

HIGH PRESSURE THERMODYNAMICS OF MIXTURES

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Abstract—In the present survey some important trends in the high pressure thermodynamics of fluid mixtures of non-electrolytes are reviewed.

First the pressure dependence of excess functions such as the excess Gibbs energy G^E , the excess enthalpy H^E , the excess entropy S^E and the excess heat capacity C_p^E is discussed. It can be obtained from the knowledge of the excess volume V^E as a function of pressure, temperature and composition. Experimental results demonstrate that the variations of V^E as a function of pressure and temperature can be important and comparable to those of the molar volumes themselves. A detailed discussion shows that further progress in this field depends on the development of an accurate equation of state for mixtures.

Since furthermore direct calorimetric measurements are practically completely lacking at high pressures most thermodynamic informations have to be deduced up to now from high pressure phase equilibria and critical phenomena where our knowledge is much better. The pressure dependence and critical phenomena of liquid-gas, liquid-liquid and gas-gas equilibria will be shortly reviewed. Mainly binary systems will be treated but phase separation phenomena in some ternary and multicomponent systems will be equally considered. Recent results concerning the rate of phase separation will be additionally presented.

New developments during recent years have shown that the limits between liquid-gas, liquid-liquid and gas-gas equilibria are not well defined and that continuous transitions occur. This continuity will be demonstrated for binary mixtures of hydrocarbons with carbon dioxide and methane and for some inert gas systems.

The significance of high pressure phase equilibria in fluid mixtures for practical applications is shortly discussed, e.g. for high pressure extractions, supercritical fluid chromatography and for some other high pressure techniques and processes.

Methods for the calculation of fluid phase equilibria in mixtures under high pressure are reviewed. They start from equations of state or from theories of mixtures using sometimes sophisticated mixing rules for the parameters. Some results are presented and compared with experimental data.

Finally a characteristic example for the pressure dependence of chemical equilibria in liquid solutions is considered and the standard value of the reaction volume ΔV^0 is determined from measurements of the equilibrium constant K as a function of pressure at constant temperature. It is shown how standard values of the reaction enthalpy ΔH^0 can be obtained from temperature jump experiments in such solutions at high pressure.

INTRODUCTION

The thermodynamics of mixtures is one of the most important fields of thermodynamics. It has been of fundamental interest to chemists for a long time especially with respect to the thermodynamic and theoretical description of mixtures and solutions, to chemical equilibria and to some important methods of separation. An enormous amount of experimental and theoretical work has already been done in the thermodynamic investigation of mixtures but up to now the pressure variable has been widely neglected although in the first decades of our century very promising efforts had been done especially by the Dutch school.

Thus the high pressure thermodynamics of mixtures is still in a developing state whereas much more research activities have already been dedicated to the high pressure properties of pure compounds, the most recent literature being regularly reported in the Bibliography of High Pressure Research¹ (for literature up to 1969, see Ref. 2).

In the present review some important trends in the high pressure thermodynamics of fluid mixtures of non-electrolytes will be discussed; the accent will be on the discussion of some special high pressure effects that might be of interest to thermodynamicists working in other fields. Polar and ionic fluids at high pressures and temperatures have been treated by Franck³ at the Third International Conference on Chemical Thermodynamics. Electrolyte solutions under pressure have been recently reviewed by Hamann⁴ and critical phenomena in electrolyte solutions by Horvath.¹¹³ Throughout this paper the pressure unit bar will be used (1 bar = 10^5 Pa = 0.1 MPa; 1 kbar = 10^3 bar; 1 Mbar = 10^6 bar).

In Fig. 1 some pressures that are important in nature and chemical industry are summarized, making use of a similar compilation by Pilz.⁵ On the left hand side some pressures relevant in nature are given in logarithmic scale: critical pressures are between 2.3 bar for helium and approximately 1.5 kbar for mercury; the deepest ocean corresponds to approximately 1 kbar and the center of the earth to approximately 4 Mbar.

More interesting for chemists is the right hand column in Fig. 1 where some high pressure processes and techniques are compiled that are relevant to the European chemical industry. Between 100 and 1000 bar we have high pressure liquid chromatography (LC) and supercritical fluid chromatography (SFC), crystal growth, some hydrogenations; the syntheses of ammonia, of methanol, of some organic compounds by oxo synthesis and of acetic acid; and additionally some polymerisations. The fabrication of polyethylene occurs between 1.5 and 3 kbar and the synthesis of diamond at approximately 50 kbar. For all these methods and processes the high pressure thermodynamics of mixtures is of fundamental importance. Hydrostatic extrusion, high pressure densification and sintering will become more and more interesting for material research. Explosive welding and plating are indispensable techniques for the fabrication of chemical reactors and tubing.

EXCESS FUNCTIONS AND EQUATION OF STATE OF MIXTURES

For the thermodynamic description of mixtures (especially of liquid mixtures) excess functions are often

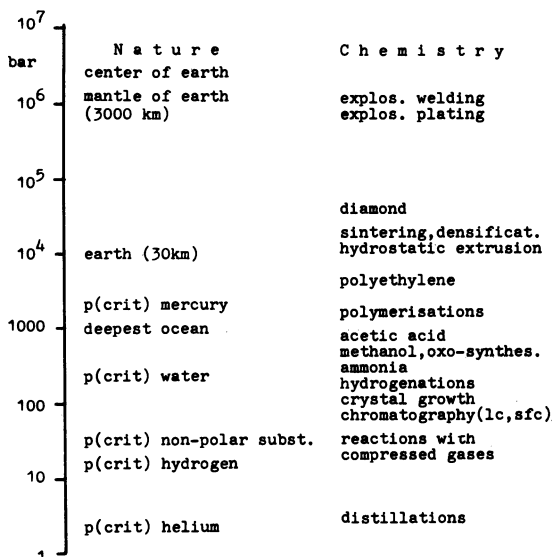


Fig. 1. Pressure scale in nature and chemistry (according to a similar compilation by Pitz²).

used.⁶⁻⁸ A molar excess function Z_m^E is defined as the difference of the molar function Z_m between a real and an ideal mixture at the same values of temperature T , total pressure p and mole fraction x_i of all constituents i , where $Z = G, H, S, V, C_p$ etc.

$$X_m^E = Z_m(\text{real}) - Z_m(\text{ideal}) \text{ for } p, T, x_i = \text{const.} \quad (1)$$

It can be easily shown that the following relations hold for the pressure dependence of the excess functions⁶⁻⁸

$$\left(\frac{\partial G_m^E}{\partial p}\right)_{T, x_i} = V_m^E \quad (2)$$

$$\left(\frac{\partial H_m^E}{\partial p}\right)_{T, x_i} = V_m^E - T \left(\frac{\partial V_m^E}{\partial T}\right)_{p, x_i} \quad (3)$$

$$\left(\frac{\partial S_m^E}{\partial p}\right)_{T, x_i} = - \left(\frac{\partial V_m^E}{\partial T}\right)_{p, x_i} \quad (4)$$

$$\left(\frac{\partial C_{pm}^E}{\partial p}\right)_{T, x_i} = - \left(\frac{\partial^2 V_m^E}{\partial T^2}\right)_{p, x_i} \quad (5)$$

It follows from the right hand sides of the relations (2-5) that the pressure derivatives of all molar excess functions are completely described by the molar excess volume V_m^E as a function of temperature, pressure and mole fractions. From this the excess functions themselves can be obtained by integration e.g. the molar excess Gibbs energy by

$$G_m^E(p) - G_m^E(p^0) = \int_{p^0}^p V_m^E dp \text{ for } T, x_i = \text{const.} \quad (6)$$

where $G_m^E(p^0)$ is the value of the molar excess Gibbs energy at the reference pressure p^0 .

Thus the problem of thermodynamics of mixtures reduces to the knowledge of the molar excess volume V_m^E as a function of pressure, temperature and composition or, more generally, to the knowledge of an equation of state for mixtures at high pressure.

Such an equation of state can be based on the excess volume V_m^E or on the molar volume V_m of the mixture

itself where

$$V_m(\text{real}) = V_m(\text{ideal}) + V_m^E = \sum_i x_i \cdot V_{mi}^* + V_m^E \quad (7)$$

According to eqn (7) V_m is made up of two terms: (1) of the ideal term taking account of the molar volumes V_{mi}^* of the pure components i and (2) of the molar excess volume V_m^E as a correction term.

For pure liquids already many pVT measurements have been undertaken up to quite high pressures. The data have been correlated with the well-known equations of state of Tait,⁹ Hudleston,¹⁰ Hayward,¹¹ Chaudhuri,¹² Witt,¹³ and others. Several authors have shown recently that among the two-parameter equations the old Tait equation does astonishingly well.^{2,7,14,15} Up to now very few measurements, however, exist on mixtures and here the equations cited are not yet well tested especially with respect to the mixing rules for the parameters. The volumes of coexisting phases at high pressures have been measured by Tsiklis *et al.*¹¹⁴

The situation is not at all good for the molar excess volumes V_m^E (for a review see¹⁶, for references see^{16,110,111}). Up to now only very few V_m^E data exist at high pressures e.g. by Hamann and Smyth,¹⁷ Engels,¹⁸⁻²⁰ Lamb and Hunt,²¹ Korpela,²² and Götze.^{23,24} V_m^E data can be obtained from very accurate pVT data measured separately on different mixtures and on all pure components or more precisely from measuring V_m^E directly as a function of pressure, temperature and composition. In Figs. 2 and 3 some results of Götze^{24,25} are shown for the system water-acetonitrile. In Fig. 2 the excess volume V_m^E in $\text{cm}^3 \cdot \text{mol}^{-1}$ is plotted against the mole fraction of acetonitrile for 100, 1000 and 2500 bar and for each pressure at 25, 50 and 75°C. The pressure influence is very remarkable: with increasing pressure the inflection point becomes more and more accentuated and at the highest pressures and temperatures the excess volume changes sign for mixtures rich in acetonitrile. In Fig. 3 the pressure derivatives of the excess functions that follow from the eqns (2-4) with the V_m^E data of Fig. 2 for $x = 0.5$ and $T = 50^\circ\text{C}$ are plotted for the water-acetonitrile system. All derivatives are negative in the pressure range 100-2500 bar. In contrast to $(\partial G_m^E/\partial p)_{T, x_i}$ is monotonous, $(\partial H_m^E/\partial p)_{T, x_i}$ and $(\partial S_m^E/\partial p)_{T, x_i}$ run through minima between 500 and 1000 bar which correspond to inflection points in the $H^E(p)$ and $S^E(p)$ curves respectively.

Figure 2 shows that the absolute values of the excess volumes V_m^E are small in comparison to the molar volumes V_m themselves whereas the variations of the excess volumes with pressure, temperature and composition can be important and comparable to those of the molar volumes. It follows that an equation of state based on the excess volume as a function of pressure, temperature and composition should be much more promising than one based on the molar volumes. Since nearly nothing is known up to now the problem of an equation of state for mixtures is still a wide field for future research activities (for a compilation see Ref. 111).

