Liquid-Liquid-Vapor Equilibria in Binary Families of SF_6, $CClF_3$, $C_2H_3F_3$ and C_2H_4 with n-alkanes [1]

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ABSTRACT

Liquid-liquid-vapor equilibria were determined experimentally for binary and quasi-binary systems of chlorotrifluormethane, and sulfur hexafluoride, 1,1,1-trifluoroethane, chlorotrifluormethane, and ethene with n-alkanes or mixtures of n-alkanes, respectively. From the location of the critical endpoints L_2=L_1+V and L_2+L_1=V of the three-phase curves, the coordinates of the tricritical point and the double critical endpoint of these families were estimated by extrapolation.

KEY WORDS: classification of fluid phase behavior, double critical endpoint, liquid-liquid-vapor equilibria; tricritical point

1. INTRODUCTION

Binary mixtures, consisting of a more volatile component like carbon dioxide, ethane or nitrous oxide and a low-volatile component like a long chain n-alkane, may exhibit liquid-liquid immiscibility phenomena extended at low and/or at high (near the critical point of the more voatile component) temperature regions [1]. These systems can be classified according according to the classification of van Konynenburg and Scott [2] as types II, III, IV, or V. A family of binary mixtures where the less-volatile component is changing systematically as a member of the same homologous series, like the n-alkanes, and even continously by appropiate mixing of two successive members of the same homologous series (quasi-binary mixtures), offers the possibility of a methodical study of the transitions between these types of fluid phase behavior.

In Fig. 1 the transition from type II to type IV is illustrated. Type II shows in the P,T-projection a low-temperature region of liquid-liquid equilibria, which is restricted to high temperature by a liquid-liquid critical curve and at low pressure by a three-phase curve liquid-liquid-vapor. These two curves intersect in the upper critical end point (UCEP) $L_2=L_1+V$ of the three-phase curve. The vapor-liquid critical is a continous curve between the critical points of the two pure components. In type IV the same low temperature region of liquid-liquid equilibria is found, but this type shows at high temperature a second region of liquid-liquid immiscibility which is bounded at low-pressure by a second branch of the three-phase curve liquid-liquid-vapor. The vapor-liquid critical curve is broken into two parts. The first part ($L_1=V$) starts in the critical point of the more-volatile component and intersects the high temperature branch of the three-phase curve in an UCEP $L_2+L_1=V$. The second part starts in the critical point of the low-volatile component and intersects the high temperature branch of the three-phase curve in a lower critical endpoint (LCEP) $L_2=L_1+V$. At low temperature this branch of the critical curve is a liquid-liquid critical curve, but its changes at high temperature gradually into a vapour-liquid critical curve. The transition between these two types of fluid phase behavior occurs via a so-called tricritical point TCP $L_2=L_1=V$, where the

LCEP and the UCEP of the high-temperature branch of the three-phase curve coincide and the three-phase curve has a zero length. Transitions between type V and type I fluid phase behavior are similar. In these types the low temperature region of liquid-liquid equilibria is missing.

The transition between type IV and type III of fluid phase behaviour is illustrated in Fig. 2. In type III the low-temperature branch and the high-temperature branch of the liquid-liquid-vapour curve are merged into one three-phase curve and also the two liquid-liquid critical curves found in type IV are joined. The transition occurs via a so-called double critical endpoint DCEP, where the UCEP of the low-temperature branch of the three-phase curve coincides with the LCEP of the high-temperature branch of this curve. The liquid-liquid critical curve is tangent to the three-phase curve in the DCEP.

In the binary families of, nitrous oxide [3], ammonia [4] and perfluoromethane [5,6] with members of the homologeous series of the n-alkanes transitions from type II to type III phase behaviour are found with increasing carbon number of the n-alkane. According to the calculations of van Konynenburg and Scott these transitions occur via the intermediate type IV, as has actually been found in the family of carbon dioxide + n-alkanes [7,8]. For a binary system the number of degrees of freedom according to the phase rule is negative in a TCP or a DCEP. This implies that it is very unlikely to find a TCP or a DCEP in a binary system. Creek et al. [9] and Goh et al. [10] have shown that the TCP can be approached very closely by studying quasi-binary systems; systems of the light component and a pseudo-component prepared by mixing of two nearest neighbours of the n-alkane series.

Investigations of this kind are important in chemical industry, e.g. in supercritical fluid technology, where the most commonly used supercritical solvent is carbon dioxide. In this paper experimental results are presented for the families of ethene (C_2H_4), chlorotrifluormethane ($CClF_3$), 1,1,1-trifluoroethane ($C_2H_3F_3$) and sulfur hexafluoride (SF_6) with n-alkanes.

2. MEASUREMENTS

2.1. Specimens

Details concerning the deliverer and the purity of the chemicals used are given in Table I. To check the purity of the gases the vapor pressure was determined experimentally and compared with literature data [11-14]. The vapor pressure of the gases used by us agreed within the experimental uncertainty with the literature data.

2.2. Procedure

The measurements were carried out in a glass-tube apparatus for use with pressures up to 15 MPa and temperatures up to 530 K described earlier by de Loos et al. [15]. With this so-called Cailletet apparatus phase envelopes of mixtures of known composition and monovariant multi-phase equilibria could be determined visually. A sample of the mixture with known composition was present in a narrow glass tube, mounted in a thermostat with circulating water or a circulating (water + alcohol) mixture, which maintained a constant temperature within 0.02 K. Mercury was used as a pressure intermediate between the sample and the oil in the pressure generating system. The temperature was measured with a 100 Ω platinum resistance thermometer (ASL F-16), calibrated against a standard thermometer. The uncertainty in the measured temperature was approximately 0.02 K. The pressure was measured with a dead-weight gauge (de Wit) with an accuracy within 2 kPa.

The mixtures are prepared by dosing the low-volatile liquid component or the mixture of two low-volatile liquid components in the sealed end of the Cailletet tube by means of a micrometer syringe. The exact mass of the liquid is determined by weighing. The liquid is thoroughly degassed by successive freezing and melting under high vaccuum. The gaseous component is added gas-volumetrically using a mercury displacement method [16].

For the measurement of the liquid-liquid-vapor equilibrium pressures the volume of the sample is adjusted until the three-phase equilibrium state is observed visually. In the case of experiments on quasi-binary systems, no variation of the three-phase equilibrium pressure could be observed within the experimental uncertainty when the

volume was varied in the interval in which the three-phase equilibrium is stable. In a L_2+L_1=V critical endpoint the three-phase curve ends in a point in which the top phase and the middle phase are critical and in L_2=L_1 +V critical endpoint the liquid-liquid-vapor curve ends in a point where the bottom phase and the middle phase are critical. The uncertainty in the experimental critical endpoint temperature is 0.02 K.

