

Figure 4 shows the variation of absorption at 400 °C between densities of 0.01 and 0.9 g/cm<sup>3</sup> or pressures from 50 to 4 000 b. At the highest density the absorption band is similar to the one observed in liquid water at room temperature. An indication of rotational structure appears only at densities lower than 0.1 g/cm<sup>3</sup>. Thus the infrared spectrum of the OD-vibration of HDO diluted in H<sub>2</sub>O gives no evidence for freely rotating water molecules at densities higher than 0.1 g/cm<sup>3</sup>. This may imply that dipole-dipole interaction and remaining hydrogen bonding at densities higher than one tenth of the density of normal liquid water are sufficient to impede water molecules from rotating freely long enough to produce a discernible rotational structure in the spectrum. This apparent strong intermolecular interaction which is retained in supercritical water is of consequence for the electrolytic solvent properties of this fluid.

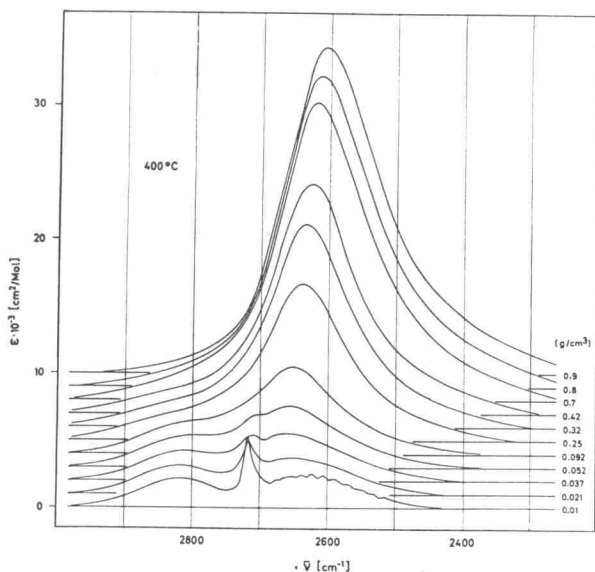


Fig. 4. — Molar extinction coefficient  $\epsilon$  of the OD-stretching vibration as a function of frequency  $\tilde{\nu}$  in  $\text{cm}^{-1}$  at 400 °C and at different densities of water ( $\text{g}/\text{cm}^3$ )<sup>(9)</sup>. Note the different base lines of the individual curves.

### III. — Solubility.

The miscibility of gases at low pressures can be expected to exist also at high pressures and elevated temperatures if the components are not too different. It has to be examined, however, whether complete miscibility is also possible if dense, gaseous supercritical water is combined with a nonpolar fluid or a solid. The discussion of these phenomena requires the knowledge of the phase boundaries in the pressure-temperature-composition ( $P-T-x$ ) diagram of such two-component systems.

A system of two components has a critical curve which in simple cases connects the critical points of the pure components in the  $P-T-x$ -diagram without interruption. If the components are more different the critical curve is divided into two branches origi-

nating at the two critical points. The branch which begins at the higher critical point may eventually extend to temperatures and pressures which are higher than the respective values of that critical point. This behavior has been predicted by KAMERLINGH ONNES<sup>(12)</sup> and first demonstrated experimentally by KRICHEVSKII *and al.*<sup>(13)</sup>. A detailed discussion is given by SCHNEIDER and by ZIKLIS<sup>(14, 14a)</sup>.

A typical example is the system  $\text{CO}_2-\text{H}_2\text{O}$ , the phase behavior of which is qualitatively represented in fig. 5. The dimensions are distorted in

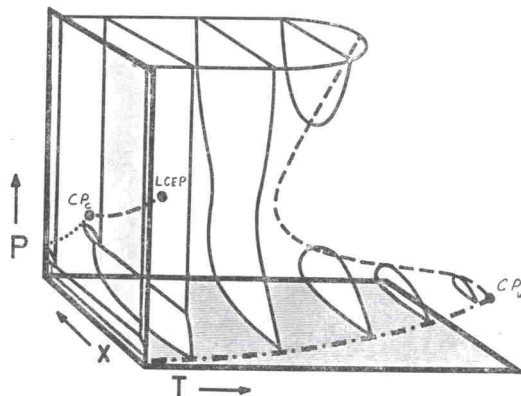


Fig. 5. — Schematic pressure-composition-temperature ( $P, T, x$ )-diagram of the system water-carbon dioxide.  $CP_c$  = critical point of  $\text{CO}_2$ ;  $CP_w$  = critical point of water. ---: critical curve.

this figure in order to show the characteristic properties more clearly. The lower branch of the critical curve ends at the « lower critical end point », LCEP at 31.5 °C and 74 b. The upper branch of the critical curve passes a minimum temperature of 266 °C and 2.45 kb and proceeds to higher temperatures with increasing pressure. This curve has been determined up to 268 °C and 3.6 kb. An upper critical end point, UCEP, has not been found in this range. To the left of the critical curve is the two phase region indicated by isotherms which have the shape of two separate loops above the minimum temperature. Above 266 °C and at pressures of one kb and more, mixtures of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  of all compositions can exist with a total density approaching that of normal liquid water. Earlier measurements of PVT-data of the homogeneous phase gave no conclusive information about possible chemical association between the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules<sup>(16)</sup>. The electric conductance of such mixtures is not appreciably higher than that of pure water at similar conditions.

It would be inferred from the behavior of  $\text{CO}_2-\text{H}_2\text{O}$ -mixtures that beyond about 400 °C dense homogeneous mixtures could also be prepared of water with inert second components such as argon or simple hydrocarbons. With the addition of argon for example one should be able to alter continuously the electrolytic properties of dense supercritical water.

