

Fluids at high pressures and temperatures

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Abstract - With high pressures, supercritical fluids can be studied over a very wide range of density. Fluids with strongly interacting polar molecules - for example water - are of particular interest. Results for several thermophysical properties are discussed. Density, dielectric constant and self-ionization of water have been determined or predicted to 1000 °C. Beyond 20 GPa very hot water appears to become a dense ionic fluid. - Dense, supercritical gases are increasingly applied as solvents. Pressure-temperature-composition diagrams and critical curves to 400 °C and 200 MPa have been determined for binary systems of water with helium, argon, xenon, nitrogen, oxygen, methane, carbon dioxide, benzene and others. An equation of state based on a defined molecular interaction model permits computation of such phase diagrams with polar partners and at high temperature. Extension to ternary systems is possible. Of geochemical interest are the ternary systems water-carbon dioxide-sodium chloride and water-methane-sodium chloride. Within the dense, supercritical aqueous mixtures, oxidation reactions are possible. Steadily burning "hydrothermal flames" have been produced at pressures to 100 MPa by introducing a slow flow of oxygen into supercritical dense water-methane fluids with excess water at 400 °C and above.

INTRODUCTION

Dense fluids at elevated and supercritical temperatures provide a unique field to study extensive and continuous variations of physico-chemical properties with temperature, pressure and composition. Knowledge of thermodynamic properties of the material under study is indispensable either as an end in itself or to define precisely the state of the substances at working conditions.

In order to generate substantial density variations, application of high pressure is necessary, although pressure values up to several hundred MPa will be sufficient in most cases. It should be remembered, that pressures of this magnitude normally do not appreciably deform molecular and electronic structures. - Fluids with pronounced intermolecular interaction are often of particular interest. Such fluids will have relatively high critical temperatures and may be corrosive at such conditions. Thus experimental arrangements may often be required which permit precise measurements at simultaneous conditions of elevated pressures, temperatures and corrosion resistance.

In the supercritical region one obviously has the possibility to vary thermophysical properties continuously from gas-like to liquid-like values. This could - for example - mean the transition from non-electrolyte to electrolyte behaviour of a solvent. There is a wide range of complete miscibility of otherwise immiscible partners like water and hydrocarbons, and there is an extended range of supercritical solvents for extraction processes. Many examples have been presented during this Conference. Studies of chemical reaction kinetics can be envisaged which take advantage of the combination of high material density and high "gas-like" transport coefficients.

In the course of this lecture selected results of more recent experimental research and of calculations shall be presented. Water and aqueous systems will be principle examples. At first some thermophysical - in particular dielectrical - properties of pure water will be shown. Binary mixtures will be more extensively discussed. Selected ternary systems will follow, and finally the feasibility of "hydrothermal combustion" shall be demonstrated.

PURE WATER

Pure water is probably the best investigated polar fluid as far as the pressure-volume temperature relations are concerned. Modern editions of steam-tables for engineering purposes provide density data in dependence of temperature and pressure to nearly 1000 °C

and 1000 MPa. Above about 3000 MPa shock wave data can be used (ref. 1). The intermediate region must for the present be covered by interpolations. It appears, however, that recent efforts to design equations of state for high temperature water, based on simple, rational molecular models can be successful (ref. 1a).

The static dielectric constant is a function of temperature and density only. The knowledge of this quantity at high and supercritical temperature is of importance for the evaluation and prediction of the solvent characteristics of water and other polar fluids. Miscibility with other partners, ionic dissociation of solutes and the possible self-ionization depend on the dielectric constant. Experimental data are available to 550 °C and 500 MPa (ref. 2). They have been critically reviewed and used to construct an equation for interpolation purposes (ref. 3). Efforts have also been made to predict the dielectric constant to higher temperatures and pressures (ref. 4,5,6,7). Such data are particularly useful for geochemical purposes. Figure 1 gives a three-dimensional diagram of the dielectric constant to 1000 °C and a water density of 1 g·cm⁻³. Above 550 °C it is based on approximate calculations. It is evident, that the familiar high values occur only within a limited range of moderate temperature and high density. For comparison, values for liquid methyl cyanide, methanol and ammonia are indicated. It is also to be seen, however, that an extended region of supercritical conditions exists, with dielectric constants between 10 and 25, where ionic dissociation of solutes can be expected.

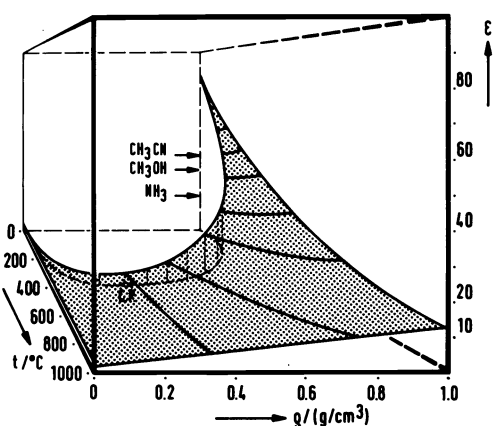


Fig. 1. The static dielectric constant of water, ϵ , as a function of temperature t and density ρ in an approximate presentation (ref. 2,3).

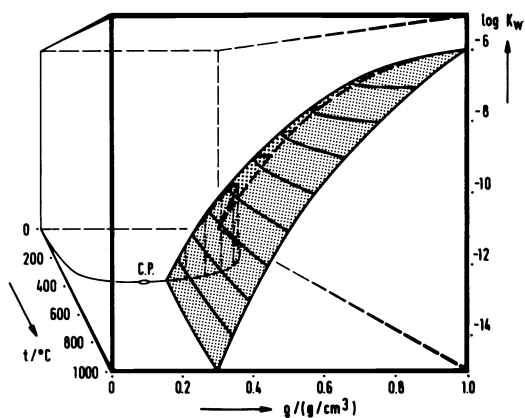


Fig. 2. The ion product of water, $\log K_w = \log [a(\text{H}^+) \times a(\text{OH}^-)]$ as a function of temperature t and density ρ in an approximate presentation (ref. 8).

