

POLAR AND IONIC FLUIDS AT HIGH PRESSURES AND TEMPERATURES

E. U. FRANCK

*Institut für Physikalische Chemie und Elektrochemie,
Universität Karlsruhe, GFR*

ABSTRACT

A survey and critical discussion is given of recent experimental investigations of thermodynamic and related properties of water, aqueous mixtures, other polar fluids, certain fused salts and fluid metals. Results cover a range of pressures to several kbar and of temperatures extending to 1000°C and beyond.

For supercritical water, *PVT*-data, thermal conductance, Raman spectra, dielectric constant and ionic dissociation are discussed and in part compared with the properties of dense supercritical hydrogen chloride and ammonia. Recently determined critical curves of binary systems with water or ammonia combined with non-polar second components such as rare gases and hydrocarbons are given. Vapour pressure, density and conductance measurements are presented for fluid and supercritical bismuth trichloride and ammonium chloride. The last salt may be the first example of a predominantly ionic fluid at critical conditions. For mercury, caesium and potassium the vapour pressure curve has been measured to the critical point. Conductance measurements at supercritical conditions show the continuous transition from insulating to metallic states with increasing density. Certain experimental details for high pressure-high temperature cells are presented, which may be useful for various applications.

INTRODUCTION

Polar and ionic fluids receive increasing attention for several reasons. It is of interest to study fluids of particles with far-reaching intermolecular forces. They may have peculiar critical properties and some of them possess high electrical conductance even at supercritical temperatures. In the dense supercritical state polar fluids can be good solvents for a variety of solutes ranging from non-polar hydrocarbons to inorganic salts. In certain cases semiconductor and metallic behaviour occurs at very high temperatures and pressures¹.

Dense polar and ionic fluids, particularly aqueous 'hydrothermal' fluids, are important transport media in the earth's crust and are studied extensively by geochemists². Certain properties of such hydrothermal solutions are of interest for high pressure power plant operation. Several crystal growth methods depend on polar fluids at high pressures and temperatures. New electrochemical processes which take advantage of the unusual properties of these fluids may become feasible. The available knowledge is still limited, however, particularly for non-aqueous fluids and at supercritical conditions. The necessity to use high pressure equipment at high temperatures and to

overcome unusual corrosion problems limits progress in this field. Evidence from spectroscopic, dielectric, electrochemical and other sources must be used to supplement the thermodynamic knowledge. Transport properties are also of considerable interest. Therefore a selection of results from various fields will be presented and discussed in this paper.

The polar fluids to be considered here have small molecules with dipole moments of about one debye unit or more. Many of them have high critical temperatures and also high critical pressures. *Figure 1* is a schematic P - T -diagram³, showing a number of phenomena which can be expected in super-

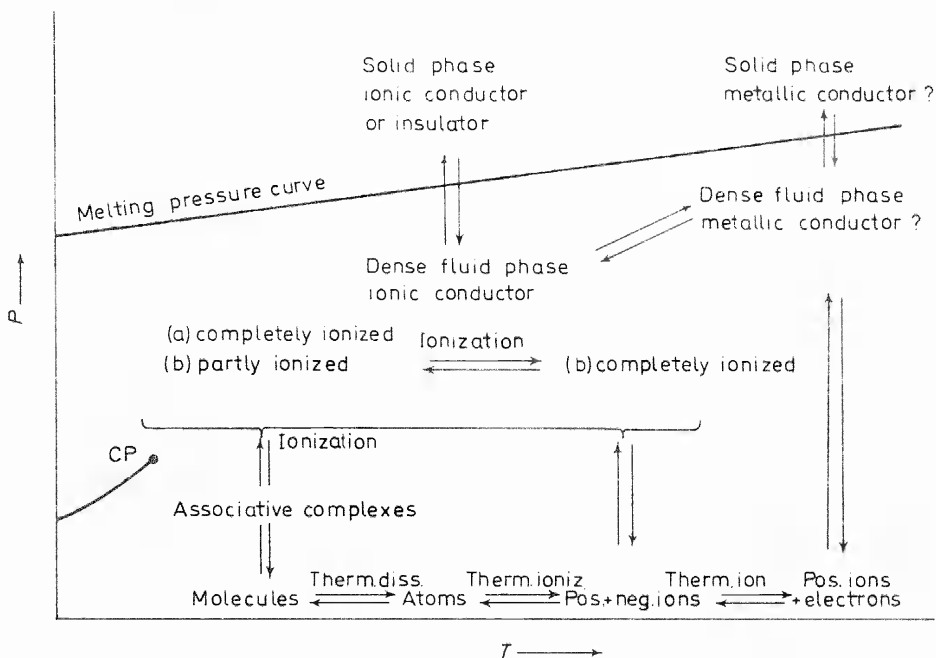


Figure 1. Schematic presentation of phenomena to be expected in polar fluids at supercritical temperatures and pressures. Vapour pressure curve and critical point at lower left³

critical polar fluids. At low pressure, increase of temperature leads to thermal dissociation, ionization and finally to plasma states. At higher pressures, molecular association and subsequently ion formation and ion solvation can be expected. Completely ionized dense fluids can occur in the upper right region of the diagram and at extreme conditions transition to metallic states in certain cases has been predicted.

Selected examples of critical temperatures and pressures for a few groups of fluids are shown in *Table 1*. The critical temperatures of polar fluids are usually higher than those of non-polar fluids, and particularly high values are found for substances which solidify to ionic crystals. Thus only a small number of salts have been investigated as yet in their liquid-gas critical regions. This is also true for metals. At present experimental determinations of critical data are available only for mercury and alkali metals. For other

POLAR AND IONIC FLUIDS AT HIGH PRESSURES AND TEMPERATURES

Table 1. Critical temperatures and pressures of selected polar, ionic and metallic fluids

Substance	$T_{cr}(\text{K})$	$P_{cr}(\text{bar})$
HCl	325	82
H ₂ O	647	221
NH ₄ Cl	1 155	1 635
BiCl ₃	1 178	119
NaCl	3 500*	240*
Hg	1 760	1 510
Cs	2 020	110
K	2 200	155
Pb	5 400*	850*
Fe	10 000*	—
W	23 000*	> 10 000*

* Estimated.

metals estimates have been made, which depend largely on density values of coexisting gaseous and liquid phases at much lower temperatures. Recently, new techniques and construction materials have permitted an extension of knowledge in this field. Measurements at transient conditions will be increasingly important in the future.

