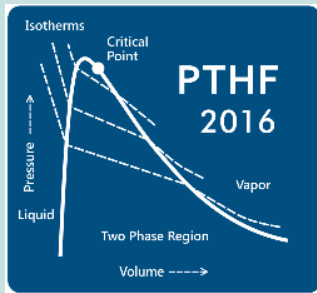


Международная конференция

**ФАЗОВЫЕ ПРЕВРАЩЕНИЯ В
УГЛЕВОДОРОДНЫХ ФЛЮИДАХ**



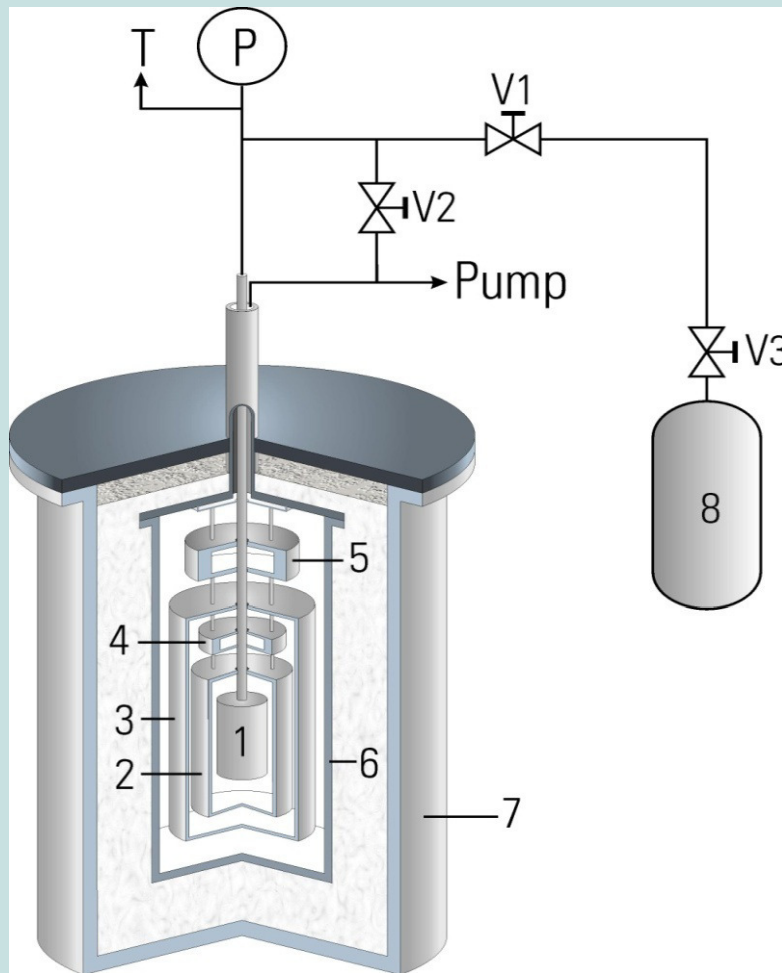
**Фазовое поведение гидратов метана
и углекислого газа и их смесей**



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PVT and calorimetry experimental setup



To decrease relaxation time:

- Cell (1) is filled by quartz sand with the grain size 8-10 μm
- After the injection of water into the cell, the cell was sealed and heated to evaporate water completely. Then the cell was cooled slowly and placed into the calorimeter. The procedure allows to distribute water homogeneously in the free volume of the cell.

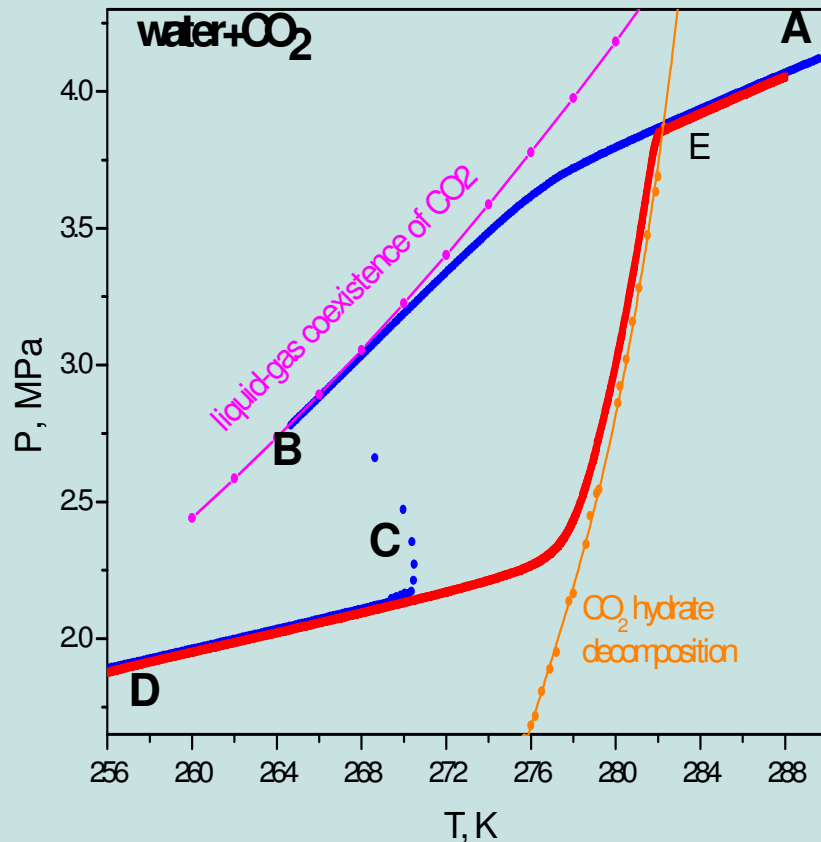
Measured properties:

Temperature (accuracy $5 \cdot 10^{-4}$ K)

Pressure (accuracy 10^{-3} MPa)

Internal energy (accuracy 1 mJ)

Accumulation and decomposition of hydrate



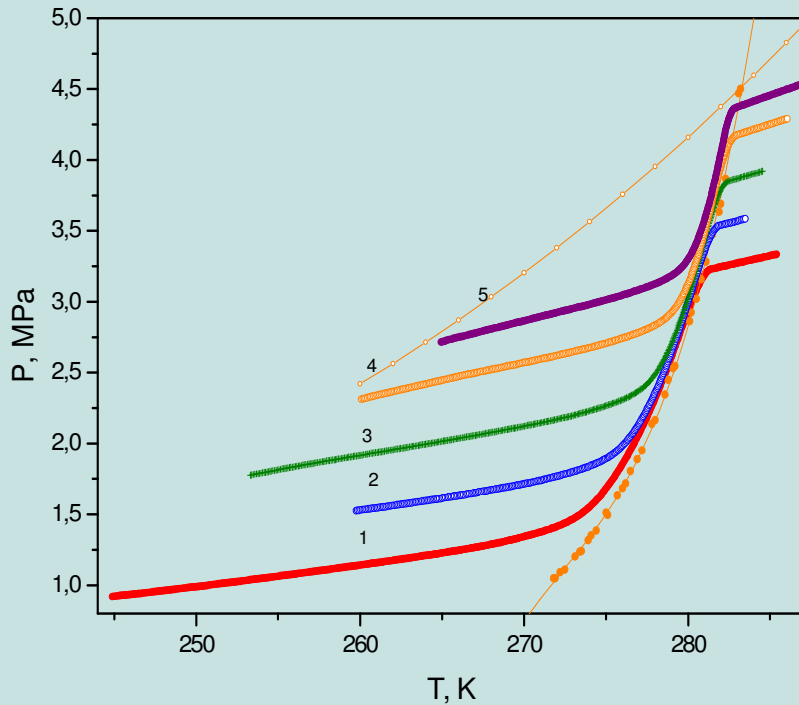
A measurement run consists of

- cooling of gas-water system A-B,
- accumulation of hydrate B-D
- heating of the cell until the complete decomposition of hydrate and return to the initial two-phase state D-E-A.

Orange line – hydrate decomposition, magenta line – liquid-gas coexistence of CO₂.

The pressure and temperature of the cell, as well as the internal energy of the system were measured and recorded.

Carbon dioxide hydrate

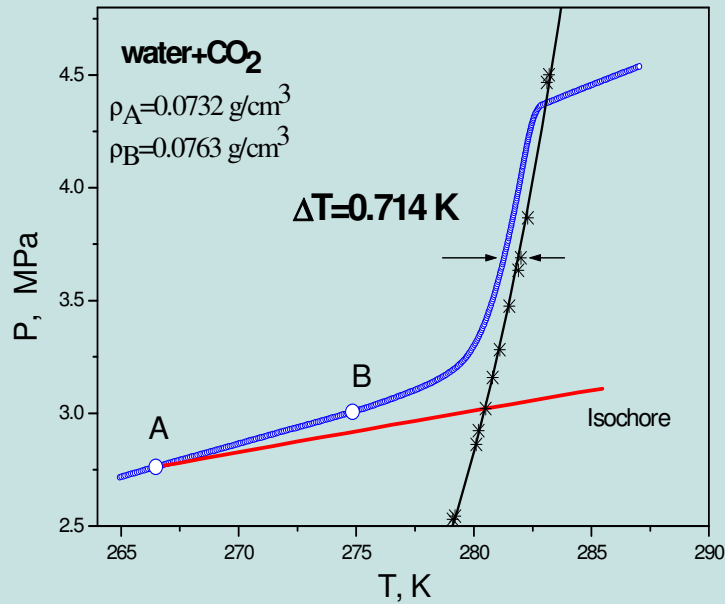


Five cycles of accumulation and decomposition of hydrate were done. The amount of water in the cell was constant, the mass of gas increased from cycle to cycle.