3. RESULTS AND DISCUSSION

In Fig. 3 the liquid-liquid-vapor three-phase pressure of the binary systems SF_6 + octane and SF_6 + nonane is presented as a function of temperature. The three-phase curve of SF_6 + octane ends in a UCEP L_2=L_1 +V, so this binary system is a type II system. The three-phase curve of SF_6 + nonane ends in an UCEP L_2+L_1=V and goes uninterrupted to low temperature. So this binary system is a type III system. To study the transition from type II to type III the phase behaviour of quasi-binary systems of SF_6 and pseudo-components composed of a mixture of octane and nonane was studied. The experimental three-phase curve for SF_6 and a mixture of octane and nonane with an average carbon number *n* of 8.5379 is also plotted in Fig. 3. This curve shows a low-temperature branch ending in an UCEP L_2=L_1 +V and a high-temperature branch starting in a LCEP L_2=L_1 +V and ending in an UCEP L_2+L_1=V. So this quasi-binary system is a type IV system. The coordinates of the critical endpoints of this and other quasi-binary mixtures are presented in Table II and plotted in Fig. 4. Although the quasi-binary systems are in fact ternary systems and for this reason these systems should show a three-phase region in stead of a three-phase curve, it was found experimentally that the width of the three-phase region could not be measured within the experimental uncertainty. This proves that the quasi-binary systems can be treated as binary system.

Figure 4 shows the transition from type II to type III via type IV phase behaviour. The same pattern was found for the familily of carbon dioxide + n-alkanes, although in this family type IV fluid phase behavior is found in a real binary system: carbon dioxide + tridecane [7, 8]. At low carbon numbers between 8 and 8.44 only an UCEP L_2=L_1 +V is found (type II phase behaviour). At carbon numbers between 8.44 and 8.55 an UCEP

L_2=L_1 +V, a LCEP L_2=L_1 +V and an UCEP L_2+L_1 =V is found (type IV phase behaviour) and at higher carbon numbers only an UCEP L_2+L_1 =V is found (type III phase behaviour). The tricritical point is found where the LCEP L_2=L_1 +V curve meets the UCEP L_2+L_1 =V curve in a beak-point. The double critical endpoint is found where the UCEP L_2=L_1 +V curve and the LCEP L_2=L_1 +V curve meet in a maximum in average carbon number. We have fitted the curve through the UCEP's and the LCEP's L_2=L_1 +V with a function of the form

$$\left(n - n_{DCEP}\right) = k(T - T_{DCEP})^2 \qquad (1)$$

It was found that this function describes the data very well. From this fit the coordinates of the DCEP were found: n_{DCEP} = 8.55 and T_{DCEP} = 335.4 K. The coordinates of the tricritical point were determined using the classical theory of tricritical points of Grittiths [17] and Scott[18], using the quasi-binary approximation [9, 10]. According to this theory the following two expressions should hold close to the tricritical point

$$\Delta T = T_{UCEP} - T_{LCEP} = 2 j_2 \left(n - n_{TCP}\right)^{3/2} \qquad (2)$$

$$T_m = \left(T_{UCEP} + T_{LCEP}\right)/2 = T_{TCP} + j_1 \left(n - n_{TCP}\right) \qquad (3)$$

The amplitudes j_1 and j_2 are system dependent constants. The carbon number in the tricritical point n_{TCP} is found from a plot of $(\Delta T)^{2/3}$ as a function of n by extrapolation to $(\Delta T)^{2/3}$ = 0, as shown in Fig. 5. The experimental points are found on a straigth line as predicted by Eq.(2). The tricritical temperature T_{TCP} is found from a plot of T_m as a function of n by extrapolationg to $n = n_{TCP}$, see Fig. 6. Again a straigth line is found as predicted from Eq.(3). We found n_{TCP} = 8.442 and T_{TCP} = 347.2 K.

The family of $C_2H_3F_3$ + n-alkanes shows the same behaviour as the family of SF_6 + n-alkanes. $C_2H_3F_3$ + undecane is a type II system, $C_2H_3F_3$ + dodecane a type IV system

and $C_2H_3F_3$ + tridecane a type III system. In table III and Fig.7 the coordinates of the critical endpoints of quasi-binary systems of $C_2H_3F_3$ + [undecane + dodecane] and $C_2H_3F_3$ + [dodecane +tridecane] are presented as function of the average carbon number of the n-alkane mixture. In this family the DCEP is found at n_{DCEP} = 12.13 and T_{DCEP} = 347.0 K and the TCP at n_{TCP} = 11.647 and T_{TCP} = 368.9 K.

In Table IV the coordinates of the critical endpoints of the liquid-liquid-vapor equilibria in the $CClF_3$ + n-alkane family are presented. The system $CClF_3$ + tridecane is a type III system. For the system $CClF_3$ + dodecane only a LCEP L_2=L_1 +V and an UCEP L_2+L_1=V are found. Based on this one would conclude that this system is a type V system. However Fig. 8, in which the critical endpoints of quasi-binary systems of $CClF_3$ + [undecane + dodecane] and of $CClF_3$ + [dodecane + tridecane] are plotted shows the same trends as Figs. 4 and 7. The open squares in Fig. 8 represent quadruple points solid-liquid-liquid-vapor, in which the low temperature branch of the liquid-liquid-vapor curve ends at low pressure. The data on which this figure are based are presented in Table IV and V. For this family we find n_{DCEP} = *12.54* and T_{DCEP} = 280.6 K and n_{TCP} = 11.353 and T_{TCP} = 319.8 K. Figure 8 clearly shows that the observation of the low temperature branch of the liquid-liquid-vapor curve for the binary system $CClF_3$ + dodecane is prevented by the occurrence of a solid phase and that $CClF_3$ + dodecane is basically a type IV system.

In Fig. 9 the temperature of the LCEP L_2=L_1 +V and the UCEP L_2+L_1=V of binary ethene + n-alkane systems are plotted. The liquid-liquid-vapor pressure as a function of temperature for these systems is given in Table VI. In this family no liquid-liquid-vapor equilibria are found for ethene + tridecane. The systems of ethene +n-alkanes with carbon numbers 14-17 show type V phase behavior. However in view of the experimental findings for the family $CClF_3$ + n-alkanes it is possible and even likely that also in this family the low temperature branch of the liquid-liquid-vapor curve is hidden below the solidification surface and that these systems are really type IV systems. In the system ethene +octadecane no LCEP L_2=L_1 +V is found because of solidification

of solid octadecane. In the system ethene +eicosane the complete liquid-liquid-vapor curve is hidden below the solidification surface, as was shown by Gregorowicz et al. [19]. For this family we find n_{TCP} = 13.93 and T_{TCP} = 291.0 K. The liquid-liquid-vapor curve in the system ethene + tetradecane is only 0.04 K long. So this binary system is very close to tricriticality.

