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Dynamical and structural behaviour of mixed molecular systems at high pressure

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Publication date
1999

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Citation for published version (APA):

Kooi, M. E. (1999). *Dynamical and structural behaviour of mixed molecular systems at high pressure*. [, Universiteit van Amsterdam]. UvA.

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The system CO₂-N₂ at high pressure and applications to fluid inclusions

4.1. Introduction

Fluid inclusions in high-grade metamorphic rocks may provide information about the p - T conditions of metamorphism in these environments. Notably binary mixtures of CO₂-N₂ have been frequently found in granulites and eclogites [57, 58] and are considered an important fluid system in the lower crust. Fluids trapped at granulite and eclogite-facies conditions may have survived uplift and form fluid inclusions of low molar volume ($< 40 \text{ cm}^3/\text{mole}$) and high pressure ($> 80 \text{ MPa}$ at room temperature). The interpretation of fluid inclusion data requires accurate p - V - T - x data, with x the mole fraction of nitrogen, for the system CO₂-N₂ over the range of p - T conditions applicable to both the metamorphic event and the conditions of the inclusion measurement, i.e. phase transitions at low temperature. Data on the system CO₂-N₂ in a pressure range applicable to fluid inclusions trapped in the lower crust are sparse. Therefore, the interpretation of V - x properties of high-density CO₂-N₂ inclusions relies on equations of state which have been extrapolated from the range of experimental data. Darimont and Heyen [59] constructed a V - T - x phase diagram with the equation of state proposed by Heyen [60] valid below 293 K and 9 MPa, but the result appeared to be inaccurate at higher pressure and higher N₂ concentrations. More recent calculations of Thiéry et al. [7, 61] achieved higher accuracy (notably in the critical region) by the compilation of experimental and fluid inclusion data and the application of the Soave-Redlich-Kwong equation of state in combination with quadratic mixing rules.

However, the topology of the system CO₂-N₂ and the extension of the critical curve towards very high pressures ($> 40 \text{ MPa}$) has been a matter of speculation [61]. Fluid-fluid immiscibility can be expected in systems characterised by very different intermolecular interactions of the constituent components such as N₂-CO₂, and occurs in a number of geologically important fluid mixtures like H₂O-CO₂, H₂O-CH₄ and H₂O-N₂. Esper et al. [62] found an open isopleth (L-G) for a CO₂-N₂ mixture of 55.3 mol % N₂ without critical conditions, which may indicate the possibility of fluid-fluid immiscibility. A similar behaviour was found by Duarte-Garza et al. [63] for 49.6 and 55.4% N₂ compositions. However, early experiments by Tsiklis [64] up to 700 MPa did not show fluid-fluid immiscibility in N₂-CO₂. In contrast with the equation of Thiéry et al. [61], Kreglewski and Hall [65] predicted fluid-fluid immiscibility in the system CO₂-N₂ above 45 MPa for a wide compositional range with a critical composition slightly higher than 50 mol % N₂. Note that Kreglewski and Hall did not take the occurrence of solid phases into account. According to the model of these authors [8, 65] two critical curves (L = G and F = F) are defined

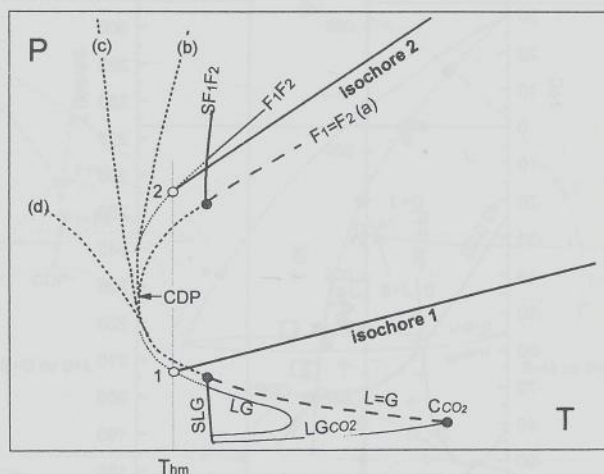


Figure 4.1. Schematic p - T diagram showing a part of the system CO₂-N₂. The L-G critical curve becomes metastable below 212 K (and ≈ 24 MPa), the intersection point with the three-phase S-L-G curve. At high pressures, four possible critical curves are shown: (a) a strongly bent critical curve giving rise to fluid-fluid immiscibility towards high temperatures and high pressures (after Ref. [65]). This critical curve grades to a $F_1 = F_2$ critical curve beyond a critical double point (CDP) and becomes stable again at a second intersection point with the three-phase line. Fluid inclusions of higher and lower molar volume at the same temperature (T_{hm}) may show L-G homogenisation or F_1 - F_2 homogenisation, respectively (c.f. Fig. 4.3). These fluids define two isochores at lower and higher pressures. (b) A moderately bent critical curve giving rise to fluid-fluid immiscibility. This assemblage however remains under the crystallisation surface. (c) A very steep asymptotic critical curve which does not form a critical double point. (d) A continuous critical curve.