In accordance with this dielectric behaviour, high electrolytic conductance of a number of salts, acids and bases dissolved in dense supercritical water has been observed. These kinetic phenomena shall not be discussed here. - A function of temperature and density alone is the self-ionisation of water, measured by the "ion product". Figure 2 gives a diagram similar to the one of Fig. 1 with the high temperature in the foreground. Near the rear, right corner the familiar value of $\log K_w = -14$ for room temperature and atmospheric pressure can be seen. Electrochemical measurements of various kinds - at high temperatures mainly the analysis of conductance determinations - lead to a function which describes $\log K_w$ in dependence of temperature and density (ref. 8), and which is shown in the diagram. At 1000 °C and a density of 1 g·cm⁻³, K_w is calculated to be 10⁻⁶ (mol·l⁻¹)². There may be an uncertainty of plus-minus one order^w of magnitude, but there is good reason to believe, that from room temperature to 1000 °C the ion product increases by a factor of 10⁷ to 10⁸. This conclusion is supported by static conductance measurements to 10 GPa (ref. 9) and more recently by conductance measurements in shock waves to several thousand K and 50 GPa (ref. 10). These shock wave experiments appear to confirm an earlier suggestion, that water at 1000 K and above and at a density of 2 g·cm⁻³ and more should become an ionic fluid like molten sodium hydroxide. It is possible, that compressed ammonia could also be brought to the state of an ionic fluid with sufficient shock compression (ref. 10).

It has been suggested, that fully ionized, high temperature, high density water may occur in the larger, outer planets (ref. 11). Uranus and Saturn, for example, may consist largely of ice or water with added helium, hydrogen and perhaps other light components. At a depth of about half the total radius, temperatures of several thousand K and pressures of 10 to 100 GPa are estimated to exist. Dense, ionic water at these conditions would have a very high electric conductivity and would accordingly be of consequence for the electric and magnetic properties of these planets. At present it does not seem likely that aqueous phases of this kind exist or earth at natural conditions.

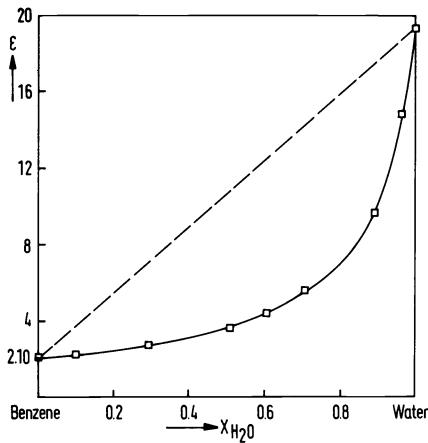


Fig. 3. The static dielectric constant of supercritical mixtures of water and benzene at 400 °C and 200 MPa as a function of the water mole fraction $x(\text{H}_2\text{O})$ (ref. 12).

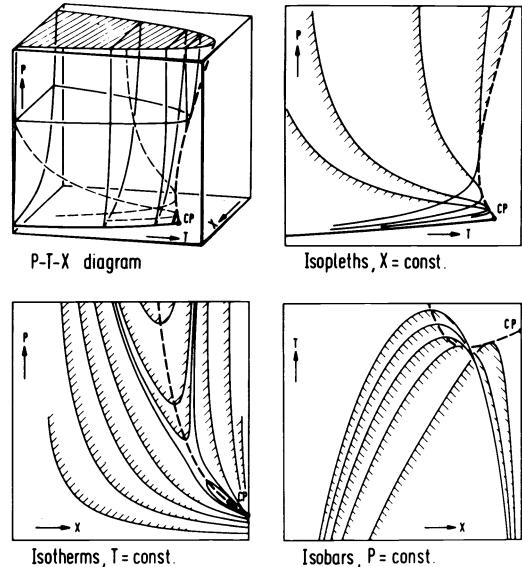


Fig. 4. Schematic phase diagram in the critical region for a binary system water-nonpolar gas. Hatched area: two-phase region. CP: Critical point of water, x : mole fraction of water, --- critical curve.

BINARY MIXTURES—EXPERIMENTAL

At sufficiently high temperature, partners of very different polarity can form homogeneous mixtures even of "liquid-like" densities, where particles are almost always within the range of their mutual interaction potentials. Thus even water can mix with entirely nonpolar gases and liquid hydrocarbons. - The dielectric constant of pure supercritical water has been discussed in the preceding paragraph. It is interesting to investigate how the dielectric constant of a supercritical binary aqueous phase would change in dependence of temperature, density and mole fraction when the composition is varied over the whole range from water to the pure nonpolar component. Measurements with such mixtures can obviously not normally be made at room temperature because of insufficient miscibility - with the exception of some cases, where the nonaqueous partner, for example, has high local dipole moments or a suitable quadrupole moment like dioxane. Besides a general interest in dielectric properties of dense supercritical polar-nonpolar mixtures, such aqueous phases with carbon dioxide, methane, nitrogen and other partners are important as hydrothermal fluids in geochemistry.

Water has a critical temperature of 374 °C. At 400 °C it is completely miscible with benzene. Figure 3 presents experimental values for the dielectric constants of water-benzene mixtures at 400 °C and a constant pressure of 200 MPa as a function of composition. The variation of the constant at these conditions is between 20 and 2 for pure benzene. The addition of 10 mole percent benzene to water reduces the value to one half. It needs 50 mole percent of water, added to benzene, to increase the constant only from 2 to 4. Relative small amounts of benzene apparently reduce the remaining water "structure" considerably (ref. 12). Existing suggestions in the literature to describe theoretically the dielectric constant of mixtures have so far not been used to include wide variations of the total density. It appears, that an uncomplicated function can describe the mixture dielectric constant with pertinent values of the pure partners using suitable defined volume fractions (ref. 12,13,14, 15). It must be mentioned, however, that very recent experimental results with methane-methanol at high pressures, but below the critical point of pure methanol, show a somewhat different behaviour.

M.L. McGlashan in his fifth Rossini Lecture (ref. 16) has presented a very instructive survey on phase equilibria and critical phenomena in fluid mixtures. The binary aqueous systems with nonpolar partners have usually interrupted critical curves, the upper branch of which begins at the critical point of pure water and then extends into the temperature-pressure composition space. Such systems belong to the groups of Fig. 13 e and 13 f of McGlashan's survey. The critical curve has either a temperature minimum ("gas-gas immiscibility of the second kind") or proceeds immediately to high temperature and pressures ("gas-gas immiscibility of the first kind").