4. CONCLUSIONS

Our experimental findings on the fluid phase behaviour of families of low-volatile components and n-alkanes support the idea that with increasing carbon number of the n-alkane practically always a transition from type II to type IV to type III fluid phase behaviour found. The only exception is maybe the family of water + n-alkanes [20]. However the occurrence of solid phases often prevent to observe the real type of fluid phase behavior.

REFERENCES

1. C.J. Peters, in *Supercritical Fluids, Fundamentals for Application,* E.Kiran and J.M.H. Levelt Sengers, eds. (Kluwer, Dordrecht, 1994), p.117.
2. P.H. van Konynenburg, and R.L. Scott, *Phil. Trans. Roy. Soc. London Ser.A* **298**:495 (1980)
3. A. Jangkamolkulchai, D.H. Lam, and K.D. Luks, *Fluid Phase Equilib.* **50**: 175 (1989).
4. E. Brunner, *J. Chem. Thermodyn.* **20**: 273 (1988).
5. M. Wirths, and G.M. Schneider, *Fluid Phase Equilib.* **15**: 257 (1985).
6. Th.W. de loos, W. Poot, and J. de Swaan Arons, *J. Chem. Thermodyn.* **21**:113 (1989).
7. R. Enick, G.D. Holder, and B.I. Morsi, *Fluid Phase Equilib.* **22**:209 (1985).
8. D.J. Fall, and K.D. Luks, *J. Chem. Eng. Data* **30**:276 (1985).
9. J.L. Creek, C.M. Knobler, and R.L. Scott, *J. Chem. Phys.* **74**:3489 (1981).
10. M.C. Goh, J. Specovius, R.L. Scott, and C.M. Knobler, *J. Chem. Phys.* **86**:4120 (1987).
11. H.P. Clegg , J.S. Rowlinson, and J.R. Sutton, *Trans. Farad. Soc.* **51**:1327 (1955).
12. J.V. Widiatmo, H. Sato, and K. Watanabe, *Int. Journal of Thermophysics* **16**: 801 (1995)
13. E. Fernandez-Fassnacht, and F. del Rio, *Cryogenics* **25**: 204 (1985).
14. R.T. Jacobsen, M. Janhangiri, R.B. Stewart, R.D. McCarty, J.M.H. Levelt Sengers, H.J. White, J.V. Sengers, and G.A. Olchowy, Ethylene, International Thermodynamic Tables of the Fluid state 10 (Blackwell, Oxford, 1988).
15. Th.W. de Loos, H.J. van der Kooi, and P.L. Ott, *J. Chem. Eng. Data* **34**: 166 (1986).
16. D. Stamoulis, Patterns of Fluid Phase Behaviour in Binary and Quasi-binary Mixtures, PhD Thesis (Delft University of Technology, Delft, 1994).

17. R.B. Griffiths, *J. Chem. Phys.* **60**:195 (1974).

18. R.L. Scott, *J. Chem. Phys.* **86**:4106 (1987).

19. J. Gregorowicz, Th.W. de Loos and J. de Swaan Arons, *J. Chem. Eng. Data* **38**: 417 (1993).

20. E. Brunner, *J. Chem. Thermodyn.* **22**: 335 (1990).

Table I Chemicals used

compound	origin	purity
ethene	Aga	99.95%
chlorotrifluoromethane	Praxair	99%
1,1,1-trifluoroethane	Intermar	99%
sulfur hexafluoride	Air Products	99.8%
octane	Fluka	99.8%
nonane	Fluka	99.5%
undecane	Fluka	99.5%
dodecane	Merck	99.5%
tridecane	Fluka	99.5%
tetradecane	Fluka	99.5%
pentadecane	Fluka	99.8%
hexadecane	Merck	99.5%
heptadecane	Janssen Chimica	99%
octadecane	Fluka	99%

Table II Temperature and pressure of the critical enpoints in the SF_6 + n-alkane family at given average carbon number *n* of the n-alkane.

	UCEP L_2=L_1+V		LCEP L_2=L_1+V		UCEP L_2 +L_1=V	
n	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)
8	300.67	2.230				
8.4573	322.28	3.460	346.37	5.180	346.60	5.200
8.4653	322.85	3.450	345.94	5.110	346.50	5.140
8.4792	323.92	3.575	345.19	5.115	346.05	5.180
8.4896	324.85	3.640	344.68	5.070	345.83	5.160
8.5103	326.57	3.760	343.30	4.960	345.35	5.125
8.5249	328.27	3.890	341.54	4.840	344.85	5.100
8.5379	330.21	4.015	340.17	4.740	344.61	5.090
8.5437	332.36	4.150	338.10	4.470	344.39	5.060
8.5485					344.27	5.065
8.7504					340.37	4.850
9					337.23	4.675

Table III Temperature and pressure of the critical enpoints in the $C_2H_3F_3$ + n-alkane family at given average carbon number *n* of the n-alkane.

	UCEP L_2=L_1+V		LCEP L_2=L_1+V		UCEP L_2 +L_1=V	
n	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)
10	287.38	0.897				
11	305.89	1.447				
11.6749	322.34	2.112	368.20	5.048	368.38	5.065
11.7498	324.66	2.215	366.63	4.926	367.49	5.002
11.8099	326.54	2.314	365.24	4.825	366.90	4.971
11.8999	329.68	2.477	362.62	4.621	365.90	4.905
11.9501	331.68	2.577	360.99	4.501	365.42	4.876
12	333.77	2.692	359.23	4.363	364.99	4.842
12.040	336.25	2.836	357.05	4.200	364.61	4.820
12.082	339.42	3.023	354.18	3.998	364.25	4.801
12.101	341.25	3.131	n.a.		n.a.	
12.113	343.34	3.259	350.54	3.735	363.91	4.773
12.125					363.84	4.773
12.148					363.56	4.752
12.201					363.15	4.727
12.396					361.52	4.630
12.445					361.28	4.617
13					385.17	4.439

Table IV Temperature and pressure of the critical enpoints in the $CClF_3$ + n-alkane family at given average carbon number *n* of the n-alkane.