PURE POLAR FLUIDS

As an example of a temperature–density diagram for a pure polar fluid the diagram for water is given in *Figure 2*. The gas–liquid critical point CP and the triple point TP are shown. The points on the dashed line extending to

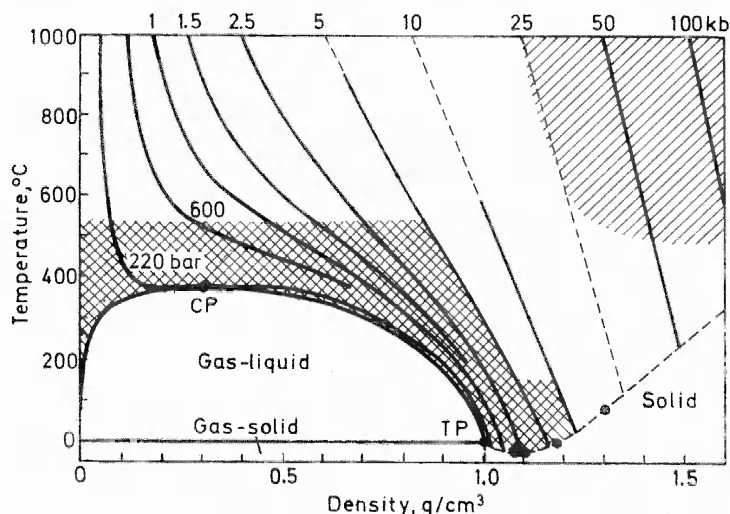


Figure 2. Temperature–density diagram of water. Full lines: measured isobars. Dashed lines: interpolated isobars. Cross-hatched area: region of most of the dielectric, transport, spectroscopic and electrolytic measurements. Single shading: ionic conductance determined

the right denote the transitions between the different modifications of ice. The cross-hatched area up to about 500 °C and 5 kbar covers the conditions at which most of the high pressure measurements of various properties, for example dielectric, transport, electrolytic and spectroscopic measurements, have been made. To about 10 kbar the water density has been determined by recent static experiments⁴⁻⁶. Above 25 kbar only shock wave data are available⁷. The intermediate range has to be covered by interpolation. At 500 and 1000 °C, pressures of about 8 and 20 kbar respectively are needed to produce the 'normal' density of liquid water of 1 g cm⁻³.

Transport properties of dense fluid phases are not only related to certain thermodynamic properties but are also of importance for the kinetics of chemical reactions in such phases. Unfortunately very little information about diffusion coefficients in water at high temperatures and pressures is available. Viscosity data, however, have been determined to 550 °C and 3.5 kbar⁸. It is interesting to observe the results plotted as supercritical isotherms from very low to liquid-like densities. Since the temperature dependence in the dilute gas is positive, and negative in the dense fluid, there is a region at about 0.8 g cm⁻³ where the temperature dependence is very small. The total increase in viscosity from nearly zero to high density at 400 and 500 °C is only by a factor of about five. Thus approximate estimates of viscosities with empirical equations are quite possible. Attempts to represent the experimental data for supercritical water with Chapman-Enskog equations using the hard sphere model were not satisfactory, however.

Anomalies of the shear viscosity in the critical region of several gases have been observed, although they are very weak. Very pronounced anomalies, however, have been found for the specific heat and also for the thermal conductivity. This applies also to polar gases such as steam. Recently the thermal conductivity of steam between 370 and 520 °C to pressures of 500 bar could be measured⁹. In *Figure 3* the 'anomalous' thermal conductivity $\Delta\lambda$ of steam is plotted as a function of density at constant temperatures. $\Delta\lambda$ is the amount by which the conductivity in the critical region exceeds the values obtained by a prescribed extrapolation from data far away from the critical point into the critical region. Even at 440 °C, that is 70 degrees above the critical temperature, a maximum in the critical density is clearly visible. The concept of scaling law relations has been applied to anomalous transport properties¹⁰. It has been shown, that the scaled anomalous thermal conductivity of steam in the range of *Figure 3* is indeed a single-valued function of a variable x , which is a combination of reduced density and reduced temperature⁹.

The anomalous thermal conductivity and the abnormally high heat capacity of supercritical water are not sufficient, however, to derive conclusive results for the extent of association by hydrogen bonds. More information about this has been obtained in recent years from infrared and Raman spectra. A number of infrared absorption cells have been designed which permit measurements with corrosive fluids to 500 °C and to about 4 kbar. Synthetic sapphire windows and one-window reflection type arrangements are particularly useful. Raman cells with two or more windows can also be built for the same temperature and pressure range.

The oxygen-hydrogen stretching vibration of water molecules is strongly

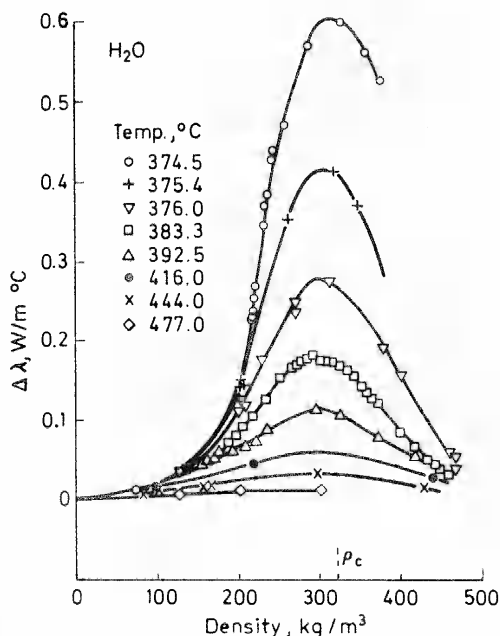


Figure 3. Anomalous thermal conductivity $\Delta\lambda$ of steam as a function of density for a number of temperatures⁹

affected by hydrogen bonds: the frequency can be lowered by several hundred wavenumbers and the intensity is increased. In the infrared one observes a continuous decrease of intensity and rise in frequency with increasing temperature and falling density. With the exception of a slight asymmetry no indication of an increasing amount of 'non-associated' molecules is visible. Rotational structure of the vibration band does not occur until the density is reduced to about one-tenth of the normal liquid value¹¹. The infrared vibration spectra of dense supercritical hydrogen fluoride¹³, hydrogen chloride¹² and ammonia¹³ have a resemblance to that of steam.

The Raman spectrum of water is different, as shown in Figure 4¹⁴. Here the relative intensity of the OD-valence vibration band of HDO molecules diluted in H₂O at a constant density of 1 g cm⁻³ is given for several temperatures. The bands were obtained with argon laser irradiation. In the dilute gas the band centre of this vibration is close to 2700 cm⁻¹, as in the infrared. At 25 °C the maximum of the Raman band is at about 2500 cm⁻¹, indicating the intermolecular association. A shoulder at 2650 cm⁻¹ is clearly visible. If the temperature is raised to 400 °C a new band seems to appear at the position of this shoulder. This shoulder and band at 2650 cm⁻¹ has been considered as an indication for water molecules which are not hydrogen bonded but which nevertheless interact strongly with each other¹⁵. The total band can be separated into two components with maximum frequencies at 2500 and 2650 cm⁻¹. Using certain assumptions one can derive from the temperature dependence of the intensity of these two bands an energy of transition between the 'bonded' and 'non-bonded' states which is about 2.4 kcal mol⁻¹ or

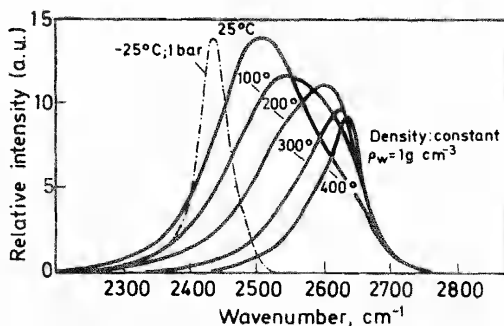


Figure 4. Relative intensity of the Raman OD-valence vibration band of HDO molecules diluted in H_2O at a constant density of 1 g cm^{-3} for several temperatures. The dashed curve is for ice¹⁴

10 kJ mol^{-1} and which is in good agreement with other sources^{14, 15}. Even at supercritical temperatures and critical density a certain degree of hydrogen-bond association can apparently be expected in water. Analogous results were obtained for hydrogen fluoride¹³.