The phase equilibria of the argon-water system have recently been determined experimentally<sup>(17)</sup>.



This was accomplished with a new method by which registration of PT-curves at constant volumes could be combined with visual observation of the fluid content of a high pressure cell. No extraction of samples from an autoclave was necessary. The cell had an observation window of synthetic sapphire. Its volume of a few  $\text{cm}^3$  could be varied by changing the position of a piston. Thus not only phase separations but also the PVT-relation in the homogeneous state could be determined. The results are shown in fig. 6 as isotherms. No separated isotherms with two loops occur.

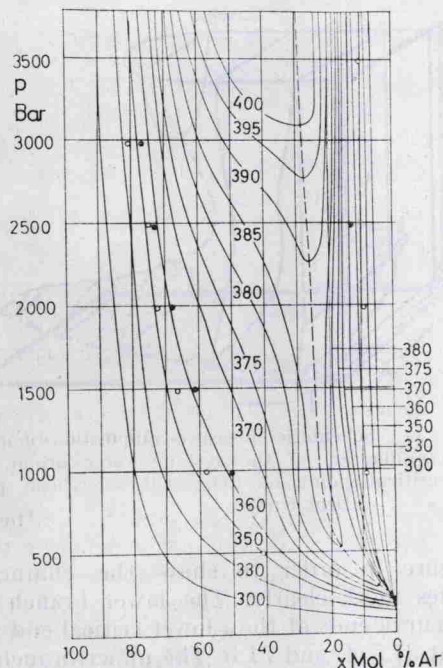


Fig. 6. — Isotherms of the two-phase boundary of the water-argon system. The heterogeneous state is within the isotherms. ---: critical curve (<sup>17</sup>).

This means that here the upper branch of the critical curve has no minimum. From the critical point of pure water it proceeds monotonously to

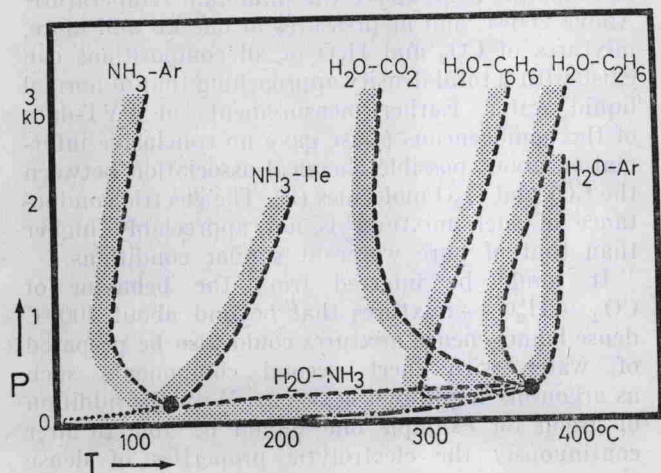


Fig. 7. — Experimentally determined critical curves for binary systems with ammonia or water combined with several nonpolar second components (<sup>17</sup>).

400 °C and 3.1 kb, the limit of these measurements. Thus high density argon-water mixtures of all compositions can be prepared beyond 400 °C. They have been used in electrolytic experiments described below.

Critical curves resembling those of the  $\text{CO}_2$ — $\text{H}_2\text{O}$  and  $\text{Ar}$ — $\text{H}_2\text{O}$  systems have also recently been observed with systems of several hydrocarbons and water. A compilation of such curves is given in fig. 7.

Obviously, very concentrated aqueous solutions of these hydrocarbons can be made between 300 and 400 °C at not too high pressures. Applications of such solutions can be imagined.

#### IV. — Spectroscopic Investigation of Complexes.

Not only volatile compounds but also inorganic salts, oxides and similar substances have a considerable solubility in dense supercritical water. According to KENNEDY *and al.* (<sup>18</sup>), the system  $\text{SiO}_2$ — $\text{H}_2\text{O}$  has an UCEP at 1080 °C and 9.8 kb. A considerable part of the phase diagram for  $\text{NaCl}$ — $\text{H}_2\text{O}$  has also been investigated (<sup>19</sup>). It may well be typical for other systems containing similar salts and water. At 600 °C and 1 kb for example, fluid mixtures appear to be possible with  $\text{NaCl}$  contents between zero and more than fifty weight percent  $\text{NaCl}$ . Accordingly concentrated aqueous electrolyte solutions can be prepared in a wide range of supercritical temperatures and pressures. Unfortunately little or nothing is known at present of the densities of such solutions. A discussion of the causes of solubility of electrolytes in supercritical water has been given earlier (<sup>20</sup>). Compilations of data and references are presented by several authors (<sup>21</sup>, <sup>22</sup>).

Not only alkali halides and other compounds with small molecules can be dissolved in supercritical water. Several heavy metals can form complex compounds which are stable enough to exist in the aqueous fluid at high temperatures. In some cases the stability of such complexes can be increased by the addition of high concentrations of alkali halides to the fluid. Some of these « hydrothermal » solutions are considered in geochemistry as having been important for the transport of heavy metals in the earth's crust. Lead chloride complexes for example have been discussed extensively from this point of view (<sup>23</sup>).

Recently the range of existence of complexes of bivalent cobalt and nickel has been investigated spectroscopically in the visible and near ultraviolet regions (<sup>24</sup>). For this purpose an absorption double cell was constructed, which could be used with aqueous solutions up to 500 °C and 6 kb. The windows were cylindrical rods from synthetic sapphire of 60 mm length. The high temperature inside the cell decreased along the length of these windows. The body of the cell was of noncorrosive steel alloy and the solutions could be pumped through the cell at high temperatures and pressures.

Dilute solutions of bivalent cobalt chloride were