	UCEP L_2=L_1+V		LCEP L_2=L_1+V		UCEP L_2 +L_1=V	
n	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)
11.5986			315.10	4.727	316.95	4.912
11.8131			311.32	4.420	315.48	4.815
12			307.36	4.100	314.25	4.735
12.1007	255.17	1.180	304.22	3.940	313.40	4.720
12.2007	258.37	1.280	301.98	3.681	312.97	4.660
12.3751	265.56	1.567	295.46	3.222	312.23	4.597
12.4807	272.44	1.895	290.08	2.860	311.86	4.558

Table V Temperature and pressure of the quadruple point solid-liquid-liquid-vapor in the $CClF_3$ + n-alkane family at given average carbon number *n* of the n-alkane.

n	*T* (K)	*P* (MPa)
12.1007	254.03	1.160
12.2007	251.26	1.052
12.3751	251.10	1.082

Table VI Liquid-liquid-vapor equilibrium pressure in binary ethene + n-alkane systems

T (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)
ethene + tetradecane		ethene + hexadecane		ethene + heptadecane	
290.91	5.885[a]	282.45	4.925[a]	277.67	4.450[a]
290.95	5.890[b]	282.91	4.980	277.81	4.460
		283.26	5.020	278.10	4.490
ethene + pentadecane		283.81	5.085	278.38	4.520
287.06	5.425[a]	284.34	5.150	278.71	4.555
287.40	5.470	284.86	5.210	279.20	4.605
287.62	5.500	285.35	5.270	280.19	4.710
287.96	5.545	285.90	5.335	281.16	4.820
288.19	5.575	286.31	5.385	282.19	4.940
288.43	5.605	286.61	5.425	283.20	5.500
288.62	5.630[b]	286.88	5.460[b]	284.14	5.160
				285.20	5.285
ethene + octadecane				285.69	5.345[b]
282.30	4.962				
283.51	5.102				
284.50	5.220				
284.94	5.272[b]				

[a] LCEP $L_2=L_1+V$

[b] UCEP $L_2+L_1=V$

FIGURE CAPTIONS

Fig. 1. Transition from type II to type IV fluid phase behavior.

Fig. 2. Transition from type IV to type III fluid phase behavior.

Fig. 3. Monovariant equilibria in the SF_6 + n-alkane family. ———— : vapor pressure curve of SF_6, - — - — : liquid-liquid-vapor curve SF_6 + nonane, -------- : liquid-liquid-vapor curve SF_6 + $C_{8.5379}$, ...: liquid-liquid-vapor curve SF_6 + octane. ○: critical point, ▲: UCEP L_2=L_1+V, ▼: LCEP L_2=L_1+V , Δ: UCEP L_2+L_1=V.

Fig. 4. The family of SF_6 + n-alkanes: critical endpoint temperature as a function of the average carbon number *n* of the n-alkane. ▲: UCEP L_2=L_1+V, ▼: LCEP L_2=L_1+V , Δ: UCEP L_2+L_1=V, ●: tricritical point, ■: double ctitical endpoint.

Fig. 5. The family of SF_6 + n-alkanes: $(\Delta T)^{2/3}$ as a function of the average carbon number *n* of the n-alkane.

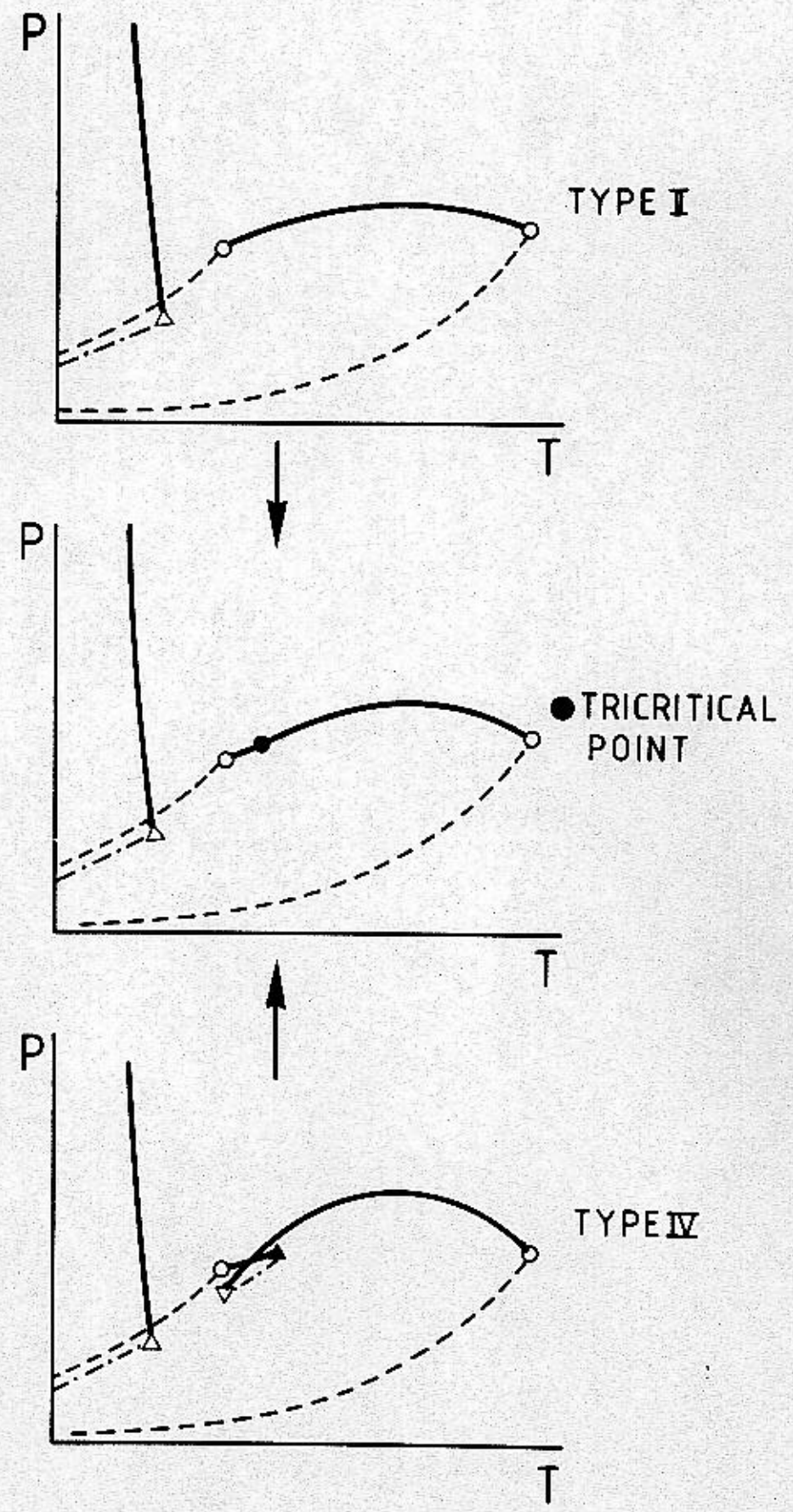
Fig. 6. The family of SF_6 + n-alkanes: T_m as a function of the average carbon number *n* of the n-alkane.

Fig. 7. The family of $C_2H_3F_3$ + n-alkanes: critical endpoint temperature as a function of the average carbon number *n* of the n-alkane. ▲: UCEP L_2=L_1+V, ▼: LCEP L_2=L_1+V , Δ: UCEP L_2+L_1=V, ●: tricritical point, ■: double ctitical endpoint.

Fig. 8. The family of CClF3 + n-alkanes: critical endpoint temperature as a function of the average carbon number *n* of the n-alkane. ▲: UCEP L_2=L_1+V, ▼: LCEP L_2=L_1+V , Δ: UCEP L_2+L_1=V, ●: tricritical point, ■: double ctitical endpoint, □: quadruple point

solid-liquid-liquid-vapor.