The static dielectric constant of polar fluids is to a certain extent determined by structural properties. This applies particularly to water, where the hydrogen bond association in the supercritical dense phase should influence the dielectric constant. This quantity could be measured with frequencies to about 1 MHz to temperatures up to 550°C and to pressures extending in some cases to 5 kbar . Gold-palladium condensers of variable geometry within a corrosion resistant cylindrical autoclave were used. Water¹⁶, pure hydrogen chloride¹⁷, methanol¹⁶ and ethanol¹⁶ have been investigated.

Figure 5 gives the two gas-liquid coexistent curves of HCl and H_2O in a diagram of reduced temperatures and densities^{16, 17}, where the two critical points coincide. Within the homogeneous region are the curves of constant values of the dielectric constant of the two fluids. It is obvious that the familiar

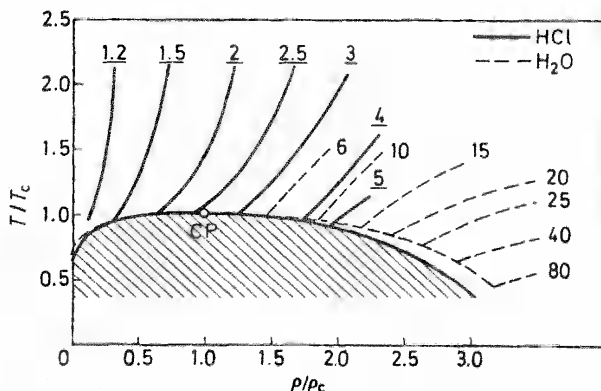


Figure 5. Curves of constant values of the static dielectric constant of HCl (full lines) and H_2O (dashed lines) in a reduced temperature and reduced density diagram. CP: critical point. T_c and ρ_c : critical temperature and density¹⁷

very high values for water occur only at low temperatures and high densities in the lower right corner of the diagram. Even at supercritical temperature and at about half the liquid density, water is still an electrolytic solvent with dielectric constants around 10 or 15. Hydrogen chloride has much lower values at corresponding states.

The 'Kirkwood correlation factor' has been evaluated for both fluids. The degree to which it exceeds unity indicates deviation from random distribution of the molecular dipoles. At the critical density and at a reduced temperature of 1.2, that is at 500°C for water and 115°C for HCl, the Kirkwood factors are 1.5 and 1.05 respectively. This expresses the considerably higher degree of orientation in water. Conclusions concerning hydrogen bond association cannot be derived from this factor with certainty, however, since the dielectric constants of these dense supercritical fluids can also be calculated by means of the 'mean spherical model' treatment, assuming hard spheres with imbedded point dipoles¹⁸.

A combined increase in temperature and pressure should enhance the ionization of such polar fluids as exhibit a small degree of ion formation already at room temperature. This has been confirmed by electrical conductance measurements in shock waves¹⁹ and under static conditions with water²⁰ and pure ammonia²¹. With water these measurements could be extended to 1000°C and to about 100 kbar, with ammonia to 600°C and 40 kbar. In water the maximum specific conductance which could be obtained is about $1 \Omega^{-1} \text{ cm}^{-1}$, comparable to the specific conductance of concentrated aqueous electrolyte solutions at room temperature. In ammonia the highest conductance was around $0.01 \Omega^{-1} \text{ cm}^{-1}$. This enormous increase in conductance in comparison with that of the fluids at normal conditions indicates a corresponding increase in the degree of ion dissociation of these pure fluids. It is caused by high volume decreases and positive enthalpies connected with the ionization reactions as shown in *Table 2*. These values

Table 2. Enthalpies, entropies and volumes of reaction for the ionization equilibria in pure liquid ammonia and water²¹

Property	Ammonia	Water
$\Delta H^\circ, \text{ kcal mol}^{-1}$	26.1 (240 K, 1 bar)	13.6 (298 K, 1 bar)
$\Delta S^\circ, \text{ cal mol}^{-1} \text{ deg}^{-1}$	-40 (240 K, 1 bar)	-18.4 (298 K, 1 bar)
$\Delta V, \text{ cm}^3 \text{ mol}^{-1}$	-98.4 (273 K, 4 bar)	-21.4 (298 K, 1 bar)

can be derived from a variety of thermodynamic measurements, independently of the conductance experiments. The next table, *Table 3*, gives negative logarithms of the ion dissociation constants, that is pK-values of NH_3 and H_2O at 700 and 1000°C and at densities of 1.12 and 1.5 g cm^{-3} respectively. Compared with boiling point conditions, the dissociation constants are raised by about thirty orders of magnitude for NH_3 and by about ten orders of magnitude for H_2O . There is an uncertainty of one or two orders of magnitude, but the results are consistent with other thermodynamic data. It has been predicted¹⁹, that water could become an ionic fluid at a density

Table 3. Negative decadic logarithms (pK values) of the ion products of pure ammonia and water at several temperatures and densities²¹

$pK_{\text{NH}_3} (\rho = 0.68; -33^\circ\text{C}) = 32.8$	$pK_{\text{H}_2\text{O}} (\rho = 0.95; 100^\circ\text{C}) = 12.3$
$pK_{\text{NH}_3} (\rho = 0.68; 700^\circ\text{C}) = 17.3$	$pK_{\text{H}_2\text{O}} (\rho = 1.0; 1\,000^\circ\text{C}) = 6.0$
$pK_{\text{NH}_3} (\rho = 1.12; 700^\circ\text{C}) = 3.6$	$pK_{\text{H}_2\text{O}} (\rho = 1.5; 1\,000^\circ\text{C}) = 2.2$

of 1.8 g cm^{-3} at high supercritical temperatures. Considering the existing results, this seems probable. An analogous transition into an ionic state may also be possible for other highly compressed polar fluids with small molecules.

MIXTURES

In dense supercritical water the intermolecular association is considerably reduced and one could expect a much higher miscibility with non-polar fluids than in ordinary water. This miscibility of non-polar components with water or other comparable fluids can be described with three-dimensional pressure-temperature-composition diagrams. Binary systems have a critical curve in such diagrams extending uninterrupted between the two critical points if the partners are not too different, as for example ethane and hexane. If there are greater differences in size, polarity or otherwise, the critical curve is often divided into two branches. The upper branch is of particular interest. It begins at the critical point of the higher boiling pure component and proceeds to lower mole fractions and higher pressures. If this branch of the critical curve remains above the critical temperature of this component, it is often classified as of 'Type I'; if it passes through a temperature minimum it would be of 'Type II'. Such phenomena were predicted by van der Waals and were demonstrated experimentally first with ammonia and nitrogen in 1940²². Since then many other examples have been found; most of them are reviewed in a comprehensive survey²³. A detailed analysis of the types of critical curves and of possibilities of predictions has recently been given²⁴. Such possibilities are as yet very restricted, however, if polar components are involved.

Figure 6 shows a number of critical curves of binary aqueous systems determined in recent years. The region of complete miscibility is always on the high temperature side. One can have homogeneous mixtures of liquid-like densities at all concentrations if the pressure can be raised to about one or two kbar in this temperature range. For all these systems a portion of the boundary surface of the two-phase region has been determined which extends to the left of these curves.

