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FOREWORD

By Prof. A. R. UBBELOHDE

(Imperial College of Science & Technology, South Kensington, S.W.7)

Until recently, equipment and techniques for work at high pressures presented formidable obstacles. Research tended to be concentrated in a few specialised laboratories. The outstanding economic importance of the Imperial Chemical Industries' process for polymerising ethylene at high pressures, first published in 1937, and the intriguing prospects of producing rare and novel solids, as in the General Electric Co's. process for converting carbon into diamonds at high temperatures and pressures, published in 1955, have added powerful incentives to the general need to augment basic research in Physics and Chemistry at High Pressures. These considerations, coupled with the aim to honour Emeritus Professor Newitt, made it timely to organise and hold a Symposium on this subject as part of the Third International Congress of the European Federation of Chemical Engineering held in London from 20th June to 29th June, 1962. Both results and techniques have been considered.

One of the clear benefits from bringing together a diversity of experts in this Symposium was to illuminate some of the craft difficulties of research and development in the field of high pressures. Even the actual measurement of pressure is not yet fully satisfactory over the whole range which can now be attained. In other aspects of experimentation, too, much still depends on 'hunches', particularly at the very highest pressures. This stresses the importance of combining engineering design with a sound knowledge of physics and chemistry, in making the most of high pressure research.

Members of the organising committee for this High Pressure Symposium were Dr. B. W. Bradford, Dr. E. Hunter, Prof. W. Jost, Mr. W. R. D. Manning, Prof. A. M. Michels, Prof. D. M. Newitt, Dr. J. A. Pople, Prof. J. S. Rowlinson, Prof. B. Vodar, with Prof. A. R. Ubbelohde as Chairman. Many contributions to efficient working of the Symposium were also made by Colonel F. J. Griffin and Dr. J. B. Brennan, and both scientific and administrative aspects were looked after with unflagging zeal by Prof. J. S. Rowlinson. We have been fortunate in obtaining strong support from the sponsoring societies, the Society of Chemical Industry, The Institution of Chemical Engineers and The Institute of Physics and the Physical Society, and particularly from the Chairman of all the co-ordinating committees of the various Symposia, Mr. Colin Spearing.

The chairmen

Wednesday, 27 June	Prof. D. M. Newitt
Thursday, 28 June	Prof. A. M. Michels
Friday, 29 June	Prof. A. R. Ubbelohde

Editor's note. All temperatures are degrees Celsius unless otherwise stated.

GROUP 1**Intermolecular Forces and Thermodynamic
Properties**

INTRODUCTION

By J. S. ROWLINSON

(Imperial College of Science & Technology, South Kensington, S.W.7).

The theme of the first eight papers of this Symposium is the balance between an applied pressure and the forces which arise from the mutual potential energy of an assembly of atoms or molecules. The nature of this balance determines the equilibrium physical properties of matter. At pressures between 10^3 and 10^5 atm. most molecules of conventional physics and chemistry retain their identity and it is useful to study the relation, which is often still obscure, between the intermolecular forces and the gross physical properties. At higher pressures the molecules lose their familiar identity and it is no longer useful to speak of the mutual potential energy of any one pair of molecules. This higher range of pressure is the theme of the third session of this Symposium.

The mean separation of two molecules at, say, 10^4 atm. is only about 7% less than their separation in the crystal at zero pressure.¹ It follows that molecules are very incompressible, and it is useful to consider first what is known about the theory of the simplest type of molecular assembly, that is, an assembly of equal-sized rigid spheres of diameter d . The equation of state of such an assembly was studied in the last century by, amongst others, van Laar and Boltzmann who obtained explicit expressions for the first four coefficients of the virial expansion.² Approximate values of the fifth³ and sixth⁴ coefficients have been derived recently from calculations on computers. The result is

$$\frac{pv}{kT} = 1 + \left(\frac{b}{v}\right) + \frac{5}{8}\left(\frac{b}{v}\right)^2 + 0.286949\left(\frac{b}{v}\right)^3 + 0.115\left(\frac{b}{v}\right)^4 + 0.05\left(\frac{b}{v}\right)^5 + \dots \quad (1)$$

where v is the mean available volume per molecule and b is four times the actual volume of one molecule

$$b = 2/3 \cdot \pi d^3 \dots \dots \dots \quad (2)$$

This appears to be a highly convergent series but is, in fact, of little use when the mean volume v approaches v_0 , the volume of a regular close-packed assembly, which is related to b by

$$v_0 = 3b/2\pi\sqrt{2} \dots \dots \dots \quad (3)$$

If the virial equation is written in a less familiar form with (v_0/v) as the independent variable then it is seen that its convergence near $(v_0/v) = 1$ is in doubt;

$$\frac{pv}{kT} = 1 + 2.9619\left(\frac{v_0}{v}\right) + 5.9218\left(\frac{v_0}{v}\right)^2 + 7.4563\left(\frac{v_0}{v}\right)^3 + 8.9\left(\frac{v_0}{v}\right)^4 + 11\left(\frac{v_0}{v}\right)^5 + \dots \quad (4)$$

Clearly this equation tells us little at $(v_0/v) \sim 1$ except that $(pv/kT) \gg 1$.

Fortunately powerful computers can be used, in at least two different ways, to find the pressure directly by following the behaviour of a model, of, say, 100 molecules. The results of such calculations³⁻⁵ are shown in Fig. 1. The calculated pressure can fall on one of two branches. The upper is the low-density branch and is satisfactorily represented by equation (4) if the volume is large. This branch appears to approach a limiting density of $(v_0/v) \sim 0.8$ at high pressures. The lower branch represents stable behaviour at high densities and is asymptotic to a density $(v_0/v) = 1$. The nature of the transition between the branches is unknown but there is probably a simple first-order transition which would be represented by a horizontal line on Fig. 1 at about $(v_0/v) = 0.6-0.7$.