which meet in a so-called critical double point ($L = F = F$) at the lowest possible critical temperature. They calculated the position of the critical double point for CO₂-N₂ at $p \approx 45$ MPa, $T \approx 202$ K, $x_{N_2} \approx 0.50$ - 0.55 , and $V \approx 42$ cm³/mole. This model implies that observed immiscibility below about 220 K can be either normal liquid-gas (at lower pressure) or fluid-fluid immiscibility (at higher pressure). For high-density/high-pressure inclusions this would imply that homogenisation (below about 223 K) can be either lower-pressure L-G or high-pressure F-F homogenisation (Fig. 4.1). For example: a CO₂-N₂ fluid inclusion containing 22% N₂ and showing a homogenisation temperature of 215 K (-58 °C) has a molar volume of 42 cm³/mole (L-G homogenisation) or 35 cm³/mole (F-F homogenisation) (Fig. 4.2). The homogenisation pressure is about 20 MPa and 150 MPa, respectively. According to the minimum homogenisation points (line c in Fig. 4.2, valid for a large compositional range) as predicted by Kreglewski and Hall [8] fluids would be *always* unmixed at low temperature. However, Klemd et al. [66] found very low homogenisation temperatures (at 183 K for $x_{N_2} = 0.39$), implying that the calculated position of the immiscibility curves cannot be correct. The topologies of

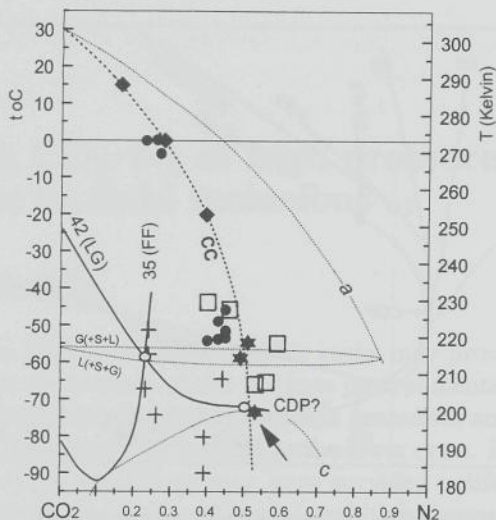


Figure 4.2. The molar volume of fluid inclusions from different models and collected critical data. Line (a) shows the maximum extension of L+G immiscibility towards higher temperature (cricondentherm) and line (c) shows the maximum extension of fluid–fluid homogenisation, i.e. fluids are always immiscible below line (c). The molar volume of an inclusion with 22% N₂ and (metastable) homogenisation temperature of 215 K can be determined as 42 cm³/mole (L–G homogenisation) or 35 cm³/mole (F–F homogenisation). The plotted data (plus-signs) represent fluid inclusions of the Münchberg Gneiss Massiv (Klemm et al. [66]). Note that liquid and critical homogenisations are observed below curve (c). The critical curve (cc) extrapolates critical experimental and fluid inclusion data from the literature: (diamonds) experimental data of Arai et al. [71]; circles, corrected critical observations of experimental (Ref. [75]) and natural fluid inclusions (stars, subcritical immiscibility in granulite from Lützow-Bay, Antarctica; squares, other measurements from the same location). The phase transitions observed in the inclusion indicated by the arrow are discussed in the text and shown in Fig. 4.4.

the system CO₂–N₂ for constant molar volume with *or* without assumed fluid–fluid immiscibility are shown in a *T*–*x* diagram (Figs. 4.3a,b respectively).

Clearly, the topology of the system CO₂–N₂ at low molar volume is uncertain. In the present study, high-pressure experiments (< 5 GPa; < 400 K) have been carried out to test for fluid–fluid immiscibility in the system CO₂–N₂. The phase behaviour has been established for 50.6% N₂ composition. Furthermore, high-density CO₂–N₂ fluid inclusions of about 50–50% N₂ composition in garnet from charnockite from Lützow-Holm Bay, Antarctica [67] have been studied by microthermometry in order to improve the topology of the system, notably the position of the critical curve.