Since calorimetric data such as heat capacities of mixtures or enthalpies of mixing²⁶ are practically completely lacking at high pressures, most thermodynamic information has to be deduced up to now from high pressure phase equilibria and critical phenomena where our knowledge is much better (for books see Refs. 7, 8, 27; for review articles see Refs. 28-35, for experimental techniques see Refs. 36, 75).

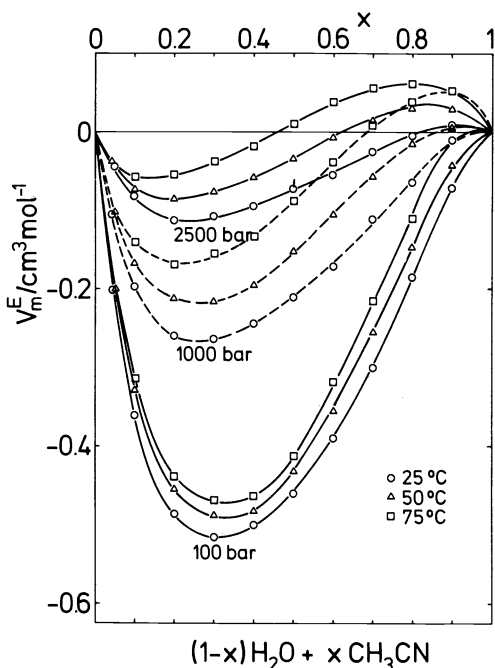


Fig. 2. Molar excess volumes V_m^E in the system $(1-x)$ water + x acetonitrile as a function of pressure, temperature and mole fraction (according to results of Götze²⁴).

LIQUID-LIQUID EQUILIBRIA

In Fig. 4 all types of pressure dependence of liquid-liquid equilibria in binary systems that are presently known are schematically represented;²⁹⁻³³ examples exist for all types except those with a question mark (Figs. 4g, 4k, 4o, 4s).

In the first vertical column on the left the different types of temperature-mole fraction isobars are represented, i.e. those with upper critical solution temperatures (UCST's, Fig. 4a), lower critical solution temperatures (LCST's, Fig. 4b), closed loops (Fig. 4c) and a hyperbolic-like type (Fig. 4d).

In the first horizontal row pressure-mole fraction isotherms (Fig. 4e-h) that belong to the types of pressure

dependence given in Figs. 4i-v are represented schematically. Their shapes correspond remarkably well to the temperature-composition diagrams for constant pressure (Figs. 4a-d) demonstrating that pressure and temperature are equivalent thermodynamic variables.

The second horizontal row shows that with increasing pressure upper critical solution temperatures will either decline (Fig. 4i) or rise (Fig. 4j) or run through a temperature minimum (Fig. 4l).

The third horizontal row demonstrates that with increasing pressure lower critical solution temperatures may either rise (Fig. 4m) or decline (Fig. 4n) or run through a temperature maximum (Fig. 4p).

The pressure dependence of closed loops is schematically shown in the fourth horizontal row: closed loops may either shrink with increasing pressure and disappear completely at a definite pressure in the three-dimensional temperature-pressure-mole fraction space (Fig. 4q) or only appear at higher pressures (Fig. 4r) or resemble hyperboloids (Fig. 4t); examples of types 2r and 4t have been found in binary mixtures of 2-, 3- and 4-methylpyridine with water and heavy water.²⁹⁻³⁴

Immiscibility surfaces of a saddle-like type such as shown in the fifth horizontal row have also been found, e.g. in mixtures of methane with hydrocarbons (Fig. 4u) or of sulfur with hydrocarbons (Fig. 4v).²⁹⁻³³

Examples for all types represented in this Figure have been summarized elsewhere.²⁹⁻³⁴ Here only one example for type 4j will be given.

In Fig. 5 some very recent results of Paas⁴⁰ are shown for the methane-tetrafluoromethane system. In Fig. 5a isobaric temperature-mole fraction profiles are plotted which exhibit upper critical solution temperatures that rise with increasing pressure. In Fig. 5b the corresponding isothermal pressure-mole fraction which exhibit lower critical solution pressures, are given.

It has been shown by several authors^{6-8,29-35,37} that some thermodynamic information can be obtained from the pressure dependence of critical solution temperatures. With the assumption that G_m is analytic† at and near a critical solution point eqn (8) and with the additional assumption of a regular solution relation (9) hold for the pressure dependence of the critical solution temperature in a demixing binary system

$$\frac{dT_c}{dp} = \frac{T_c \cdot (\partial^2 V_m^E / \partial x^2)_c}{(\partial^2 H_m^E / \partial x^2)_c} \tag{8}$$

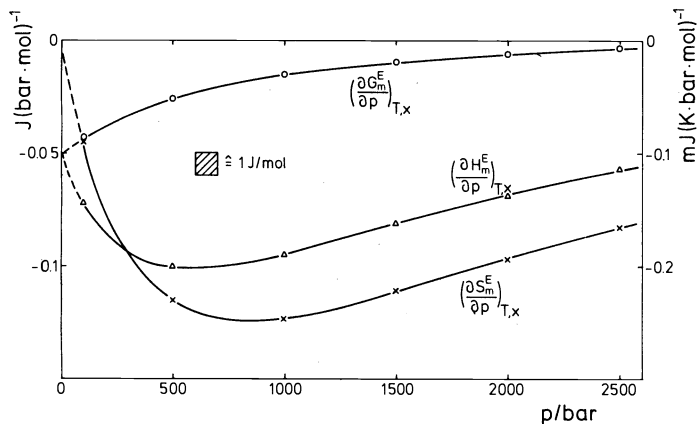


Fig. 3. Pressure dependence of the molar excess functions in the system $(1-x)$ water + x acetonitrile: $(\partial G_m^E / \partial p)_{T,x}$, $(\partial H_m^E / \partial p)_{T,x}$ and $(\partial S_m^E / \partial p)_{T,x}$ as a function of pressure at $T = 323.15$ K and $x = 0.5$ (according to results of Götze²⁴).

†It has, however, been shown that the assumption of G_m being analytical at a critical solution point is doubtful; for an explicit critical discussion see Refs. 7, 31, 35.

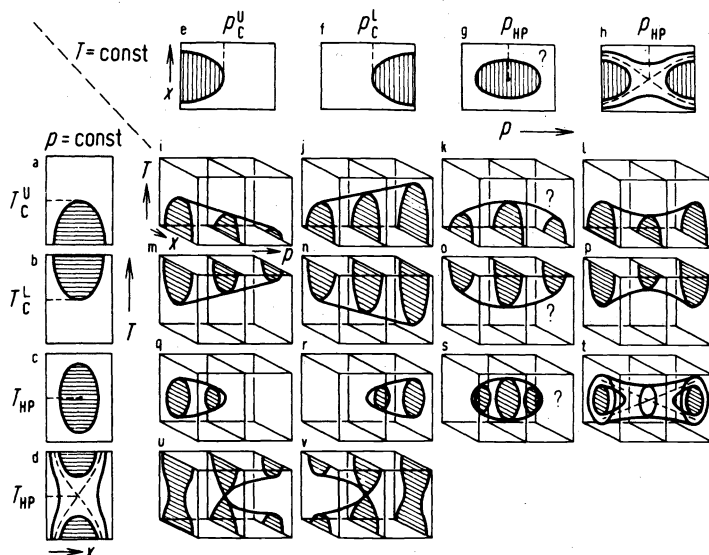


Fig. 4. Pressure effects on immiscibility phenomena in liquid binary systems (according to Refs. 30, 32; see text).

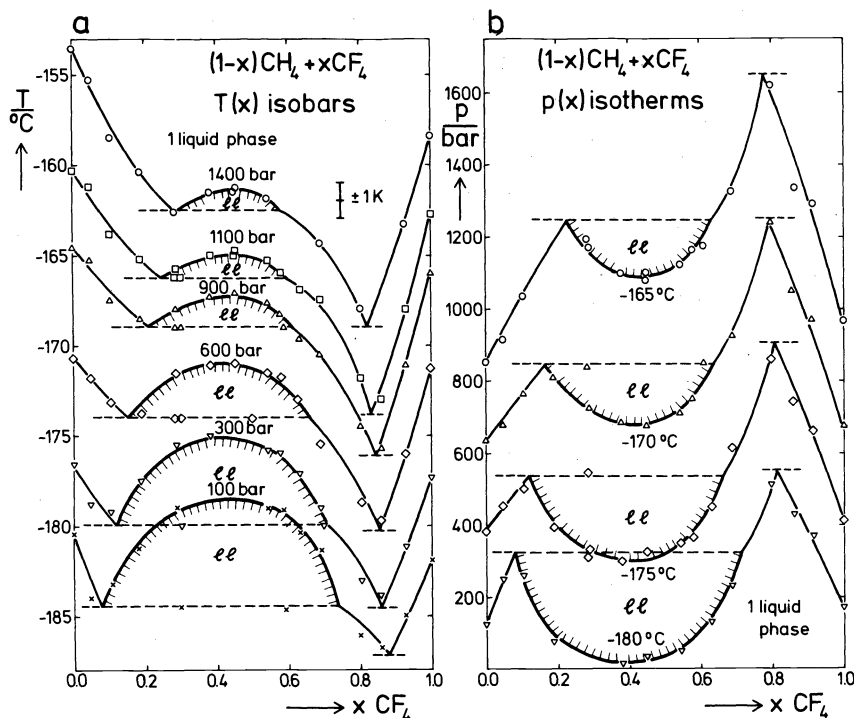


Fig. 5. Phase behaviour of the system $(1-x)$ methane + x tetrafluoromethane at elevated pressures (according to results of Paas⁴⁰). (a) $T(x)$ isobars; (b) $p(x)$ isotherms.

$$\frac{dT_c}{dp} = \frac{T_c \cdot V_{mc}^E}{H_{mc}^E} \quad (9)$$

It has to be kept in mind, however, that the conditions for the validity of relation (9) in general are largely oversimplified.† For the system methane-tetrafluoromethane it follows from the existence of upper critical solution temperatures (corresponding to $H_{mc}^E > 0$ ^{8,29-34,37}) and from the positive sign of dT_c/dp obtained

experimentally⁴⁰ that V_m^E should be positive, a result that had already been known for this system from normal pressure measurements by Croll and Scott.³⁸ Also Paas⁴⁰ could show that regular solution theory³⁹ describes quite well the sign and the order of magnitude of dT_c/dp in this system.

For systems of type t in Fig. 4 the molar excess enthalpy H_m^E should have to change its sign from minus (corresponding to LCST's) to plus (corresponding to UCST's) with increasing temperature at constant pressure and it follows from eqn (9) that the molar excess volume V_m^E should have to change its sign from minus to plus with increasing pressure at constant temperature.²⁹⁻³⁴ The

†It has, however, been shown that the assumption of G_m being analytical at a critical solution point is doubtful; for an explicit critical discussion see Refs. 7, 31, 35.

curious result is that for these systems that deviate very much from ideality, the molar excess enthalpy H_m^E and the molar excess volume V_m^E should both nearly vanish just between the two immiscibility surfaces in Fig. 4t. The change of the sign of the excess volume has already been affirmed experimentally by Engels¹⁸⁻²⁰ for the system 3-methylpyridine-H₂O.

