

CHAPTER VII

PRESSURE STUDIES OF $\bar{7}S5$, $\bar{8}S5$ AND THEIR MIXTURES

7.1 Introduction

All the compounds discussed so far have essentially C.O.O or CH=N linkage group, except in the case of re-entrant nematogens. Recently Reynold synthesised a new class of compounds, viz., p,p'-disubstituted phenyl thiol benzoates which have C.O.S as the linkage unit, i.e., 'there is a sulphur atom in the ester linkage. The 7th and the 8th member of this homologous series, viz., 4-n-pentylphenyl-4'-n-heptyloxy thiobenzoate ($\bar{7}S5$) and 4-n-pentyl phenyl-4'-n-octyloxy thiobenzoate ($\bar{8}S5$) were in fact the substances used by Johnson et al² to observe the multicritical NAO point, for the first time, in a temperature-concentration diagram (figure 7.1). We have carried out precise and detailed pressure studies on these two compounds and their 3 mixtures for several reasons: (1) to study the effect of adding a heavy atom, namely, sulphur in the linkage group on the stability of various mesophases under pressure) (2) to see if this compound which has a monolayer S_A phase, exhibits the phenomenon of reentrance as in the case of bilayer

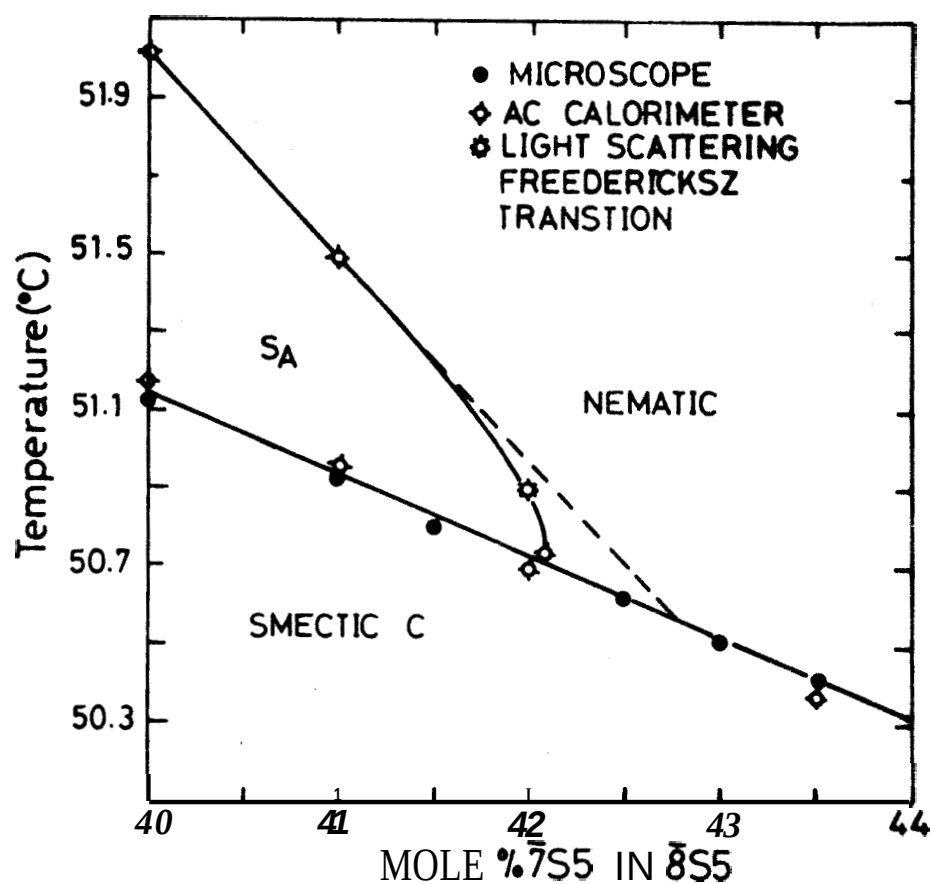


Figure 7.1: Isobaric phase diagram of the binary mixtures of 7S5 and 8S5 near the NAC point (after R. De Hoff et al⁵).

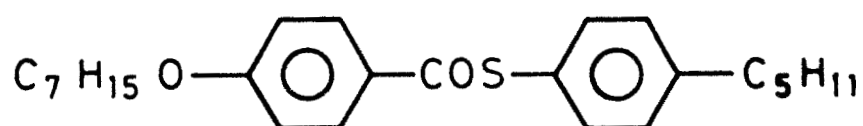
smectic A compounds since the latent heat associated with A-N transition is very small; and (3) to investigate whether NAC point observed in the temperature concentration phase diagram of these substances can also be obtained in the P-T diagram since most of the effects like tricritical behaviour,³ reentrant phenomenon⁴ observed by varying concentrations in binary mixtures can also be observed in a single component system by varying pressure.⁵⁻⁸

7.2 Compounds

The compounds 7S5 and 8S5 used in our experiment were kindly given by Prof. G. Heppke. These compounds belong to the homologous series of diaubstituted phenyl thio benzoates which were first synthesised by Reynolds et al¹ with a view to study the mesomorphic stability when an oxygen atom is replaced by sulphur in the ester linkage of benzoyl benzoates. The structural formula of the compounds are given in figure 7.2. The transition temperatures of the two pure compounds and their mixtures having molar percentage of 34, 40 and 45 of 7S5 in 8S5 as determined by thermal microscopy are given in Table 7.2. The transition enthalpies associated with the various transitions in the case of pure compounds were determined using a differential scanning

Structural Formula
of

(1) 4 - n pentyl phenyl - 4'- n Heptyloxy thio **Benzoate** (**7S5**)



(2) 4 - n Pentyl Phenyl - 4 n octyloxy thio **Benzoate** (**8S5**)