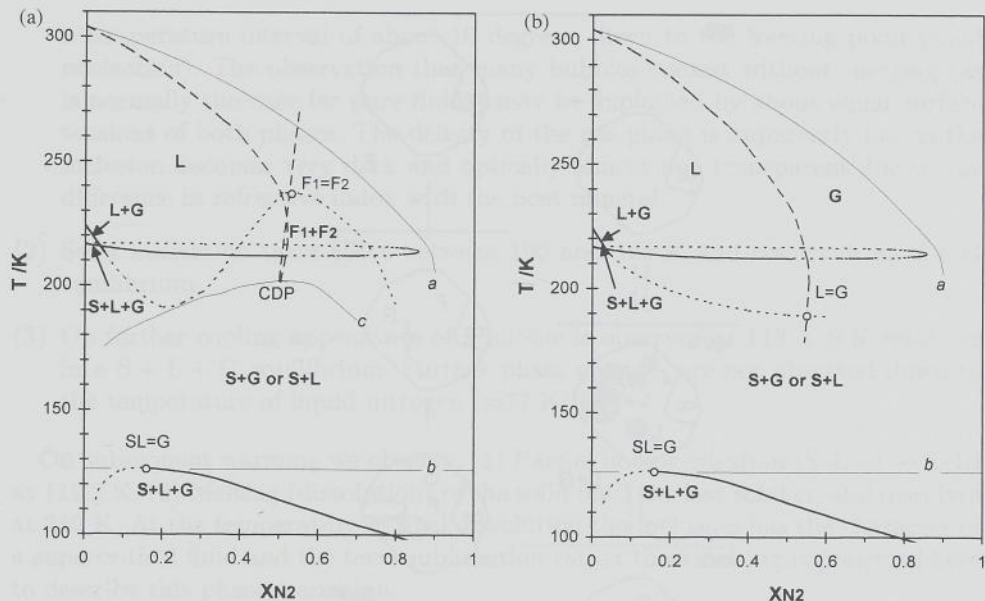


Figure 4.3. $T-x$ phase diagrams at constant volume ($38 \text{ cm}^3/\text{mole}$) (a) topology in the case of fluid–fluid immiscibility, after calculations of Kreglewski and Hall [65] (b) absence of fluid–fluid immiscibility with a continuous metastable extension of the $L+G$ field (Ref. [61]). The circles show the $V-x$ conditions for critical $L-G$ homogenisation ($L = G$) or F_1-F_2 homogenisation ($F_1 = F_2$). The point $S-L = G$ shows the conditions of critical partial homogenisation ($S-L-G \rightarrow S + \text{critical fluid}$). Line (a) shows the maximum extension of $L + G$ immiscibility towards higher temperature (cricondentherm). Line (b) shows the maximum extension of $L+G$ immiscibility in the presence of solid CO₂ and line (c) shows the maximum extension of fluid–fluid homogenisation, i.e. fluids are always immiscible below line (c).

4.2. High-density 50–50% CO₂-N₂ fluid inclusions

Fluid inclusions in garnet from charnockite from Lützow-Holm Bay, Antarctica [67] typically contain about equal amounts of CO₂ and N₂ as measured by Raman analysis (40–66 mol % N₂) and have molar volumes of 42–45 cm³/mole, according to the model of Thiéry et al. [61]. These $V-x$ properties are close to the conditions of the by Kreglewski and Hall [8] predicted critical double point ($x_{N_2} = 0.50-0.55$; $V \approx 42 \text{ cm}^3/\text{mole}$). The lowest homogenisation temperatures (199.8 K) were recorded in a 25 μm inclusion of 42 cm³/mole and 53 mol % N₂. This observation states that, contrary to the predictions of Kreglewski and Hall [8], $L-G$ homogenisation may occur below 202 K for this composition (Fig. 4.2). The $L-G$ immiscibility has an unusual character (bubbles do not merge), and in combination with the other phase transitions between 77 and 293 K, it provides information about the topology of the system CO₂-N₂.