The asymptotic density of the lower branch is clearly that of a regular close-packed crystal in which each molecule has twelve nearest neighbours. The limit of the upper branch can probably be identified with the random close-packed state studied by Bernal and colleagues,⁶ and by Scott.⁷ They studied experimentally the density and geometry of packing of rigid spheres in irregular containers, and found that there is a limiting density of $(v_0/v) = 0.86$ which is not exceeded when long-range (or crystalline) order is absent.

Thus it appears that an assembly of rigid spheres can exist in one of two phases, a fluid or irregular state at low densities and a solid or regular state at high densities. The p, T projection of the phase diagram of such a system is shown in Fig. 2. Its simplicity arises from the linearity

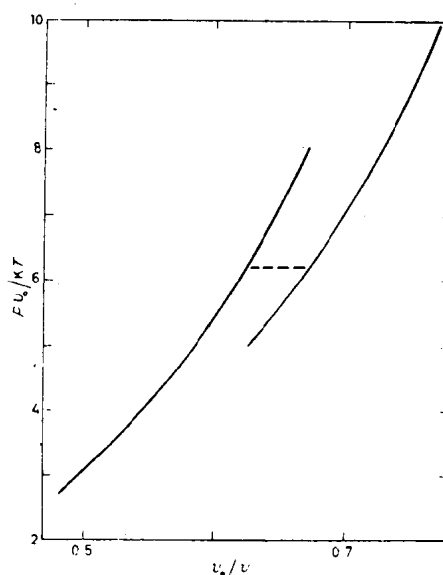


Fig. 1. Equation of state of rigid spheres, as calculated on computers³⁻⁵

The broken line represents the probable position of a first-order transition between the low- and high-density branches

of the isochores and the constant density of the coexisting phases in an assembly of rigid spheres. The phase-boundary line continues without limit as pressure and temperature are increased.

Consider now a more realistic assembly in which the molecules have attractive forces as well as repulsive forces. The phase diagram now adopts a more familiar form in which the fluid state is itself divided into liquid and gas by the vapour pressure line which ends at the well-known critical point (Fig. 3). This point lies at comparatively low pressures for pure substances. The behaviour of the rigid-sphere model suggests that the solid-fluid line continues without limit and has no critical point, since the behaviour of this model presumably becomes more realistic at high pressures. However, neither theory nor experiment has yet settled this question although there are probably few who now believe in the existence of a solid-fluid critical point. However, as Kennedy and his colleagues⁸ show for caesium, the equilibrium phase at the triple point is not always the same as that at the highest pressures, and the solid-fluid line may show extrema. The nearest counter-example is the tentative suggestion of Beecroft & Swenson⁹ that a solid-solid transition in cerium might end in a critical point at about 630°K and 20,000 atm. However this is a transition that involves only the electronic states of the ions and not a re-ordering of the positions of their nuclei.

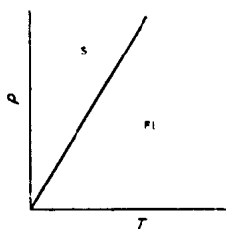


Fig. 2. Probable phase diagram of an assembly of rigid spheres, in which there are the two phases, solid and fluid

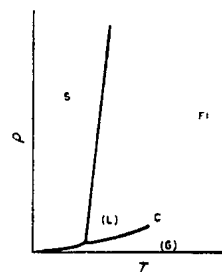


Fig. 3. Phase diagram of an assembly of molecules which have attractive forces
Part of the fluid phase is now divided into liquid and gaseous phases by the vapour pressure curve which ends at the critical point C

No direct or convincing link yet exists between the character of the attractive and repulsive forces on the one hand, and the type of phase diagram which they produce or the thermodynamic properties of the individual phases on the other. The most commonly used intermolecular potential is that named after Lennard-Jones,

$$u(r_{ij}) = \lambda r_{ij}^{-n} - \mu r_{ij}^{-6} \quad (n > 6) \quad (5)$$

where u is the mutual potential energy of two molecules at a separation r_{ij} , n is the index of the repulsive potential and λ and μ are parameters characteristic of the molecules concerned. One cannot predict directly many of the properties of an assembly of Lennard-Jones molecules although one can often make useful comparisons of the type generally called 'corresponding states relations'. However there is one direct experimental check of such an equation by which the properties of the fluid at high pressures place a lower limit on the index n . The potential energy of an assembly of Lennard-Jones molecules in an arbitrary configuration is

$$\mathcal{U} = \sum_{i>j} u(r_{ij}) \quad (6)$$

Similarly an intermolecular virial can be defined by

$$\mathcal{V} = \sum_{i>j} v(r_{ij}) \quad (7)$$

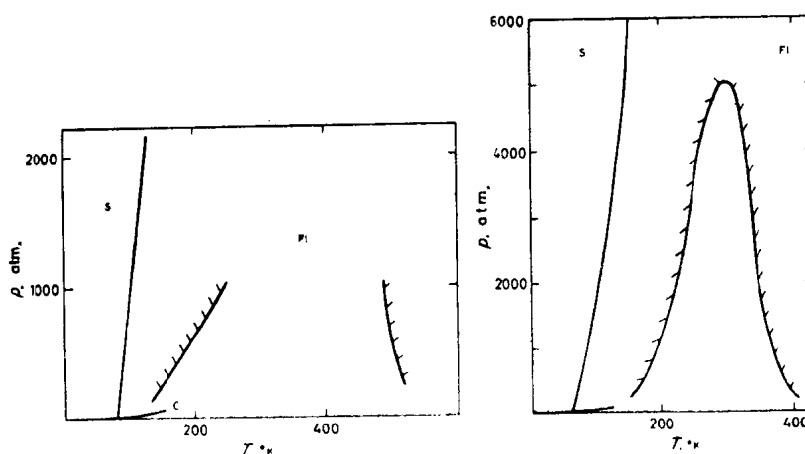
where

$$v(r_{ij}) = r_{ij} [du(r_{ij})/dr_{ij}] \quad (8)$$

The mean values of \mathcal{U}^2 , $\mathcal{U}\mathcal{V}$, and \mathcal{V}^2 in an assembly of fixed volume and temperature are expressible in terms of the thermodynamic properties of the system and, in the case of \mathcal{V}^2 , in terms of the index n . These average values must satisfy the Schwarz (or Cauchy) inequality¹⁰

$$\overline{\mathcal{U}^2} \overline{\mathcal{V}^2} - (\overline{\mathcal{U}\mathcal{V}})^2 \geq 0 \quad (9)$$