Liquid-liquid equilibria in ternary systems have been investigated most frequently at normal and low pressure, but for high pressure the experimental data are very scarce.²⁹⁻³⁴ Recently the liquid-liquid equilibria in the ternary system tetrafluoromethane-trifluoromethane-ethane have been studied as a function of pressure by Peter^{42,43} and Paas.⁴⁴

For aqueous solutions of organic compounds the influence of added salts on the mutual miscibility has also been studied under pressure in some cases.^{45,46} A rather simple example is given in Fig. 6 where the upper and the lower solution temperatures are plotted for the system 1-propanol-water-potassium chloride according to measurements of Russo;⁴⁵ the mass ratio water/1-propanol being kept constant at a value of 1.5. Figure 6a gives the solution temperatures as a function of the amount of potassium chloride added at normal pressure and Fig. 6b shows the

solution temperature as a function of pressure for a mixture of constant composition. There is a striking analogy between Figs. 6a and 6b, increasing the pressure having a similar effect as decreasing the salt content.

Systems such as shown in Fig. 6 are well suited to study the rate of liquid-liquid phase separation. Starting from concentrations, temperatures and pressures in the homogeneous region just below the plotted curves heterogeneous states can be reached by a relatively small temperature increase and the rate of demixing is obtained from measuring the turbidity as a function of time. Measurements were made by Jost⁴⁷ and Limbach⁴⁸ with a temperature jump apparatus that has been developed for the investigation of fast reactions in solution under high pressure.⁴⁹ Here the temperature jump was created within microseconds by discharging a high voltage capacitor through the solution. The measuring cell with optical windows was mounted in a high pressure autoclave. The intensity of the transmitted light and of the light scattered through an angle of 90 degrees could be measured simultaneously as a function of time, stored in a transient recorder and registered afterwards with a normal recorder. In Fig. 7 the recorder traces thus obtained are presented for one experiment on the system 1-propanol-water-potassium

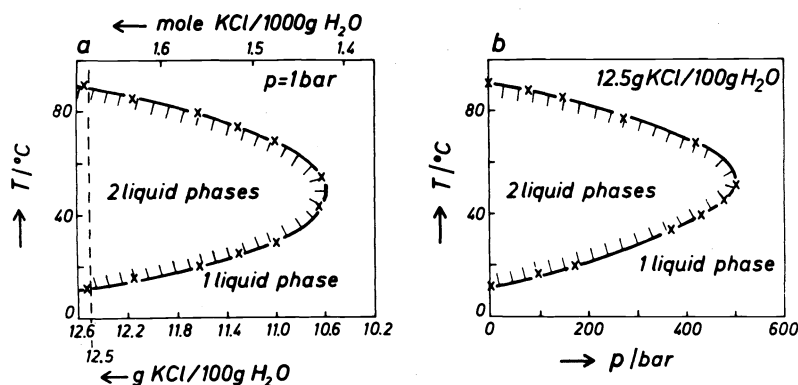


Fig. 6. Salt and pressure effects on liquid-liquid immiscibility phenomena in the system 1-propanol-water-potassium chloride (according to results of Schneider and Russo⁴⁵; w% water/w% 1-propanol = const. = 1.5).

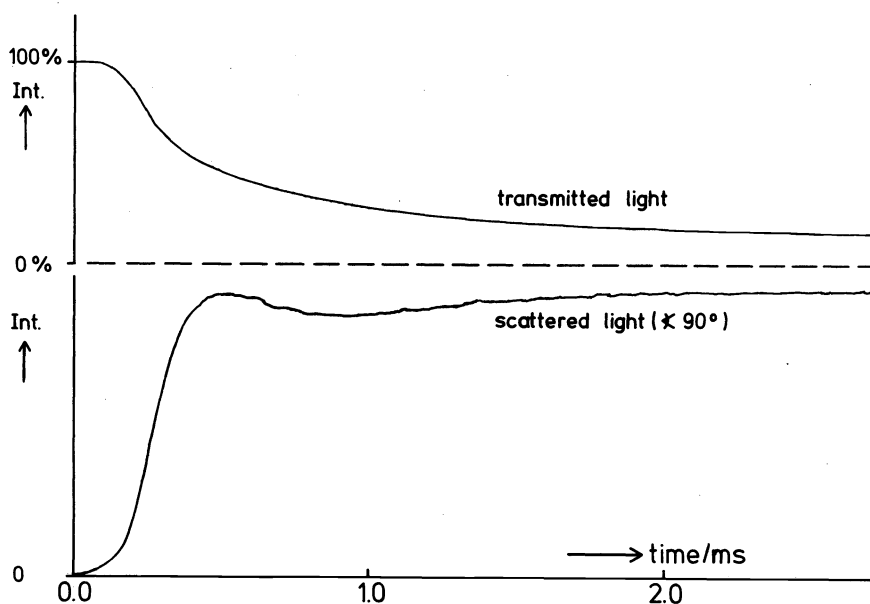


Fig. 7. Rate of liquid-liquid phase separation in the system 1-propanol-water-potassium chloride (according to results of Limbach⁴⁸; $\Delta T = 13^\circ\text{K}$; $\lambda = 497\text{ nm}$; $p = 1\text{ bar}$; concentrations: 50.3 wt% 1-propanol, 44.5 wt% water, 5.2 wt% potassium chloride).

chloride at 1 bar;⁴⁶ similar measurements have also been performed on the system pyridine-water-potassium chloride at elevated pressures.⁴⁷ In the upper diagram of Fig. 7 the intensity of the transmitted light and in the lower diagram the intensity of the scattered light are registered as a function of time. The transmitted light decreases to nearly zero transmission and the scattered light accordingly increases to a nearly constant value within less than one millisecond. The initial maximum in the intensity of the scattered light can be explained qualitatively from the growth of the scattering particles during the time of the experiment. The curves show that induction times greater than some tenth of a millisecond are absent and it follows from a rough estimation that the formation and the ageing of the scattering droplets of a second liquid phase is essentially diffusion controlled.

LIQUID-GAS EQUILIBRIA

In Fig. 8a the well-known three-dimensional pressure-temperature-mole fraction surface is represented for the liquid-gas equilibria of a binary system in a simple case, x being the mole fraction of the less volatile component II. The dashed lines are the vapour pressure curves of the pure components I and II. They end at the gas-liquid critical points CP I and CP II of the pure components. For

each pressure-mole fraction isotherm the binary critical point is situated at the maximum of the isothermal pressure-mole fraction profile; the line that connects the critical points of all isotherms is the binary critical curve.

The phase equilibria and the critical phenomena in binary fluid mixtures are most easily discussed with the aid of the pressure-temperature projection of this critical line, the so-called critical locus curve. Here the critical locus curve is not interrupted; some important types are schematically represented in Fig. 8b. At temperatures and pressures beyond the critical locus curve the two components of the binary system are miscible in all proportions (for examples and Refs. see Refs. 7, 8, 29-33, 50).

GAS-GAS EQUILIBRIA

The critical phase behaviour of binary mixtures, however, is not always so simple as that represented in Figs. 8a and 8b. In Fig. 9a the phase behaviour of systems exhibiting gas-gas equilibria is schematically shown in a three-dimensional representation. Here the critical locus curve is interrupted. The branch that starts from the critical point CP II of the less-volatile component II does not end at the critical point of pure component I as in Fig. 8 but runs through a temperature minimum corresponding to a so-called gas-gas equilibrium of the second type

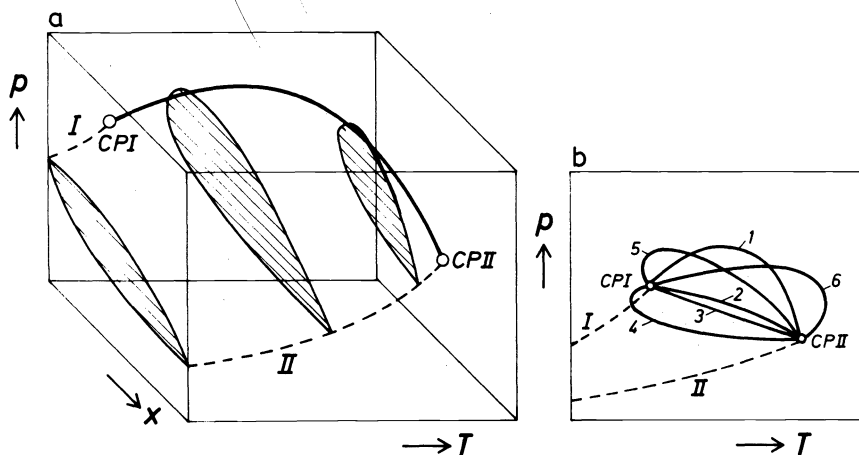


Fig. 8. Liquid-gas equilibria in binary systems (schematically; see text). (a) Three-dimensional representation in the T - p - x space; (b) $p(T)$ projection of the diagram in (a).

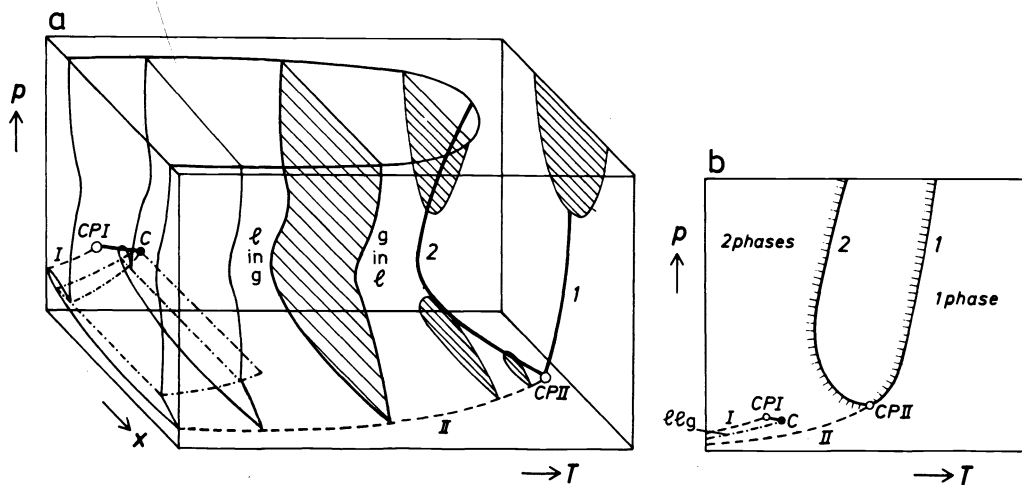


Fig. 9. Gas-gas equilibria in binary systems (schematically; see text). (a) Three-dimensional representation in the T - p - x space; (b) $p(T)$ projection of the diagram in (a).

(curve 2) or directly tends to increasing temperatures and pressures corresponding to a gas-gas equilibrium of the first type (curve 1). The corresponding $p(T)$ projections are represented schematically in Fig. 9b.

