69-7610

SAPSE, Anne-Marie, 1939-
SOME THEORETICAL PROBLEMS IN STATISTICAL
THERMODYNAMICS OF MIXTURES.

The City University of New York, Ph.D., 1969
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

SOME THEORETICAL PROBLEMS IN STATISTICAL THERMODYNAMICS OF MIXTURES

by

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A dissertation submitted to the
Graduate Faculty in Chemistry in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy,
The City University of New-York.

1968

This manuscript has been read and accepted for the University Committee in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Aknowledgments

I wish to express my deep gratitude to my Thesis Advisor, Professor Charles E. Hecht for his highly intelligent and perceptive guidance and to the committee members for their help.

I also wish to express my gratitude to my husband Marcel Sapse without whose moral support I could not accomplish my work.

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Advisor:
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ABSTRACT

Part 1

An augmented Van der Waals theory for binary mixtures of real fluids

Thermodynamic perturbation theory is applied to a binary mixture of real fluids. The unperturbed case is that of hard cores of diameter σ and the perturbing potential is an attractive square well of depth ε and width 0.5σ. Excess functions of isobaric, isothermic mixing and critical points are calculated for a mixture of hard spheres and hard spheres with tails and for a mixture of points (ideal gas component) and hard spheres with attractive tails. All the hard sphere core are of the same diameter. In the former case, our model exhibits "gas-gas" equilibria.

Part 11

Phase-separation temperatures in solid isotopic mixtures

Phase-separation temperatures for solid isotopic mixtures are calculated taking into account first and second nearest neighbor interactions for simple cubic, body centered and face centered lattices. Application is made to He^3-He^4 and to H_2-D_2.

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Part 1

An augmented Van der Waals theory for binary mixtures of real fluids

Chapter 1

Introduction

It is known experimentally that real gases do not obey the perfect gas law : $PV/NkT = 1$. The deviation of the PV/NkT ratio from 1 varies from gas to gas at any given temperature and pressure. This arises from the fact that the equation of state for an ideal gas being derived from the assumptions that' molecules are mathematical points with no potential energy of interaction between them, must be corrected for the breakdown of the assumptions to different extents, depending on the particular gas under study.

At low pressures and high temperatures, the deviations from ideality are small, and the virial equation:

$$PV/NkT = 1 + B(T)/V + C(T)/V^2 + \ldots\ldots$$

is quite a good approximation, even if virial coefficients beyond $B(T)$ are neglected.

For denser systems, other methods have to be used. The molecules of a real gas have to be considered as occupying a volume by themselves. Due to the impenetrability of matter, or more basically to the Pauli Principle, at small intermolecular distances the potential energy will become very large and positive.

For the so-called "hard sphere model" at intermolecular distances smaller than the sum of approximate gas molecule radii, the potential energy is taken as infinite, while for larger distances it is zero. Much work has been done on the hard sphere model in determining thermodynamic properties of the pure gas or of mixtures. The "exact results" which serve as a standard of comparison for other methods, were obtained by following on an electronic computer, the detailed molecular dynamics of a comparatively few hard spheres in a cell considered to be periodically repeated through space. This type of calculations was done for a pure gas [1a] and for mixtures of spheres with different diameters[1b]. Other methods used were: the Monte-Carlo method for pure gas[2] and for mixtures[3], the virial series expansion using for instance the superposition approximation for the radial distribution function (which is a poor approximation)[4] used for mixtures and the Percus-Yevick equation which gives good results for mixtures of spheres with different diameters[5,6].

The hard sphere model is only a very crude approximation to the real intermolecular potential.

The exact calculations by molecular dynamics for a mixture of hard spheres do not account for many experimental facts of real gas mixtures, particularly those having to do with phase separation. This is to be expected, since it is known that besides the hard-core repulsive potential, molecules interact with an attractive potential part. This potential has been described in various ways, often by the well known Lennard-Jones form, or by square wells of different widths and depths.

Thermodynamic perturbation theory can be used to describe real gaseous properties - including critical points, in terms of reduced pressures and reduced temperatures[7,8].