Fig. 9. The family of ethene + n-alkanes: critical endpoint temperature as a function of the average carbon number *n* of the n-alkane.▼: LCEP L_2=L_1+V, Δ: UCEP L_2+L_1=V, ●: tricritical point.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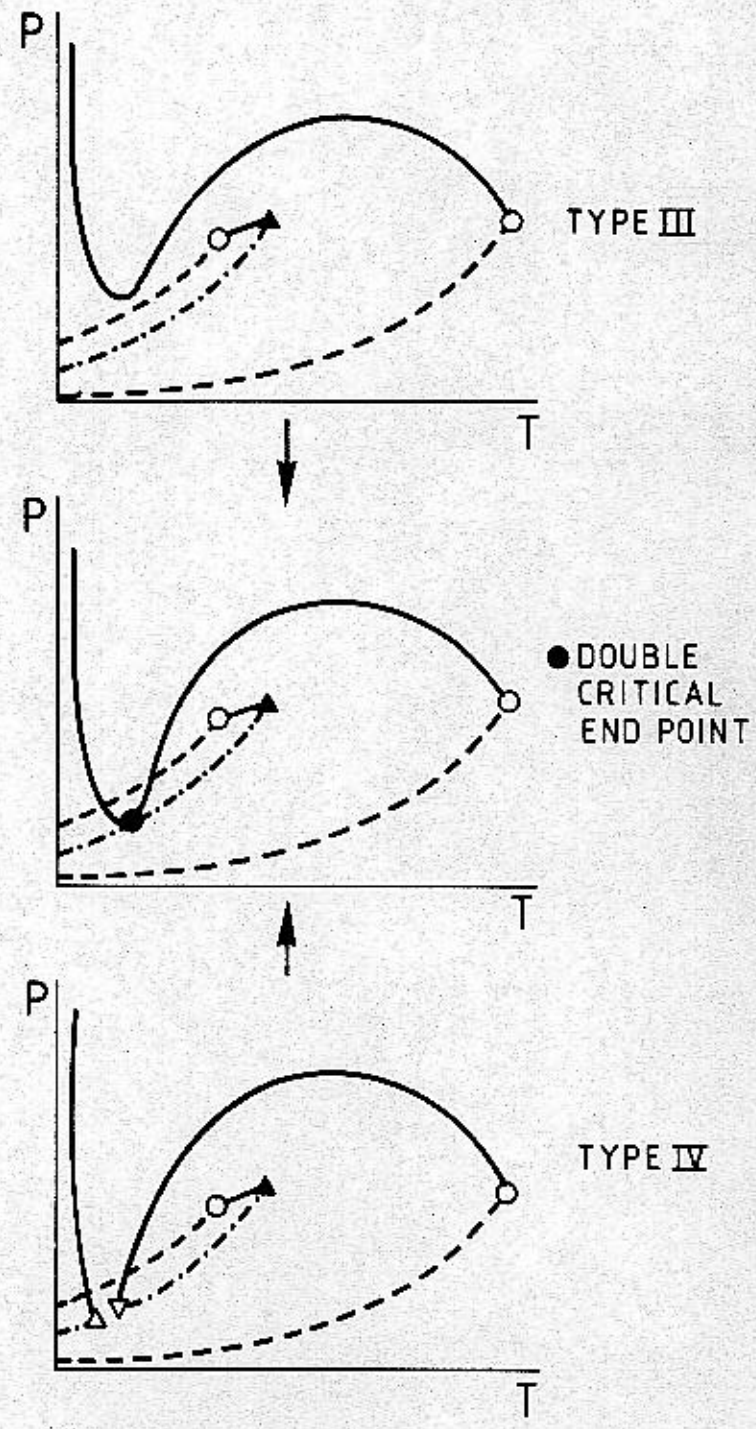
de Loos and Poot
Fig. 2



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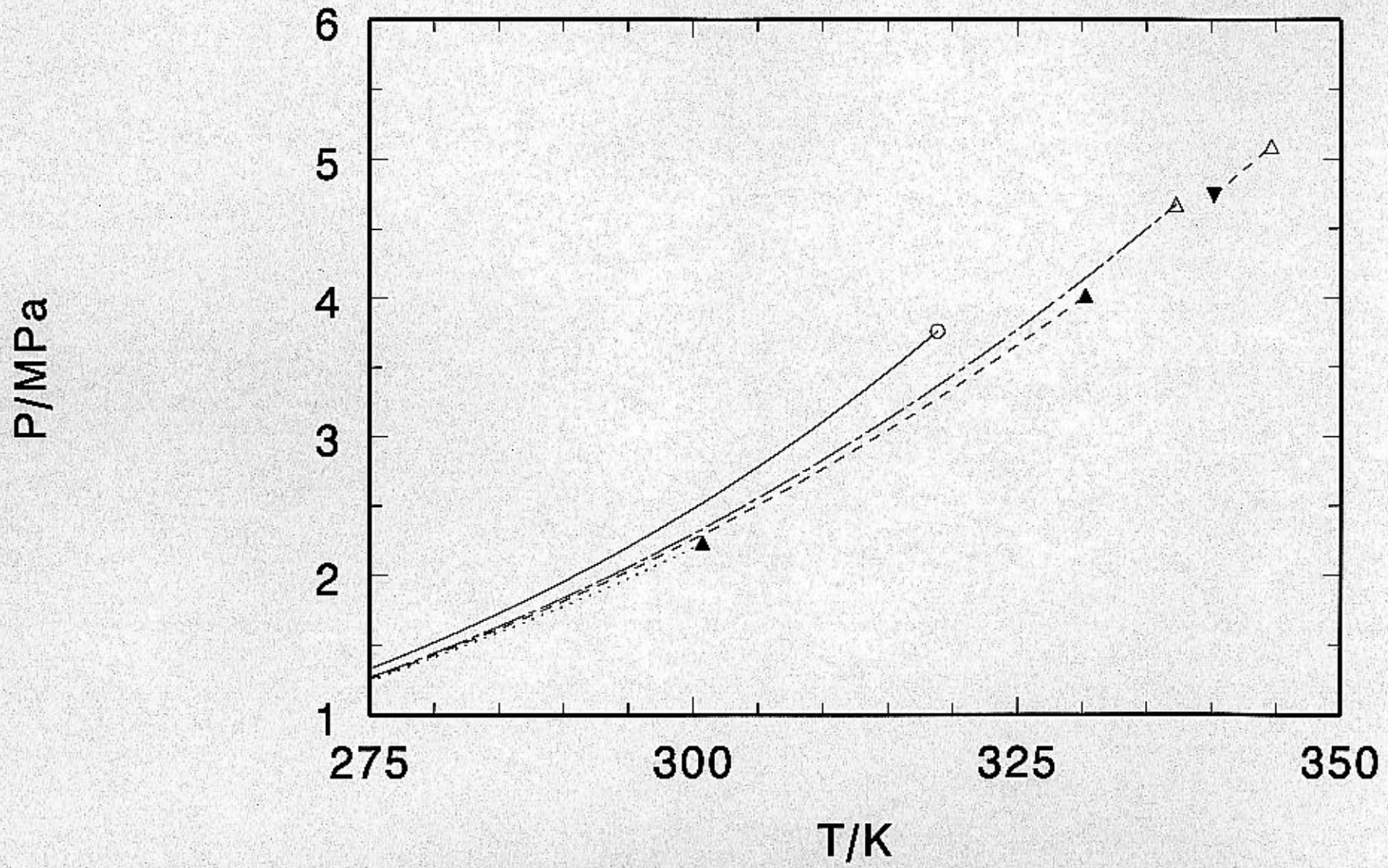