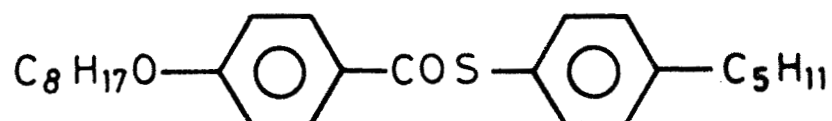


Figure 7.2

Structural formula of 7S5 and 8S5

calorimeter (Perkin Elmer Model DSC-II) and are tabulated in Table 7.1. Transition temperatures as well as the heats of transition are in good agreement with those determined by previous workers.^{9,10,11}

$\bar{7}S5$ exhibits a nematic phase in addition to the monotropic smectic C phase. On the other hand, $\bar{8}S5$ has nematic and smectic A phases which are enantiotropic. In addition to this, it shows two monotropic phases, viz., smectic C and a higher order smectic. This higher order smectic phase exhibits mosaic textures and in their recent studies, Mary Neubert et al.¹¹ classified it as S_y phase. It should be pointed out here that Chruściel and Rachwalska,⁹ while doing adiabatic calorimetric studies on $\bar{7}S5$, observed the metastable nature of the smectic C phase. They did not find any specific heat anomaly corresponding to the smectic C - nematic transition temperatures which may be due to the spontaneous crystallisation directly from the nematic phase. Further, the dielectric relaxation studies carried out by Chruściel et al.¹² also indicate that smectic C is not stable but transforms spontaneously to the solid phase. However, this metastability of the phase did not pose any problems in our pressure study experiment since the technique

adopted, viz., optical transmission is a dynamic one wherein the **sample** temperature is being continuously varied at a constant rate of about 1 to 2°C/minute, whereas in the dielectric studies the temperature **is** to be kept constant **for** a long period of **time**.

Since **NAC** point for the binary mixture of $\bar{7}S5$ and $\bar{8}S5$ lies very close to the 42% molar concentration of $\bar{7}S5$ in $\bar{8}S5$ (refer figure 7.1), we have selected **three** mixtures with molar concentration of $\bar{7}S5$ **close** to 42%, **viz.,** 34%, 40% and 45%. The transition **temperatures** of these mixtures measured at room **pressure** are given in **Table 7.2**. Two of these mixtures (34% and 40% mole **fraction** of $\bar{7}S5$) show **smectic C**, smectic A and nematic **phases** while the mixture having 45% molar **concentration** of $\bar{7}S5$ shows only a smectic C and nematic **phase**. **More-**over, **all** the **phases** are **enantiotropic** unlike in pure compounds wherein smectic C is monotropic in character.

7.3 Experimental

Measurement of transition **temperatures** at various **pressures**: As already described, the **transition** **tempe-**ratures at various pressures were determined by light **transmission** technique using a **high** pressure optical cell.

In all, two independent sets of **readings** were taken using fresh samples in each case and it was found that the data points for the two independent sets of **measurements** all fall on the same curve and therefore practically indistinguishable from one another.

7.4 Results and discussion

7.4.1: 7S5: The P-T data of this compound **are** given in Table 7.5 while the phase diagram **is shown** in figure 7.3. It is seen that all the phase boundaries are essentially straight **lines**. **The** range of the nematic phase increases with the increase of pressure. **The** smectic **C** phase **which** is monotropic at room pressure remains so even at high pressures, but its range **decreases** with the increase of pressure and **finally** the nematic - smectic **C** **phase** boundary joins the crystallisation line at a pressure of 1.61 kbar. It is to be noted that the crystallization point at different pressures fall on a smooth straight line, The smectic **C** is therefore '**bounded**' resulting in solid - **nematic** - smectic **C** triple point at 1.61 kbar and 62°C. **The** data points for the various transitions are fitted to the polynomial equation suggested by Horn¹³, viz.,