In Figure 7 an analogous set of three critical curves is shown for systems containing ammonia. All the curves of Figures 9 and 10 except one are of Type II. So far only helium-xenon and water-argon have been found as examples for Type I. Two of the curves of Figure 6 deviate significantly from the remaining group: the minimum temperature for water-benzene is particularly low and occurs at about 200 bar. Comparable behaviour has been found for other aromatic components, which suggests that interaction of aromatic π -electrons with the water dipoles creates the remarkable mutual solubility. Attempts to investigate this effect further by high pressure

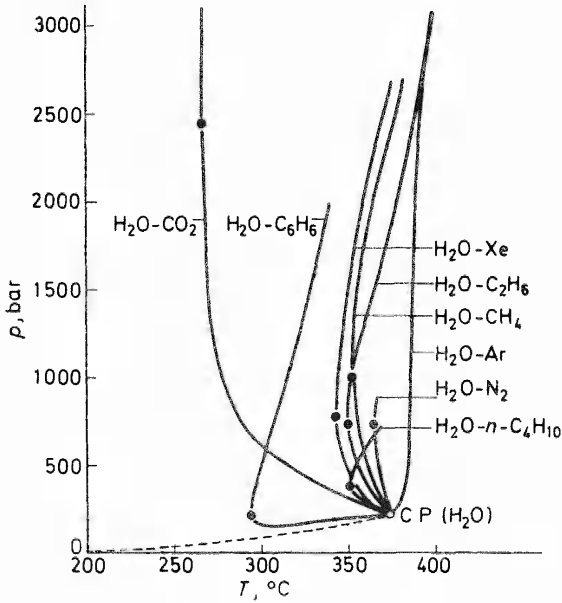


Figure 6. Critical curves of several binary aqueous systems (upper branches beginning at the critical point of pure water)

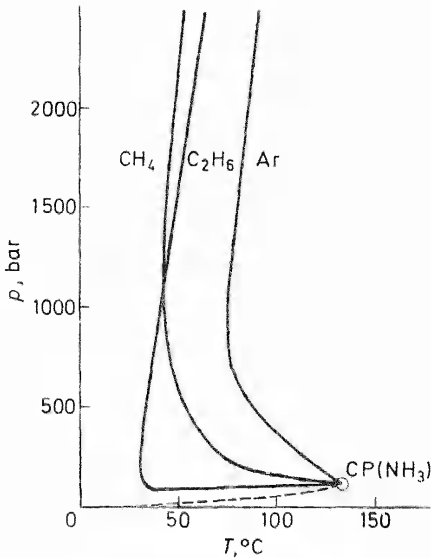


Figure 7. Critical curves of several binary ammonia systems (upper branches beginning at the critical point of pure ammonia)

Raman studies have so far been unsuccessful because of fluorescence. Infrared investigations may be fruitful. Another special case is water-carbon dioxide, where the low critical temperatures at high pressures indicate a specific interaction, which is apparently verified by infrared absorption as shown below (*Figure 9*).

The proposed procedure²⁴ to calculate critical curves for van der Waals binary mixtures was tried with three systems containing a polar component, namely water-argon, water-xenon and water-methane. A quantitative description could not be obtained, but it is correctly predicted that $\text{H}_2\text{O}-\text{Ar}$ should be of Type I and both $\text{H}_2\text{O}-\text{Xe}$ and $\text{H}_2\text{O}-\text{CH}_4$ of Type II²⁵. It is interesting to observe in *Figure 6* that at 2 kbar the critical temperatures of five systems with non-aqueous partners as different as benzene and argon are within a range of only 50 degrees and close to 647 K, the critical temperature of pure water. The slope of the curves in this region is also similar. A theoretical description of phase separation in this region of dense fluids may be easier than at lower pressures.

For several of the above-mentioned systems the density in the supercritical homogeneous state has been measured and excess volumes could be calculated. *Figure 8* gives an example: the experimentally determined excess

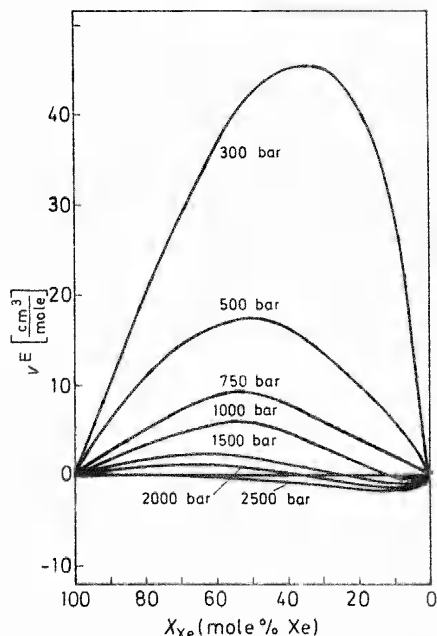


Figure 8. Excess volumes of supercritical water-xenon mixtures at 400°C and various pressures²⁵

volumes for $\text{H}_2\text{O}-\text{Xe}$ mixtures at 400°C and constant pressures²⁵. These isobars are qualitatively similar to those determined previously with other aqueous systems. Above 1500 bar the excess volume often does not exceed a few per cent of the molar volume of the mixture and may even be slightly negative.

The critical curves of *Figure 6* indicate the possibility of a specific interaction between water and carbon dioxide. To obtain more information about this, infrared spectra have been measured as shown in *Figure 9*, with the absorption caused by the OD-valence vibration of HDO in H₂O with added Xe and CO₂²⁶. The water density, 0.17 g cm⁻³, is constant for all curves and the concentration of the second component is increased. Xenon changes the absorption band only slightly, while carbon dioxide in high concentrations produces a second band around 2700 cm⁻¹. Since Xe and CO₂ are comparable in size, the spectrum indicates a specific CO₂-H₂O interaction. The nature of it is not yet sufficiently understood, however. Raman spectra at these conditions should be useful.

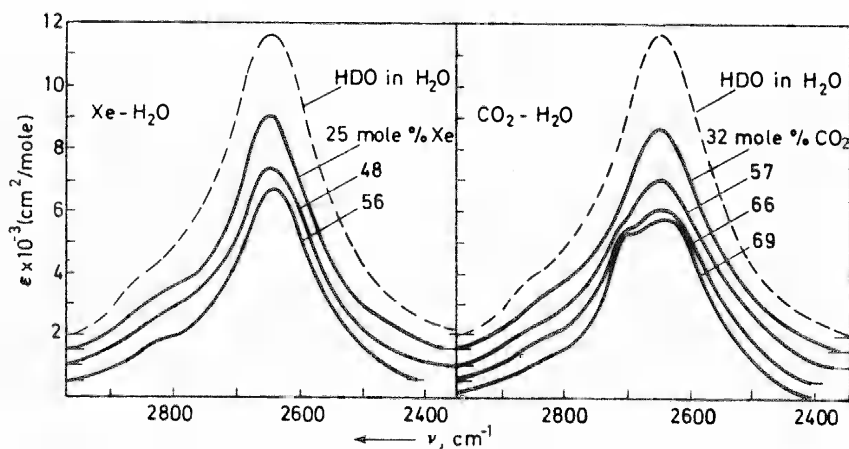


Figure 9. Infrared absorption bands of the OD-valence vibration of HDO diluted in H₂O with added xenon and carbon dioxide at 400°C. Water density is constant at 0.17 g cm⁻³ for both diagrams²⁶