The 25 μm fluid inclusion is monophasic at room temperature (except for a daugh-

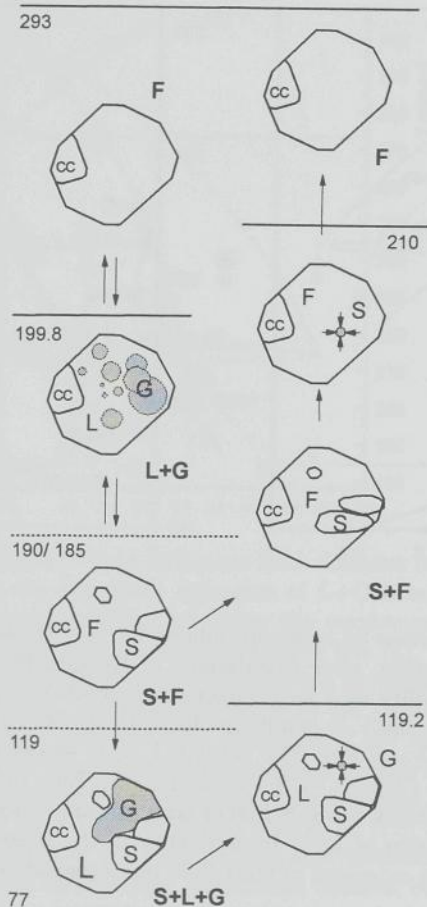


Figure 4.4. A $25\ \mu\text{m}$ fluid inclusion in garnet from granulite from Lützow-Holm Bay, Antarctica. V - x properties are $42\ \text{cm}^3/\text{mole}$ and $53\ \text{mol}\ \% \text{N}_2$, i.e. close to the predicted critical double point. On cooling from room temperature to about $77\ \text{K}$ we observe the following phase transitions: L-G immiscibility characterised by violent subcritical effervescence ($200\ \text{K}$); “boiling” down to the temperature of solid nucleation (190 – $185\ \text{K}$); immiscibility of the N_2 -rich fluid ($119\ \text{K}$). On warming between $77\ \text{K}$ and room temperature partial homogenisation to liquid ($119.2\ \text{K}$), and “dissolution” of the solid ($210\ \text{K}$) are observed.

ter calcite crystal which does not effect the low-temperature phase equilibria) and has an estimated pressure of $139\ \text{MPa}$ at room temperature. During cooling we observed the following phase transitions (Fig. 4.4):

- (1) Immiscibility at $199.8\ \text{K}$ seems to have a (sub)critical character: violent bubble appearance, large bubble size just below the homogenisation temperature, and the almost absence of “undercooling”. Below the temperature of first immiscibility continuous subcritical “effervescence” was observed, which pertains over

a temperature interval of about 10 degrees, down to the freezing point (solid nucleation). The observation that many bubbles coexist without merging (as is normally the case for pure fluids) may be explained by about equal surface tensions of both phases. The density of the gas phase is apparently low as the inclusion becomes very dark and optically almost non-transparent due to the difference in refractive index with the host mineral.

- (2) Solid nucleation takes place between 190 and 185 K and results in an S + G equilibrium.
- (3) On further cooling appearance of a bubble is observed at 118–119 K resulting in a S + L + G equilibrium. Further phase changes are not observed down to the temperature of liquid nitrogen (≈ 77 K).

On subsequent warming we observe: (1) Partial homogenisation (S–L–G \rightarrow S–L) at 119.2 K. (2) Melting (dissolution) of the solid until the last solid crystal dissolves at 210 K. At the temperature of final dissolution the inclusion has the character of a supercritical fluid and the term sublimation rather than melting is preferred here to describe this phase transition.

The molar volume of 42 cm³/mole as obtained from Thiéry et al. [61] is in good agreement with the partial homogenisation at 119.2 K (corresponding to nitrogen molar volume $V_{N_2} = 52.2$ cm³/mole) and the total composition: from these data the molar volume can be derived from the simple correlation $V_t = (1 - x_{N_2})28.2 + x_{N_2}V_{N_2}$ (taking the molar volume of solid CO₂ as 28.2 cm³/mole). The stability of other solid phases would make this assumption invalid. The experimental data of Tsiklis [64] show that N₂ dissolves in solid CO₂, but at pressures higher than about 330 MPa. These pressures are not realistic in natural fluid inclusions at low temperatures.