Now the left-hand side of this inequality increases with n and no potential which gives negative values for the discriminant is acceptable. Fig. 4 shows the regions of pressure and temperature in which the experimental results for argon satisfy equation (9) with the choice $n = 12$. Fig. 5 shows similar results for nitrogen. It is seen that the inequality is strongly satisfied around the gas-liquid critical point, where the influence of the attractive forces is paramount, but that it is satisfied neither at high pressures nor at high temperatures where the influence of the repulsive forces becomes paramount. It appears to be satisfied in the solid but here quantal effects make verification difficult.



Phase diagram of (Fig. 4, left) argon, (Fig. 5, right) nitrogen

The inequality (equation 9) is satisfied for $n = 12$ only in that part of the diagram within the hatched line¹⁰

A larger value of n would extend slightly the region in which equation (9) is satisfied, but it must be concluded that the Lennard-Jones potential is no longer sufficiently flexible to accommodate the best modern results, even for so simple molecules as argon and nitrogen. There is now a growing body of evidence to show that the repulsive potential is harder than $n = 12$ at separations near the collision diameter and softer at much shorter separations.¹¹⁻¹³

The phase diagrams of mixtures differ from those of pure substances in several ways, and I would like to emphasise two of these.

The first is their complexity, which arises from the increased degrees of freedom of the systems. The complexities to be discussed briefly are those of the fluid-fluid equilibria and the interruption of such equilibrium lines by the solidification of one of the components. Fig. 6 shows p, T projection of the phase diagram of a simple binary mixture, in which it is seen that the single gas-liquid critical point of a pure substance is replaced by a locus of critical points which has generally a maximum in the pressure. The greater the difference of the intermolecular energies and sizes, then the higher is this maximum. If the two components are very different or if the mean mutual intermolecular energy is unusually small, then the liquid phase separates into two immiscible phases. The phase diagram is now as in Fig. 7. If the differences are only just sufficient to cause immiscibility, as for example with ethane + methanol, then the critical locus still has a maximum but has also a further rise at low temperatures. As far as is known this curve continues indefinitely to the highest pressures attainable unless it is interrupted by the solidification of one of the components.

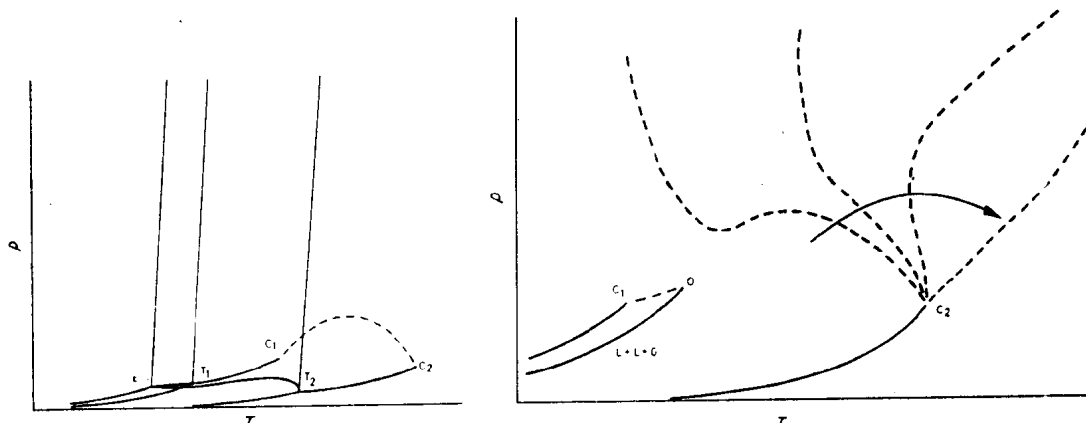


Fig. 6, (left). p, T projection of the phase diagram of a simple binary mixture

T_1 and T_2 are the triple points of the two pure components and C_1 and C_2 are the critical points. E is the eutectic point. The three lines rising to high pressures are the boundaries between the pure solids and their melts, and between a eutectic mixture and its melt. The broken line is the locus of the critical points of the mixtures.

Fig. 7, (right). p, T projection of the phase diagrams of systems which form immiscible liquids

The three-phase line ($L+L+G$) ends at a critical end-point O where the liquid phase rich in component 1 becomes identical with the gas phase. The critical line that starts from C_2 rises to higher pressures (apparently without limit) as the proportion of component 1 increases. The arrow shows schematically the change of shape of this line as the disparity of the two components increases.

This rise is the second feature of mixtures which should be emphasised. The vapour pressure curve of a pure substance rarely reaches to 100 atm., and so it is of little interest in this Symposium, but the vapour pressure curves (and hence the critical points) of mixtures of dissimilar molecules can apparently increase without any limit, except for that imposed in many cases by solidification. Fig. 8 shows the p, T projection of a diagram in which the critical locus is interrupted by a solid phase. Van Hest & Diepen¹⁴ have studied methane + naphthalene near the upper critical end-point of such a diagram and the highest pressure they find for a fluid-fluid critical point is 1303 atm. in equilibrium with solid naphthalene at 87°. Were it not for this solid phase, then there is no doubt that the pressure would rise without limit as the temperature falls, for liquid methane is immiscible with all hydrocarbons that have more than six carbon atoms.¹⁵ The highest fluid-fluid point in equilibrium with a solid found so far seems to be that for water + silica, which Kennedy and his colleagues¹⁶ reported to be at 9600 atm. and 1080°.