Although the dielectric constant of dense supercritical water is much lower than at normal conditions, it is still high enough to permit the electrolytic dissociation of dissolved salts, and ion hydration is possible. Thus ion formation can be demonstrated in many ways, particularly by conductance measurements. Numerous such determinations have been made with acids, bases and salts, dissolved in subcritical and supercritical water, which cover a very wide range of electrolyte concentrations. As an example only a summary of results for dilute aqueous KCl solutions obtained by several authors and laboratories is given in *Figure 10*²⁷. Isotherms of the specific conductance of KCl for pressures from one to twelve kbar are shown, which extend to 800°C. The data have been compiled and critically reviewed. The initial increase of the isobars is to be expected as a consequence of the decreasing viscosity and increasing ion mobility. Above about 400°C the isobars decrease strongly at lower pressures and slightly at the highest pressures. Qualitatively it can be assumed that ion pair association becomes important above 400°C and that the product of dielectric constant and temperature at constant density varies little under these conditions. Furthermore, the viscosity

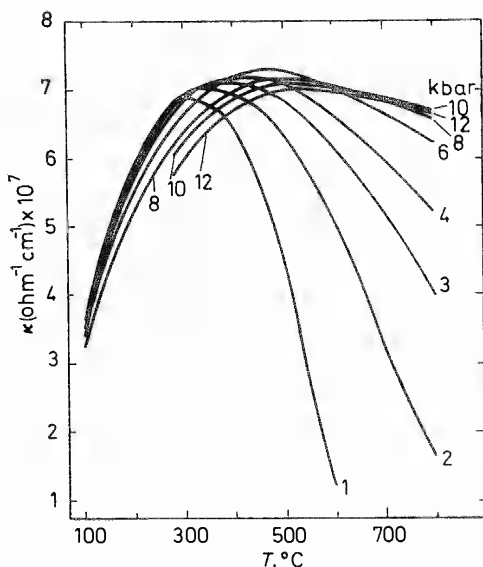


Figure 10. Specific conductance of 0.01 molal aqueous KCl solutions as a function of temperature for constant pressures²⁷

does not change very much at densities higher than about 0.5 g cm^{-3} and supercritical temperatures. Thus it appears that it will not be possible to raise the specific conductance of strong electrolytes at given concentrations in dense supercritical water higher than tenfold the value at ordinary conditions. New determinations with salt concentrations up to about ten molal show that the conductance of such aqueous solutions at several hundred degrees centigrade and several kbar approaches the conductance of fused salts at comparable conditions²⁸.

IONIC FLUIDS

Experimental work on thermodynamic properties at critical or supercritical conditions for ionic fluids is still very limited. The reasons are obvious: corrosion of such fluids is severe, critical temperatures are high and unusual materials and structures may be necessary to contain the high pressure fluid. Knowledge of the density as a function of temperature and pressure over a wide range of conditions is not only desirable as such but also as a basis for the theoretical discussion of electrical, spectroscopic and other data. Partial molar volumes, derived from density measurements of mixtures, permit conclusions on structural and solvation phenomena. Partial molar volumes of subcritical concentrated aqueous solutions at elevated temperatures and pressures have been determined by several authors in recent years²⁹.

Figure 11 schematically shows an apparatus developed recently to measure densities of concentrated aqueous electrolyte solutions up to 1000°C and 4000 bar ³⁰. The main pressure vessel has an internal heater and is filled with pressurized argon gas. Within the heater is a water filled cylinder which

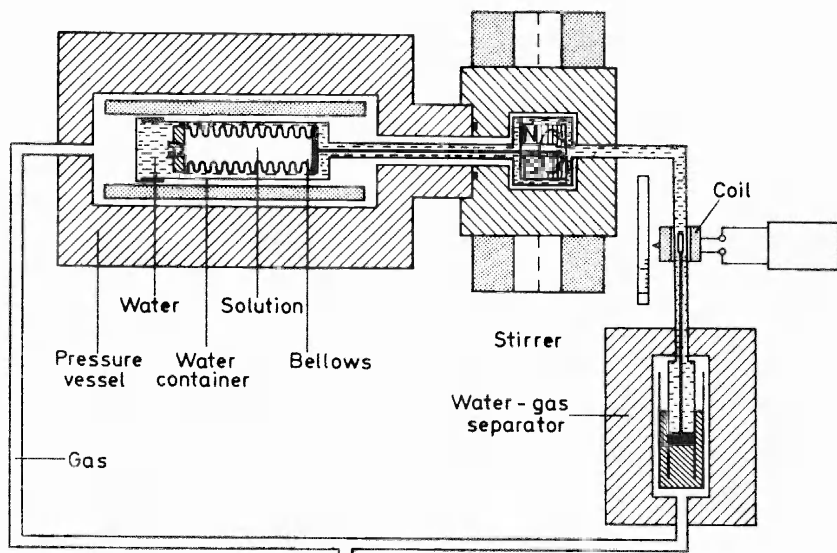


Figure 11. Schematic diagram of an apparatus to measure densities of concentrated aqueous electrolyte solutions to 1000 °C and 4 kbar³⁰

contains the sample cell which consists of a nickel bellows. This cell can be charged at room temperature with liquid solution or a solid salt. It can be rotated magnetically to stir the contents at high temperatures and pressures. Argon gas, water and sample are always maintained at equal pressure by means of a separator using mercury. Since the amount of water in the heated cylinder can be determined with a magnetic float on the mercury, the density of the sample can be derived from the volume of the cylinder and the known *PVT* data of pure supercritical water.

Among the more simple salts, bismuth trichloride is one with a relatively low critical point at 905 °C as shown in *Table 1*. Its specific electric conductance as a liquid above the melting temperature at 250 °C is high: $0.4 \Omega^{-1} \text{cm}^{-1}$. It can be considered as almost completely ionized at these conditions. It is interesting to investigate the ionic dissociation at supercritical temperatures and densities and try to obtain information about ionization in the critical region. For this purpose, electric conductance and density were measured to 1200 °C and 4 kbar, that is over a range of about 300 °C in the supercritical region³¹. An internally heated and argon filled autoclave with silica sample cells was used. Results are summarized in *Figure 12*, where the logarithm of a 'degree of dissociation' α of bismuth trichloride is plotted as a function of salt density at constant and partly supercritical temperatures. In order to calculate α it had to be assumed that BiCl_2^+ and BiCl_4^- are the dominant ions in the fluid and estimates of the ion mobilities had to be made. The assumptions involved can be well justified. It appears that in the critical region the fluid bismuth trichloride is a good conductor but the degree of ionization is only around one per cent. Increase of density, however, leads to an almost completely ionized fluid. Thus it can be expected that bismuth trichloride in

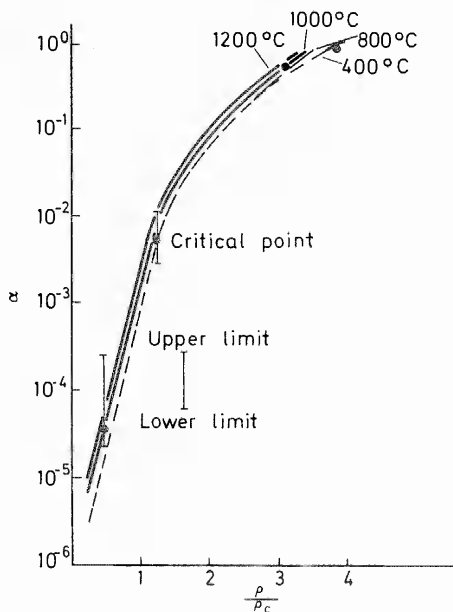


Figure 12. Degree of dissociation, α , of bismuth trichloride as a function of reduced density ρ/ρ_c at several constant sub- and super-critical temperatures³¹

the vicinity of the critical point should have rather normal thermodynamic properties. The critical exponent β , derived from the relation (liquid density–gas density) = $(T - T_{\text{critical}})^\beta$, was indeed found to be 0.33 as for many non-polar fluids.