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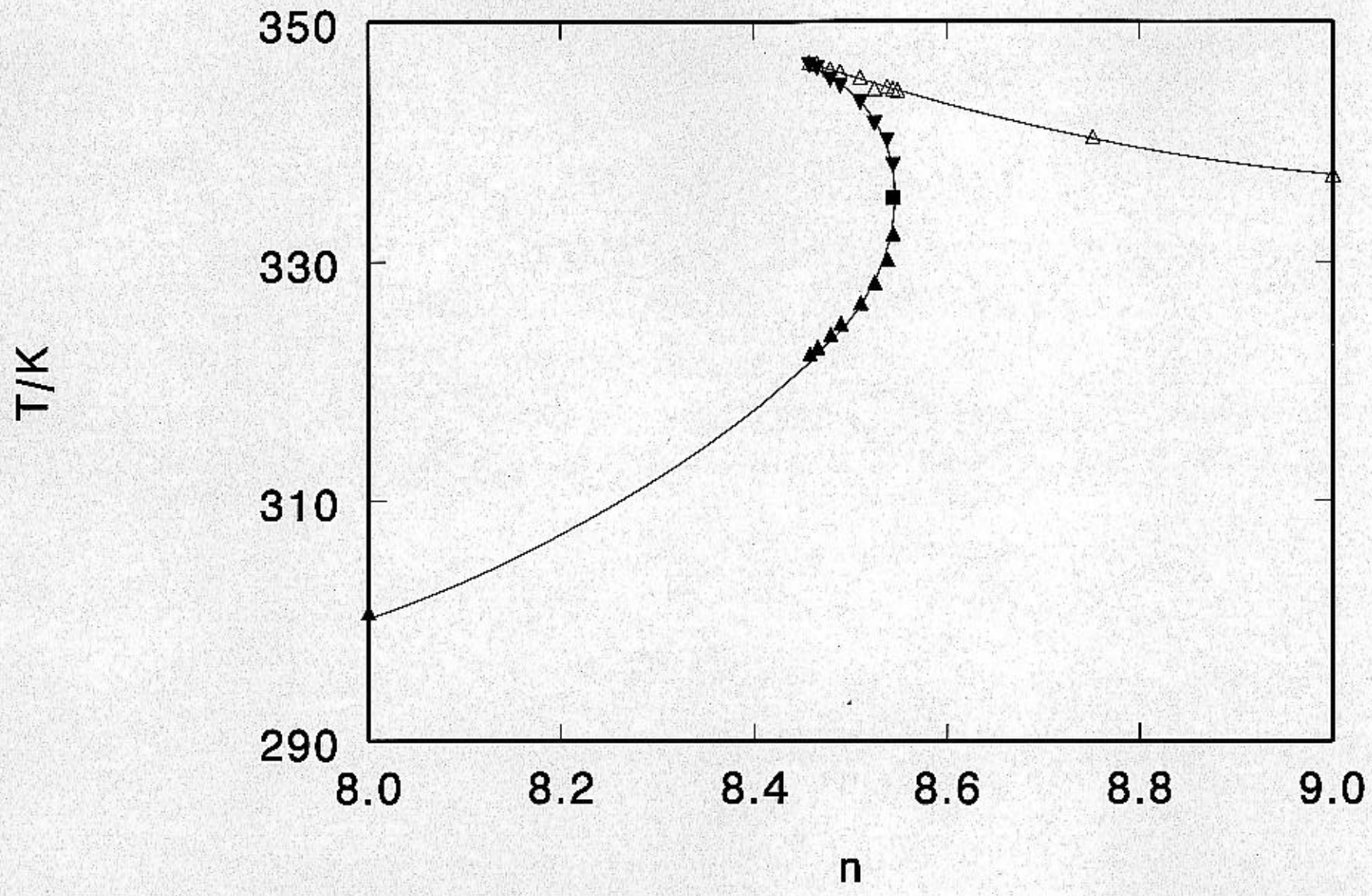