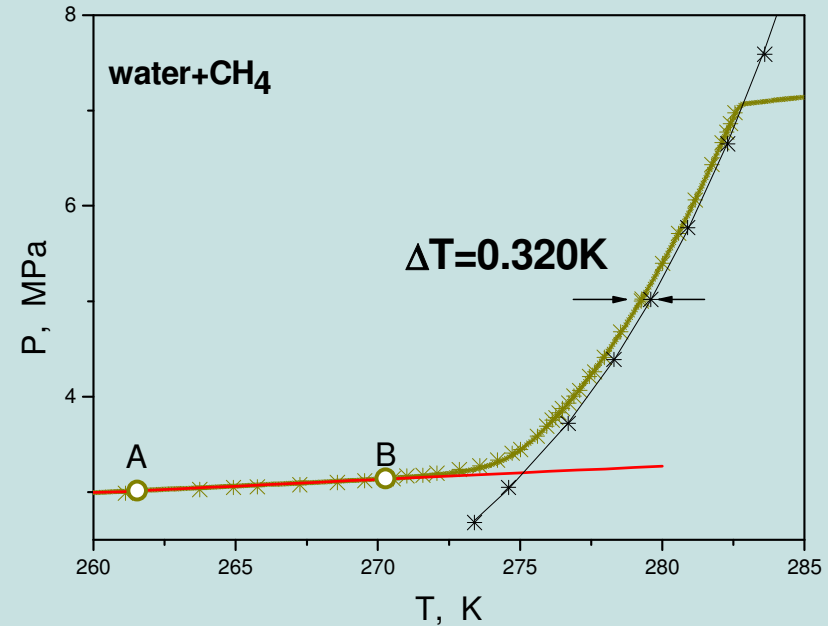
Number of cycle	1	2	3	4	5
Mass of CO ₂ , g	0.5683	0.6380	0.7168	0.8086	0.875