A number of such aqueous systems have been studied more recently and examples shall be presented. Figure 4 shows schematically a typical case which resembles water-nitrogen or

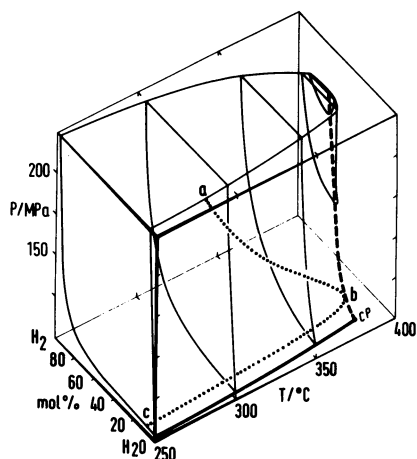


Fig. 5. Experimentally determined PTx phase diagram of the system water-hydrogen. The isotherms outline the two-phase equilibrium surface. abc: Isopleth for 90 mole percent water. ---: Critical curve (ref. 17).

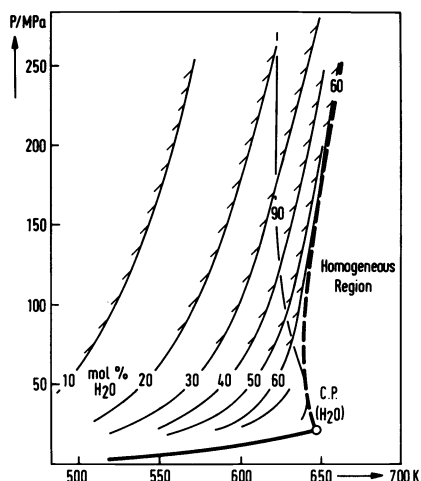


Fig. 6. The phase diagram water-oxygen. Experimentally determined curves for constant water contents (isopleths) which outline the two-phase region in the PTx-space, ---: critical curve (ref. 18).

water-methane (see below). The upper left quarter gives a three-dimensional PTx-diagram. The composition is described by mole fractions x . The two-phase region is shaded. The critical curve has a shallow temperature minimum. The remaining three quarters of the diagram show the three two-dimensional projections: Isotherms, isobars and curves for constant mole fractions x , isopleths.

A real example is given in Fig. 5 with the system water-hydrogen (ref. 17). The curve abc is an actual isopleth for 90 mole percent of water. The projection of the critical curve in the temperature pressure plane rises almost vertically. The critical curve would be of the "first kind" (see above). Another system, investigated quite recently, is water-oxygen. A set of isopleths is shown in Fig. 6. The critical curve has a slight temperature minimum around 367 °C and 75 MPa (ref. 18). The PTx-diagram for the water-nitrogen system is very similar, the minimum of the critical curves occurs at almost the same pressure and temperature (ref. 19). At room temperature and atmospheric pressure the solubility of oxygen in water is nearly twice as high as that of nitrogen, which is important for biological systems.

Accordingly the Henry-constant at 25 °C for water-nitrogen is twice as high as for water oxygen. Near the critical point of water, however, the two Henry-constants are almost equal. Differences in molecular interaction have largely been levelled out. Working with oxygen and water to 400 °C and 250 MPa needs certain precautions in order to prevent rapid corrosion and burning of metal parts. The fact of complete miscibility, however, opens up possibilities of oxidation and other chemical reactions in dense, hydrothermal phases.

One further example is the system water-helium, Fig. 7. Here the critical curve is clearly of the type one (ref. 20). For comparison, a part of the critical curve of the water-hydrogen system is also shown. The dashed strip marked "Uranus" has been calculated (ref. 21) as the possible pressure-temperature relation with increasing depth in the outer planet Uranus. Since the planet is believed to contain, besides highly compressed water, also helium and hydrogen, the knowledge of the intersection of the calculated pT-relation with the critical curve may permit conclusions concerning possible phase separation and stratification - provided the concentrations of helium or hydrogen can be estimated.

BINARY MIXTURES - CALCULATIONS

It is desirable, to have the possibility to calculate the important features of the binary systems: The fluid-fluid equilibria in PTx-space, the critical curve and excess properties in the supercritical homogeneous region. Tests of molecular interaction models can be made, predictions given, and the number of tedious experiments reduced. Van der Waals (ref. 22) in 1900 has for the first time systematically discussed binary fluid mixtures at high pressures and elevated temperatures. Scott and van Konynenburg (ref. 23) have given a classification of critical curves based on the van der Waals equation for nonpolar components. Recent comprehensive discussions have been given by Schneider (ref. 24) and Rowlinson and Swinton

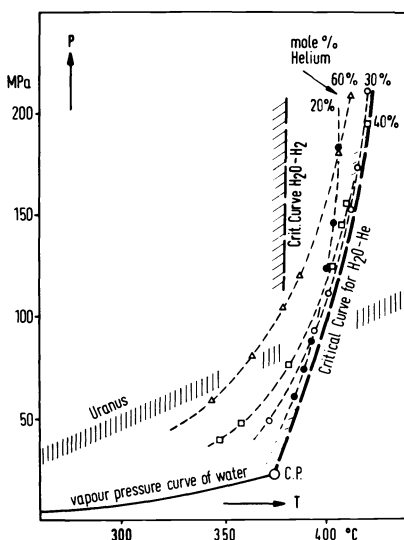


Fig. 7. The phase diagram water-helium (ref. 20). Experimentally determined constant helium contents (isopleths) which outline the two-phase region in the PTx-space. ---: The critical curves for water-helium and water-hydrogen. ||||: Pressure-temperature relation inside Uranus, suggested by D.J. Stevenson (ref. 21).