$$T_p = T_o + AP - BP^2 \quad (1)$$

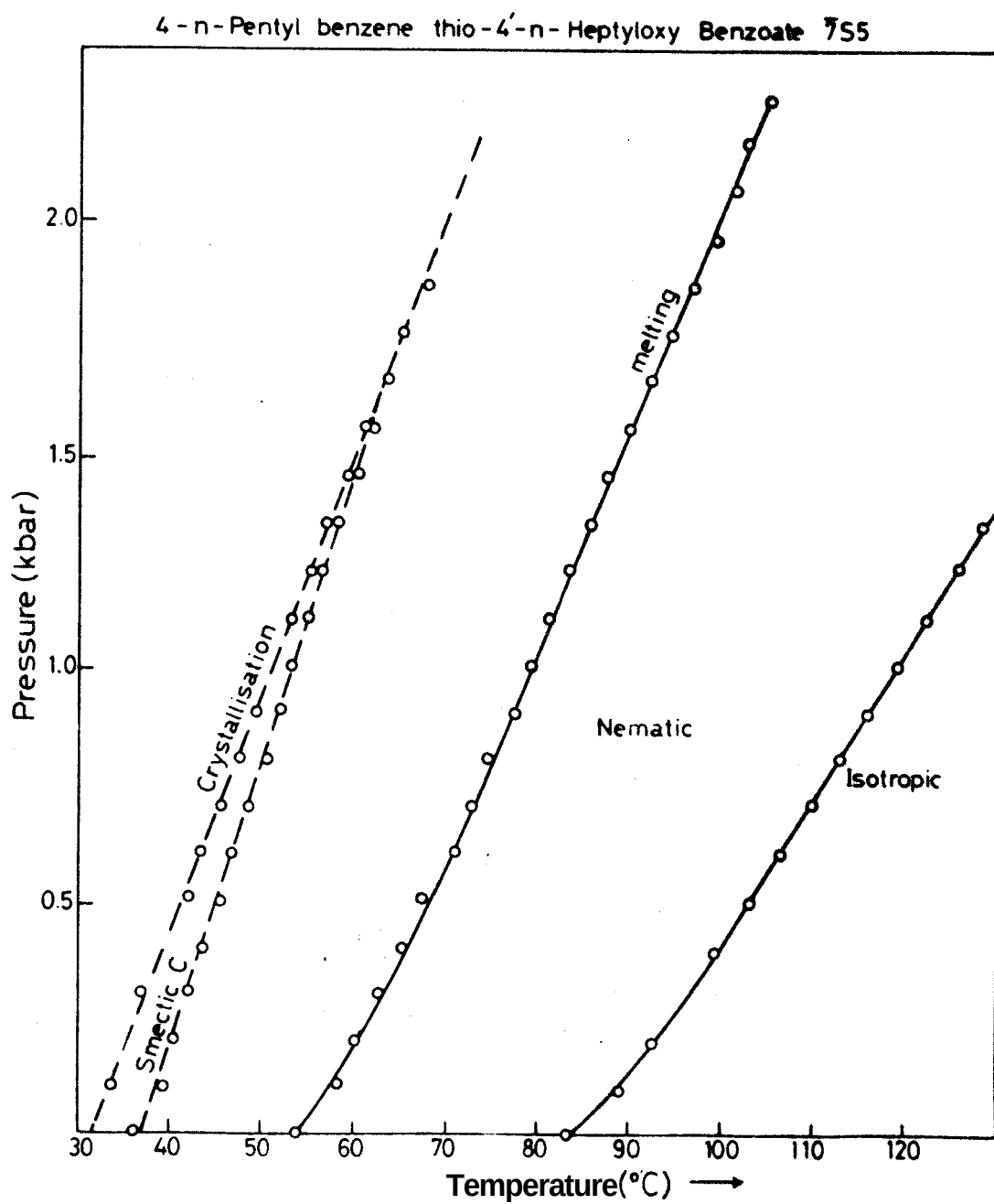


Figure 7.3: P - T diagram of $\bar{7}S5$

where T_P and T_0 are the transition temperatures in absolute at a pressure P and at atmospheric pressure respectively, A & B are empirical constants which are evaluated by the method of least square fit using Hewlett Packard 9821 programmable calculator. The value of constants A and B are tabulated in Table 7.3 along with the R.M.S. error. It may be noted that the dT/dP at 1 bar given by the value of A is rather low for nematic - smectic C transition, when compared to nematic to isotropic or solid - nematic transitions.

7.4.2 8S5: The (P-T) data for 8S5 are given in Table 7.6 while the corresponding phase diagram is shown in figure 7.4. The smectic A - smectic C as well as smectic C - S_{mosaic} phase boundaries remain monotropic in character throughout the pressure range studied and are shown by dotted line in the figure. Here again, the range of nematic phase increases with the increase of pressure. What is more interesting is that there is rather a steep increase in the smectic A range with increase in pressure which is accompanied by a decrease in the range of smectic C phase. The smectic C phase is ultimately bounded resulting in S_{mosaic} - Smectic C - Smectic A triple point at 4.1 kbar, and 65°C. Thus, although, the stability of smectic C phase