4.3. High-pressure experiments in a diamond-anvil cell

4.3.1. Experimental procedure

A diamond-anvil cell (DAC) connected to a temperature control system, as described by Schouten et al. [68], has been used to study the phase behaviour of the system CO₂-N₂ at various temperatures and pressures. The different phases were visually observed through a microscope. In addition, the phase behaviour has been investigated by measuring the pressure in steps of about 2 K while heating or cooling the sample, a so-called p - T scan. This quasi-isochoric scanning method can be used to detect three-phase lines in binary mixtures. Note that the volume of the sample chamber slightly changes while heating or cooling the DAC, due to thermal effects of the various parts of the DAC. To obtain more information about the various phases we measured the vibrational Raman spectra of N₂ and CO₂. Similar to the above mentioned p - T scans, we have performed quasi-isochoric ν - T scans in which the Raman frequencies, ν , have been measured as a function of temperature.

Since Kreglewski and Hall [65] predicted fluid–fluid immiscibility with a critical composition slightly higher than 50%, the cell has been loaded with a 50.6 mol % nitrogen mixture. The mixture has been prepared in a gas compressor as described by Van den Bergh [69]. First, carbon dioxide has been supplied to the compressor. The partial pressure was determined with a calibrated mirror manometer with an absolute precision of 0.02 bar. Subsequently, nitrogen has been added and the final temperature and pressure of the mixture were recorded after thermal equilibrium had been achieved. After an equilibration time of one day the mixture is still not completely mixed. The mixture proved to be inhomogeneous, since we found different solid–fluid isopleths for samples loaded at different equilibration times. This behaviour is in contrast to our experience with binary mixtures of helium, hydrogen, nitrogen, and methane (see e.g. Ref. [69]). In these mixtures equilibrium is reached within one day. When the $\text{CO}_2\text{-N}_2$ mixture is left to equilibrate for 14 days the composition of the sample loaded in the DAC does not depend on the equilibration time any longer and the experimental solid–fluid isopleths are reproducible. Therefore, it is assumed that the mixture is then in equilibrium, which is the homogeneous state under these conditions [70, 71]. In addition, it has been verified that the mixture is still homogeneous at the usual loading conditions of 300 MPa and room temperature: since a 50 mol % $\text{CO}_2\text{-N}_2$ mixture is known (from literature) to be homogeneous at 20 MPa and room temperature, we loaded the DAC once at these conditions, and subsequently raised the pressure, while studying the phase behaviour through the microscope. The sample remained homogeneous until at least 500 MPa.

The temperature of the DAC is measured using copper–constantan thermocouples with an accuracy of about 1 K. The pressure is determined by using the ruby technique with the pressure scale of Mao et al. [20], and the temperature correction from Vos and Schouten [21]. The accuracy of the pressure measurements is about 50 MPa and the accuracy of the position of the Raman peak is about 0.2 cm^{-1} . The spectrograph was calibrated after each measurement.

The experimental procedure is as follows. The pressure in the DAC is set at a predetermined value and the temperature is raised so that the p - T conditions are well into the homogeneous region. Subsequently, the temperature is slowly decreased and the phase behaviour is observed through the microscope. When a phase separation takes place, the temperature is increased again to determine the range of metastability. This range is very large in the case of solidification. The transition temperatures have been obtained on heating. After a predetermined temperature has been reached, sufficient time was allowed for temperature equilibrium in the DAC. The transition temperatures are independent of the rate of heating.

4.3.2. Experimental results and discussion

The phase behaviour has been investigated up to 400 K and at pressures up to 5 GPa. At low temperatures two solid phases have been visually observed in the sample chamber. On raising the temperature one of the solid phases starts to melt. The three-phase line $S_1\text{-}S_2\text{-}F$ is followed in a range of a few K until the two-phase

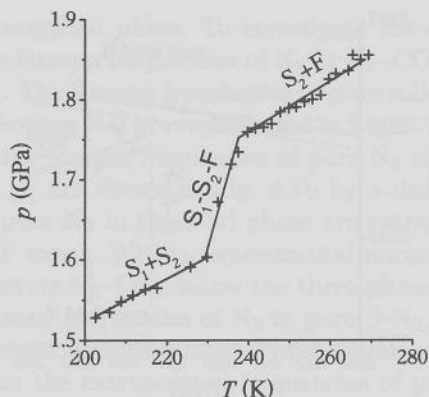


Fig. 4.5

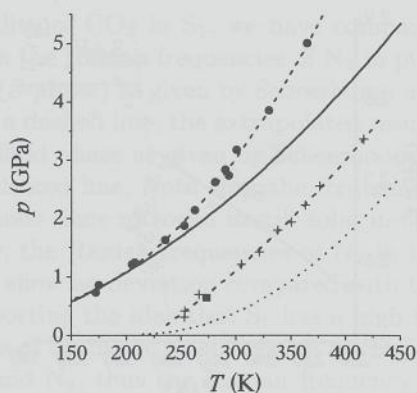


Fig. 4.6

Figure 4.5. A typical p - T scan (plus-signs) in which the three-phase line S_1 - S_2 - F is followed in a range of 10 K. Solid lines are guides to the eyes.