These phase separation effects were predicted by van der Waals⁵¹ and discussed in detail by Kamerlingh Onnes and Keesom as early as 1907.⁵² Type 2 was found for the first time in 1940 by Krichevskii and co-workers⁵³ in the system nitrogen-ammonia and type 1 in 1952 by Tsiklis⁵⁴ in the system helium-ammonia. In the mean time similar phase separation effects have been detected in some fifty other systems;^{7,27-34,50} up to now no temperature maximum on the critical curve, however, has been found such as originally predicted by van der Waals.

At a first glance these somewhat exotic types of phase behaviour might seem to be of academic interest only to normal thermodynamicists. One has to realize, however, that the exhibition of gas-gas equilibria will rather be the rule than the exception for mixtures where the components differ more and more in size, structure and/or polarity e.g. for solutions of a gas in a liquid. Here the right branch of the middle isotherm in Fig. 9a (marked with "g in 1") corresponds to the solubility of gas I in liquid II as a function of pressure, whereas the left hand branch (marked with "1 in g") corresponds to the solubility of liquid II in gas I, both on a mole fraction basis. It is an interesting fact that for systems of this type, both solubilities will run through a maximum mole fraction value with increasing pressure; here the numerator of the right hand side of the coexistence eqn (10)^{6,7}

$$\left(\frac{\partial x_2}{\partial p}\right)_{T,\sigma} = \frac{x_1''(V_1' - V_1'') + x_2''(V_2' - V_2'')}{(\partial^2 G_m / \partial x_2^2)_{T,p} (x_2' - x_2'')} \quad (10)$$

will become zero, V_i being the partial volume and ' and '' the indices for the coexisting phases.

Examples for gas-gas equilibria have been summarized in some books, e.g. by Tsiklis²⁷ and Rowlinson⁷ and in several review articles.²⁸⁻³⁴ Here only some results on inert gas systems will be reviewed in Fig. 10 where parts of the critical locus curves of some helium binaries, and of the vapour pressure curves of the less volatile components respectively are plotted making use of a compilation by Streett.⁵⁵ Whereas helium-hydrogen,⁵⁶ helium-nitrogen⁵⁷ and helium-argon^{55,58} exhibit gas-gas equilibria of the second type and helium-neon⁵⁹ shows a tendency for such a phase behaviour, gas-gas equilibria of the first type have been found in the systems helium-methane,⁶⁰ helium-xenon⁶¹ and helium-carbon dioxide.⁶² According to Schouten and Trappeniers neon-krypton⁶³ resembles to the helium-argon system.

The gas-gas equilibria found in the helium-hydrogen system seem to have important consequences for planetary atmospheres as has been recently reported by Streett.⁵⁶ The same author has also discussed the limits of gas-gas equilibria.⁶⁴ In principle there is no limit of the gas-gas critical curve at higher temperatures and pressures. In many cases it will disappear below the crystallization surface of the system at very high pressures but it may also persist up to very high temperatures and pressures perhaps even to the limits at which atomic and molecular structure begin to break down.⁶⁴

TRANSITIONS BETWEEN LIQUID-GAS, LIQUID-LIQUID AND GAS-GAS EQUILIBRIA

Up to now the three different types of two-phase equilibrium in fluid mixtures namely liquid-liquid, liquid-gas and gas-gas equilibria have been discussed separately. During the last decade systematic high-pressure investigations, however, have shown that the limits between these three forms of heterogeneous phase equilibrium in fluid mixtures are not well defined and that continuous transitions occur³⁰⁻³⁴ the transition types sometimes being of considerable practical interest.

The discussion of this question will start from Fig. 11 where the phase behaviour and the critical phenomena are schematically represented for a binary system exhibiting separation into two liquid phases.³³ For the type in Figs. 11a and 11b the critical curve liquid-gas (lg) is not interrupted and runs through the usual pressure maximum. At temperatures far below the critical temperature of the pure more volatile component I separation into two liquid phases additionally takes place. The branch II of the critical curve corresponds to upper critical solution temperatures as a function of pressure that are slightly raised with increasing pressure.

The more the mutual miscibility of the two components decreases the more the branch II of the critical curve is displaced to higher temperatures. It can finally penetrate the ranges of temperature and pressure for the critical phenomena liquid-gas and may pass continuously into the critical curve lg whereas the branch of the critical curve starting from the critical point of the pure component I ends at a so-called critical end point C on the three-phase line liquid-liquid-gas (Figs. 11c and 11d).

For still lower mutual miscibility of the components critical locus curves without any pressure maximum or minimum may be obtained such as indicated in Fig. 11d by a dotted line. Since a phase behaviour of this type is attributed to gas-gas equilibria of the second type, continuous transitions between liquid-gas, liquid-liquid and gas-gas equilibria should be possible.

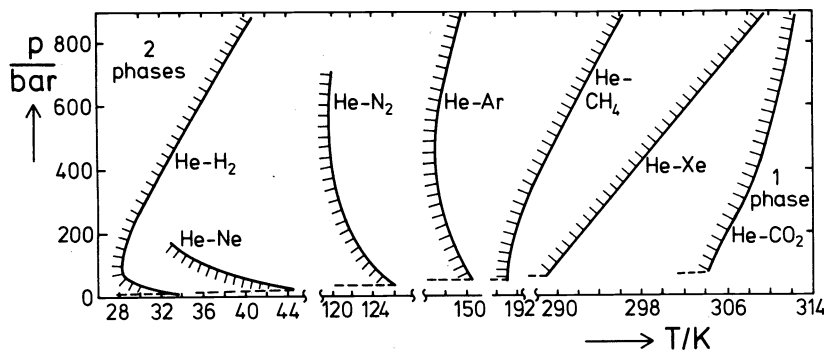


Fig. 10. Critical locus curves of binary helium systems (according to a similar compilation by Streett⁵⁵; for details and references see text).

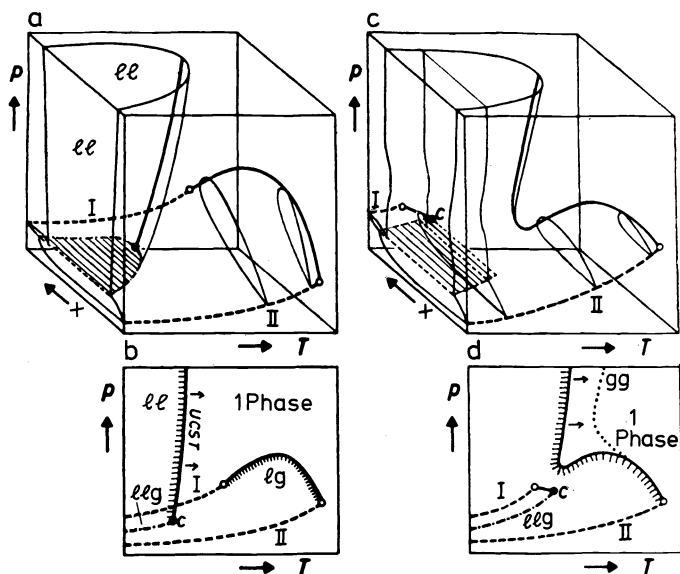


Fig. 11. Phase behaviour of a binary system showing liquid-liquid immiscibility (schematically; see text). (a) and (c) Three-dimensional representation in the T - P - X space; (b) $p(T)$ projection of the diagram in (a); (d) $p(T)$ projection of the diagram in (c).

In order to prove this hypothesis series of binary systems were studied where one constant component I such as carbon dioxide, methane, ethane, ethylene, water etc. was combined with a component II that was systematically altered in size, structure and polarity, the phrase "family" being proposed for such a series of related binary systems.⁶⁴

In Fig. 12 the carbon dioxide family is discussed as a first example. For binary mixtures of carbon dioxide with octane⁶⁶ the liquid-gas critical curve lg runs through the usual pressure maximum. At much lower temperatures additionally separation into two liquid phases is found, the upper critical solution temperatures rising steeply with increasing pressure. No superposition of the critical phenomena liquid-gas and liquid-liquid occurs in this system. If octane is replaced by a higher alkane the mutual miscibility decreases and the branch of the

critical curve that corresponds to liquid-liquid equilibria is displaced to higher temperatures. For carbon dioxide-hexadecane⁶⁶ it penetrates the ranges of temperature and pressure for the critical phenomena liquid-gas and the critical curve liquid-liquid (II) merges continuously into the critical curve liquid-gas (lg), a pronounced pressure minimum and a slight temperature minimum being found. For carbon dioxide-squalane⁶⁷ (=2,6,10,15,19,23-hexamethyltetracosane) the mutual miscibility is still lower and the critical curve liquid-liquid (II) is displaced to even higher temperatures, the pressure minimum of the critical curve becoming less pronounced. For even higher alkanes than squalane critical locus curves without any pressure maximum or minimum may be obtained.⁶⁷

The phase behaviour of carbon dioxide-2-hexanol⁶⁵ and of carbon dioxide-2-octanol⁶⁵ corresponds completely to that of carbon dioxide-octane, whereas the system carbon dioxide-2,5-hexanediol⁶⁵ resembles that of carbon dioxide-squalane without showing, however, any pressure minimum or maximum. According to measurements of Tödheide and Franck⁶⁸ the critical curve of the carbon dioxide-water system runs through a temperature minimum at approximately 1500 bar showing thus a typical gas-gas phase behaviour of the second type.

These types of phase behaviour in fluid carbon dioxide systems are of increasing practical interest since supercritical carbon dioxide may become an important solvent for industrial extractions, especially in the food and pharmaceutical industry where substances with low thermal stability have to be separated or purified.^{94,5} Some patents have already been given in this field.⁶⁹ Additionally supercritical carbon dioxide is the favourite mobile phase in supercritical fluid chromatography (SFC).⁷⁰⁻⁷⁴

In Figs. 13 and 14 the methane family is treated.^{30-33,76,77,79,80} Figure 13 shows the pressure-temperature projections of the phase diagrams of several binary hydrocarbon systems and of the systems methane-ammonia⁷⁸ and helium-methane.⁶⁰ The critical curve of the rather curious type of Fig. 13c consists of two branches. That at low temperatures corresponds to upper critical solution temperatures; the other branch of the critical

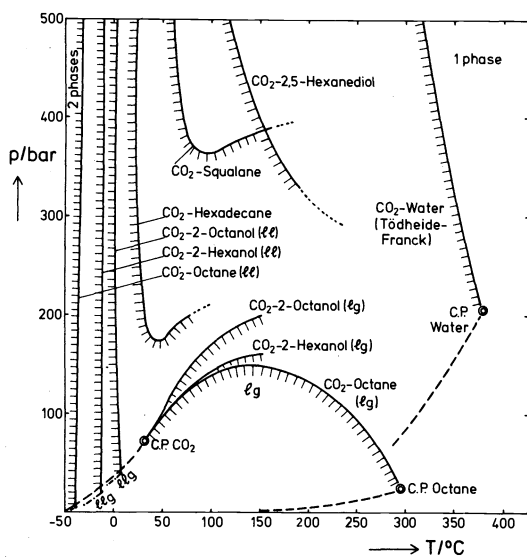


Fig. 12. Critical locus curves of binary carbon dioxide systems (for details and references see text).