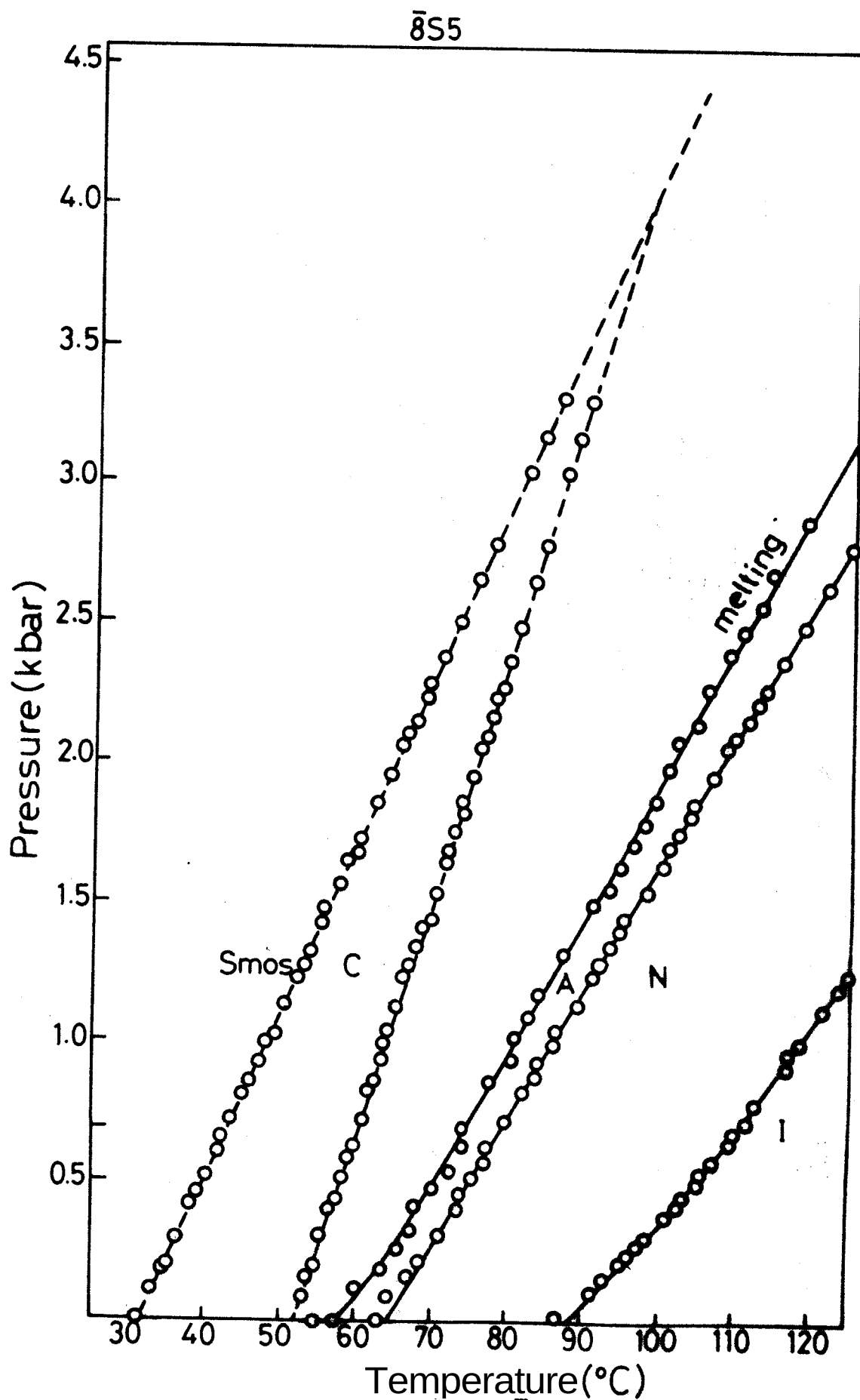


Figure 7.4: P - T Diagram of $\bar{8}S5$

at 1 bar for $\bar{8}S5$ is greater than that of $\bar{7}S5$, it also ultimately gets bounded at a pressure which is much higher than that for $\bar{7}S5$. Therefore, it is not possible to have an NAO point in $\bar{8}S5$ under pressure.

It must also be pointed out that Cladis et al¹⁴ have also studied this compound as a function of pressure up to 2kbar. The latent heat associated with smectic A - nematic transition is very small so that it can be regarded as weakly first order. This is attributed to a flexible aromatic part of $\bar{8}S5$. This has led Cladis et al to carry out high pressure studies of this compound with a view to observe the reentrant behaviour as in bilayer smectic A compound. Our studies have shown that the smectic A - nematic transition does not show any sign of curvature towards the pressure axis. In other words, there is no sign of reentrance even up to a pressure of 4 kbars. Since Xray studies of Cladis et al have shown that the measured layer spacing of smectic A of $\bar{8}S5$ is consistent with a monolayer smectic A phase, we can conclude, therefore, that the bilayer smectic A is essential for the reentrant nematic phase to appear.

The constants A and B for the various transitions obtained by the least square fit of the data to the poly-

nomial equation are given ⁱⁿ table 7.3 along with the corresponding R.M. S. error. The dT/dP values at 1 bar for various transitions are given in Table 7.4. It is to be noted that our values of dT/dP measured at 1 bar for smectic C - smectic A and smectic A - nematic transitions are $14.0^{\circ}\text{C/kbar}$ and $23.2^{\circ}\text{C/kbar}$ respectively which agree very well with those of Gladis et al. However, our value of dT/dP at 1 bar for nematic - isotropic transition, namely, $43.2^{\circ}\text{C/kbar}$ differs very much from that of Gladis ($= 30.14^{\circ}\text{C/kbar}$). This rather large difference is, perhaps attributed to the difference in the ΔH values for this transition at atmospheric pressure. The ΔH reported by Gladis et al is 0.87 kJ/mole while for our sample it is 1.30 kJ/mole , although the transition temperatures are practically the same in both the cases.

7.5 Binary mixtures of $\bar{7}S5$ and $\bar{8}S5$

As mentioned earlier, pressure studies were undertaken for 3 binary mixtures of $\bar{7}S5$ and $\bar{8}S5$ having a molar fraction of 34%, 40% and 45% of $\bar{7}S5$ in $\bar{8}S5$ which are in the vicinity of the critical concentration at which NAC point is observed. Since our interest is to see whether smectic A phase is bounded or not under pressure, we have concentrated only on smectic C - smectic A and smectic A - nematic phase transitions. The P-T data for these mixtures

are given in Table 7.7 to 7.9 respectively, while figures 7.5 to 7.7 represent the corresponding phase diagrams.

For the mixture having 34% molar fraction of 7S5 in 8S5, smectic A phase has a range of about 2°C at 1 bar which increases to 13°C at a pressure of 2.4 kbar, i.e., the range or the stability of the smectic A phase increases monotonically with the increase of pressure. The 40% mole fraction mixture also shows a similar behaviour (figure 7.8) except that the rate of increase of the range of smectic A phase is slower in this case, being about 1°C at 1 bar and 9°C at 2.5 kbar. It is therefore seen that neither the pure compound nor the mixtures show the NAC point under pressure. It appears as though the monolayer smectic A phase cannot be bounded by applying pressure. On the other hand, pressure has the effect of increasing the stability of such a monolayer smectic A phase. For the sake of completeness, pressure studies have also been conducted on the mixtures of 45% molar fraction of 7S5 in 8S5 which does not have smectic A but only smectic C and nematic phases partly with a view to see if smectic A can be induced at high pressures. The unusual aspect of the phase diagram (figure 7.7) is that smectic C phase which is enantiotropic at one bar becomes