(ref. 25). Computer simulation and perturbation theory have been successfully applied (ref. 26,27,28,29,30). Semi-empirical functions - mainly extended van der Waals equations - have been developed, for example those of the Redlich-Kwong type (ref. 31) or the very useful Peng-Robinson equation (ref. 32). It is beyond the scope of this paper to discuss the great number of existing equations. Recent surveys are available (ref. 30). In the present field of interest, progress was achieved with the equation of McGlashan with a Carnahan-Starling (see below) repulsion and van der Waals attraction term (ref. 33,34). Several other equations and procedures to calculate three-dimensional phase boundary surfaces and critical curves of binary systems have been published in recent years, which were shown to be successful in several ways. Among others there are the equations of Deiters (ref. 35), of Kleintjens and Koningsveld (ref. 36,37) of Peter and Wenzel (ref. 38,39) or the one used by Brunner (ref. 40). See also the presentations by Boublik (ref. 41). These equations can provide good descriptions of systems, but need generally a certain number of experimental points for adjustment. The relation to defined molecular models is not always straight-forward. The equations are mostly not well suited for mixtures with highly polar molecules, like aqueous systems. A systematic investigation of the influence of the polarity of one of the two partners on the character of the critical curve was made by Gubbins and Twu (ref. 42).

For the special purpose to predict phase equilibria and critical curves of binary mixtures which include highly polar partners to high temperatures and pressures, a new equation was designed (ref. 43). This equation ("CF") contains only a limited number of parameters which can be interpreted on the basis of molecular models. It is of a modular type to permit later extensions and refinements. The equation is extensively discussed elsewhere (ref. 43,44). Figure 8 shows the main characteristics of the equation. As in the van der Waals equation it

$$p(T, V_m) = \frac{RT}{V_m} \cdot \frac{V_m^3 + V_m^2 \beta + V_m \beta^2 - \beta^3}{(V_m - \beta)^3} - \frac{4\beta RT}{V_m^2} (\lambda^3 - 1) \left[\exp\left(\frac{\epsilon}{kT}\right) - 1 \right]$$

with $\beta(T) = \frac{\pi}{6} N_0 \sigma^3(T)$;

$\beta(T) = \beta(T_c) \left(\frac{T_c}{T}\right)^{3/m}$

$\beta(T_c) = 0.04682 \frac{RT_c}{p_c}$; $\frac{\epsilon}{k} = T_c \cdot \ln \left[1 + \frac{2.6503}{(\lambda^3 - 1)} \right]$

λ : preferably from 15 to 25 ; $m = 10$

For mixtures : $\epsilon_{12} = \xi \sqrt{\epsilon_1 \cdot \epsilon_2}$; $\sigma_{12} = \zeta (\sigma_1 + \sigma_2) / 2$

Fig. 8. Proposed new equation of state (CF-equation)(ref. 43,44) to calculate phase equilibria and thermodynamic functions of fluid mixtures with water or other polar components at high temperatures and pressures. V_m = Molar volume, N_0 = Avogadro number.

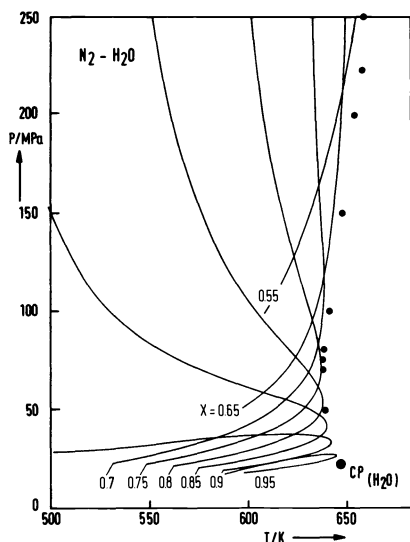


Fig. 9. Pressure-temperature diagram for the binary system water-nitrogen. CP: Critical point of pure water. ●●●: Experimental points on the critical curve (ref. 19). Curves: Spinodal isopleths for several water mole fractions x , calculated with the CF-equation (see Fig. 8). $\zeta=1.0$, $\xi=0.75$, $\lambda=2.5$, $m=10$.

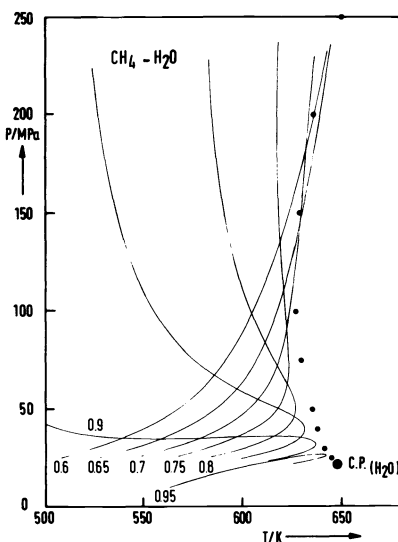


Fig. 10. Pressure-temperature diagram for the binary system water-methane. CP: Critical point of pure water. ●●●: Experimental points on the critical curve (ref. 47,44). Curves: Spinodal isopleths for several water mole fractions x , calculated with the CF-equation (see Fig. 8). $\zeta=1.0$, $\xi=0.75$, $\lambda=2.5$, $m=10$.

has a repulsion term and an added attraction term. The repulsion term is of the form derived by Carnahan and Starling from computer simulations (ref. 45). Only the particle diameter σ has been made slightly temperature dependent. For the attraction term a square well potential is used. The diameter σ and the depth of the square well ϵ are derived from critical data of the pure partners. The relative width of the potential well λ can be set at values between 1.5 and 2.5 or can be derived from vapour pressure curves (ref. 44). There is a relation to the Pitzer acentric factor (ref. 46). ξ and ζ are adjustable parameters defined by combination rules. It appears, that within certain groups of systems ξ and ζ can remain constant or may vary only modestly and systematically. It should be emphasized, that because of the relative simplicity of the CF-equation its main field of application may be that of elevated temperatures. It turns out, however, that equation and procedure are applicable to ternary aqueous systems like water-nitrogen-hexane or others, where the usefulness may be even higher because of the otherwise high number of necessary experimental data points.