At present there is perhaps only one known group of fluids where ions prevail in the critical region: some of the ammonium halides. Recent experimental results for ammonium chloride will be discussed here. The equilibrium pressure of the solid–gas system of NH_4Cl has been measured by several authors³². The triple point temperature and pressure have been determined to be 520°C and 47.5 bar³³. The melting pressure curve was determined to about 40 kbar³⁴.

Recent measurements have shown that ammonium chloride has a normal vapour pressure curve above the triple point and behaves as a one-component system in this respect. The critical point was found at $882 \pm 15^\circ\text{C}$ and $1635 \pm 20 \text{ bar}^{35}$. In addition, density measurements could be made in the coexisting gaseous and liquid phases to about 850°C. Several high pressure cells made mainly from sapphire and gold–platinum parts were used for these measurements. A number of results are shown in Figure 13 which gives equilibrium densities at subcritical temperatures.

This coexistence curve is narrower at higher temperatures than corresponding curves for non-polar fluids. Figure 14 shows in a double logarithmic plot the liquid–gas density difference as a function of $(T_c - T)$ for a variety of different substances. The slope, β , is given for each of the almost linear curves. The typical value for ‘normal’ non-polar fluids is $\beta = 0.33$.

Xenon is an example. Even unusual fluids like B_2H_6 , HF and BiCl_3 have

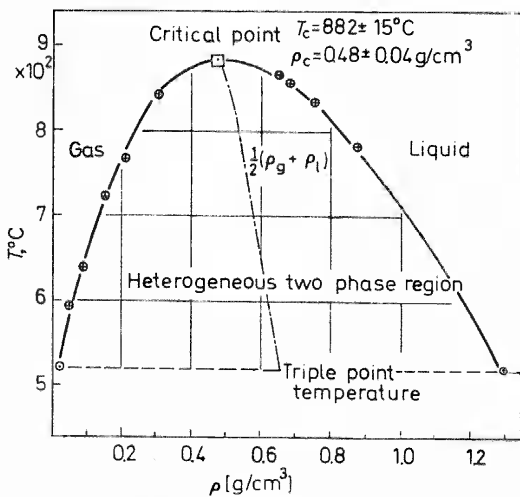


Figure 13. Gas-liquid coexistence curve of ammonium chloride in the temperature-density diagram³³

similar slopes. For NH_4Cl , however, one obtains $\beta = 0.50$. Only the fluid metals, Hg and Na, also have higher values: 0.40 and 0.50. In this regard it is interesting that electric conductance measurements could also be made in liquid ammonium chloride at equilibrium pressures from the triple point to about 850°C . The conductance indicates predominant or almost complete ionization in the liquid phase at least to 850°C and probably in the critical region. It is suggested that long range coulomb interaction is responsible for the high value of $\beta = 0.50$ in the case of NH_4Cl . The van der Waals equation, which is applicable for substances with far reaching intermolecular interactions, also predicts $\beta = 0.50$. Ammonium chloride does not obey the

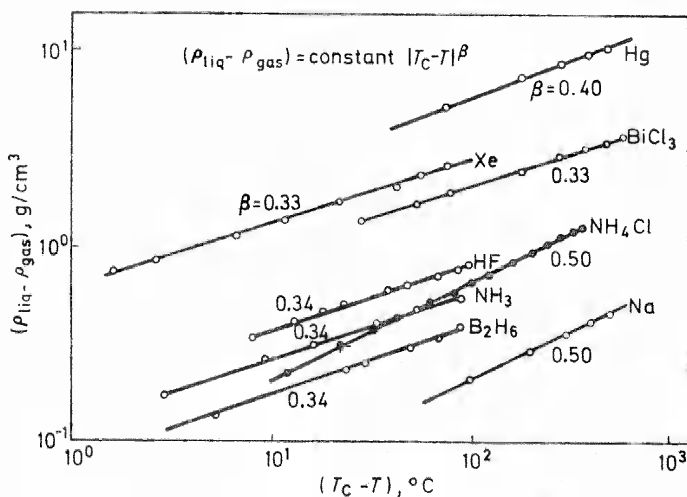


Figure 14. Double logarithmic plot of the liquid-gas density difference as a function of the distance from the critical temperature for several substances

van der Waals equation in other respects, however. The critical coefficient $P_c V_c / RT_c$, for example, has the value of 1.85 for NH_4Cl instead of 0.375 for a van der Waals fluid. Therefore, the equality of $\beta(\text{NH}_4\text{Cl})$ and $\beta(\text{v.d. Waals})$ may be fortuitous. An estimate of $\beta(\text{NaCl})$ from measured liquid densities and the extrapolated critical temperature yields $\beta = 0.7$. It may be added that density measurements with NH_4HF_2 at high equilibrium pressures gave $\beta = 0.48$ for this fluid. Corresponding measurements with NH_4F could not be made, because it behaved like a two-component system.

The critical temperature of NH_4Cl can be used to estimate critical temperatures of alkali halides. It is assumed that NH_4Cl , NaCl and KCl have the same reduced boiling temperature. With $T_b/T_c = 0.52$ for NH_4Cl one obtains $T_c(\text{NaCl}) = 3330 \text{ K}$ and $T_c(\text{KCl}) = 3225 \text{ K}$. Both values agree within two per cent with the critical temperatures derived earlier from rectilinear diameter considerations.

The small number of polar substances for which the conditions of complete ionization in the dense supercritical fluid have been investigated can perhaps be divided into three groups³¹. The reduced density $\rho_r = \rho/\rho_c$ necessary to achieve complete ionization is $\rho_r \approx 1$ for NH_4Cl , $\rho_r \approx 3$ to 4 for BiCl_3 and mercury halides, $\rho_r \approx 6$ to 7 for H_2O and NH_3 . The triple point liquid density is usually $\rho_r \approx 3$.

METALS

Fluid metals are another group of substances with high electric conductance at dense supercritical conditions. There are, however, fundamental differences between the properties of these and those of the polar compounds discussed above. Gaseous metals at low density already undergo normal thermal ionization at relatively moderate temperatures. If the density is increased, one observes a growth of conductance indicating a concentration of charge carriers much higher than what could be expected from the ionization energy of the isolated metal atoms. This increase of conductance with density by many orders of magnitude can be followed continuously at supercritical temperatures. The critical points of metals, however, are unusually high and only very few are known at present. *Table 1* gave examples of critical temperatures and pressures for metals. Experimental data exist only for mercury and alkali metals. Values for heavier metals are based on estimates using gas and liquid densities, rectilinear diameter considerations and real gas corrections^{36, 37}.