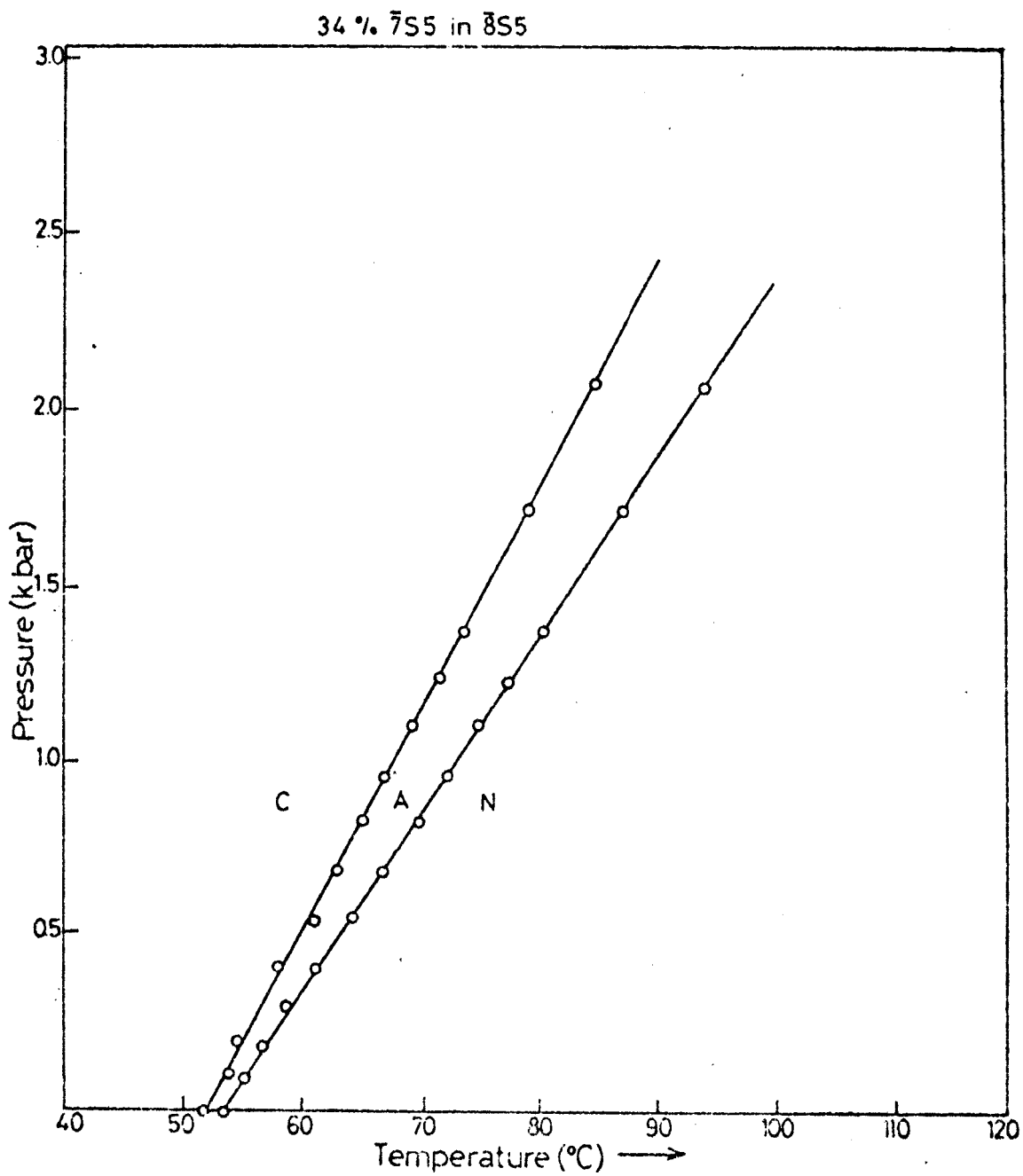


Figure 7.5: P - T diagram of C - A and A - N phase boundaries of 34% mole fraction of $\bar{7}S5$ in $\bar{8}S5$.