Figure 9 demonstrates a first test of the equation with the system water-nitrogen which was recently redetermined experimentally (ref. 19). The full black points were measured and show the course of the critical curve. The curves are calculated spinodal isopleths for constant mole fractions. The spinodals determine the boundary surface for diffusional or material instability. This surface coincides with the surface of mechanical stability or binodal surface along the critical curve. Thus the critical curve can be determined as an envelope of calculated spinodals in the pT-projection. The parameters λ , m and ζ were taken as 2.5, 10 and 1.0 respectively. ξ was left as the only adjustable parameter. The best possible presentation of the critical curve was obtained with $\xi = 0.75$. The agreement is good and probably within the range of experimental accuracy. It can be expected, that other binary aqueous systems with partners, for which similar interactions with water are probable, can be described with the same unchanged set of parameters. As a test, the two systems water-methane and water-xenon were chosen, for which high pressure experimental data are available (ref. 47,48). Figure 10 demonstrates the results for water-methane. As before, the envelope of the calculated spinodal isopleths agrees well with the experimental points. This is true also for water-xenon at high pressure. At lower pressure the deviation amounts to 15 K.

An important and interesting binary aqueous system is water-carbon dioxide. One can expect, that it is more difficult to describe, because of stronger interaction between water and carbon dioxide molecules. The latter have a considerable quadrupole moment. The two-phase equilibrium surface in the PTx-space and the critical curve have been determined experimentally to 250 MPa (ref. 49). The temperature along the critical curve changes by more than 100 K within this pressure region. To calculate the critical curve in this case the

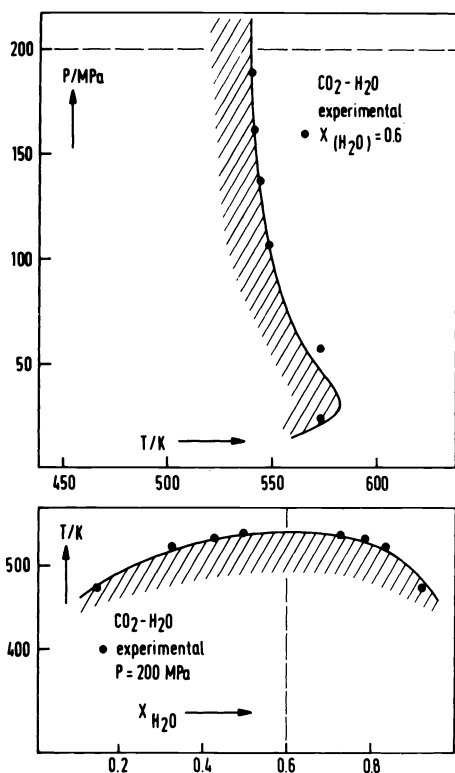


Fig. 11. The binary system water-carbon dioxide upper part: The two-phase boundary curve (isopleth) for $x(\text{H}_2\text{O}) = 0.6$. Lower part: The two-phase boundary curve (isobar) for $p = 200$ MPa. ●●●: Experimental points (ref. 49). Curves: Calculated with the CF-equation (see Fig.8). $\zeta=0.99$, $\xi=0.94$, $\lambda=1.5$, $m=10$.

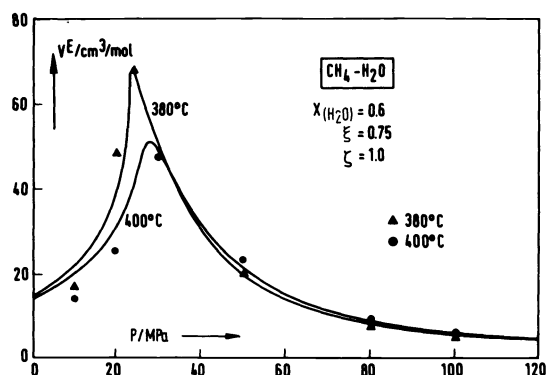


Fig. 12. The binary system water-methane. The molar excess volume v^E at the two supercritical temperatures 380 and 400 °C as a function of pressure. ●●●: Experimental points (ref. 58). Curves: Calculated with the CF-equation. Parameters as in Fig.10.

adjustment had to be made using a changed set of parameters as shown in the legend. In Fig. 11 one calculated binodal isopleth (two phase boundary curve) for 60 mole percent water is shown with experimental points. The lower part of the Fig. 11 gives one isobaric cross section at 200 MPa, again with experimental points. The agreement is satisfactory.

In addition to the prediction of phase equilibria and critical curves it is interesting to know whether an equation and its underlying model can also describe thermodynamic properties of homogeneous supercritical mixtures. This question was examined with the excess volume of the water-methane and other aqueous systems. Molar volume data of several such mixtures have been determined experimentally to 400 °C and 200 MPa and above. These mixture volumes are compared with values calculated by the addition of molar volumes of the pure partners, multiplied by their respective mole fractions. The differences are generally called excess volumes, v^E , which represent the deviation of the mixture from ideal, additive behaviour as far as the volume is concerned. For the polar-nonpolar aqueous mixtures discussed here, the excess volumes are usually positive, that is the mixture volume is higher than expected for ideal behaviour. The amounts of the excess volume decreases if one approaches high pressure. One example, the excess volume of water-methane mixtures as a function of pressure at 400 °C and two compositions is shown in Fig. 12. Calculations were made with the same set of parameters given in Fig. 10. The agreement is again within the range of experimental uncertainties, with the exception, perhaps of values around 10 MPa. These low pressure data depend to some extent on binary second virial coefficients. A very recent investigation indicates that calculated high pressure excess volumes are comparatively insensitive to small parameter changes.

In conclusion it should be emphasized again, that with aqueous systems the CF-equation cannot be expected to give good predictions at moderate and normal temperatures. It has been applied successfully, however, for the methanol-methane critical curve between 300 and 500 K and to 300 MPa.

TERNARY SYSTEMS

Ternary fluid systems at elevated pressures and temperatures are receiving increased attention not only because of their obvious technical importance, but also because computational methods make them more tractable as far as the phenomenological description and the test of molecular interaction models is concerned. Functions like the CF-equation mentioned above can help to reduce the number of necessary experimental data points if a kind of concerted procedure is applied, where calculated predictions suggest the conditions where measurements of particular consequence should be made. Projects of investigation of water-carbon dioxide-benzene and water-nitrogen-hexane as model systems are presently being pursued in this way with promising results.