The zero-order approximation is taken to be the hard core model and the perturbing potential is the attractive tail of the intermolecular energy . For gaseous mixtures, the theory provides a useful description of material instability (phase-separation) in the gas phase at high pressures and at temperatures above the critical point of both components. This phenomenon was termed "immiscibility of two gases"[9], but it should be recalled[10] that for mixtures there is no absolute distinction between critical solution points (phase-separation with both phases in the same state of aggregation) and gas-liquid critical points (phase-sepabation with one phase gaseous, one phase liquid) since both are points of incipient material instability rather than of mechanical instability.

The perturbation theory used for the case of pure gases [8], relates the thermodynamic properties of different systems of molecules with various attractive tails added to a common hard core potential to those of a system of hard cores alone.

According to the results of the expansion of the classical partition function in inverse powers of the temperature (with the required conditions that the perturbation energy per particle be small compared to kT) and keeping only the first order corrections to the Helmholz free energy A[11.12], we have:

$$A = A_o + (2\pi N^2/V) \int_0^\infty g_0(R,V)\ U(R)R^2dR \tag{1}$$

and for the pressure, P :

$$P = P_0 - \frac{\partial}{\partial V}\left[(2\pi N^2/V) \int_0^\infty g_0(R,V)U(R)R^2dR \right] \tag{2}$$

The correction term is here the perturbing energy U(R) as averaged over the unperturbed system. The averaging is carried out by use of the radial distribution function $g_0(R,V)$ for the unperturbed system.

V is the volume of the system and N is the number of molecules present.

For the unperturbed system, the expansion to the 6th virial coefficient was used according to[13],

$$P_0v_0/NkT = 1/X + 2.9619/X^2 + 5.4831/X^3 + 7.455/X^4 + 8.443/X^5 + 8.80/X^6 \qquad (3)$$

in which $X=V/v_0$ and $v_0=N\sigma^3/\sqrt{2}$, the closed packed volume for N hard spheres of diameter σ.

For more convenience in numerical work, AH* expanded $g_0(R,V)$ in a series of the form :

$$g_0(R,V) = 1 + \rho g_0^{(1)}(z) + \rho^2 g_0^{(2)}(z) + \rho^3 g_0^{(3)}(z) + \rho^4 g_0^{(4)}(z) \qquad (4)$$

for $z \geqslant 1$

and : $g_0(R,V) = 0$ for $z < 1$; in which $\rho = N/V$ and $z = R/\sigma$ the number density and the reduced interparticle distance respectively.

The equation of state assumes the form :

$$Pv_0/NkT = P_0v_0/NkT - (2\pi\sqrt{2}/T^*X^2)\left(I - X\frac{\partial}{\partial X}I\right) \qquad (5)$$

with T^* being the reduced temperature kT/ε where ε is an energy parameter of the attractive tail which was taken in the form of a square well of attractive width 0.5σ beyond the hard core:

$$\begin{aligned} U(z) &= \infty \qquad z < 1 \\ U(z) &= -\varepsilon \quad 1 < z < 1.5 \\ U(z) &= 0 \qquad z > 1.5 \end{aligned} \qquad (6)$$

I is the integral $\varepsilon I = \int_1^{1.5} g_0(R,V)U(z)z^2dz$ (7)

AH used several other potentials for U(z) as well. Molecular dynamics results are available for comparison.[14] So, the limits of the integral I were from 1 to 1.5σ for our choice of U(R)

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* AH refers to reference 8, AH being the initials of the authors Alder and Hecht.

in equation 6 . The equation of state from AH in this case is:

$$Pv_0/NkT = f(X) - a(X)/T^* \qquad (8)$$

where f(X) is P_0v_0/NkT from eq.3 and a(X) is an expansion of the form :

$$a(X) = 7.0346/X^2 + 14.546/X^3 + 3.748/X^4 + 24.35/X^5 - 24.9/X^6 \qquad (9)$$

The two conditions fixing the critical point are :

$$(\partial P/\partial V)_{T_c} = 0 \qquad (10)$$

$$(\partial^2 P/\partial V^2)_{T_c} = 0 \qquad (11)$$

which lead to the following critical parameters :

$T_c^* = 1.41$ $\quad P_c^* = 0.139$ $\quad X_c = 4.49$

where P_c^* is the critical reduced pressure according to :

$P^* = Pv_0/N\varepsilon$

The methods of AH for pure gases are applied to mixtures of gases.