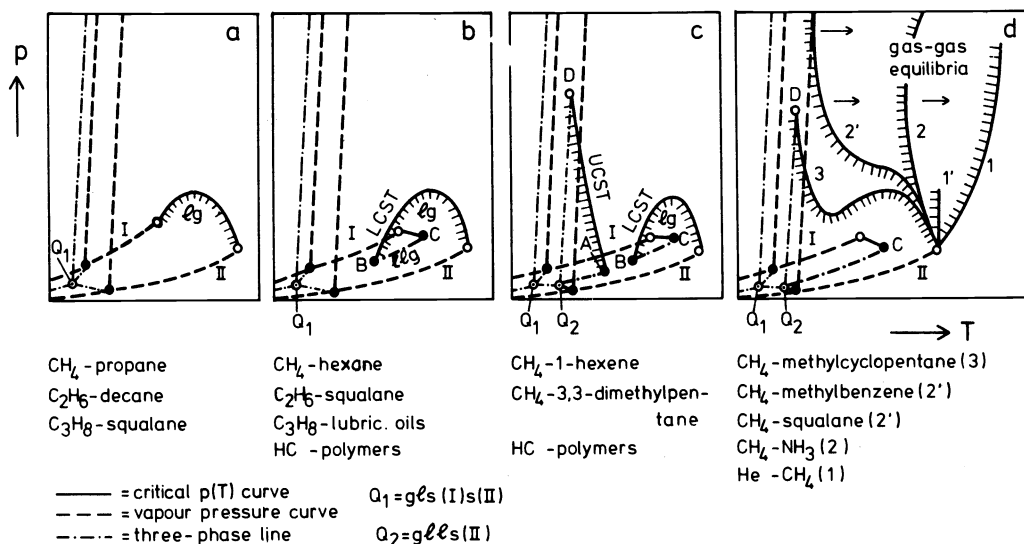


Fig. 13. $p(T)$ projections of the phase diagrams of binary hydrocarbon systems (schematically; see text).

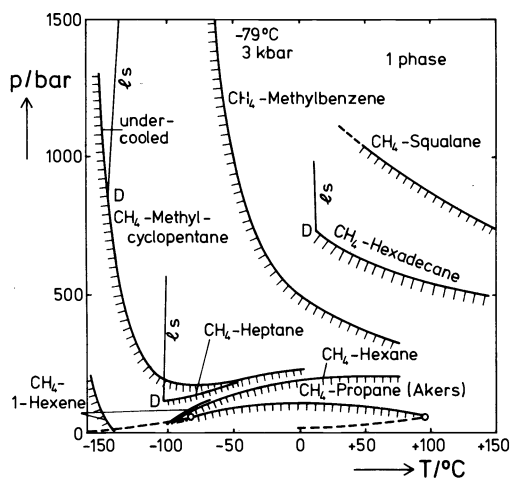


Fig. 14. Critical locus curves of binary methane-hydrocarbon systems (for details and references see text).

curve first corresponds to lower critical solution temperatures for liquid-liquid phase separation and then merges continuously into the critical curve liquid-gas that ends at the critical point of the less volatile component II (e.g. methane-1-hexene,⁷⁹ methane-3,3-dimethylpentane⁸⁰). This somewhat exotic type of phase behaviour is of considerable practical interest and seems to be the fundamental type of phase behaviour for mixtures of hydrocarbons differing very much in size, e.g. for solutions of polymers in hydrocarbon solvents (see Refs. 7, 81).

With increasing mutual miscibility (e.g. for smaller differences in size and/or polarity) the branch that corresponds to upper critical solution temperatures in Fig. 13c is displaced to lower temperatures and may disappear below the crystallization surface such as shown in Fig. 13b (e.g. methane-hexane,⁷⁶ ethane-squalane,⁸² propane-lubricating oils,⁷ polymers in a hydrocarbon solvent^{7,81}); for further increasing mutual miscibility the common type of Fig. 13a results (e.g. methane-propane,⁸³ ethane-decane,⁸⁴ propane-squalane⁶⁵). Figure 13d corresponds to decreasing mutual miscibility in comparison to type 13c: Consecutively type 3 (e.g. methane-methylcyclo-

pentane^{76,77}), type 2' (e.g. methane-methylbenzene,⁷⁷ methane-squalane⁶⁵) and type 2 result, the latter corresponding to a gas-gas system of the second type (e.g. methane-ammonia⁷⁸); finally type 1 is obtained, which corresponds to a gas-gas system of the first type (e.g. helium-methane⁶⁰).

Experimental data for the schematic types of Fig. 13 are given in Fig. 14, where the critical locus curves for methane binaries with hydrocarbons of sizes from propane to squalane are plotted. Methane-propane⁸³ has a non-interrupted critical curve liquid-gas according to type 13a. Methane-hexane⁷⁶ belongs to type 13b and methane-1-hexene^{77,79} to type 13c. The critical curves of the methane-heptane⁷⁶ and the methane-methylcyclopentane^{76,77} systems run through pressure minima according to type 3 in Fig. 13d whereas the critical curves of methane-methylbenzene,⁷⁷ methane-hexadecane⁶⁵ and methane-squalane⁶⁵ have a monotonous shape such as type 2 in Fig. 13d. This kind of phase behaviour is of great practical importance for the fabrication of high-pressure polyethylene since the methane-hexadecane⁶⁵ form has also been found for solutions of polyethylene in ethylene by Ehrlich⁸⁵ and Steiner and Horlé.⁸⁶

It has been shown in Figs. 11-14 that a large pattern of transition types between typical liquid-gas, typical liquid-liquid and typical gas-gas equilibria exist in fluid mixtures at high pressures that are of considerable practical interest in some cases. Quite similar phenomena have also been found in mixtures of helium with inert gases (see Fig. 10), of hydrocarbons of medium size with water at much higher temperatures,^{25,29-34} in ammonia binaries^{27-34,53,54,78,109} etc.; similar investigations on ethylene and ethane binaries are underway.⁶⁵ All these results give evidence that the hypothesis of transitions between all types of two-phase equilibrium in fluid mixtures is useful in understanding the great variety of phase relationships and in giving a certain order to many different types of critical phenomena in fluid mixtures.

Scaling law studies in mixtures (see Ref. 35) have not yet been performed at high pressures since the high accuracy necessary for these investigations is difficult to obtain under these conditions; just the pressure dependence of the scaling parameters, however, should be of considerable

experimental and theoretical interest, e.g. because of the great variety of the different $p(x)$ isotherms and/or $T(x)$ isobars that can be sometimes obtained in the same system at high pressures. Although critical phenomena seem to be more or less understood in fluid binary mixtures⁸⁷ much progress is to be expected in the investigation of the phase diagrams and critical phenomena of ternary and multicomponent mixtures under high pressures, e.g. with respect to tricritical points.⁴¹

CALCULATION OF HIGH-PRESSURE PHASE EQUILIBRIA IN FLUID MIXTURES

The continuity between all types of two-phase equilibria in fluid mixtures demonstrated in the preceding section is also of interest from a theoretical point of view especially for the calculation of high-pressure phase equilibria in fluid mixtures.

These calculation methods start from the fact that the conditions for phase equilibrium and for critical points are essentially the same for all types of two-phase equilibria in fluid mixtures. For a binary system the conditions for phase equilibrium are given in eqn (11)

$$G'_m - x'_m(\partial G_m / \partial x_i)_{p,T} = G''_m - x''_m(\partial G_m / \partial x_i)_{p,T} \quad (11)$$

or

$$\mu'_i = \mu''_i$$

with

$$i = 1 \text{ or } 2 \quad \text{for } T' = T'' \text{ and } p' = p''$$

and for a binary critical point in eqn (12)

$$(\partial^2 G_m / \partial x_i^2)_c = 0 \quad (\partial^3 G_m / \partial x_i^3)_c = 0 \quad (12)$$

$$\text{for } i = 1 \text{ or } 2.$$

From the phase equilibrium conditions the phase diagram is deduced, while from the conditions of a critical point the critical curve can be obtained. In most cases, however, the simple conditions for the molar Gibbs energy G_m given in (11) and (12) are not applicable but the more complicated corresponding conditions for the molar Helmholtz energy A_m have to be used.^{6,7,35,37} Because of difficulties in the definition of standard states generally no excess functions are used.

The molar Gibbs energy G_m or the molar Helmholtz energy A_m necessary for the calculations are obtained:

(1) from an equation of state that is often a modified version of the Redlich-Kwong^{88-95,106} or of the van der Waals^{35,80} equation, using sometimes rather sophisticated combining rules for the parameters of the mixtures, or

(2) from theories of mixtures with the use of different combining rules for the potential parameters in a mixture.⁹⁸⁻¹⁰⁵

Calculations of high-pressure phase diagrams in fluid mixtures from an equation of state have been carried out by Wilson,⁸⁸ Prausnitz and Chueh,⁸⁹ Zudkevitch and Joffe,⁹⁰ Joffe, Schroeder and Zudkevitch,⁹¹ Peter and Wenzel,⁹² Wenzel and Peter,⁹³ Peter, Brunner and Riha,^{94,95} Scott and van Konynenburg,⁸⁰ Scott,³⁵ Breedveld and Prausnitz,⁹⁶ Renon, Chandron and Asselineau⁹⁷ and others.

Calculations from theories and models have been per-

formed by de Swaan Arons and Diepen,⁶¹ Zandbergen, Knaap and Beenakker,⁹⁸ Tan, Luks and Kozak,⁹⁹ Rigby *et al.*,¹⁰⁰ Trappeniers, Schouten and Ten Seldam,¹⁰¹ Schouten, Ten Seldam and Trappeniers,¹⁰² Mulholland and Rehr,¹⁰³ Neff and McQuarrie,¹⁰⁴ Bartis and Hall¹⁰⁵, McGlashan, Stead and Warr¹¹² and others.

Here only the calculation method using the Redlich-Kwong equation of state will be treated in more detail for a binary system (see Refs. 92-95). From condition (11), eqn (13) can be deduced

$$RT \ln(x'_i/x''_i) = \int_{p^0}^p (V''_i - V'_i) dp = \int_{V(p^0)}^{V(p)} (p'_i - p''_i) dV. \quad (13)$$

Here p_i is not the partial pressure but is defined as $p_i = (\partial p / \partial n_i)_{T, V, x_j(j \neq i)}$; p^0 is a (low) reference pressure.