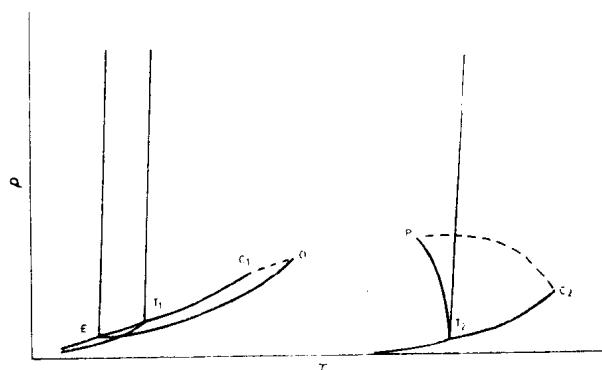


Fig. 8. p, T projection of the phase diagram of a system in which the critical locus is cut twice, at the end-points O and P , by the vapour pressure curve of the saturated solution of component 2 in component 1. If the components are very dissimilar then the pressure at P may be many times that at C_1 or C_2 .

The measurements of Franck¹⁷ on the alkali halides in supercritical water are studies of the opposite end of such a critical line, that is the end at the critical point of the more volatile component. However the great solubility of these salts in water ensures that the vapour pressures of the saturated solutions are too low for the system to show a fluid–fluid critical point in equilibrium with the solid salt.

As the disparity between the molecules of the two components increases, then the fluid–fluid critical line of Fig. 7 moves to higher temperatures. When it has moved sufficiently far for part or all of it to lie at temperatures above the gas–liquid point of both components, then we are in the region of so-called gas–gas immiscibility. This is the region of study of Tsiklis & Vasiliev.¹⁸ The striking name given to such systems should not obscure the fact that the critical line is still of the same type as, for example, that studied by van Hest & Diepen. It is only its disposition in p, T, x space that is unusual. Here again there is no reason to believe that this line reaches a maximum pressure. The earlier measurements of Tsiklis¹⁹ show that in nitrogen + ammonia the line is still rising at 17,000 atm.

It may be concluded that there are at least two types of phase-boundary curves which, as far as we know, persist to the highest pressures at which molecules retain their identity. The first is that between a solid and a fluid in a pure substance, and the second is the critical locus that terminates the vapour pressure curves of mixtures of molecules which are (or would be) immiscible in the liquid state at zero pressure.

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SOLUBILITY OF NAPHTHALENE IN SUPERCRITICAL METHANE

By J. A. M. van HEST and G. A. M. DIEPEN

(Technical University, Delft, Netherlands)

The phase behaviour of the methane-naphthalene system was investigated in the range 0–100 moles-% of naphthalene at 70–130° and 0–2000 atm. For this purpose an autoclave was developed provided with glass windows, which permitted visual observation of phase-transitions.

Solubilities of naphthalene in supercritical methane, dew points and bubble points were measured with a high degree of accuracy. From the results the P - T - x space model was derived.

The three-phase equilibrium of solid naphthalene (S_B)-solution of methane in molten naphthalene (L_2)-solution of naphthalene in methane (G), the critical curve $L_2 = G$, the heat of fusion of naphthalene along the melting curve and the accurate conditions of the upper critical end-point, viz., 1303 atm. and 87.3° at a naphthalene concentration of 18.5 moles-%, have all been established indirectly.

Introduction

In the P - T curves for a binary system of a volatile component A and a slightly volatile component B, the possibility exists that the critical line $L = G$ is intersected twice by the three-phase line S_B - L - G . At the points of intersection, the lower and upper critical end points, the critical phenomenon $L = G$ will occur as well as the solid substance B. This will occur when the melting point of B is above the critical temperature of A and also when the solubility of solid B in liquid A is low. For a detailed discussion of a similar phase-diagram, reference should be made to Zernike.¹

With such systems, two pressure and temperature regions can be indicated in which the three-phase equilibrium S_B - L - G exists, with an intermediate temperature range in which the pure solid substance B is in equilibrium with a liquid phase whatever the pressure may be. For measuring the solubility of solid substance in the liquid phase, this region is very suitable, as is the region near the upper critical end-point for pressures exceeding those of the critical line $L_2 = G$.

This region has not been much investigated because of experimental difficulties. Solubility measurements between the lower and upper critical end-points have only been carried out for the systems: ether-anthraquinone,² ammonia-melamine,³ ethylene-hexachloroethane,⁴ ethylene-*p*-iodochlorobenzene,⁵ ethylene-naphthalene⁶ and ethane-naphthalene.⁷

As an extension of our study on the solubility of solid substances in supercritical gases, the methane-naphthalene system has been examined in the neighbourhood of the upper critical end-point, which according to preliminary measurements was expected to be at a pressure between 1000 and 2000 atm.

Experimental

Apparatus

For the high-pressure measurements of the methane-naphthalene system an apparatus was developed (Fig. 1) for use with pressures up to 2000 atm. and temperatures up to 130°, which had the special feature that extreme phase-transitions could be observed visually.

At the top of a glass measuring vessel, a weighed quantity of naphthalene is sealed with a stirrer. After being filled with methane, which is subsequently isolated from the surroundings by pouring mercury into the U-tube, the vessel is connected to the closing plug by means of the movable container and the stationary outer bush and thus centred, and then placed in the stainless steel autoclave (i.d. 60 mm.) which is partly filled with mercury.