A very different group of ternary aqueous systems are those, where an electrolyte - for example a salt - is added to a combination of water with a nonpolar partner. Water and carbon dioxide for example have a two-phase region extending to the critical curve which begins at 647 K, passes through a temperature minimum at 540 K and about 250 MPa and proceeds to higher temperatures and pressures. The addition of sodium chloride extends this two-phase region towards higher temperatures - a kind of unusual "salting out" effect. This was first shown by Takenouchi and Kennedy (ref. 50). A more extensive investigation of the same system was performed later (ref. 51). The result is, that a concentration of six weight percent of sodium chloride, relative to water, shifts the maximum temperature of the occurrence of two fluid phases to higher temperatures by about one hundred degrees K at 100 MPa pressure. This effect is of considerable importance in geochemistry, for example in the interpretation of fluid inclusions in natural quartz crystals.

More recently the system water-methane-sodium chloride was investigated to 500 °C and 250 MPa (ref. 52,53). At several constant values of water-salt ratios, curves on the three-dimensional PTx-two phase boundary surface for ten different methane concentrations, isopleths, were determined. Figure 13 shows the high temperature shift of the boundary curves for 17 and 51 mole percent methane caused by an addition of only 0.53 and 2.61 mole percent of sodium chloride relative to water. The effect of such small amounts of salt is very pronounced, particularly around 50 % of methane. The curve at the bottom of the diagram is the first part of the critical curve for the binary water-sodium chloride system (ref.54). It may be possible to treat the ternary system with moderate salt contents as quasi-binary if one makes use of appropriate points on the water-sodium chloride critical curve. Figure 14 is a tentative diagram of the water-methane-sodium chloride system at a constant pressure of 200 MPa. The prismatic diagram extends to the melting temperature of sodium chloride. The left front side shows the binary water-methane subsystem at 200 MPa which has been

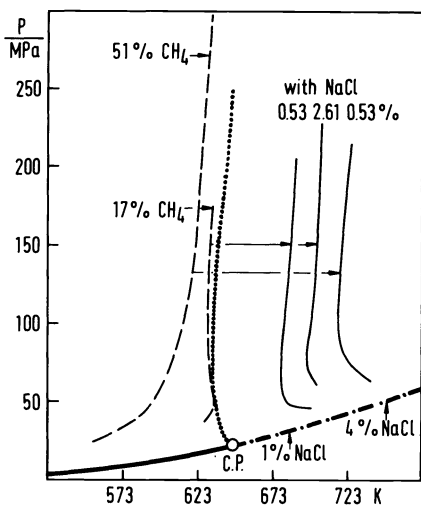


Fig. 13. The ternary system water-methane-sodium chloride. Two isopleths (dashed curves) for the binary system water-methane with 17 and 51 mole percent methane. Two critical curves for water-methane (...) and water-sodium chloride (-.-.). Full curves show the temperature shift caused by the addition of sodium chloride.

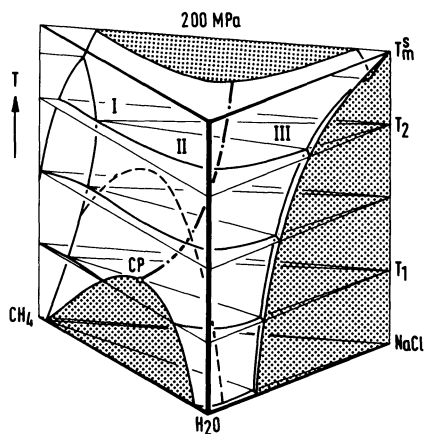


Fig. 14. The ternary system water-methane-sodium chloride. Tentative composition-temperature diagram for a constant pressure of 200 MPa. Shaded areas on two prism sides are two-phase regions. The course of measurements is indicated by the (---) curve. (ref. 52,53).

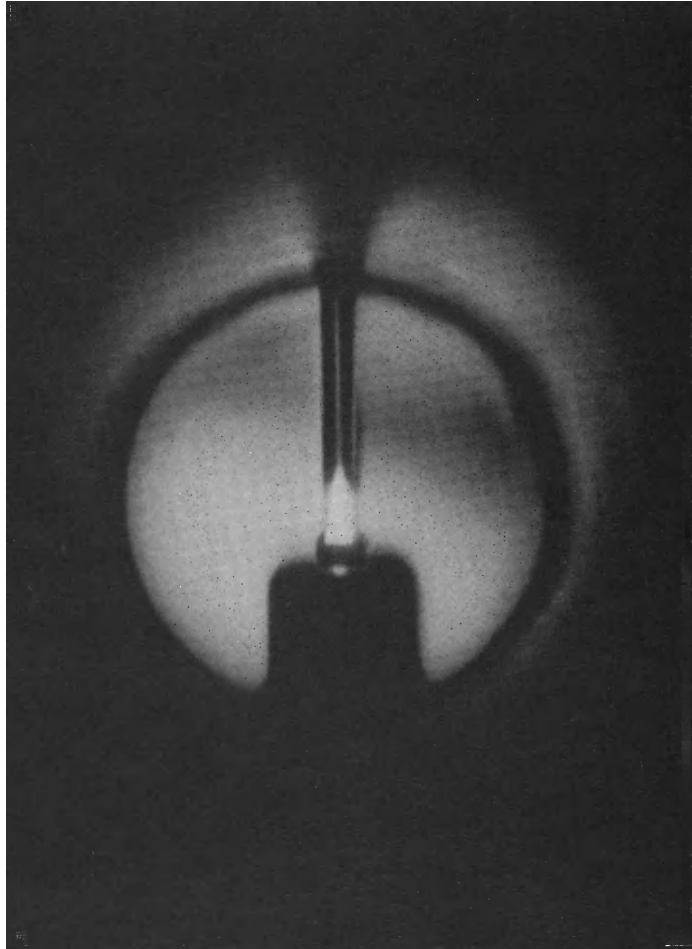


Fig. 16. "Hydrothermal flame" at 100 MPa. Oxygen is injected at about $3 \text{ mm}^3 \text{ s}^{-1}$ into a supercritical homogeneous fluid of 70 mole percent water and 30 mole percent of methane at $450 \text{ }^\circ\text{C}$. The spontaneously ignited flame is 3 mm high and 0.5 mm wide. Sapphire windows. (Observations by W. Schilling.)