The Redlich-Kwong equation of state (14)

$$p = \frac{nRT}{(V - nb)} - \frac{an^2}{T^{1/2}V(V + nb)} \quad (14)$$

is then used for the calculation of the integrals in (13) with the mixing rules (15) and (16) for the parameters a and b

$$a = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2 \quad (15)$$

$$b = b_{11}x_1 + b_{22}x_2. \quad (16)$$

a and b for the pure components are obtained from pVT data and critical data a_{12} is calculated from (17)

$$a_{12} = (1 - k_{12})(a_{11}a_{22})^{1/2} \quad (17)$$

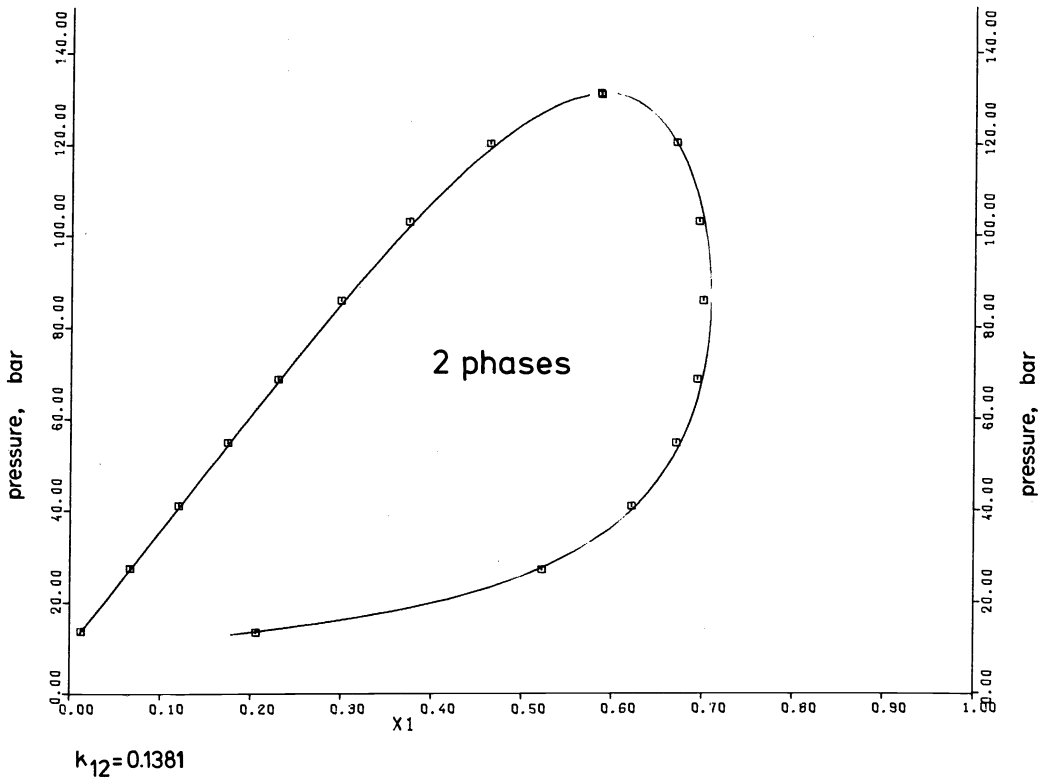
where the correction parameter k_{12} is generally fitted to one binary experiment.

In Figs. 15 and 16 some characteristic results are shown that have been obtained with this method by Deiters.¹⁰⁶ In Fig. 15 experimental¹⁰⁷ and calculated¹⁰⁶ data are compared for the pressure-mole fraction isotherm of the system methane-heptane at 477.60°K; a k_{12} value of 0.1381 was used. The agreement between the experimental data and the calculated curve is quite satisfactory. In Fig. 16 experimental⁶¹ and calculated¹⁰⁶ values are compared for helium-xenon at 293.15°K, this system exhibiting gas-gas equilibria of the first type (see Fig. 10). Here the agreement is not bad, but a k_{12} value of 1.2561 had to be used, the physical meaning of which being doubtful.

In Fig. 17 some results of the theoretical approach of Neff and McQuarrie¹⁰⁴ are compiled where reduced critical locus curves predicted from the van der Waals one-fluid theory are plotted; here pressure and temperature are reduced with the Lennard-Jones 6-12 intermolecular potential parameters ϵ_{22} and σ_{22} of the less volatile component 2. The first row corresponds to $R_\sigma = \sigma_{11}/\sigma_{22} = 0.6$ and the second row to $R_\sigma = 0.8$, the curves are labelled with the ratio $\epsilon_{11}/\epsilon_{22}$, and k_{12} is defined by

$$\epsilon_{12} = (1 - k_{12})(\epsilon_{11}\epsilon_{22})^{1/2}. \quad (18)$$

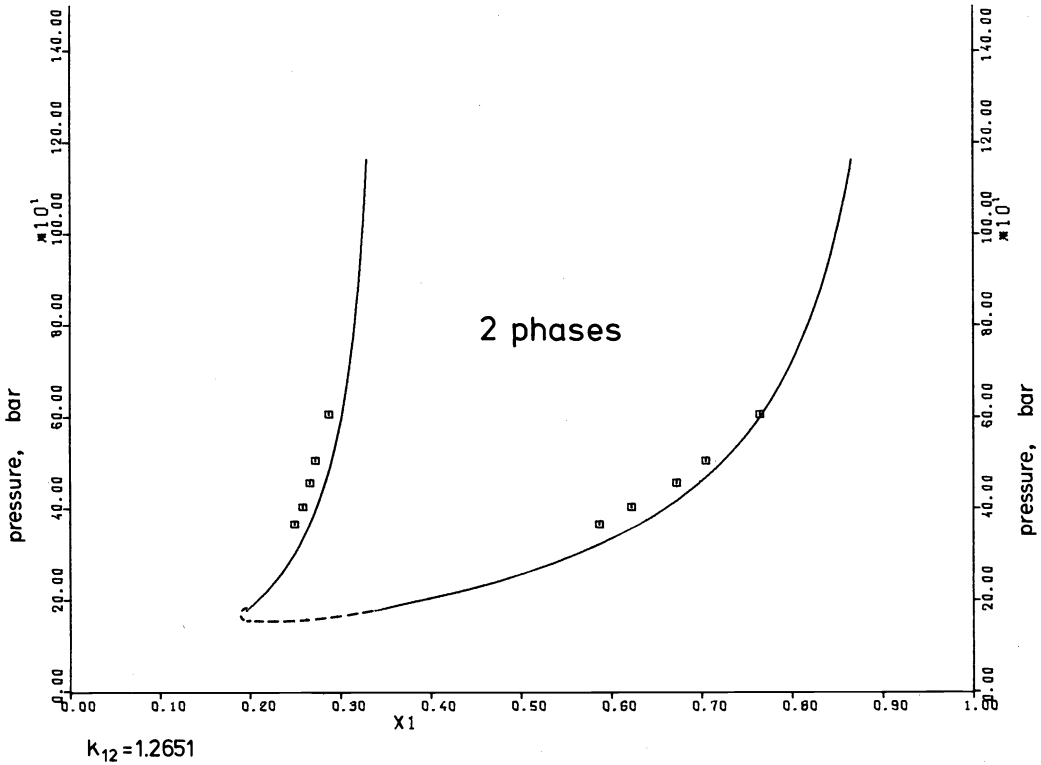
A whole sequence of different critical locus curves result, ranging from curves having a negative initial slope without any temperature minimum, through types with a temperature minimum corresponding to gas-gas equilibria of the second type, up to curves that run directly to increasing temperatures and pressures such as are attributed to gas-gas systems of the first type. Decreasing values of



METHANE/HEPTANE

TEMPERATURE: 477.60 K

Fig. 15. Calculation of high-pressure phase equilibria in binary fluid systems: $p(x)$ isotherm at 477.6°K for methane-heptane (\square = experimental data¹⁰⁷, full line = calculated curve¹⁰⁶; original computer plot; for details see text).



..HE...XE..

TEMPERATURE: 293.15 K

Fig. 16. Calculation of high-pressure phase equilibria in binary fluid systems: $p(x)$ isotherm at 293.15°K for helium-xenon (\square = experimental data⁶¹, full line = calculated curve¹⁰⁶; original computer plot; for details see text).

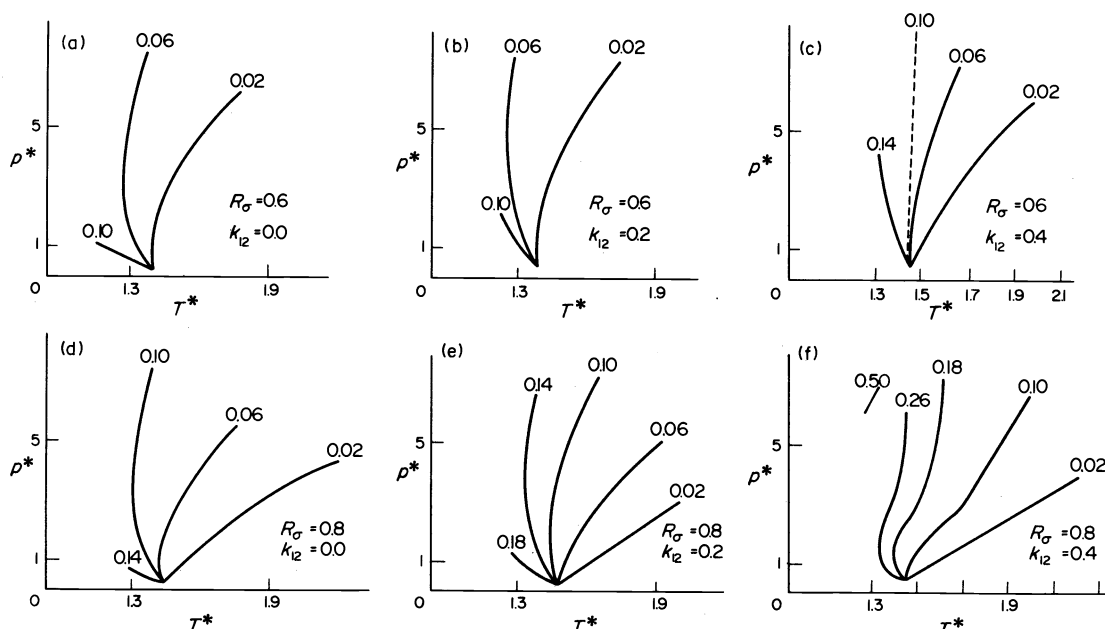


Fig. 17. Critical locus curves predicted by the van der Waals one-fluid theory (according to Neff and McQuarrie¹⁰⁴; curves are labeled with $\epsilon_{11}/\epsilon_{22}$; $R_\sigma = \sigma_{11}/\sigma_{22}$; for k_{12} see text; 2 = less volatile component).

$\epsilon_{11}/\epsilon_{22}$ and increasing values of k_{12} increase the tendency to the formation of gas-gas equilibria of the first type; this tendency is partly compensated, however, by increasing difference in size for this model.¹⁰⁴

PRESSURE DEPENDENCE OF CHEMICAL EQUILIBRIA IN SOLUTIONS

Since the treatment of reacting mixtures is somewhat outside the scope of the present lecture only some results that have been recently obtained in the field of chemical equilibria in solutions under pressure will be presented in order to give a characteristic example.

In Fig. 18 the spectrum of an aqueous solution containing nickel and murexide ions is plotted at 1, 500, 1000 and 1500 bar according to measurements of Jost.¹⁰⁸ An isobestic point is observed by application of pressure only;

the peak at 460 nm corresponds to the nickel-murexide complex.