Water is forced into the autoclave, by means of a hand-pump and, after the air exhaust has been shut off, the system can be compressed at the top of the measuring vessel.

The movable container is mounted on a piston in such a way that the vessel can be moved upwards in a vertical direction in front of the windows during the measurements by forcing in water to the bottom of the apparatus. The cylindrical window of Securit glass (30 × 16 mm.) is mounted with a locking ring in the window mounting, and sealed with O-rings. To secure equilibrium, intensive stirring is effected both inside and outside the vessel top, by means of an electromagnet which is periodically excited to apply a reciprocating movement to a soft-iron cover in the shaft of the closing plug. At the bottom of this cover are two button magnets which cause the same movement on both sides of the vessel top and in doing so lift and depress the ferrochromium stirrer surrounded with glass.

The autoclave is wound with heating wire and insulated with asbestos. The temperature is

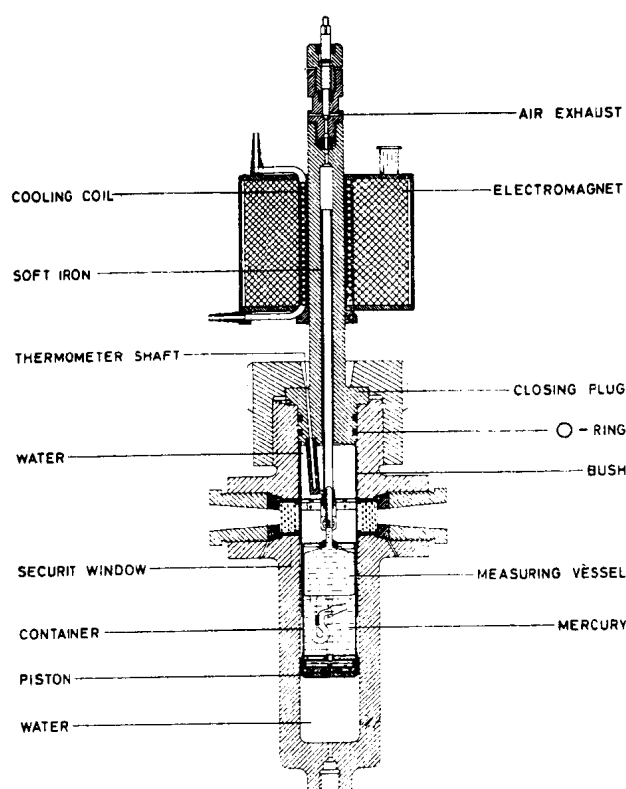


Fig. 1. Diagram of autoclave with windows

measured with a platinum resistance thermometer, which is placed in a shaft inserted in the closing plug. A high-pressure bench is connected with the unit by means of an oil-water separator. A pressure balance is used to measure the pressure and to keep it constant in accordance with Michels.^{7a} The events occurring at the top of the vessel are observed through a magnifying glass.

Method of measurement

Data on the P - T - x space model of the methane-naphthalene system have been obtained by determining visually the extreme phase transitions mentioned below for a large number of mixtures of known composition:

(a) *Dew and bubble points*.—The pressure on the liquid phase was gradually decreased at constant temperature until there was observed a liquid (for mixtures less concentrated than those in the upper critical end-point x_q) or formation of gas (for mixtures more concentrated than those at x_q). The average of these pressures measured during the originating and disappearance of de-mixing was taken as the correct value.

(b) *Solubilities of naphthalene in supercritical methane*.—Starting from the liquid phase containing solid naphthalene, the temperature was slowly raised at constant pressure, until with stirring the last crystal was dissolved. Also, the melting curve of naphthalene was measured up to 2000 atm. In this case the starting point was molten naphthalene containing some crystals. By varying the pressure in small stages at constant temperature, the melting pressure could be determined from the mass of crystals increasing or decreasing at the fixed temperature.

Components

The naphthalene (m.p. 80.20°) used was obtained by recrystallisation several times from a large quantity of molten naphthalene. The methane (minimum purity 99.65 moles-%) was a Philips Petroleum Co. Research Grade Product. To purify it further, this gas was condensed several times with removal of the most and least volatile fractions.

Results

The results are shown in Fig. 2. To avoid confusion, the observations of all P - T sections measured are not incorporated; however, all measurements obtained were employed for drawing sections. All the results obtained are tabulated in a thesis by van Hest.⁸ Compositions are expressed in moles-% of naphthalene. The relative error is not more than 1%; accuracy is greater as the proportion of naphthalene is increased. The error in measuring temperature amounts to $\sim 0.05^\circ\text{C}$. The accuracy of the pressure measurement with the pressure balance is better than