Figure 4.6. S_2 - F points, three-phase line and the melting lines. Circles, S_1 - S_2 - F three-phase line (this work); plus-signs, S_2 - F points, 50.6 mol % N₂ (this work); squares, S_2 - F point (Ref. [64]); dotted line, melting line pure CO₂ (Ref. [76]); solid line, melting line pure N₂ (Ref. [24]). The dashed lines are empirical fits to the data.

region $S_2 + F$ is reached. Considering the melting order, S_1 should be a nitrogen-rich solid and S_2 a carbon dioxide-rich solid. The three-phase line has also been measured by p - T scans along quasi-isochores. Since the three-phase line is uniquely defined in the p - T plane, it should be followed in a p - T scan as long as the three phases coexist. This leads to a strong increase of the slope of the pressure versus the temperature at the three-phase line. The discontinuity in the slope in p - T scans corresponds with a pressure jump of about 150 MPa. A typical p - T scan at this three-phase line is shown in Fig. 4.5. One can observe that in a single scan the heating path coincides with the three-phase line over a 10 K interval. At a higher temperature, the second solid starts to melt. The temperature is increased very slowly, while the sample chamber is observed through the microscope, in order to determine the temperature of final solid disappearance accurately. The point at which the two-phase region is left is called the solid-fluid (S_2 - F) point. At the S_2 - F point the temperature and pressure are determined. The S_2 - F points and the three-phase line have been plotted in Fig. 4.6 in a pressure-temperature diagram. The S_2 - F isopleth of the 50.6 mol % N₂ mixture lies between the melting lines of pure N₂ and CO₂. Our data are in agreement with the low pressure measurements of Tsiklis [64]. Above the S_2 - F point a clear homogeneous sample has been observed through the microscope. In the case of fluid-fluid immiscibility one should observe a bubble within the sample chamber.

In Figs. 4.7a-c a p - T scan and ν - T scans near the S_1 - S_2 - F three-phase line are shown. The pressure and the Raman frequencies have been measured in the same