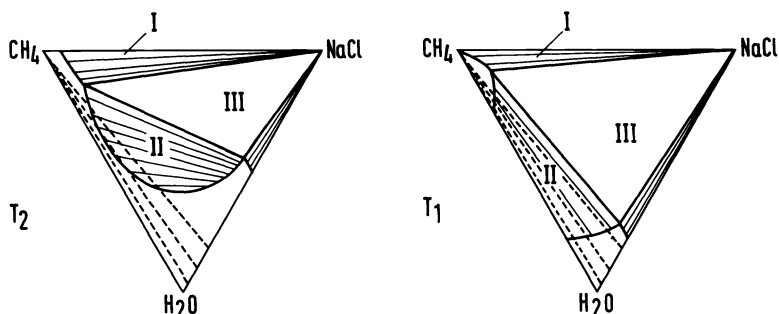


Fig. 15. The ternary system water-methane-sodium chloride. Schematic triangular diagram for the two temperature T_1 and T_2 indicated in Fig. 14. Regions I and II: Two phases. Region III: Three phases. ---: Lines indicating the course of measurements (ref. 52,53).

investigated (ref. 47). The right front side shows the estimated temperature dependence of sodium chloride solubility at high pressure. The dash-point curve from CP marks the presumed course of a critical curve. The dashed curve shows schematically the trace of one set of phase equilibrium measurements with constant water to salt ratio. The two isothermal triangles at T_1 and T_2 are shown in Fig. 15 with the homogeneous and the two and three phase regions. The tie lines in the two phase regions have only schematic value. They have not yet been measured. Measurements (see above) have only been made along the straight dashed lines. Where these meet the boundary of region II, the phase separation was determined and the three-dimensional surface around the region II with one methane-rich and one water-rich phase in the isobaric diagrams can be outlined. Similar new measurements, which are under way with the system water-hexane-sodium chloride seem to indicate, however, that the water-hexane two-phase region is much less shifted to higher temperature by added salt. This may be related to the fact that at given pressure and concentration the critical curve of the binary water-hexane system extends already to much higher temperatures than the curve for water-methane. - A limited number of experiments have been made with water, methane and calcium chloride. The results seem to indicate, that the calcium chloride around 400°C forms mainly mono-valued ions.

COMBUSTION AND FLAMES

It has been shown, that at 400°C methane and oxygen are both completely miscible with the dense supercritical water. Very probably also a mixture of both these two gases can form a homogeneous phase with water. Thus one should assume that "hydrothermal combustion" could be supported in such phases. A project has been started to investigate such combustion. An autoclave with sapphire windows was designed to hold and observe water-gas mixtures to 500°C and 100 MPa or more. Through a narrow nozzle injection of methane or oxygen into the 100 MPa water is possible at slow flow rates of a few microliters per second. Around room temperature unusual phenomena of clathrate formation are observed. If oxygen is slowly injected into a homogeneous mixture of water and 30 mole percent methane, spontaneous ignition occurs already at temperatures as low as 430°C . Steadily burning hot flames are observed at 100 MPa, about 3 mm high and 0.5 mm wide. A photograph of such a flame is shown in Fig. 16. No phase separation occurs around this "supercritical flame". The formation of the flames is remarkable, since normally spontaneous ignition temperatures for oxygen-methane mixtures are reported to be around 550°C (ref. 55,56,57). The quenching effect of the dense water is not as pronounced as could be expected. The burning velocity of these flames is exceptionally small: of the order of 1 cm sec^{-1} or even less. High pressure flames described in the literature, seem not to exceed about 7 MPa of pressure. Certainly, because of the high miscibility other combinations with more components can be brought to reaction in the hydrothermal fluid and oxidation below the flame temperature is also feasible.

In conclusion it may be mentioned again that the dense fluids at supercritical conditions are media which provide an unusual variation of phenomena. Extensive and continuous change of physico-chemical properties, combination of "liquid-like" and "gas-like" behaviour, unusual miscibility, high chemical reaction rates and also continuous transitions like those from molecular to ionic and even to metallic states can be observed.

REFERENCES

1. Felix Franks, Ed. "Water, a Comprehensive Treatise", Vol. 1, Plenum Press, New York, 1972.
- 1a. F.H. Ree, *J.Chem.Phys.* **76**, 6287 (1982).
2. K. Heger, M. Uematsu, E.U. Franck, *Ber.Bunsenges.Phys.Chem.* **84**, 758 (1980).