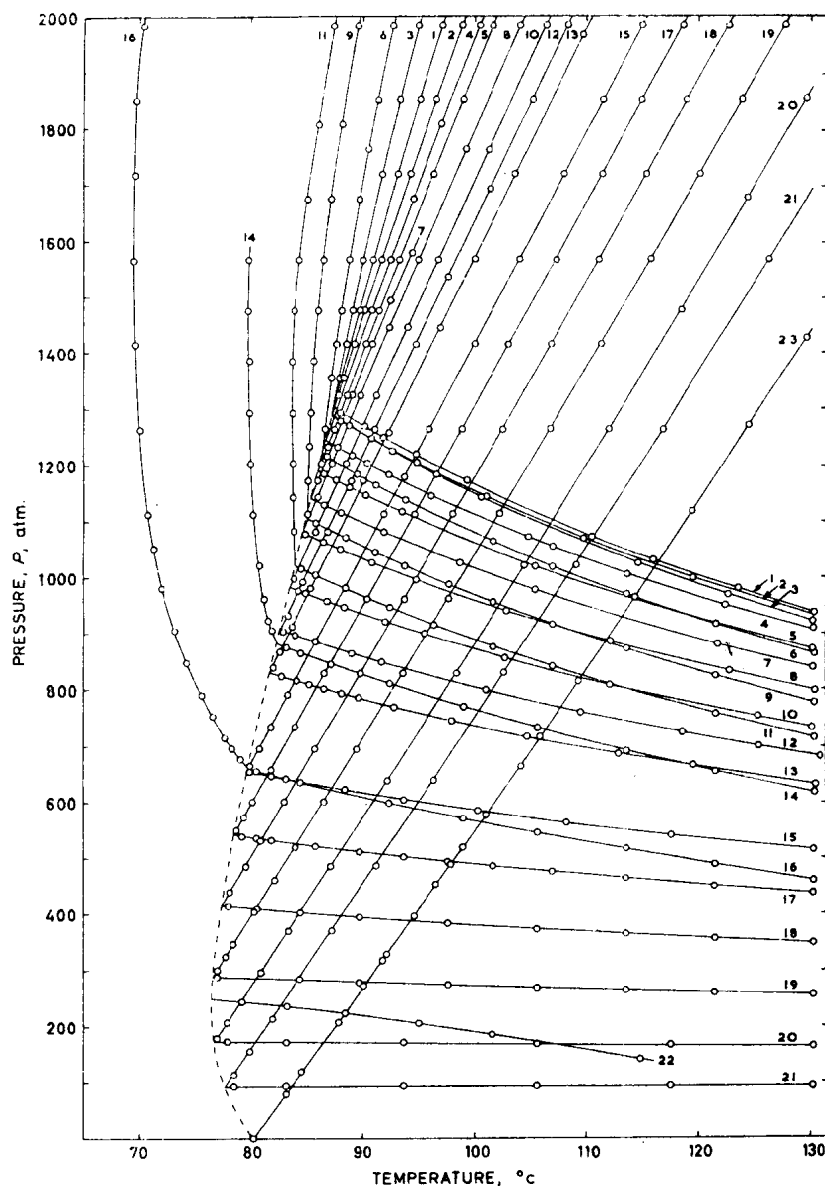


Fig. 2. P - T measurements for different compositions
 --- three-phase curve, solid naphthalene-liquid-gas-naphthalene
 (moles-% of naphthalene)

curve no.	curve no.	curve no.	curve no.
1 18.9	2 25.1	3 12.2	4 29.6
5 33.1	6 8.46	7 35.8	8 38.7
9 6.18	10 43.1	11 5.05	12 46.3
13 49.3	14 3.63	15 56.5	16 2.03
17 61.6	18 67.3	19 74.1	20 81.9
21 89.1	22 0.30	23 100.0	

1 : 10,000. Determination of pressure while measuring the L-G boundary curve was, however, made with an error of ~ 0.3 atm. From Fig. 2, as the experimental points lie on a smooth curve, it is concluded that the method applied is reliable.

An efficient check of the temperature measurement is that the melting curve of naphthalene measured with the resistance thermometer up to 2000 atm. corresponds very well with the melting curve measured with a mercury thermometer up to 1000 atm.,⁷ the deviations being not more than 0.1°C .

Discussion

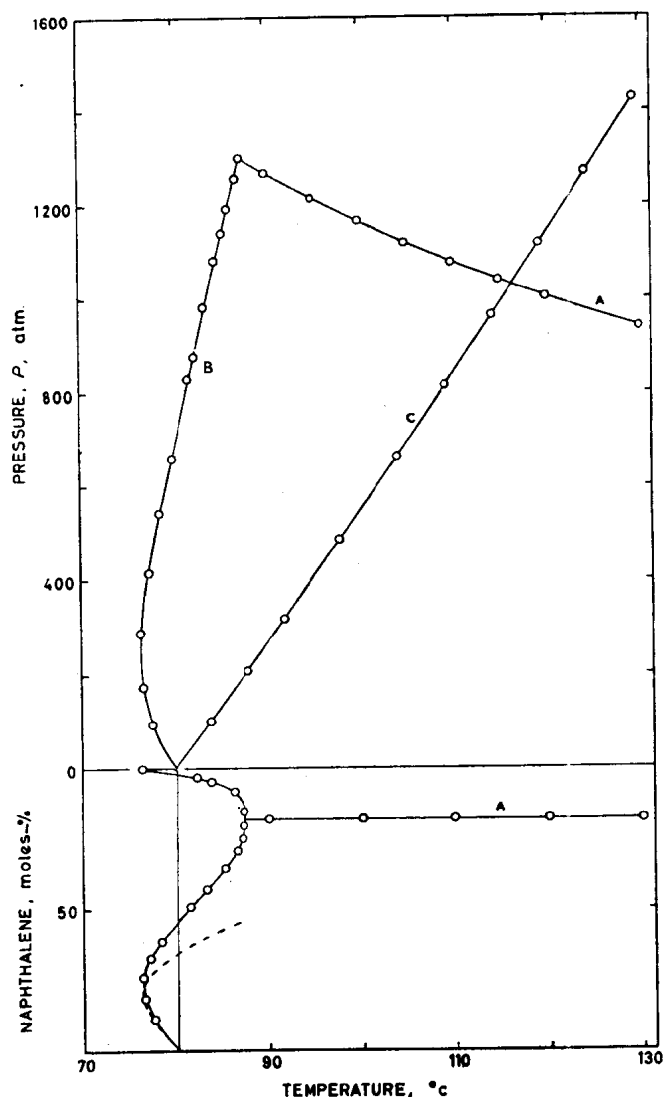
The experimental results (Fig. 2) enable the P - T - x space model of the methane-naphthalene system to be derived in the region under investigation, viz. of 0 - 2000 atm., 0 - 100 mole-% and $70 - 130^\circ$.