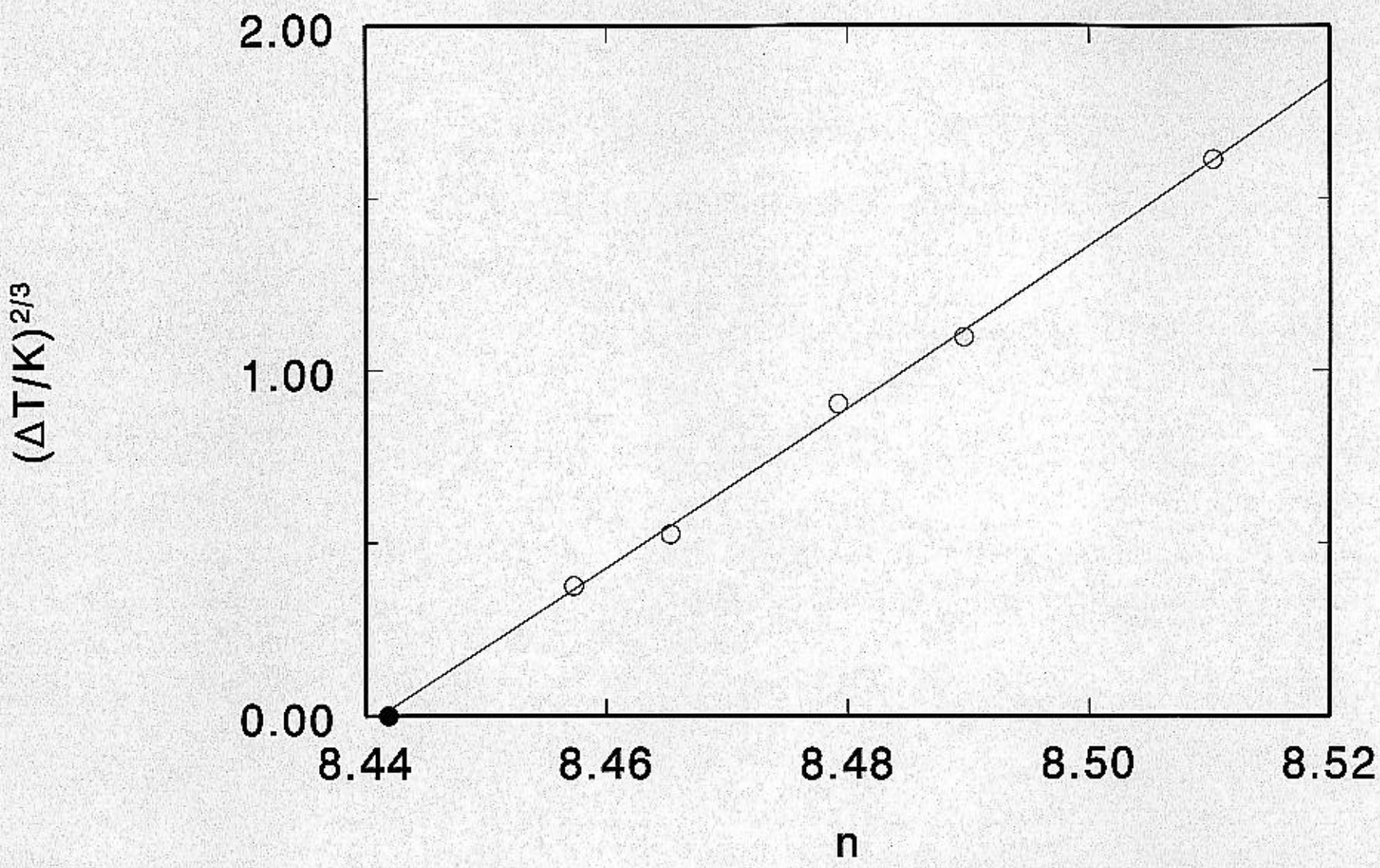
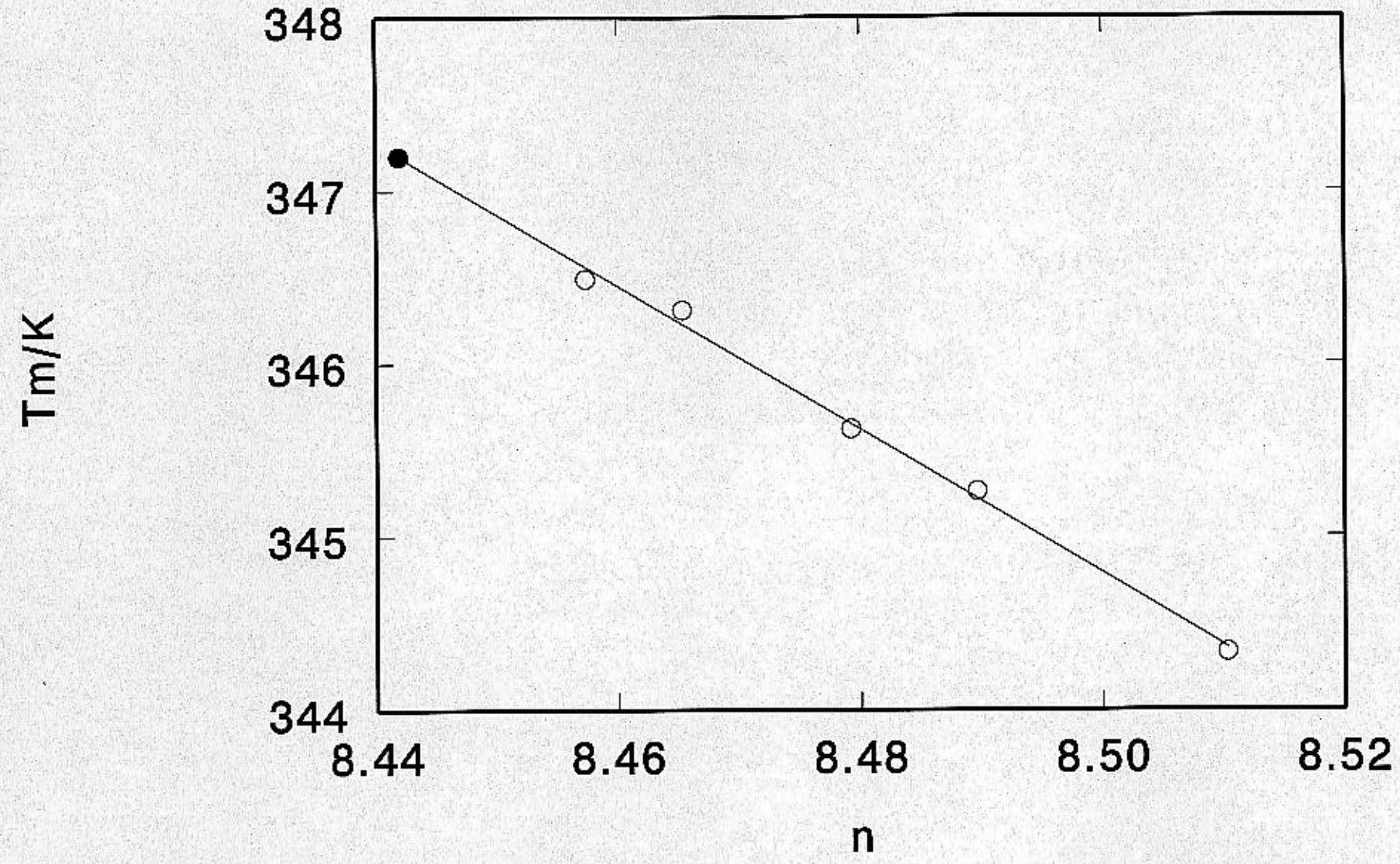
Figure 4