Hydrate dissociation in porous medium

CO₂ hydrate



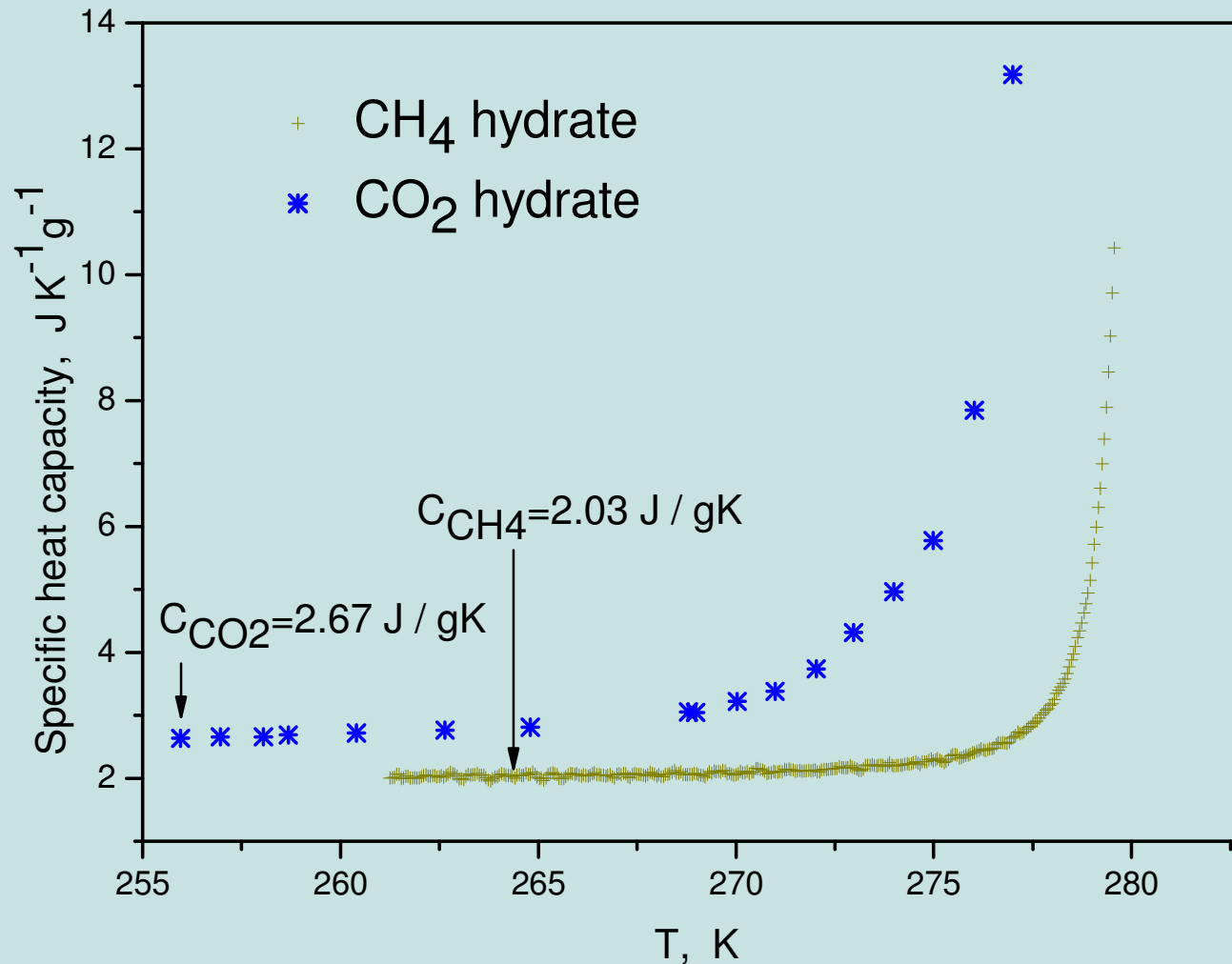
CH₄ hydrate



Red lines present the isochores passing through the point A. The initial part of heating curve coincides with the isochore for methane hydrate but differs from it for CO₂ hydrate. Thus, the hydrate number is constant for methane hydrate, but it increases for CO₂ hydrate.

The shift of three-phase equilibrium curve in a porous medium for the CO₂ hydrate is two times greater than the shift for the methane hydrate. The surface tension of CO₂ hydrate-water is three times larger than for methane hydrate – water.

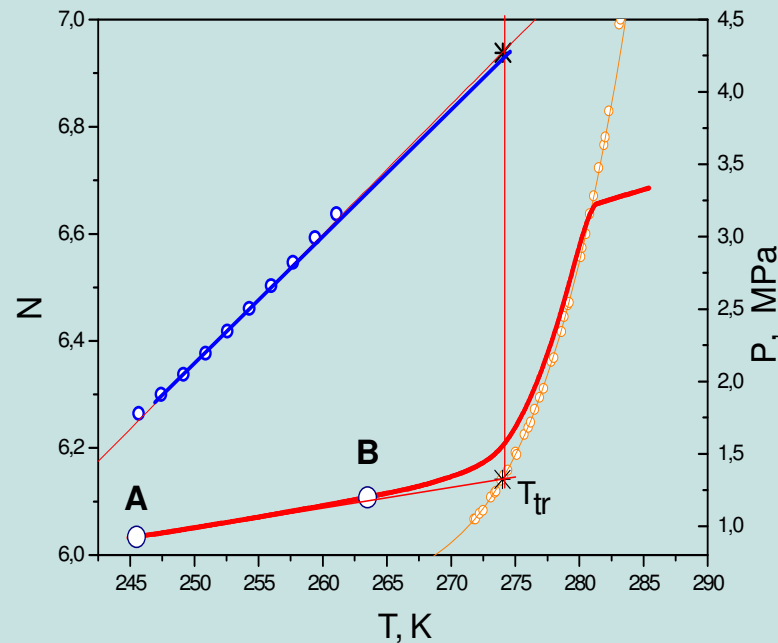
Heat capacity of hydrates of methane and CO₂



Specific heat of CO₂ hydrate is 30% larger than the specific heat of methane hydrate.