The three-phase equilibrium solid naphthalene-liquid-gas (S_B - L_2 -G)

The equilibrium conditions of this three-phase equilibrium were indirectly determined from the P - T graphs (Fig. 2) by tracing for each composition at what temperature and pressure the boundary curves of the solid-fluid (S_B -F) and liquid-gas (L-G) region intersect. The results thus obtained are represented in Fig. 3.

Fig. 3. P - T and T - x projections of the three-phase curve, solid naphthalene-liquid-gas, and critical curve. liquid = gas

— — — ideal liquid curve
A critical curve B three-phase curve
C melting curve of naphthalene



From the P - T projection it appears that the three-phase line has a temperature-minimum at 76.4° and 250 atm. To indicate the development of the gas branch at very low compositions in the T - x projection for some temperatures in the immediate neighbourhood of the triple point of naphthalene, corresponding gas compositions were calculated on the assumption that the gas behaves ideally.

It is seen that the gas curve and the liquid curve commencing at the triple point at the minimum temperature (76.4°) diverge and then coincide at the temperature of the upper critical end-point in such a way that $dT/dx = 0$. At the minimum temperature, the naphthalene concentration in the gas phase of the three-phase equilibrium is 0.3 mole-% (= 2 wt.-%) and in the liquid 76 moles-% (= 96 wt.-%).

The temperature and pressure at the upper critical end-point can be determined fairly accurately from Fig. 3 and are respectively, $87.3 \pm 0.1^\circ$ and 1303 ± 1 atm.

The critical composition can be read off less accurately because near the critical end-point the T - x curve is very flat.

The value obtained, $x_q = 18.5 \pm 0.5$ moles-%, agrees well with the fact that in the determination of the L-G boundary curve for the composition 18.9 moles-%, critical phenomena occurred practically all over the temperature range. It agrees moreover with the fact that in Fig. 2 the gradient of the naphthalene solubility line of 18.9 moles-% and that of the three-phase curve S_B - L_2 -G are practically equal at the intersection point. In the P - T section, at the critical composition, the gradients of both curves mentioned coincide at the upper critical end point, as here the critical phase $L_2 = G$ is in equilibrium with the solid substance.

As a point on the liquid branch of the three-phase equilibrium in the T - x projection indicates to what temperatures the melting point of pure naphthalene is reduced when a certain quantity of methane is dissolved at a certain pressure, it is clear that in the ideal case the liquid curve can be calculated from the freezing point depression formula:

$$-\ln x_{id} = \frac{\Delta H_m}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \quad (1)$$

in which ΔH_m represents the molecular heat of fusion and T_m the melting temperature of naphthalene and T the temperature of the three-phase equilibrium at the same pressure. As the heat of fusion along the melting curve changes very slightly with pressure, 4540 cal./mole was used each time. The ideal curve calculated from equation (1) agrees with the experimental line for the dilute solutions. After that, at a given temperature, obviously more methane is dissolved in the fluid than in the ideal case. The composition at the upper critical end-point is found in this way to be $x_{id} = 0.54$.

When a rough estimate was made originally, the pressure at the upper critical end-point for the methane-naphthalene system, equation (1) was employed. At that time data about the melting curve of naphthalene and about the P - T projection of the three-phase curve both to ~ 1000 atm. were available. From this it was apparent that the three-phase curve at high pressure was practically a straight line in accordance with the equation

$$T = 344.4 + 0.0115 P \quad (2)$$

The melting curve could be represented by:

$$T_m = 354.0 + 0.0347 P \quad (3)$$

assuming that at higher pressures the curve was rectilinear. Substitution of equations (2) and (3) into equation (1) gives

$$-\ln x = \frac{\Delta H_m}{R} \left(\frac{1}{344.4 + 0.0115 P} - \frac{1}{354.0 + 0.0347 P} \right) \quad (4)$$

Calculation of the composition at the upper critical end-point with the ideal melting curve (equation 1) gave $x_{id} = 0.51$ ($p_q = 174$ atm.; $t_q = 52.1^\circ$) for the ethylene-naphthalene system and for ethane-naphthalene $x_{id} = 0.58$ ($p_q = 122.5$ atm.; $t_q = 56.6^\circ$).⁷

From equation (4) the corresponding pressures were determined subsequently for some values of x_{id} in this concentration region. The influence of a change of 5% in the heat of fusion

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($\Delta H_m = 4540$ cal./mole) was also traced. From the results (Table I) it was concluded that, assuming that in the system methane-naphthalene the ideal critical composition should be of the same order of magnitude as in the systems mentioned above, the pressure in the second critical end-point had to be below 2000 atm.

Table I

Effect of change of heat of fusion (ΔH_m) on pressure at different compositions at the upper critical end-point (x_{id})

x_{id}	P , atm. ($\Delta H_m - 5\%$)	P , atm. (ΔH_m)	P , atm. ($\Delta H_m + 5\%$)
0.45	2050	1900	1750
0.50	1640	1500	1390
0.55	1280	1180	1090
0.60	990	900	830

T - x curves

Fig. 4 contains a number of T - x curves for a series of pressures varying from 100 to 2000 atm. These were derived from the P - T sections (Fig. 2) and the compositions of the gas and liquid phases of the three-phase equilibrium from Fig. 3.

The maximum in the L-G line, corresponding with a point of the critical line $L_2 = G$, moves to lower temperatures when the pressure increases and at 87.3° becomes identical with the horizontal point of inflexion of the solubility line at 1300 atm.