From the spectrum in Fig. 18 the equilibrium constant K has been calculated¹⁰⁸ as a function of pressure according to well-known techniques. In Fig. 19 the logarithm of the equilibrium constant K thus obtained is plotted against the pressure in bar. Within the limits of experimental error a straight line results; from the slope the standard value of the reaction volume ΔV° has been calculated by Jost¹⁰⁸ to be $22.6 \text{ cm}^3 \cdot \text{mol}^{-1}$ using the well-known thermodynamic relation (19)

$$\Delta V^\circ = -RT \left(\frac{\partial \ln K}{\partial p} \right) T. \quad (19)$$

These measurements have been carried out with a high

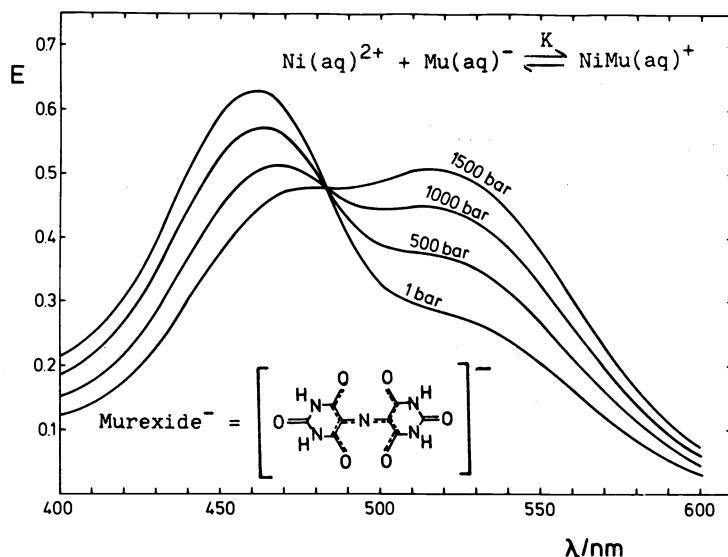


Fig. 18. Spectrum of the system $\text{Ni}^{2+} + \text{murexide}^-/\text{water}$ at 25°C and at different pressures (according to results of Jost¹⁰⁸; $c_0(\text{Ni}^{2+}) = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$; $c_0(\text{Mu}^-) = 5.66 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.1 \text{ mol dm}^{-3}$ (NaClO_4 ; ionic strength); $\text{pH} = 5.0$).

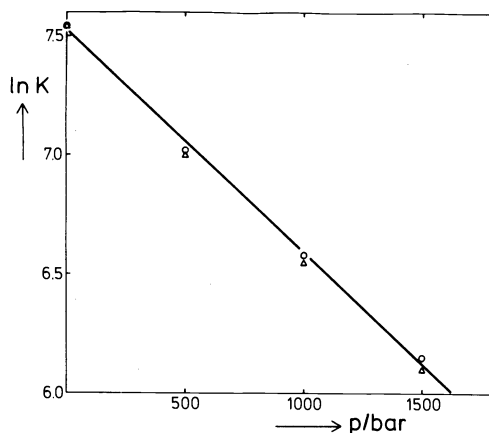


Fig. 19. Pressure dependence of the overall equilibrium constant K for the system $\text{Ni}^{2+} + \text{murexide}^-/\text{water}$ at 25°C (according to results of Jost¹⁰⁸; K in mol dm^{-3}).

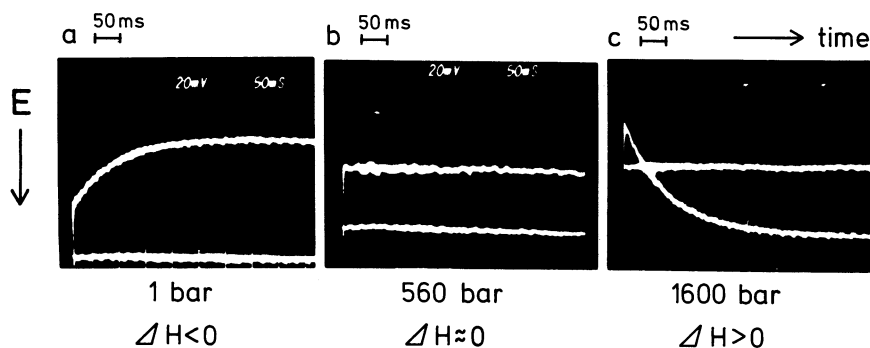


Fig. 20. Temperature-jump relaxation traces at 1, 560 and 1600 bar for the system $\text{Ni}^{2+} + \text{murexide}^-/\text{water}$ (according to results of Jost¹⁰⁸; $\Delta T = 8.0^\circ\text{K}$; $T(\text{final}) = 298.15^\circ\text{K}$; $\lambda = 460 \text{ nm}$; $c_0(\text{Ni}^{2+}) = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$; $c_0(\text{Mu}^-) = 5.4 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.1 \text{ mol dm}^{-3}$ (NaClO_4 ; ionic strength)).

pressure optical cell in a commercial spectrometer; they were made in connection with kinetic investigations of very fast reactions in solution at high pressure using the temperature jump relaxation technique and will be published elsewhere.^{49,108} A result that is interesting from a thermodynamic point of view, however, is shown in Fig. 20. Here the traces on the screen of an oscilloscope showing the optical extinction of the solution as a function of time after a temperature jump are represented at 1, 560 and 1600 bar. Whereas the optical extinction and consequently the complex concentration *decreases* with time after the temperature jump at 1 bar, it remains practically unchanged by the temperature jump at 560 bar and on the contrary *increases* at 1600 bar. The consequence is that the reaction enthalpy ΔH° must change its sign from minus to plus with increasing pressure at constant temperature in this system; this is a very remarkable pressure effect for a reaction in liquid solution, where often pressure effects are widely neglected. From the relaxation curves in Fig. 20 approximate values of ΔH° can be calculated.¹⁰⁸

It was the aim of this lecture to stimulate the interest in the thermodynamic properties of mixtures at high pressures which really merit to be investigated to a greater extent in the future.

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REFERENCES

- ¹L. Merrill, *Bibliography on High Pressure Research*. Brigham Young University, Provo, Utah, USA.
- ²E. Kuss, *Fortschr. Verfahrenstech.* **9**, 32 (1968/69).
- ³E. U. Franck, Plenary lecture presented at the 3rd Int. Conf. on Chemical Thermodynamics, 3–7 September, 1973, Baden, Vienna, Austria. *Pure Appl. Chem.* **38**, 449 (1974).
- ⁴S. D. Hamann, in *Modern Aspects of Electrochemistry* (editors J. O'M. Bockris and B. E. Conway), Vol. 9, Chap. 2. Plenum, New York (1974).
- ⁵V. Pilz, *Verfahrenstech.* **9**, 280 (1975).
- ⁶R. Haase, *Thermodynamik der Mischphasen*. Springer, Berlin (1956).
- ⁷J. S. Rowlinson, *Liquids and Liquid Mixtures*. 2nd Edn, Butterworth, London (1969).
- ⁸J. M. Prausnitz, *Molecular Thermodynamics of Fluid Phase Equilibria*. Prentice Hall, Englewood Cliffs (1969).
- ⁹P. G. Tait, *Physics and Chemistry of the Voyage of H.M.S. Challenger*. Vol. 2, Part 4 (1888); G. Tammann, Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen, Hamburg (1907).
- ¹⁰C. J. Hudleston, *Trans. Faraday Soc.* **33**, 97 (1937).
- ¹¹A. T. J. Hayward, *Brit. J. Appl. Phys.* **18**, 965 (1967).
- ¹²P. M. Chaudhuri, *Can. J. Chem. Eng.* **46**, 132 (1968).
- ¹³K. Witt, *Antriebstech.* **12**, 137 (1973).
- ¹⁴F. Hötte, *Chem. Ingr.-Tech.* **46**, 762 (1974).
- ¹⁵E. Kuss, *Chem. Ingr.-Tech.* **46**, 750 (1974).
- ¹⁶B. Battino, *Chem. Rev.* **71**, 5 (1971).
- ¹⁷S. D. Hamann and F. Smyth, *Aust. J. Chem.* **24**, 2431 (1971).
- ¹⁸P. Engels, Ph.D. thesis, University of Karlsruhe, GFR (1970).
- ¹⁹P. Engels and G. M. Schneider, *Ber. Bunsenges. phys. Chemie*, **74**, 931 (1970).
- ²⁰P. Engels, G. Götze and G. M. Schneider, Paper presented at the