Determination of hydrate number

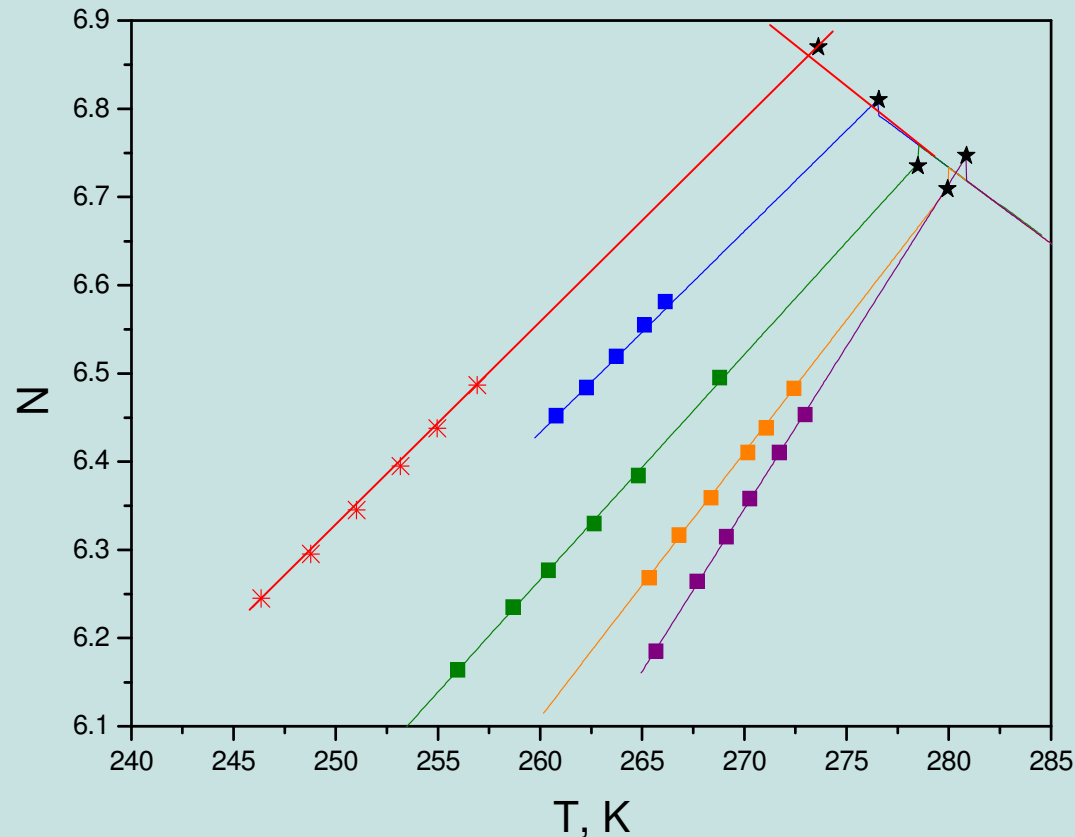
Hydrate number N determines the composition of hydrate: $N = v_w / v_G$.



Part AB of the hydrate heating curve is different from the isochore. The amount of gas in the hydrate decreases. We assume and control that all water in the cell is in hydrate. Thus, the mass of the water in the hydrate is constant, while the hydrate number changes.

Dissociation of the hydrate into water and gas starts at point B. Blue circles present the dependence of the hydrate number on the temperature at the part AB of the heating curve. Solid blue line is the extrapolation of these points to the transition temperature T_{tr} .

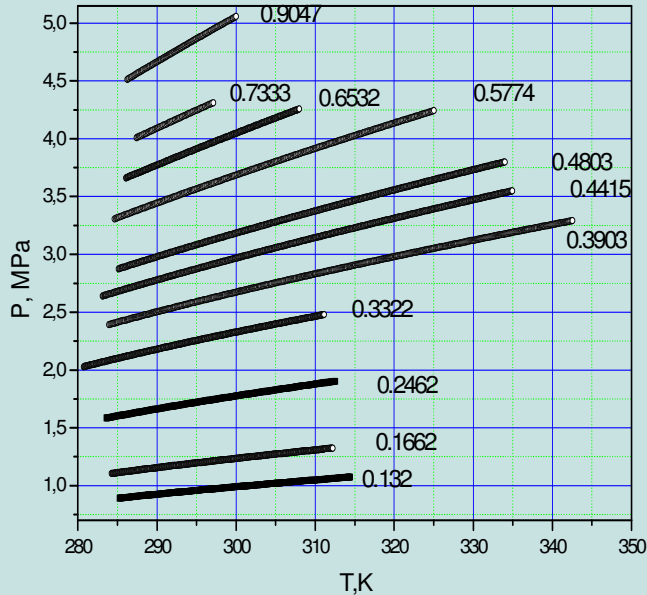
Temperature dependence of CO₂ hydrate number



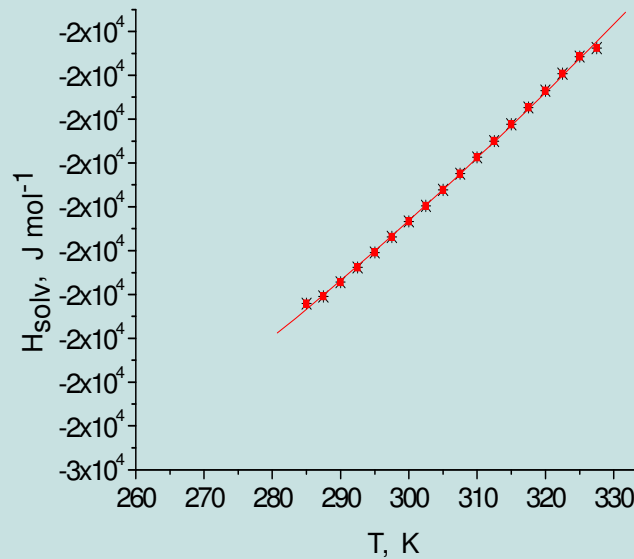
The hydrate numbers for other cycles were obtained analogously. The hydrate number values on the hydrate-gas-water equilibrium line are presented by stars.

