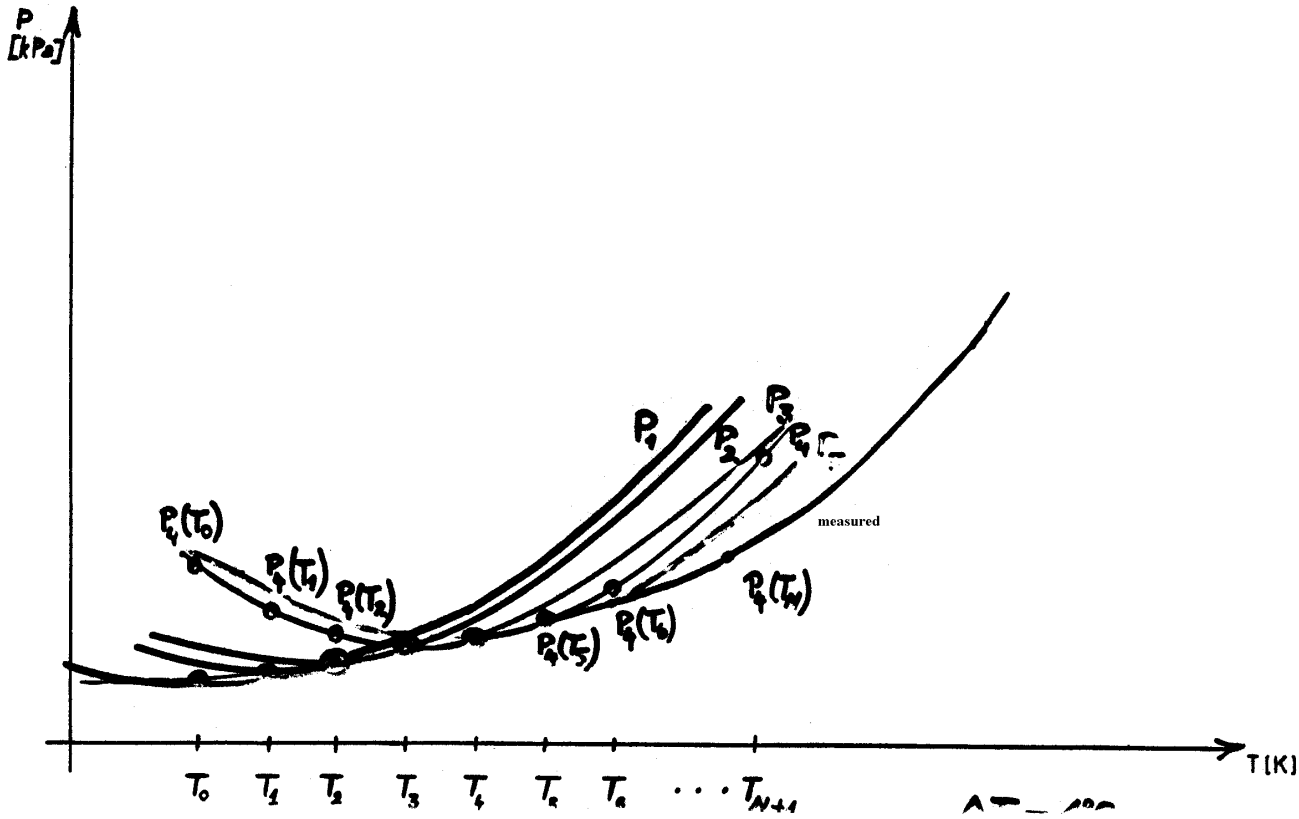
n is constant on P_i $(i \leq N)$



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Calculation of free enthalpy and entropy

For the decomposition reaction

$$K=\frac{a_{\text{hydrate}}}{a_{\text{ice}} * a_{\text{chlorine gas}}}$$

and considering, that the solid ice and hydrate activity equal to be unit,

$$K_p=\frac{1}{p_{Cl_2}}$$

Thus,

$$\Delta G=-RT\ln K_p$$

and

$$\Delta S=\frac{\Delta H-\Delta G}{T}$$

Checking the calculation method

For the chlorine hydrate formation reaction from chlorine gas and liquid water at 0 °C (from literature data) we took the value $-\Delta H_1=-80.567$ kJ/mole. From our calculations for formation of chlorine hydrate from chlorine gas and ice we was taken a $-\Delta H_2=-30.452$ kJ/mole.

Taking these values and using the melting heat of water at 0 °C from the

$$n=\frac{\Delta H_1-\Delta H_2}{\Delta H_m}$$

we obtained the n = 8.34. We carried out our calculations from p,T-data of chlorine hydrate, which are characterized with n=8.35 value (experimentally measured value).