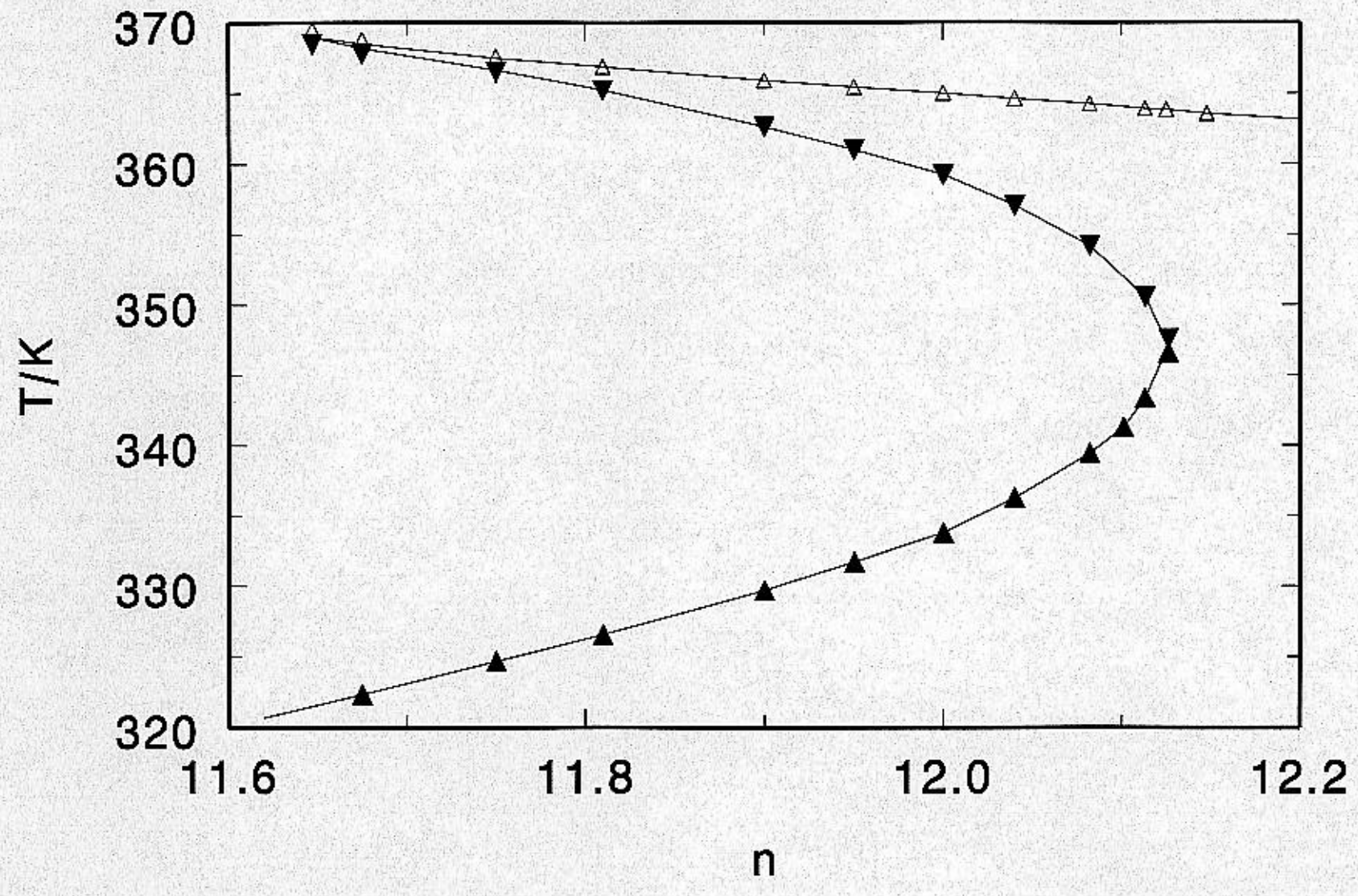
de Loos and Post
Figure 5



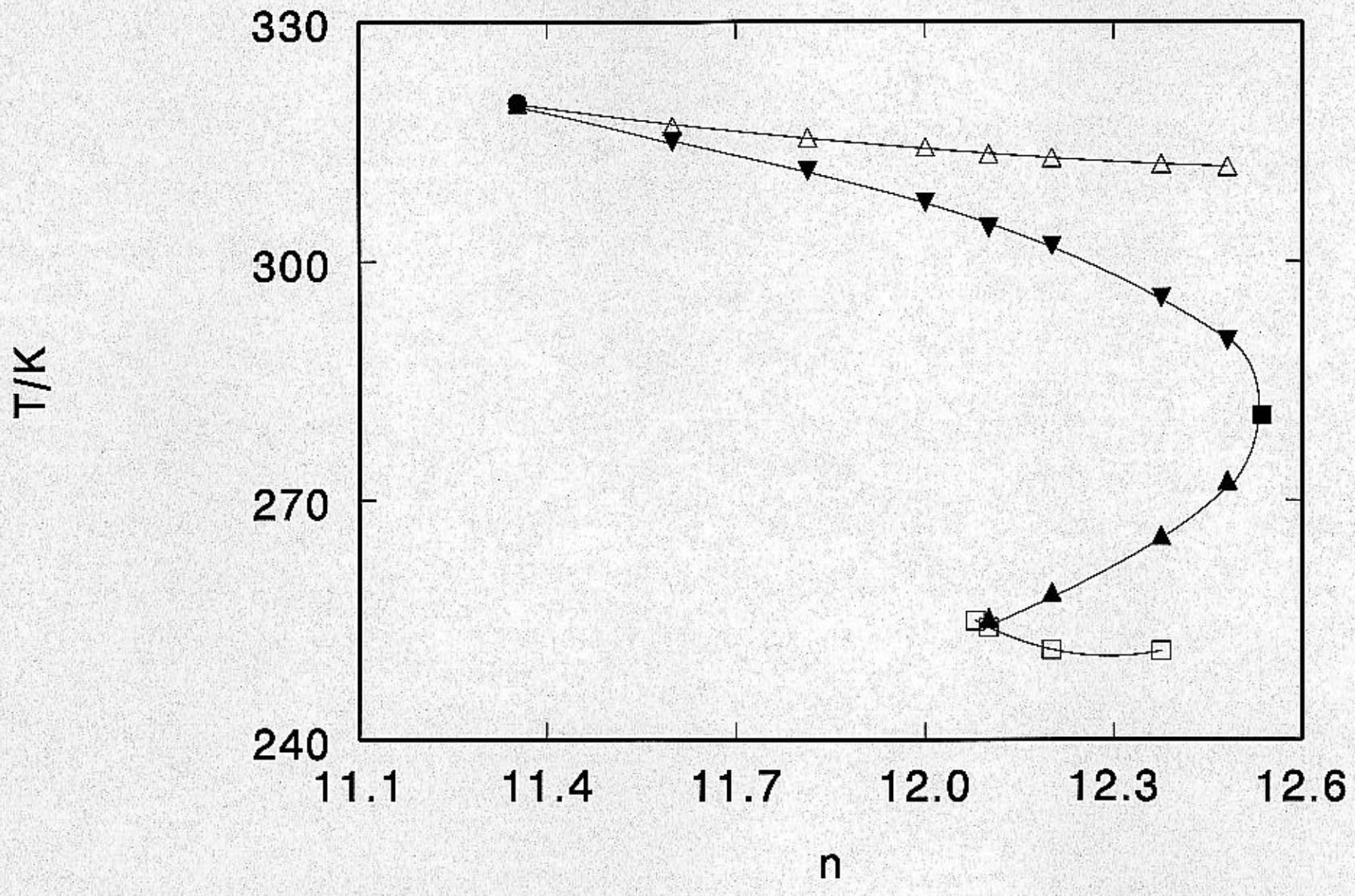
de Loos and Post
Figure 6



de Loos and Peet
Figure 7



de Loos and Poot
Figure 8



de Lous and Post
Figure 9