- 3rd Int. Conf. Chemical Thermodynamics, 3-7 September, 1973, Baden, Austria; section V/21.
- ²¹J. A. Lamb and A. F. Hunt, *Chem. Engng J.* To be published.
- ²²J. Korpela, *Acta Chem. Scand.* **25**, 2852 (1971).
- ²³G. Götze, Diplom thesis, University of Bochum GFR (1972); G. Götze, P. Engels and G. M. Schneider, *Chem. Ingr.-Tech.* **46**, 750 (1974).
- ²⁴G. Götze, Ph.D. thesis, University of Bochum, GFR, In preparation.
- ²⁵G. Götze, R. Jockers and G. M. Schneider, Paper presented at the 4th Int. Conf. Chemical Thermodynamics, 26-30 August, 1975, Montpellier, France; section IV/9.
- ²⁶H. Lentz, paper presented at the *Ulmer Kalorimetrietage*, 3-4 April, 1975, Ulm, GFR.
- ²⁷D. S. Tsiklis, Phasentrennung in Gasmischen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (1972).
- ²⁸D. S. Tsiklis and L. A. Rott, *Russ. Chem. Rev.* **36**, 351 (1967).
- ²⁹G. M. Schneider, *Ber. Bunsenges. phys. Chemie* **70**, 497 (1966).
- ³⁰G. M. Schneider, *Fortschr. Chem. Forsch.* **13**, 559 (1970).
- ³¹G. M. Schneider, *Advan. Chem. Phys.* **17**, 1 (1970).
- ³²G. M. Schneider, *Ber. Bunsenges. phys. Chemie* **76**, 325 (1972).
- ³³G. M. Schneider, in: *Chemical Thermodynamics*. Vol. 2, Chemical Society Specialist Reports. To be published.
- ³⁴G. M. Schneider in *Water—A Comprehensive Treatise*. (editor F. Franks), Vol. 2, Chap. 6, Plenum, New York (1973).
- ³⁵R. L. Scott, *Ber. Bunsenges. phys. Chemie* **76**, 296 (1972); R. L. Scott, paper presented at the 3rd Int. Conf. Chemical Thermodynamics, 3-7 September, 1973, Vienna, Austria, section IV/11a.
- ³⁶D. S. Tsiklis, *Handbook of Techniques in High-Pressure Research and Engineering*. Plenum, New York (1968).
- ³⁷I. Prigogine and R. Defay, *Chemical Thermodynamics*. Longmans, Green, London (1954); I. Prigogine and R. Defay, *Chemische Thermodynamik*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (1962).
- ³⁸I. M. Croll and R. L. Scott, *J. Phys. Chem.* **62**, 954 (1968).
- ³⁹J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, *Regular and Related Solutions*, Van Nostrand, New York (1970).
- ⁴⁰R. Paas, Ph.D. thesis, University of Bochum, GFR, In preparation.
- ⁴¹G. D. Efremova and A. V. Shvarts, *Russ. J. Phys. Chem.* **46**, 237 (1972); R. B. Griffiths, *Physica* **73**, 174 (1974).
- ⁴²K. Peter, Ph.D. thesis, University of Bochum, GFR (1974).
- ⁴³K. Peter and G. M. Schneider, Paper presented at the 3rd Int. Conf. Chemical Thermodynamics, 3-7 September, 1973, Baden, Austria, section IV/10; K. Peter and G. M. Schneider, *Ber. Bunsenges. phys. Chemie* **77**, 1013 (1973).
- ⁴⁴R. Paas, Diplom thesis, University of Bochum, GFR (1974); *J. Chem. Thermodyn.*, To be published.
- ⁴⁵G. M. Schneider and C. Russo, *Ber. Bunsenges. phys. Chemie* **70**, 1008 (1966).
- ⁴⁶J. P. Novak and G. M. Schneider, *Ber. Bunsenges. phys. Chemie* **72**, 791 (1968).
- ⁴⁷A. Jost and G. M. Schneider, *J. Phys. Chem.* **79**, 858 (1975).
- ⁴⁸U. Limbach, Diplom thesis, University of Bochum, GFR (1975).
- ⁴⁹A. Jost, *Ber. Bunsenges. phys. Chemie* **78**, 300 (1974).
- ⁵⁰J. Zernike, *Chemical Phase Theory*. Kluwer, Deventer Djakarta (1955).
- ⁵¹J. D. van der Waals, *Zittingsversl. Koninkl. Akad. Wetenschap. Proc. Ser. B133* (1894); (see also J. de Boer, *Physica* **73**, 1 (1974)).
- ⁵²H. Kamerlingh Onnes and W. H. Keesom, *Comm. Phys. Lab. Univ. Leiden*, Suppl. No. 15 (1907); *Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B9*, 786 (1907), **10**, 231 (1907).
- ⁵³I. R. Krichevskii, *Acta Phys. Chim. USSR* **12**, 480 (1940); I. R. Krichevskii and P. E. Bol'shakov, *Zh. Fiz. Khim.* **15**, 184 (1941); I. R. Krichevskii and D. S. Tsiklis *Zh. Fiz. Khim.* **15**, 1059 (1941), **17**, 126 (1943); D. S. Tsiklis, *Dokl. Akad. Nauk SSSR* **86**, 993 (1952).
- ⁵⁴D. S. Tsiklis, *Dokl. Akad. Nauk SSSR* **86**, 1159 (1952).
- ⁵⁵W. B. Streett, *Trans. Faraday Soc.* **65**, 696 (1969).
- ⁵⁶W. B. Streett, *Astrophys. J.* **186**, 1107 (1973).
- ⁵⁷W. B. Streett, *Chem. Eng. Progr. Symp. Ser.* **81**, 63, 37 (1967).
- ⁵⁸W. B. Streett and J. L. E. Hill, *Trans. Faraday Soc.* **67**, 622 (1971).
- ⁵⁹C. K. Heck and P. L. Barrick, *Advan. Cryog. Eng.* **12**, 714 (1967).
- ⁶⁰W. B. Streett, A. L. Erickson and J. L. E. Hill, *Phys. Earth Planet. Interiors* **6**, 69 (1972).
- ⁶¹J. de Swaan Arons and G. A. M. Diepen, *J. Chem. Phys.* **44**, 2322 (1966).
- ⁶²D. S. Tsiklis, *Dokl. Akad. Nauk SSSR* **86**, 1159 (1952).
- ⁶³N. J. Trappeniers and J. A. Schouten, *Physica* **73**, 546 (1974).
- ⁶⁴W. B. Streett, *Can. J. Chem. Eng.* **52**, 92 (1974).
- ⁶⁵Z. Alwani, University of Bochum, GFR, Unpublished results.
- ⁶⁶G. M. Schneider, Z. Alwani, W. Heim, E. Horvath and E. U. Franck, *Chem. Ingr.-Tech.* **39**, 649 (1967).
- ⁶⁷K. G. Liphard and G. M. Schneider, *J. Chem. Therm.* **7** (1975), in press.
- ⁶⁸K. Tödheide and E. U. Franck, *Z. Physik. Chem. (Frankfurt)* **37**, 387 (1963).
- ⁶⁹K. Zosel, Offenlegungsschrift 1,493,190, Deutsches Patentamt München; O. Vitzhum *et al.*, Patentschrift 2,127,618, Deutsches Patentamt München. T. P. Zhuze and M. A. Kapelyushnikov, USSR patent No. 113,325 (1958); H. V. Hess *et al.*, US patent No 3,318,805 (1967).
- ⁷⁰T. H. Gouw and R. E. Jentoft, *J. Chromatog.* **68**, 203 (1972); *Advan. Chromatog.*, in press.
- ⁷¹M. N. Myers and J. C. Giddings, *Progr. Separ. Purif.* **3**, 133 (1970).
- ⁷²D. Bartmann, *Ber. Bunsenges. phys. Chemie* **76**, 336 (1972).
- ⁷³D. Bartmann and G. M. Schneider, *J. Chromatog.* **83**, 135 (1973).
- ⁷⁴U. van Wasen and G. M. Schneider, *Chromatographia* **8**, 274 (1975).
- ⁷⁵G. M. Schneider, *Experimental Thermodynamics*. (editors B. Le Neindre and B. Vodar), Vol. 2, Chap. 16, part 2. Butterworth, London (1975).
- ⁷⁶G. M. Schneider, *Z. Physik. Chem. (Frankfurt)* **46**, 375 (1965).
- ⁷⁷D. Oeder and G. M. Schneider, *Ber. Bunsenges. phys. Chemie* **73**, 229 (1969); **74**, 580 (1970).
- ⁷⁸I. R. Krichevskii and D. S. Tsiklis, *Zh. Fiz. Khim.* **17**, 126 (1943).
- ⁷⁹A. J. Davenport, J. S. Rowlinson and G. Saville, *Trans. Faraday Soc.* **62**, 322 (1966).
- ⁸⁰R. L. Scott and P. H. van Konynenburg, *Dis. Faraday Soc.* **49**, 87 (1970); P. H. van Konynenburg, Ph.D. thesis, UCLA (1968).
- ⁸¹B. A. Wolf and G. Blum, paper presented at the 4th Int. Conf. Chemical Thermodynamics, 26-30 August, 1975, Montpellier, France, section IV/8.
- ⁸²E. Horvath, Diplom thesis, University of Karlsruhe, GFR (1965).
- ⁸³W. W. Akers, J. F. Burns and W. R. Fairchild, *Ind. Eng. Chem.* **46**, 2531 (1954).
- ⁸⁴H. H. Reamer and B. H. Sage, *J. Chem. Engng Data* **7**, 161 (1962); H. H. Reamer and V. Berry, *J. Chem. Engng Data* **7**, 486 (1962).
- ⁸⁵P. Ehrlich, *J. Polym. Sci.*, **A3**, 131 (1965).
- ⁸⁶R. Steiner and K. Horlé, *Chem. Ingr.-Tech.* **44**, 1010 (1972).
- ⁸⁷J. S. Rowlinson, Plenary lecture presented at the 3rd Int. Conf. Chemical Thermodynamics, 3-7 September, 1973, Baden, Austria; *Pure Appl. Chem.* **38**, 495 (1975).
- ⁸⁸G. M. Wilson, *Advan. Cryog. Eng.* **9**, 168 (1964).
- ⁸⁹J. M. Prausnitz and P. L. Chueh, *Computer Calculations for High-Pressure Vapor-Liquid Equilibria*. Prentice Hall, Englewood Cliffs (1968).
- ⁹⁰D. Zudkevitch and J. Joffe, *A.I.Ch.E. J.* **16**, 112 (1970).
- ⁹¹J. Joffe, G. M. Schroeder and D. Zudkevitch, *A.I.Ch.E. J.* **16**, 469 (1970).
- ⁹²S. Peter and H. Wenzel, *Chem. Ingr.-Tech.* **43**, 623 (1971).
- ⁹³H. Wenzel and S. Peter, *Chem. Ingr.-Tech.* **43**, 856 (1971).
- ⁹⁴S. Peter, G. Brunner and R. Riha, *Dechema Monograph*, **73**, 197 (1974).
- ⁹⁵S. Peter, G. Brunner and R. Riha, *Chem. Ingr.-Tech.* **46**, 623 (1974).
- ⁹⁶G. J. F. Breedveld and J. M. Prausnitz, *A.I.Ch.E. J.* **19**, 783 (1973).
- ⁹⁷H. Renon, J. Chandron and L. Asselineau, Paper presented at the CHISA congress, Prague (1972).

- ⁹⁸P. Zandbergen, H. F. P. Knaap and J. J. M. Beenakker, *Physica* **33**, 379 (1967).
- ⁹⁹P. Y. Tan, K. D. Luks and J. J. Kozak, *J. Chem. Phys.* **55**, 1012 (1971).
- ¹⁰⁰M. Rigby, B. J. Alder, A. M. Sapse and C. E. Hecht, *J. Chem. Phys.* **52**, 3665 (1970).
- ¹⁰¹N. J. Trappeniers, J. A. Schouten and C. A. Ten Seldam, *Chem. Phys. Lett.* **5**, 541 (1970).
- ¹⁰²J. A. Schouten, C. A. Ten Seldam and N. T. Trappeniers, *Physica* **73**, 556 (1974).
- ¹⁰³G. W. Mulholland and J. J. Rehr, *J. Chem. Phys.* **60**, 1297 (1974).
- ¹⁰⁴R. O. Neff and D. A. McQuarrie, *J. Phys. Chem.* **79**, 1022 (1975).
- ¹⁰⁵J. T. Bartis and C. K. Hall, Cornell University, Ithaca, N.Y., To be published.
- ¹⁰⁶U. Deiters, Diplom thesis, University of Bochum (1975).
- ¹⁰⁷B. H. Sage and W. N. Lacey, *Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen*. American Petrochemical Institute, New York (1950).
- ¹⁰⁸A. Jost, *Ber. Bunsenges. phys. Chemie* **79**, 850 (1975).
- ¹⁰⁹M. Elborai, Ph.D. thesis, University of Karlsruhe, GFR (1974).
- ¹¹⁰J. Timmermans, *The Physico-chemical Constants of Binary Systems in Concentrated Solutions*. Vol. 1-4, Interscience, New York (1960).
- ¹¹¹Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology*. New Series, Group IV, Vol. 1, Densities of liquid systems, Part a, Springer, New York (1974).
- ¹¹²M. L. McGlashan, K. Stead and C. Warr, paper presented at the 3rd Int. Conf. Chemical Thermodynamics, 3-7 September, 1973, Baden, Austria; section IV/11b.
- ¹¹³A. L. Horvath, *Chem. Ingr-Tech.* **47**, 859 (1975).
- ¹¹⁴D. S. Tsiklis *et al.*, *Zh. Fiz. Khim.* **48**, 217 (1974).