Mixture of 40% $\bar{7}S5$ in $\bar{8}S5$

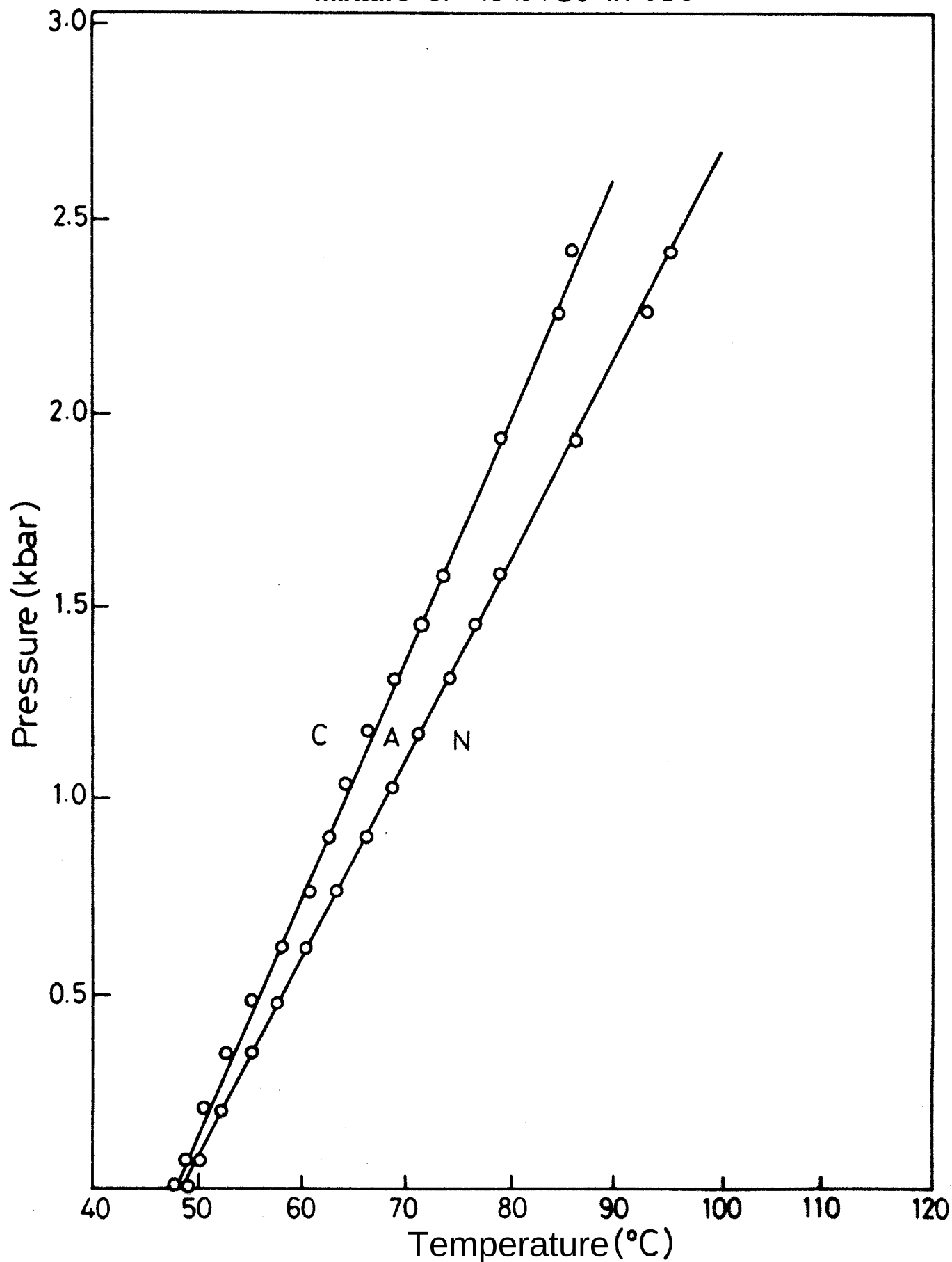


Figure 7.6: P-T diagram of C-A and A-N phase boundaries of the b —
e — of 7S5 (40% mole fraction) and 8S5.

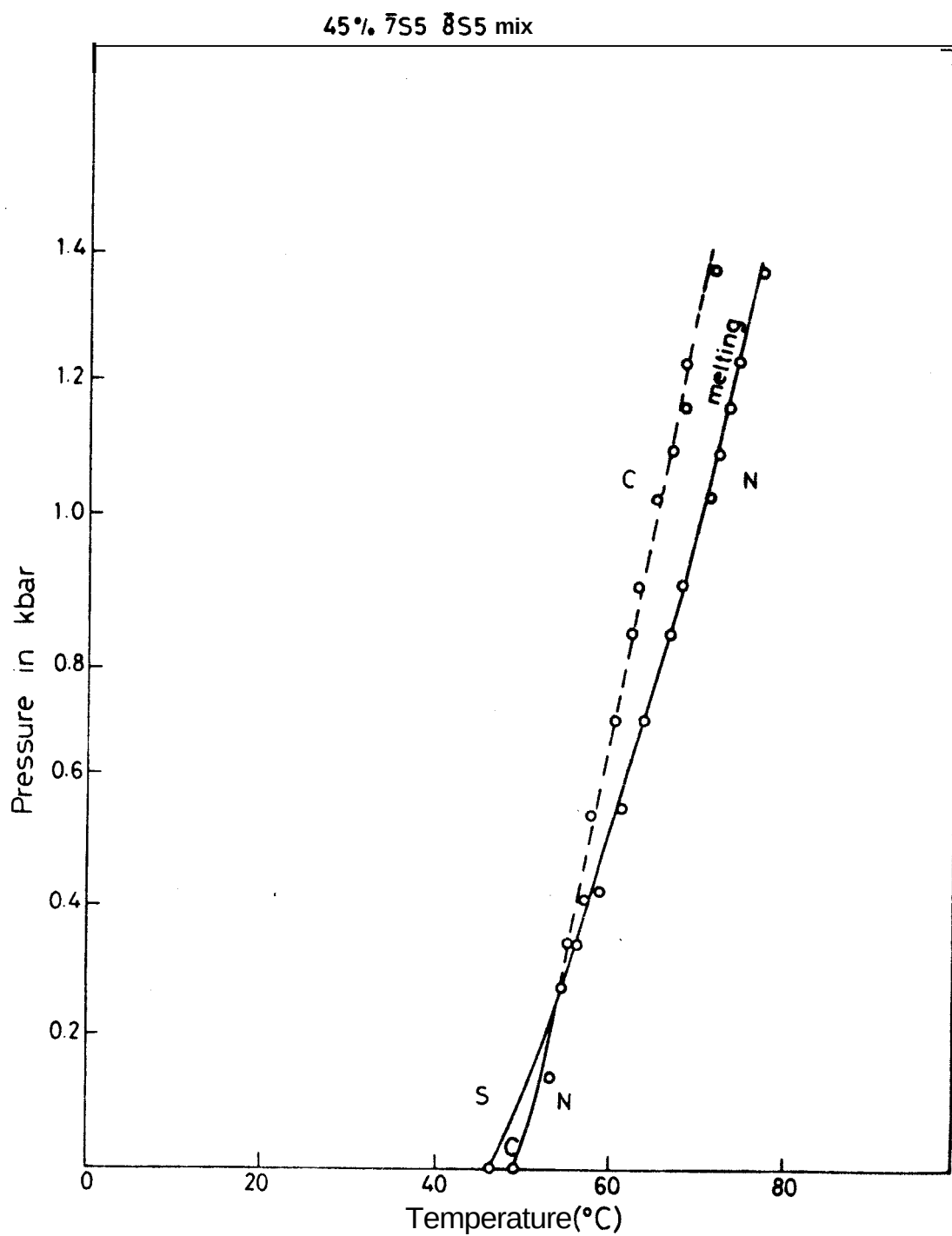


Figure 7.7: P-T diagram of solid-C and C-N phase boundaries of the binary mixture of 7S5 (45% mole fraction) and 8S5.

monotropic for pressures beyond 0.22 kbar. As far as we know this is the first instance of the smectic C - nematic transition showing a change in character from enantiotropic to monotropic, although similar change has been observed for smectic A - nematic transition before.^{8,15} It may also be recalled that the case of smectic C - nematic transition changing its character from monotropic to enantiotropic under pressure has already been observed.¹⁶ The constants A and B for the mixtures evaluated by least square fit of the data points to the polynomial equation are given in Table 7.3.

7.6 Evaluation of volume change ΔV at the transition using the Clausius-Clapeyron equation

The available data on the volume change ΔV at transitions involving different kinds of liquid crystal phases are rather sparse. Hence it is of interest to calculate ΔV for the substances studied. From the initial linear portion of the pressure-temperature diagrams, dT/dP at one bar for the various transitions have been calculated. Using these values and the ΔH values given in Table 7.1, ΔV at one bar has been evaluated. These are tabulated in table 7.4.