Henry's constant. Heat of dissolution

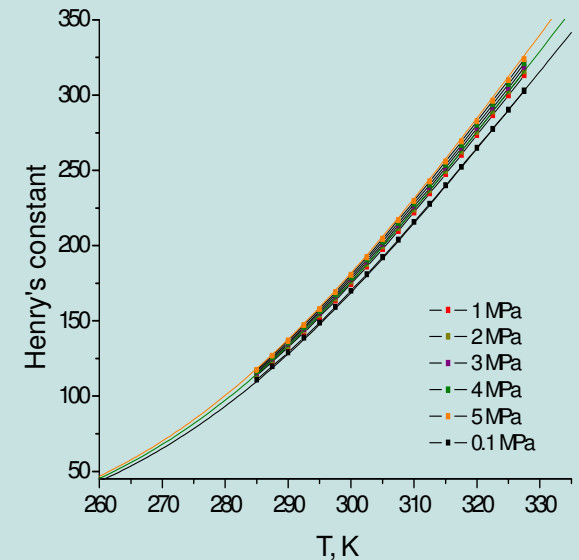
CO₂-water isochores



Heat of CO₂ dissolution

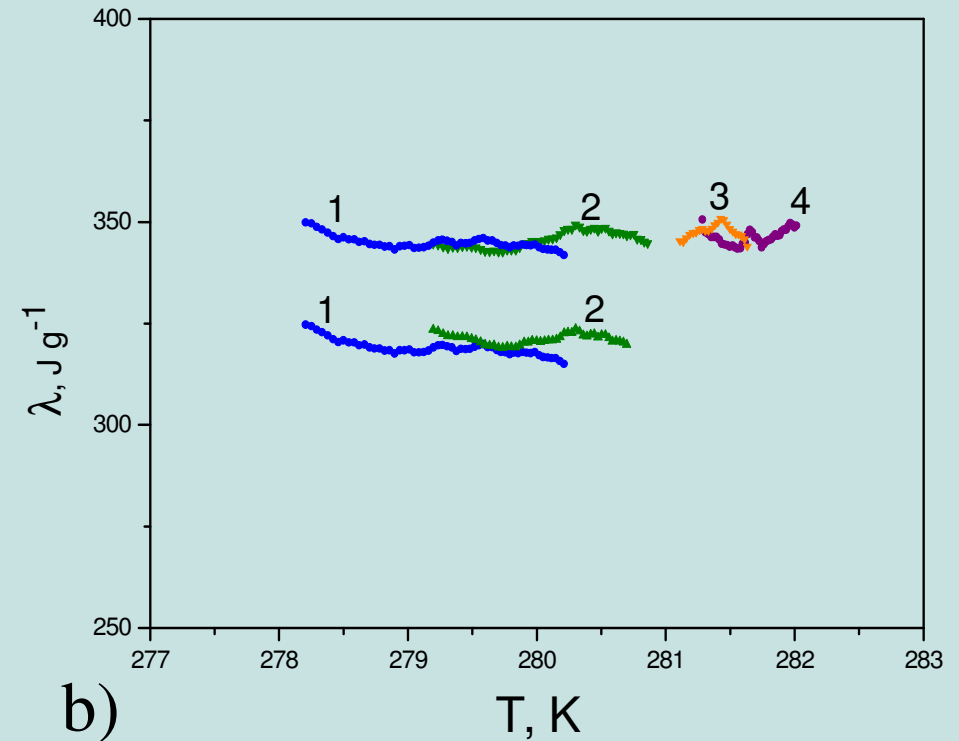
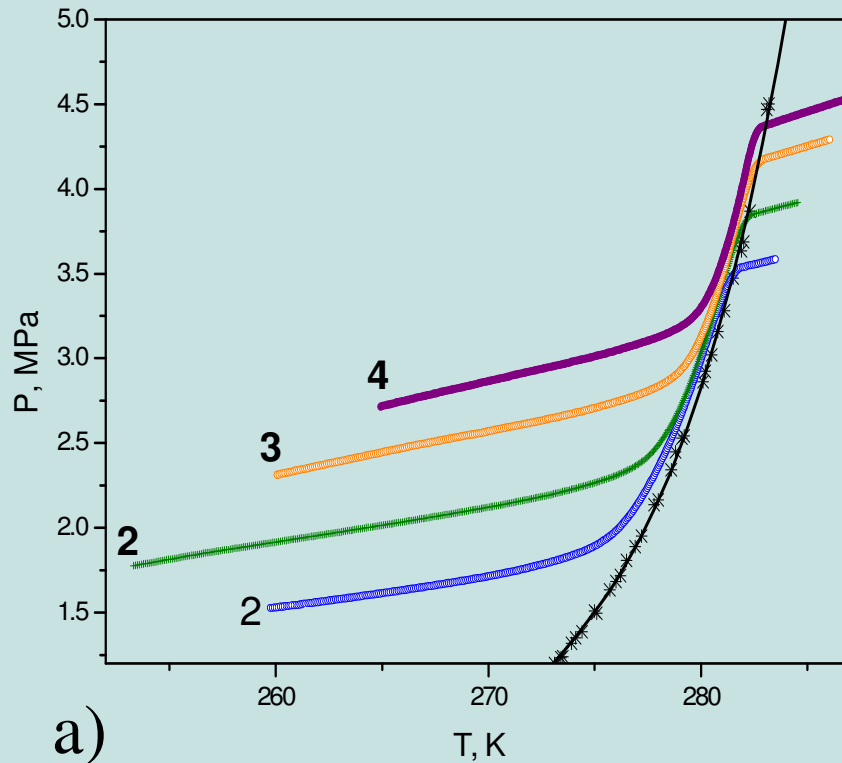