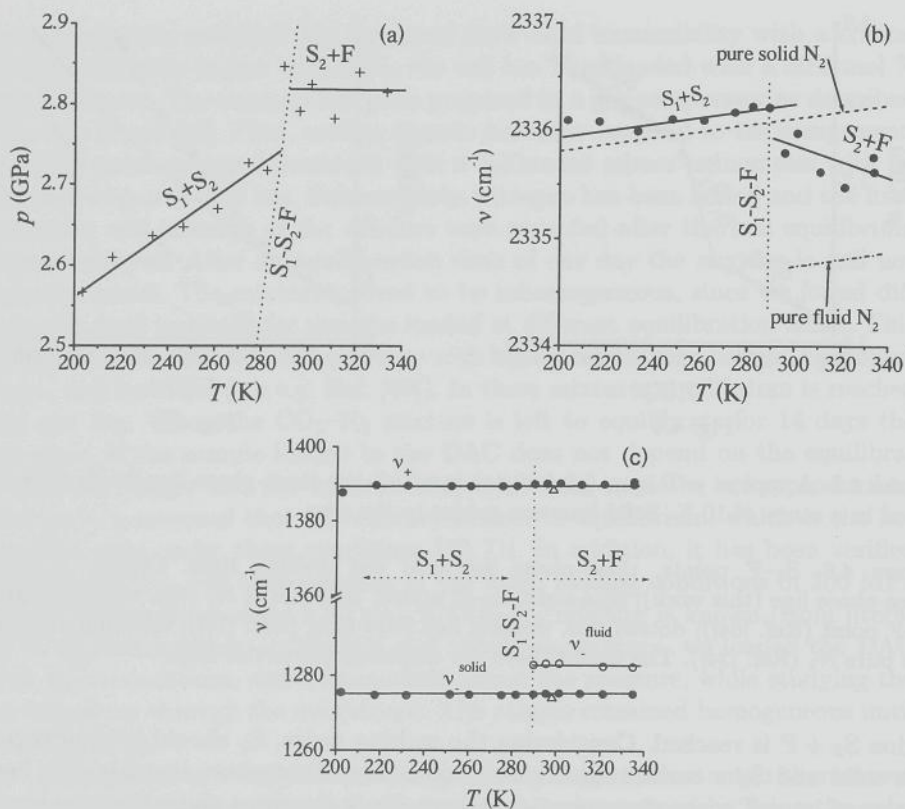


Figure 4.7. Scans near the three-phase line. The solid lines are guides to the eyes. The dotted line represents the S_1 - S_2 - F three-phase line. (a) The p - T scan (plus-signs), was measured in the same run as the ν - T scans. (b) ν - T scan (circles) of the vibrational mode of N_2 . The dashed line represents the vibrational frequencies of pure solid N_2 (Ref. [44]). The dashed-dotted line represents an extrapolation of the vibrational frequencies of pure fluid N_2 (Ref. [1]). (c) ν - T scan (circles) of the vibrational modes of CO_2 . The triangles represent the vibrational modes of pure solid CO_2 at room temperature (Ref. [73]).

run. In Fig. 4.7b, it is observed that the vibrational Raman frequency of N_2 shows a discontinuity at the three-phase line. The Raman frequency of N_2 in the $S_1 + S_2$ coexistence region is higher than in the solid-fluid coexistence region. Moreover, at both sides of the three-phase line we have observed only a single peak within experimental accuracy. This suggests hardly any solubility of N_2 in solid CO_2 (S_2). If S_2 would contain a measurable amount of N_2 , then the Raman frequency of N_2 in S_2 should behave continuously at the three-phase line or it should increase due to the increase of the pressure. Note that in the solid phase the Raman frequency generally increases when the pressure increases. In pure nitrogen the Raman frequency of the solid phase (β - N_2) is higher than the frequency of the fluid phase [72]. Therefore, the decrease is attributed to a difference in frequency of N_2 in S_1 and N_2 in the

mixed fluid phase. To investigate the solubility of CO₂ in S₁, we have compared the Raman frequencies of N₂ in N₂-CO₂ with the Raman frequencies of N₂ in pure N₂. The Raman frequencies of pure solid N₂ (β -phase) as given by Scheerboom and Schouten [44] are represented in Fig. 4.7b by a dashed line; the extrapolated results of the Raman frequencies of pure N₂ in the fluid phase as given by Scheerboom et al. [1] are shown in Fig. 4.7b by a dashed-dotted line. Note that the frequencies of pure N₂ in the fluid phase are extrapolations since nitrogen is still solid in this p - T range. Within experimental uncertainty, the Raman frequencies of N₂ in the mixture N₂-CO₂ below the three-phase line, show no deviation compared with the Raman frequencies of N₂ in pure β -N₂, supporting the idea that S₁ has a high N₂ content. One can observe that the frequencies of N₂ in the S₂ + F region are higher than the extrapolated frequencies of pure fluid N₂, thus the Raman frequency of the nitrogen molecules is increased due to the presence of carbon dioxide molecules.

The internal ν_- and ν_+ modes of CO₂ show a slight discontinuity to higher frequencies at the three-phase line in a heating scan, which is hardly visible in Fig. 4.7c due to the relatively large scale in frequency in this plot. The increase of the frequency of the Raman peaks of CO₂ at the three-phase line is attributed to the increase of the pressure. In the solid-fluid coexistence region the Raman peak corresponding to the ν_- mode of CO₂ is split into two peaks. The low-frequency ν_- Raman peak corresponds to the Raman frequency that is observed in the S₁ + S₂ coexistence region. At higher temperatures the intensity of this peak decreases until it disappears at the S₂-F point. The intensity of the high-frequency ν_- peak of CO₂ increases at increasing temperature. It corresponds to the frequency that is observed for the homogeneous fluid mixture. The Raman peak corresponding to the ν_+ mode of CO₂ does not show splitting within experimental uncertainty. We attribute the splitting of the ν_- mode of CO₂ in the S₂ + F coexistence region to a difference of the internal mode of CO₂ in the fluid and in the solid phase. We have compared the Raman frequencies of CO₂ in N₂-CO₂ with the Raman frequencies of pure solid CO₂ at room temperature as measured by Hanson and Bachman [73]. Their measurements have been represented in Fig. 4.7c by triangles. Within experimental uncertainty, there is no deviation between ν_+ and ν_- of pure solid CO₂ and ν_+ and the lower frequency mode of ν_- in the S₂ + F region in this work. This again suggests a low solubility of N₂ in solid CO₂ (S₂). The fact that the Raman peak of CO₂ does not show splitting in the S₁ + S₂ coexistence region suggests, as before, that the solubility of CO₂ in solid N₂ (S₁) is low. The present work shows that the internal mode ν_+ of CO₂ in S₂ does not show any shift with respect to ν_+ of CO₂ in the fluid phase within the experimental uncertainty.