It is to be noted that in smectic C - nematic

transition in $\bar{7}S5$ and in smectic A - nematic transition in $\bar{8}S5$ change in the volume associated during the transition is very small. In fact, volume change associated with smectic C - nematic transition in $\bar{7}S5$ is perhaps the lowest observed so far for this transition.

Table 71

Transition temperatures and heats of transition of
 $\bar{7}S5$ and $\bar{8}S5$

S.No.	Compound	Transition	Transition temperature °C	Heats of Transition ΔH in kJ/mole
1	$\bar{7}S5$	K - N	54.5	29.47
		N - I	83.0	1.08
		N - C	(36)	0.26
2	$\bar{8}S5$	K - A	59.0	34.68
		A - N	63.0	0.09
		N - I	86.5	1 e30
		A - C	(55.5) ^a	~0
		C - S _{mos}	(31)	2.89

^aby optical microscopy

() monotropic transition

K - solid, A - smectic A, C - smectic C,

S_{mos} - Smectic (mosaic), N - nematic, I - isotropic

TABLE 7.2

Transition temperatures of the binary mixtures of
 $\bar{7}\text{S5}$ and $\bar{8}\text{S5}$

Sl. No.	Molar concentration of $\bar{7}\text{S5}$ in $\bar{8}\text{S5}$	Transition	Transition temperatures °C
1	34%	$\text{S}_\text{C} - \text{S}_\text{A}$	52.0
		$\text{S}_\text{A} - \text{N}$	53.0
2	40%	$\text{S}_\text{C} - \text{S}_\text{A}$	48.0
		$\text{S}_\text{A} - \text{N}$	48.5
3	45%	$\text{K} - \text{S}_\text{C}$	46.4
		$\text{S}_\text{C} - \text{N}$	49.0

Table 7.3

Constants A and B of the polynomial eqn. $T_p = T_o + AP - BP^2$

Sl. No.	Compound	Transition	A (kbar)	B (kbar ²)	RMS error δ_c
1	$\bar{7}S5$	K - N	25.90	1.63	± 0.54
		N - I	42.87	6.72	± 0.53
		N - C	17.77	0.74	± 0.52
2	$\bar{8}S5$	K - A	26.72	3.10	± 0.48
		A - N	23.22	0.52	± 0.54
		N - I	43.23	12.25	± 0.51
		A - C	14.01	0.69	± 0.48
		C - S _{mos}	17.06	0.21	± 0.36
3	35% mole fraction of $\bar{7}S5$ in $\bar{8}S5$	C - A	16.36	0.016	± 0.46
		A - N	19.21	0.26	± 0.52
4	40% mole fraction of $\bar{7}S5$ in $\bar{8}S5$	C - A	15.99	0.028	± 0.51
		A - N	19.64	0.015	± 0.50
5	45% mole fraction of $\bar{7}S5$ in $\bar{8}S5$	K - C	27.33	3.11	± 0.40
		C - N	15.91	0.185	± 0.35

Table 7.4 $(dT/dP)_{1\text{bar}}$ and volume change (ΔV) at transition

Sl.No.	Compound	Transition	$(dT/dP)_{1\text{bar}}$ °C/kbar	$\Delta V \times 10^{-4}$ cc/gm
1	$\bar{7}\text{S5}$	K - N	25.90	585.6
		N - I	42.87	32.67
		N - C	17.77	3.0
2	$\bar{8}\text{S5}$	K - A	26.70	569.2
		A - N	23.20	1.50
		N - I	43.20	37.91
		A - C	14.0	~0
		C - S _{mos}	17.06	39.20

Table 75

Transition temperatures of $\bar{7}S5$ as a function of
pressure

Set I

Sl. No.	Pressure in kbar	Transition temperatures °C			
		Heating		Cooling	
		S - N	N - I	N - S ₀	S ₀ - crystal
1	room pressure	54.5	83	36	31
2	0.10	—	89.68	—	33.89
3	0.21	60.3	93.17	40.42	34.9
4	0.31	63.28	96.27	41.68	36.41
5	0.41	65.52	100.9	43.44	39.67
6	0.52	68.26	103.38	45.19	42.18
7	0.62	69.75	106.37	46.96	43.2
8	0.72	71.75	110.61	48.46	45.95
9	0.9	75.23	113.35	49.72	47.45
10	0.93	77.48	116.39	51.48	49.47
11	1.04	79.47	119.58	53.09	50.7
12	1.14	81.71	122.32	55.5	52.53
13	1.24	84.45	125.81	56.75	55.00
14	1.35	86.69	128.55	58.76	56.74
15	1.45	88.68	131.29	60.52	59.5
16	1.55	90.18	134.03	61.77	61.72
17	1.66	92.67	—	—	63.28
18	1.76	94.67	—	—	65.28
19	1.87	97.16	—	—	67.3
20	1.97	99.4	—	—	68.5
21	2.07	101.39	—	—	69.81

Table 7.5

**Transition temperatures of $\bar{7}S5$ as a function of pressure
Set II**

Sl. No.	Pressure in kbar	Transition temperatures			
		Heating		Cooling	
		S - N	N - I	N - S_C	S_C - Crystal
1	room pressure	54.5	83	36	31
2	0.10	58.36	89.28	39.42	33.89
3	0.21	60.35	92.27	40.42	35.40
4	0.31	62.6	95.77	41.68	36.91
5	0.42	65.1	99.51	43.94	39.9
6	0.52	67.6	103.05	45.45	42.18
7	0.62	70.0	106.5	46.46	43.19
8	0.72	72.3	109.98	48.71	45.7
9	0.90	74.3	113.22	50.47	47.71
10	0.93	76.56	115.72	51.98	49.47
11	1.04	79.3	118.96	52.98	50.73
12	1.14	81.0	-	55.0	52.98
13	1.24	83.3	-	56.5	54.99
14	1.25	85.5	-	58.01	56.5
15	1.45	87.3	-	60.02	59.26
16	1.55	89.78	-	61.53	61.52
17	1.66	92.0	-	-	63.03
18	1.76	94.8	-	-	65.29
19	1.87	97.0	-	-	67.8