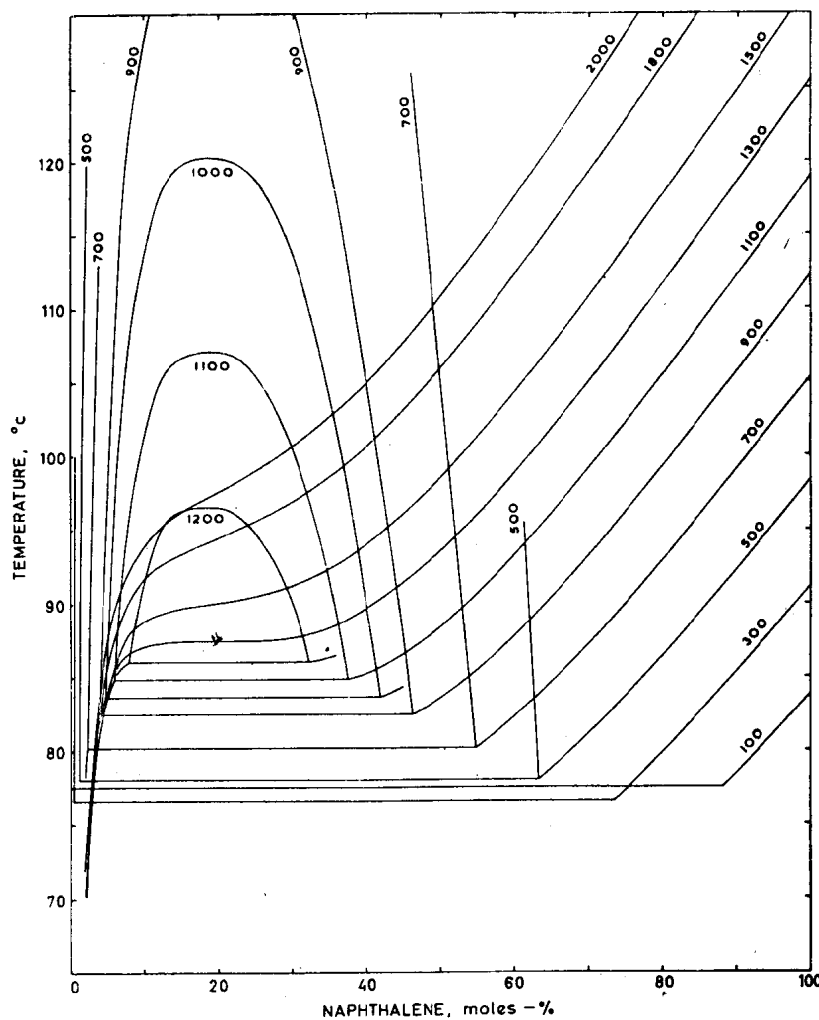


Fig. 4. T - x curves for various constant pressures
numerals on curves are pressures in atm.

The solubility lines are almost straight at very high naphthalene concentrations and terminate at the melting point of naphthalene at the corresponding pressure, obtained from the melting curve.

From the gradient of the solubility lines in the neighbourhood of pure naphthalene the heat of fusion of naphthalene was calculated along the melting curve from the freezing point depression formula:

$$-dT/dx = RT_m^2/\Delta H_m \quad (5)$$

The results are summarised in Table II. This contains also the heat of fusion calculated from the T - x graphs for the system ethylene-naphthalene.^{6e}

Table II
Heat of fusion of naphthalene at different pressures

P_{atm}	$T_m, ^\circ\text{K}$	dT/dx	$\Delta H_m, \text{cal./mole}$
Methane-naphthalene			
100	357.05	5.55	4560
300	364.35	5.85	4510
500	371.45	6.10	4490
700	378.50	6.40	4450
900	385.35	6.60	4460
1100	392.10	6.90	4420
1300	398.70	7.10	4450
1500	405.15	7.35	4430
1800	414.75	7.70	4430
2000	420.90	8.00	4390
Ethylene-naphthalene			
200	360.70	5.75	4490
400	367.95	6.00	4480
600	375.00	6.20	4500
800	381.95	6.50	4460
1000	388.80	6.75	4440

The ΔH_m values thus obtained show some divergence, but the deviation from the most obvious line through these points amounts in no case to more than 1%. It is seen that in the pressure range investigated, the heat of fusion gradually decreases along the melting curve and that this decrease for a pressure change of 2000 atm. amounts to $\sim 3\%$. A similar change of ΔH_m was found by Tammann⁹ and Deffet.¹⁰ They determined the heat of fusion indirectly from volume changes measured during melting. According to Tammann, the decrease of ΔH_m across a pressure difference of 2000 atm. is about 5%. After extrapolation we find that the heat of fusion of naphthalene at 1 atm. is $4540 \pm 1\%$ cal./mole. Some literature values are: 4440,¹¹ 4500,¹² 4540,¹³ 4610.¹⁴

P - x graphs

In Fig. 5 some P - x graphs for temperatures between 75° and 130° are represented, as obtained from Figs. 2 and 4, and from Fig. 3 for plotting the equilibrium concentrations.

Fig. 5 shows that the graph for 87.3° through the S_B - F boundary plane has a horizontal point of inflexion at 1303 atm. which is the maximum in the intersection with the plane enclosing the L - G region. Also from this figure it follows that the composition at the upper critical end-point amounts to 18.5 ± 0.5 moles-% naphthalene. It is remarkable that in the neighbourhood of this upper critical end-point, the solubility of naphthalene in the fluid phase decreases considerably when the pressure is raised at constant temperature; this is contrary to what happens under analogous conditions in the systems ethylene-naphthalene and ethane-naphthalene.^{6,7} On the 87.3° isotherm a difference in solubility of 6 moles-% can occur with a pressure difference of only 2 atm. At higher temperatures, the solubility lines become more and more straight, although at 90° the influence of the upper critical end-point is still clearly present.

However, it is not true that in all cases the solubility decreases when pressure increases. As is apparent from the P - T curves (Fig. 2), some S_B - F lines have a temperature minimum for very low molar percentages of naphthalene. This change in direction along the S_B - F line means that,