Extensive density and electrical conductance measurements with mercury were made by several authors³⁸⁻⁴⁰. *Figure 15* presents isotherms of the specific conductance of mercury as a function of pressure. In the critical region the values are high (between 0.1 and $1.0 \Omega^{-1} \text{ cm}^{-1}$) but still four or five orders of magnitude lower than in a normal liquid metal.

The most probable value for the critical density is 5.3 g cm^{-3} . It has been shown by absorption spectroscopy that with increasing pressure the minimum gap between the widened $\sigma^1 S_0$ and $\sigma^3 P_1$ levels of mercury atoms narrows and approaches zero at a density between 5.0 and 5.5 g cm^{-3} ⁴¹. Thus the overlap of the $6 S$ and $6 P$ levels of mercury begins near the critical density. A detailed

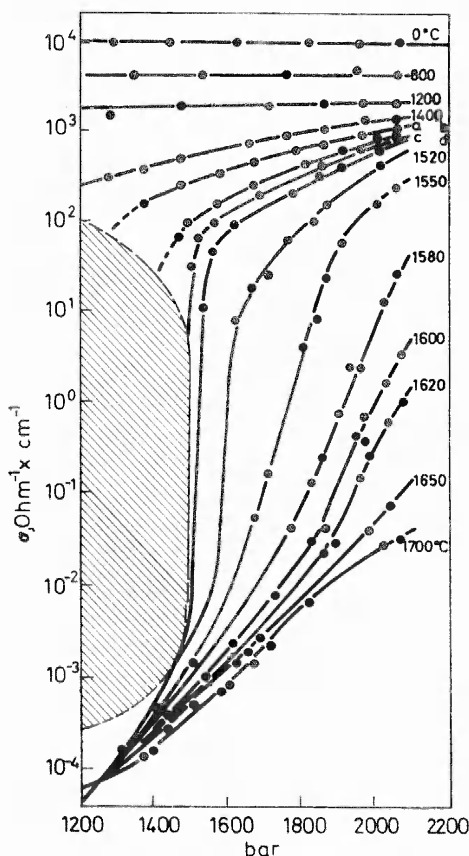


Figure 15. Specific conductance σ of fluid mercury as a function of temperature and pressure^{1,43}

examination reveals, however, that genuine metallic behaviour for bivalent fluid mercury does not necessarily already occur when this overlap is still small. Because of a certain degree of electron localization, the appearance of metallic conductance and the first overlap of the valence band with the next higher unoccupied band does not coincide. In the critical region mercury is not dense enough to be called a 'metallic gas'. This state is reached only at densities of $9\text{--}10\text{ g cm}^{-3}$. The situation is different for caesium and the other monovalent alkali metals.

Apart from mercury, caesium⁴² and potassium⁴³ are the only metals for which the complete vapour pressure curves and the critical data have as yet been determined experimentally. Well-founded estimates for the critical points of the remaining alkali metals are available, however^{44,45}. The most recent experimental determination of a full vapour pressure curve was made for potassium⁴³. The authors have used an autoclave with internal heater into which the cell containing liquid potassium was placed. The remaining internal space of the autoclave was filled with pure argon gas, the pressure of which was equilibrated with the potassium pressure inside the cell. At moderate temperatures the liquid potassium in the cell was subjected to a constant

pressure and then heated. The formation of a vapour phase could be detected by sharp decreases of electric conductance and thermoelectric power.

In *Figure 16* the essential part of the cell is shown. It is made from 75% W:25% Re alloy and of cylindrical shape. Since no insulating material compatible with potassium above 1000°C was available, the resistance of the whole cell between top and bottom, that is the parallel resistances of the solid wall and the fluid contents, had to be determined simultaneously. In

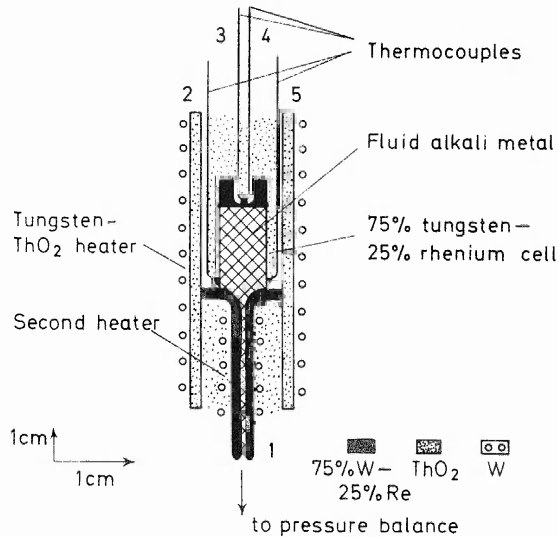


Figure 16. Cell for conductivity, thermoelectric power and vapour pressure measurements with alkali metals to 2500 K at elevated pressures³⁸

order to facilitate the subsequent derivation of the potassium conductances from these resistances, the cylindrical wall of the W/Re alloy was machined to a thickness of only 0.13 mm. Diameter and length of the cylindrical cell were 7.1 and 26 mm. The thin cell wall was electron-beam welded to the cell base and capillary, also of W/Re. Four thermocouple wires of 97%W:3% Re and 76%W:24% Re were fixed to the cell to create a four-terminal resistance for conductance measurements. Temperatures at the top and bottom of the cell and the thermoelectric voltage for a given temperature gradient between top and bottom could thus be measured.

Figure 17(a) and (b) gives results as a plot of isotherms of the logarithm of specific conductance over the pressure and also a vapour pressure curve. Above 155 ± 15 bar discontinuous changes in resistance and thermoelectric power could no longer be observed. This value was assumed to be the critical pressure with a corresponding critical temperature of $1925 \pm 30^\circ\text{C}$. An earlier prediction from gas and liquid density data was that the critical temperature should be at about 1950°C ⁴⁴. The $\log p - 1/T$ plot along the vapour pressure curve is linear to the critical temperature within experimental uncertainty. The curves of calculated vaporization entropies as functions of the reduced temperature T/T_{crit} are very different for potassium and for

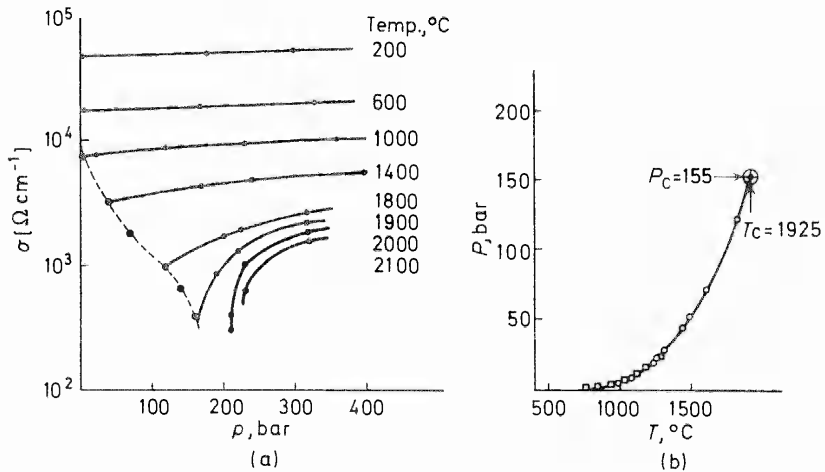


Figure 17. Fluid potassium: pressure dependence of the specific conductivity to 2100 °C and vapour pressure curve to the critical point³⁸

argon. This suggests that corresponding state considerations cannot be applied taking metals and non-metals as one group. It may be feasible, however, to derive properties of one metal from those of others.