In Fig. 4.8 the Raman frequencies of CO₂ near the S₂-F point at 1.5 GPa have been plotted. The lower frequency mode of ν_- indeed disappears at the S₂-F point. Above the S₂-F point the Raman peaks do not show splitting anymore, indicating that the fluid is now homogeneous, in agreement with observations through the microscope. The Raman frequency of N₂ behaves smoothly at the S₂-F point.

From these measurements, we conclude that, in contrast to the prediction of Kreglewski and Hall [8], fluid-fluid phase separation, if it occurs at all, certainly does not occur in a 51 mol % N₂ mixture at pressures below 3300 MPa at any temper-

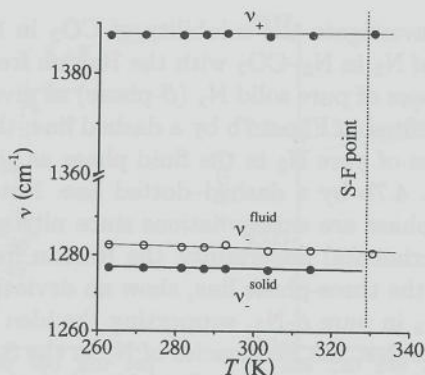


Figure 4.8. ν - T scan (circles) of the vibrational Raman peak of CO_2 near the S_2 -F point at about 1.5 GPa. Dashed line represents the S_2 -F point which has been detected by visual observation. The solid lines are guides to the eyes.

ature. This does not completely exclude the existence of a fluid–fluid immiscibility region at other concentrations. The system nitrogen–methane for example shows a very small fluid–fluid immiscibility region at the nitrogen-rich side of the phase diagram [74]. However, since the S_2 -F isopleth of the 51 mol % N_2 mixture lies between the melting lines of the pure components, it is very unlikely that fluid–fluid phase separation appears at much higher temperatures than the melting line of CO_2 . Taking into account the results of the 51 mol % mixture, this would lead to a very unusual T - x phase diagram, although the intermolecular forces between the dissimilar molecules are not of exceptional character.

In addition, it is shown that there is a very low solubility or no solubility at all of carbon dioxide in solid nitrogen and vice versa. It is interesting to compare this system to argon–nitrogen, since the molecular diameter ratios of these two systems are about the same. Note that in the system carbon dioxide–nitrogen, carbon dioxide is the largest component, while in the system argon–nitrogen, nitrogen is the largest component. In Chapter 2, it was shown that a large amount of argon dissolves into the solid phases of nitrogen, and in Chapter 5 we will show that also a large amount of nitrogen dissolves into solid argon. Therefore, it is concluded that although argon and carbon dioxide both have about the same diameter as nitrogen, the solubility of argon and carbon dioxide in nitrogen and vice versa is very different.

4.4. Conclusions

The experiments show that fluid–fluid immiscibility does not occur for the system CO_2 - N_2 , at least for a 50.6% N_2 composition. Therefore, a critical curve bending towards higher temperatures, with a critical composition of about 0.5, as predicted by Kreglewski and Hall [65], is excluded. Fluid–fluid immiscibility at other concentrations is highly unlikely, considering the S_2 -F isopleth for 50.6% N_2 . Ob-

servations in fluid inclusions with V - x properties corresponding to the predicted critical double point show an unusual (subcritical) effervescence phenomenon down to the temperature of solid nucleation. Although the results of Esper et al. [62] and Duarte-Garza et al. [63] suggest a (metastable) critical double point at higher pressures, the lack of observing fluid-fluid immiscibility in our experiments suggests that the critical curve remains under the crystallisation surface (Fig. 4.1). The molar volume ($< 32 \text{ cm}^3/\text{mole}$) of CO₂-N₂ inclusions found in a number of eclogite and granulite-facies rocks can be determined by assuming L-G immiscibility. Such inclusions have a minimum pressure of 57 MPa at room temperature. L-G homogenisation is always into gas phase (L-G \rightarrow G) for $x_{\text{N}_2} > \approx 0.55$, except for pure N₂. Models based on L-G immiscibility only (e.g. Ref. [61]) are applicable for molar volume calculations, also in the high-pressure range.