Henry's constants



To determine the mass and dissociation heat of the hydrate it is necessary to measure the solubility of carbon dioxide in water and the specific heat of dissolution. For this the temperature dependencies of the pressure of CO₂ along isochores in the presence of a fixed amount of water were measured.

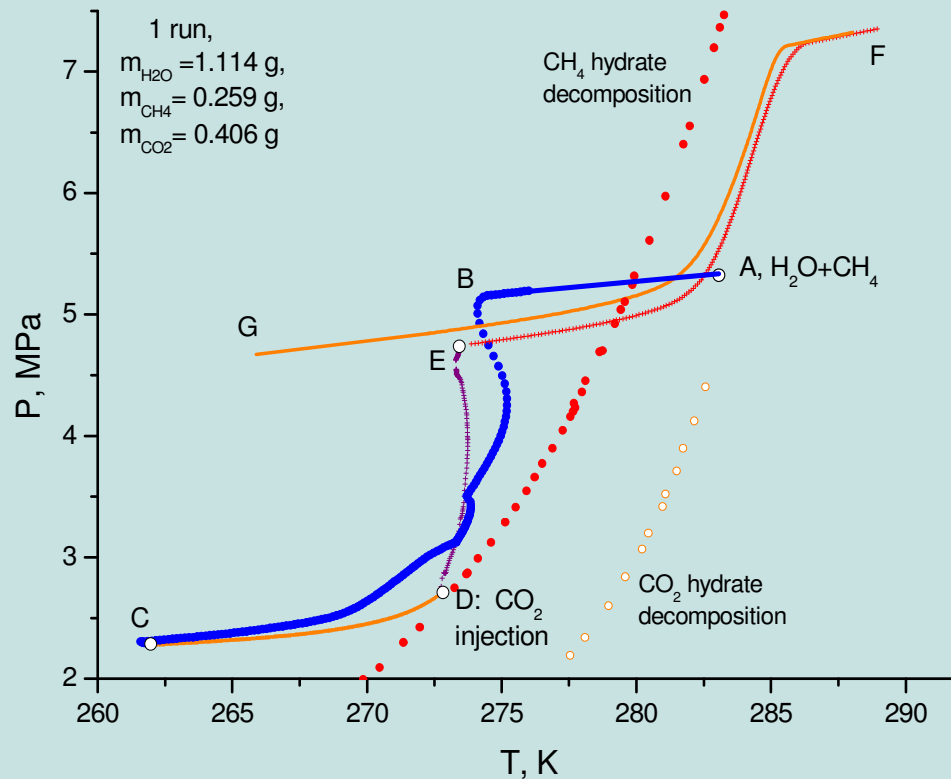
Dissociation heat of CO₂ hydrate



a) The heating curves of CO₂ hydrate.

b) The hydrate dissociation heat on the three-phase equilibrium line. Upper curves were obtained with the account of dissolution of CO₂, lower curves – ignoring effect of CO₂ dissolution.