Table 7.6

**Transition temperatures of $\bar{8}85$ as function of pressure
Set I**

Sl. No.	Pressure in kbar	Transition temperatures				
		Heating			Cooling	
		S - S _A	S _A - N	N - I	S _A - S _C	S _C - S _{mos}
1	room pr.	59	63	86.5	55.3	31
2	0.10	61.38	65.59	91.49	52.23	31.13
3	0.17	63.25	67.22	94.29	53.5	34.4
4	0.31	66.75	71.08	98.96	55.24	36.4
5	0.45	68.85	73.82	103.16	56.75	38.67
6	0.57	73.05	77.06	107.13	58.76	41.68
7	0.72	78.42	79.92	111.57	60.53	43.45
8	0.86	81.46	83.42	-	62.04	45.45
9	1.00	84.72	86.16	118.33	63.56	47.21
10	1.14	87.06	88.79	120.90	65.00	50.73
11	1.29	88.43	92.03	-	66.55	53.24
12	1.41	92.66	94.79		68.57	55.00
13	1.55	94.21	98.2		70.32	57.51
14	1.69	95.93	101.03		71.83	59.52
15	1.82	97.56	103.63		73.84	-
16	1.97	98.96	106.26		74.59	64.03
17	2.10	102.23	109.46		76.85	65.8
18	2.24	104.56	112.03		78.36	68.31
19	2.38	106.66	115.03		79.86	71.31
20	2.52	110.16	117.93		81.88	73.1
21	2.66	114.83	121.3		82.90	74.6
22	2.79	116.93	124.64		85.14	77.86
23	3.04	119.5	129.6		86.5	81.37
24	3.17	121.6			88.5	83.9
25	3.31	123.93	134.57		90.5	86.5

TABLE 7.6

Transition temperatures of $\bar{S}S5$ as function of pressure
Set II

Sl. No.	Pressure in mkbar	Transition temperatures ($^{\circ}C$)				
		Heating			Cooling	
		$S - S_A$	$S_A - N$	$N - I$	$S_A - S_C$	$S_C - S_{mos}$
1	room pr.	59.	63	86.5	55.3	31
2	0.10	61.38	65.35	91.60	52.23	33.13
3	0.21	65.59	69.02	95.5		34.65
4	0.31	67.69	70.95	99.1	54.99	36.16
5	0.41	70.02	72.82	102.15	56.00	37.91
6	0.52	72.35	75.06	104.93	57.75	39.67
7	0.62	74.00	77.52	108.1	58.75	41.93
8	0.72	76.56	79.12	111.43	60.76	42.69
9	0.83	77.2	82.06	114.32	61.53	44.7
10	0.93	82.39	84.02		63.28	46.96
11	1.04	83.66	86.29		64.03	49.22
12	1.14	86.12	87.06		64.84	50.47
13	1.24	87.76	90.96		66.05	51.98
14	1.35	88.70	92.93		67.20	53.70
15	1.45	89.63	95.33		69.06	55.25
16	1.55	91.49	98.16		70.31	56.75
17	1.66	94.06	100.22		71.1	58.27
18	1.76	95.93	102.06		73.5	59.77
19	1.86	98.26	104.56		74.08	61.83
20	1.97	99.9	106.43		75.34	63.78
21	2.07	101.0	109.0		76.1	65.30
22	2.17	102.7	111.0		77.59	67.55
23	2.28	104.33	113.0		78.36	68.31
24	2.39	105.03	115.47		79.86	71.00

Table 7.7

Transition temperatures of mixture of $\bar{7}S5$ (34% mole fraction) in $\bar{8}S5$ as function of pressure

Sl. No.	Pressure in kbar	Transition temperature °C	
		$S_G - S_A$	$S_A - N$
1	room pressure	52.0	53
2	0.10	54.15	55.82
3	0.21	54.27	57.18
4	0.31	55.67	58.58
5	0.41	58.12	61.63
6	0.55	60.92	64.42
7	0.69	63.00	66.87
8	0.83	65.59	69.90
9	0.97	67.72	72.00
10	1.10	69.32	74.57
11	1.24	71.89	77.61
12	1.38	73.17	80.17
13	1.73	78.77	87.29
14	2.07	86.12	94.41

Table 7.8

Transition temperatures of mixture of $\bar{7}S5$
(40% mole fraction) in $\bar{8}S5$ as function of
pressure

Sl. No.	Pressure in kbar	Transition temperatures (°C)	
		$S_C - S_A$	$S_A - \text{Nematic}$
1	room pressure	48.00	48.5
2	0.07	49.42	50.23
3	0.21	50.53	52.51
4	0.35	53.33	55.31
5	0.48	55.43	57.65
6	0.62	57.8	60.6
7	0.76	60.6	63.25
8	0.9	62.66	66.52
9	1.03	64.65	68.73
10	1.17	66.52	71.09
11	1.31	68.68	73.98
12	1.45	71.28	76.6
13	1.59	73.52	78.77
14	1.93	78.88	85.89
15	2.27	84.37	93.13
16	2.41	85.89	95.22

Table 7.9

Transition temperatures of mixture of $\bar{7}S5$ (45% mole fraction) in $\bar{8}S5$ as function of pressure

Sl. No.	Pressure in kbar	Transition temperatures (°C)	
		Solid - S_C	S_C - Nematic
1	room pressure	46.4	49
2	0.069	48.0	52.45
3	0.14	50.5	53.46
4	0.28		54.96
5	0.35	56.13	55.22
6	0.41	58.35	57.22
7	0.55	60.92	57.73
8	0.69	63.86	60.39
9	0.83	66.61	62.35
10	0.9	68.46	63.00
11	1.04	70.95	65.52
12	1.10	71.84	66.77
13	1.17	72.63	67.95
14	1.24	74.66	68.03
15	1.38	77.16	71.29

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