3. M. Uematsu, E.U. Franck, J.Phys.Chem.Ref.Data 9, 1291 (1980).
4. E.U. Franck, Z.Phys.Chem.N.F. 8, 107 (1956).
5. A.S. Quist, W.L. Marshall, J.Phys.Chem. 69, 3165 (1965).
6. D.J. Bradley, K.S. Pitzer, J.Phys.Chem. 83, 1599 (1979).
7. R.P. Beyer, B.R. Staples, in print in J.Solution Chemistry (1986).
8. W.L. Marshall, E.U. Franck, J.Phys.Chem.Ref.Data, 10, 295 (1981).
9. W.B. Holzapfel, E.U. Franck, Ber.Bunsenges.Phys.Chem. 70, 1105 (1966).
10. A.C. Mitchell, W.J. Nellis, J.Chem.Physics, 76, 6273 (1982).
11. D.J. Stevenson, Ann.Rev.Earth and Planet. Sci. 10, 257 (1982).
12. R. Deul, "Dielectric Constant and Density of Water-Benzene-Mixtures to 300 °C and 3000 bar", Thesis (1984), Institute of Physical Chemistry, University of Karlsruhe, BRD.
13. C.J.F. Böttcher: "Theory of Electric Polarisation" Vol. 1, Elsevier, Amsterdam (1973).
14. L. Landau, F. Lifschitz, "Electrodynamics of Continuous Media", Addison-Wesley, New York (1960).
15. H. Looyenga, Physica 31, 401 (1965).
16. M.L. McGlashan, J.Chem.Thermodynamics 17, 301 (1985).
17. T.M. Seward, E.U. Franck, Ber.Bunsenges.Phys.Chem. 85, 2 (1981).
18. M.L. Japas, E.U. Franck, Ber.Bunsenges.Phys.Chem. 89, 1268 (1985).
19. M.L. Japas, E.U. Franck, Ber.Bunsenges.Phys.Chem. 89, 793 (1985).
20. N.G. Sretenskaja, M.L. Japas, E.U. Franck, to be published in Ber.Bunsenges.Phys.Chem. (1986).
21. D.J. Stevenson, Ann. Rev.Earth and Planet Sci. 10, 257 (1982).
22. J.D. van der Waals "Die Kontinuität des gasförmigen und flüssigen Zustands", 2. Ed. Vol. 2 (Binary Mixtures), Barth, Leipzig (1900).
23. R.L. Scott, P.H. van Konynenburg, Discuss.Far.Soc. 49, 87 (1970). P.H. van Konynenburg, R.L. Scott, Phil.Trans. A298, 495 (1980).
24. G.M. Schneider, "High Pressure Phase Diagrams and Critical Properties of Fluid Mixtures" Spec.Per.Rep. Chem. Thermodynamics, Vol. 2, The Chemical Society, London (1978).
25. J.S. Rowlinson, F.L. Swinton: "Liquids and Liquid Mixtures", III. Ed. Butterworth Scientific, London (1982).
26. J.P. Hansen, J.R. McDonald: "Theory of Simple Liquids", Academic Press, London (1976).
27. C.G. Gray, K.E. Gubbins: "Theory of Molecular Fluids", Vol.1, Clarendon, Oxford (1984).
28. B.J. Alder, T.E. Wainwright, J.Chem.Phys. 27, 1208 (1957), 31, 459 (1959).
29. K.E. Gubbins, K.S. Shing: "A Review of Methods for Predicting Fluid Phase Equilibria: Theory and Computer Simulation", in J.M. Haile, G.A. Mansoori (Eds): "Molecular-Based Study of Fluids", Adv. in Chem.Series No. 204, Am.Chem.Soc. Washington D.C. (1983).
30. S.M. Walas, "Phase Equilibria in Chemical Engineering", Butterworth Publishers, Boston (1985).
31. O. Redlich, J.N.S. Kwong, Chem.Rev. 44, 233 (1949).
32. D.Y. Peng, D.B. Robinson, Ind.Eng.Fund. 15, 59 (1976). A.J. Ch.E. Journal 23, 726 (1977).
33. M.L.McGlashan, K. Stead, C. Warr, J.Chem.Soc.Faraday Trans. 2, 73, 1889 (1977).
34. M.L.McGlashan, J.Chem.Thermodynamics, 17, 301 (1985).
35. U. Deiters, Chem.Eng.Sci. 37, 855 (1982), Fluid Phase Equilibria, 10, 173 (1983).
36. L.A. Kleintjens, R. Koningsveld, Colloid Pol.Sci. 258, 711 (1980).
37. L.A. Kleintjens, Fluid Phase Equilibria 10, 183 (1983).
38. H. Hederer, S. Peter, H. Wenzel, Chem.Eng.J. 11, 183 (1976).
39. S. Peter, H. Wenzel, Symp. "Phase Equilibria and Fluid Properties in the Chemical Industry", EFCE Publ. Series No 11 (1980).
40. S. Peter, G. Brunner, R. Riha, Chem.Eng.Technik 46, 623 (1979).
41. T. Boublik, J. Nezbeda, Chem.Phys.Letters 46, 315 (1977), Mol.Physics 51, 1429 (1984).
42. K.E. Gubbins, C.H. Twu, Chem.Eng.Sci. 33, 863, 879 (1978).
C.H. Twu, K.E. Gubbins, C.G. Gray, J.Chem.Phys. 64, 5186 (1976).
43. M. Christoforakos, E.U. Franck, Ber.Bunsenges.Phys.Chem. 90, Sept. (1986).
44. M. Christoforakos: "Überkritische Systeme unter hohem Druck", Thesis, Institute of Physical Chemistry, University of Karlsruhe, BRD (1985).
45. N.F. Carnahan, K.E. Starling, J.Chem.Physics 51, 635 (1969).
46. K.S. Pitzer, D.Z. Lippmann, R.F. Cure, C.M. Huggins, D.E. Petersen, J.Amer.Chem.Soc. 77, 3427, 3433 (1955) 79, 2369 (1957).
47. H. Welsch, "Die Systeme Xenon-Wasser und Methan-Wasser bei hohen Drücken und Temperaturen", Thesis, Inst. of Physical Chemistry, University of Karlsruhe (1973).
48. E.U. Franck, H. Lentz, H. Welsch, Z.Phys.Chem.N.F. 93, 95 (1974).
49. K. Tödheide, E.U. Franck, Z.Phys.Chem.N.F. 37, 387 (1963).
50. S. Takenouchi, G.C. Kennedy, Am.J.Sci. 263, 445 (1965).
51. M. Gehrig, H. Lentz, E.U. Franck, Ber.Bunsenges.Phys.Chem. 90, 525 (1986).
52. T. Krader, "Das ternäre System Wasser, Methan und Natriumchlorid bis 2.5 kbar und 800 K", Univ. of Karlsruhe (1985).
53. T. Krader, E.U. Franck, Physica, 139 - 140 B, 66 (1986).
54. S. Sourirajan, G.C. Kennedy, Amer.J.Sci., 260, 115 (1962).
55. W. Jost, "Explosions- und Verbrennungsvorgänge in Gasen", Springer, Berlin (1939).
56. A.G. Gaydon, H.G. Wolfhard, "Flames", 4. Ed., Chapman and Hall, London (1979).
57. R.A. Strehlow, "Combustion Fundamentals", McGraw Hill, New York (1984).
58. V.M. Shmonov, E.U. Franck, "Excess volumes of water-methane mixtures to 400 °C and 200 MPa", to be published Ber.Bunsenges. (1987).