Replacement of methane in hydrate by carbon dioxide



A-..-F – cycle of replacement

A - starting point, water + CH₄

B - hydrate formation starts

C - heating of hydrate+CH₄

D - CO₂ injection

E - end of replacement,

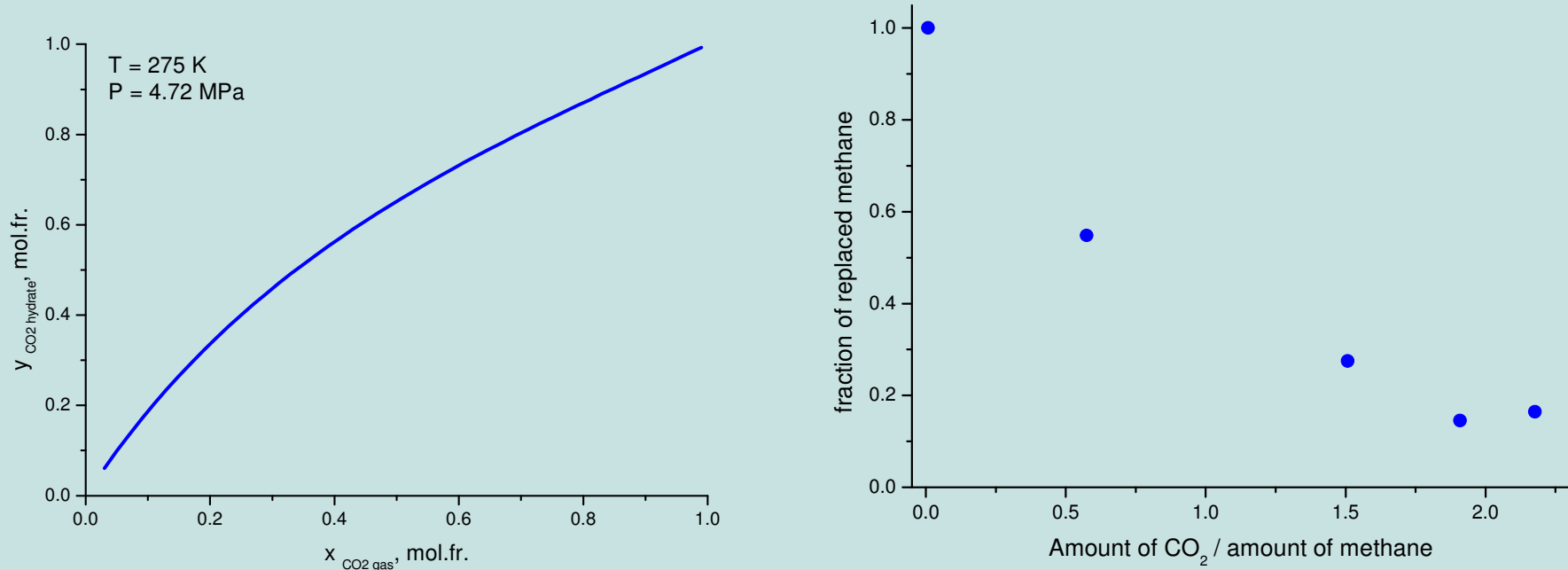
DE - about 24 hours

F - end of cycle

GF - heating of hydrate, formed **directly** from the same CH₄-CO₂ mixture

The dissociation curves of the hydrate formed by the replacement of methane by carbon dioxide E-F and for the hydrate formed directly from the same CH₄-CO₂ gas mixture G-F. At the first cycle the curves E-F and G-F are close, at the second cycle they practically coincide.

Replacement of methane in hydrate by carbon dioxide



The left figure presents the dependence of the equilibrium composition of gas in the hydrate on the composition of gas phase, determined according to the Van der Waals – Platteeu model.

The replacement extent can be calculated using the equation of state of the gas mixture and mass balance equations. The right figure presents the calculated replacement extent as a function of the amount of carbon dioxide, used for the replacement.

Conclusions

- The heat capacity and decomposition heat of the methane and carbon dioxide hydrates were determined.
- It is demonstrated that the hydrate number of carbon dioxide hydrate depends considerably on the temperature and pressure.
- It is shown that the account of dissolution heat of carbon dioxide in water is relevant for accurate determination of the hydrate dissociation heat.
- The dissolution heat and Henry's constant of carbon dioxide are determined for various pressures and temperatures.

Conclusions

- The composition of the hydrate after the replacement of methane by CO₂ is determined, it agrees with the tuned Van der Waals –Platteeu model. The dependence of the replacement extent on the amount of carbon dioxide was studied.
- Kinetics of the methane replacement from hydrate by carbon dioxide is controlled by two relaxation modes, the ratio of characteristic times of these modes is about ten. The replacement process is faster in the presence of liquid water in the system.