Figure 17(a) can be compared with the analogous diagram for mercury (Figure 15). Because of experimental reasons specific conductances σ of fluid potassium could only be measured above $300 \Omega^{-1} \text{ cm}^{-1}$ and the data for this metal are more limited. It is nevertheless obvious that in the critical region σ will be around $100 \Omega^{-1} \text{ cm}^{-1}$, that is two orders of magnitude higher than in the critical region of mercury. This and additional evidence from the isochoric temperature dependence of the conductance and from the thermoelectric power show that potassium in the critical region can be considered as 'metallic'. Mercury has to be compressed to about 9 g cm^{-3} to reach this state. This is consistent with the theoretical conclusion that metallic behaviour should begin when the density of electron states in the vicinity of the Fermi energy approaches and exceeds 30 per cent of the free electron density of states.

CONCLUSION

Finally, returning to Figure 1, one can see that examples for most of the phenomena expected in supercritical phases have been observed, although with different substances. It appears that a comprehensive description of the diverse aspects of high temperature fluid behaviour will become possible in the future. A great deal of interesting exploratory experimental work remains to be done. Critical points of heavier metals investigated by transient methods, mixtures of metals with fluid hydrides, mixtures of fluid salts with non-polar and polar gases at high pressures, metal complex compounds in supercritical aqueous solutions, critical surfaces of selected ternary systems, may be some of the fields in which future research could produce results of considerable basic and practical interest.

REFERENCES

- ¹ E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **76**, 341 (1972).
- ² H. L. Barnes (ed.), *Geochemistry and Hydrothermal Deposits*, Holt: New York (1967).
- ³ K. Tödheide, *Naturwiss.* **57**, 72 (1970).
- ⁴ S. Maier and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **70**, 639 (1966).
- ⁵ H. Köster and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **73**, 716 (1969).
- ⁶ C. W. Burnham, J. R. Holloway and N. F. Davies, *Amer. J. Sci.* **267** A, 70 (1969); The Geological Society of America, Special paper No. 132 (1969).
- ⁷ M. H. Rice and J. M. Walsh, *J. Chem. Physics*, **26**, 824 (1957).
- ⁸ K. H. Dudziak and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **70**, 1120 (1966).
- ⁹ B. Le Neindre, R. Tufeu, P. Bury and J. V. Sengers, *Ber. Bunsenges. phys. Chemie*, **77**, 262 (1973).
- ¹⁰ J. M. H. Levelt Sengers and S. C. Greer, *Int. J. Heat and Mass Transfer*, **15**, 1865 (1972).
- ¹¹ E. U. Franck and K. Roth, *Disc. Faraday Soc.* **43**, 108 (1967).
- ¹² M. Buback and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **75**, 33 (1971).
- ¹³ M. Buback, Thesis, Institute of Physical Chemistry, University of Karlsruhe (1972).
- ¹⁴ H. Lindner, Thesis, Institute of Physical Chemistry, University of Karlsruhe (1970).
- ¹⁵ G. E. Walrafen, *J. Chem. Physics*, **52**, 4174 (1970); *Hydrogen-bonded Systems*, Taylor and Francis, London, 1968.
- ¹⁶ K. Heger, Thesis, Institute of Physical Chemistry, University of Karlsruhe (1969).
- ¹⁷ W. Harder, Thesis, Institute of Physical Chemistry, University of Karlsruhe (1973).
- ¹⁸ V. M. Jansoone and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **76**, 943 (1972).
- ¹⁹ H. G. David and S. D. Hamann, *Trans. Faraday Soc.* **55**, 72 (1959); S. D. Hamann and M. Linton, *Trans. Faraday Soc.* **65**, 2186 (1969).
- ²⁰ W. Holzapfel and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **70**, 1105 (1966).
- ²¹ D. Severin, Thesis, Institute of Physical Chemistry, University of Karlsruhe (1971).
- ²² J. R. Krichevski, *Acta Physicochimica (USSR)*, **12**, 480 (1940).
- ²³ G. M. Schneider 'Gas-Gas-Gleichgewichte' in *Topics in Current Chemistry*, vol. 13, p. 559, Springer: Heidelberg, New York (1970).
- ²⁴ R. L. Scott, *Ber. Bunsenges. phys. Chemie*, **76**, 296 (1972); R. L. Scott and P. H. van Konynenburg, *Discuss. Faraday Soc.* **49**, 87 (1970).
- ²⁵ H. Welsch, Thesis, Institute of Physical Chemistry, University of Karlsruhe (1973).
- ²⁶ W. v. Osten, Thesis, Institute of Physical Chemistry, University of Karlsruhe (1971).
- ²⁷ A. S. Quist, W. L. Marshall, E. U. Franck and W. v. Osten, *J. Phys. Chem.* **74**, 2241 (1970).
- ²⁸ J. U. Hwang, H. D. Lüdemann and D. Hartmann, *High Temperatures-High Pressures*, **2**, 651 (1970).
- ²⁹ A. J. Ellis, *J. Chem. Soc. (London)*, 1579 (1966); 660 (1967).
- ³⁰ R. Hilbert, Thesis, Institute of Physical Chemistry, University of Karlsruhe (1974).
- ³¹ G. Treiber and K. Tödheide, *Ber. Bunsenges. phys. Chemie*, **77**, 540 (1973).
- ³² H. Braune and S. Knoke, *Z. phys. Chemie*, **135**, 49 (1928); W. H. Rodebush and J. C. Michalek, *J. Amer. Chem. Soc.* **51**, 752 (1929); G. J. Novikow and O. G. Polyachenok, *Z. neorg. Chem. (USSR)*, **6**, 1951 (1961).
- ³³ M. Buback and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **76**, 350 (1972).
- ³⁴ C. W. F. T. Pistorius, *J. Chem. Phys.* **50**, 1436 (1969).
- ³⁵ M. Buback and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **78** (1974).
- ³⁶ A. V. Grosse, *Rev. Hautes Temp. et Refr.* **3**, 115 (1966).
- ³⁷ A. V. Grosse, *Inorg. Nucl. Chem. Letters*, **4**, 261 (1968).
- ³⁸ W. F. Freyland and F. Hensel, *Ber. Bunsenges. phys. Chemie*, **76**, 16 (1972).
- ³⁹ J. K. Kikoin and A. R. Sechenko, *Phys. Metals USSR*, **24**, 74 (1967).
- ⁴⁰ R. G. Ross and D. A. Greenwood, *Progr. Mater. Sci.* **14**, 173 (1969).
- ⁴¹ F. Hensel, *Ber. Bunsenges. phys. Chemie*, **75**, 619, 847 (1971).
- ⁴² H. Renkert, F. Hensel and E. U. Franck, *Ber. Bunsenges. phys. Chemie*, **75**, 507 (1970).
- ⁴³ F. Hensel and E. U. Franck, *Rev. mod. Physics*, **40**, 697 (1968).
- ⁴⁴ J. G. Dillon, P. A. Nelson and B. S. Swanson, *Rev. Sci. Instr.* **37**, 614 (1966); *J. Chem. Phys.* **44**, 4229 (1966).
- ⁴⁵ G. F. Oster and C. F. Bonilla, *Proc. Fifth Symp. on Thermophysical Properties*, ASME, Boston, pp. 468-474 (1970).