Gaseous systems in which there is a large disparity between the separate force fields of the components, exhibit immiscibility. The phenomenon was demonstrated experimentally for the first time by Kricevskii[15] and had been predicted by Van der Waals in 1894[16]. This behavior has been observed in mixtures of helium with CO_2[17], NH_3[18], ethylene[19].

Some theoretical predictions of this phenomenon using only the Van der Waals equation of state for mixtures can be found in Temkin's work[20]; these are incorrect because the Helmholtz free energy is used for the critical point conditions instead of the Gibbs free energy.

More recently, experimental data were given for mixtures of He-Xe and He-N_2, in the works of De Swaan Arons[21] and Streett[22]. De Swaan Arons describes the two types of behavior described also by Rowlinson[10]. In one case, the locus of critical temperatures increases monotonically with the pressure, for pressures above the critical pressure of the less volatile component, while the critical mole fraction of the less volatile component keeps decreasing with the rise of the pressure, although slowly as the pressure becomes very large, as can be seen from Fig 1. As can be seen from Fig 1, at temperatures below the critical temperature of the pure less volatile component, the spread between the coexistent mole fractions does not decrease with the rise of the pressure at fixed temperature and no critical point behavior occurs, these curves merely representing solubility curves that do not meet. This is the behavior found experimentally by De Swaan Arons for a mixture of He-Xe.

The other type of behavior experimentally observed is the one seen in Fig 2. Here the critical temperature starts by decreasing with the increase of the pressure, from the value corresponding to the less volatile component and then starts increasing again. At fixed temperatures below the critical temperature of the less volatile component, and above the minimum on the critical temperature vs pressure curve, the coexistent mole fractions form loops with a critical pressure being at the maximum of the loop. This type of behavior was observed by Kricevskii[23] for a mixture of N_2-NH_3 and recently by Streett[22] for a mixture of He-N_2

In order to describe theoretically these phenomena, we have chosen model mixtures in which one component has always the hard sphere potential and the square well tail attraction of eq 6 and the second component is either hard spheres of same diameter as component one - which case will be referred to as a

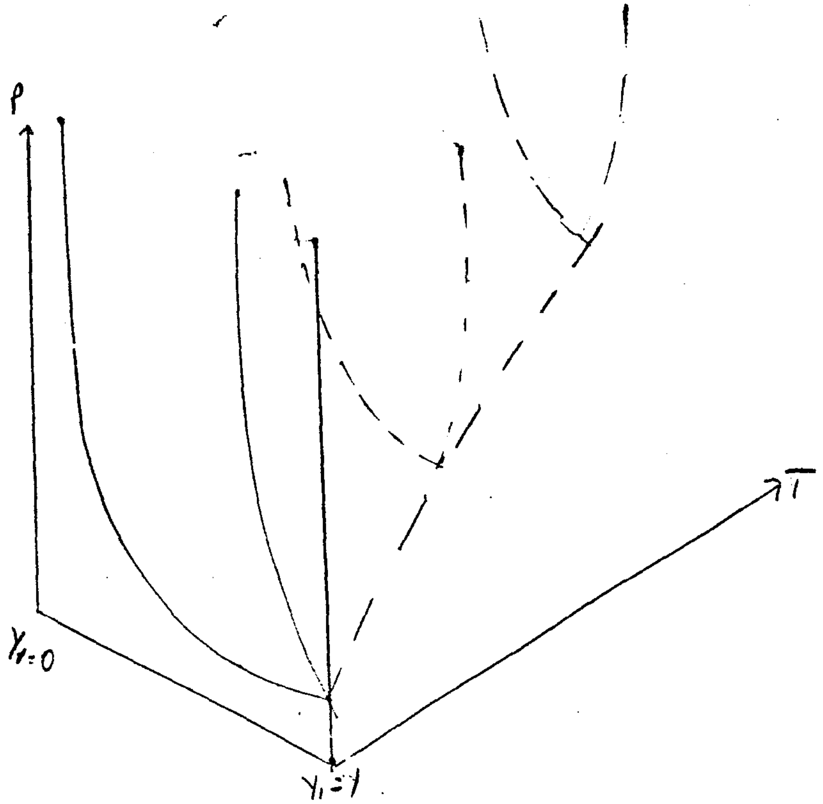


FIG 1

Dependence of the coexistent mole fractions of the pressure and temperature Systam of He-Xe (Ref 21)

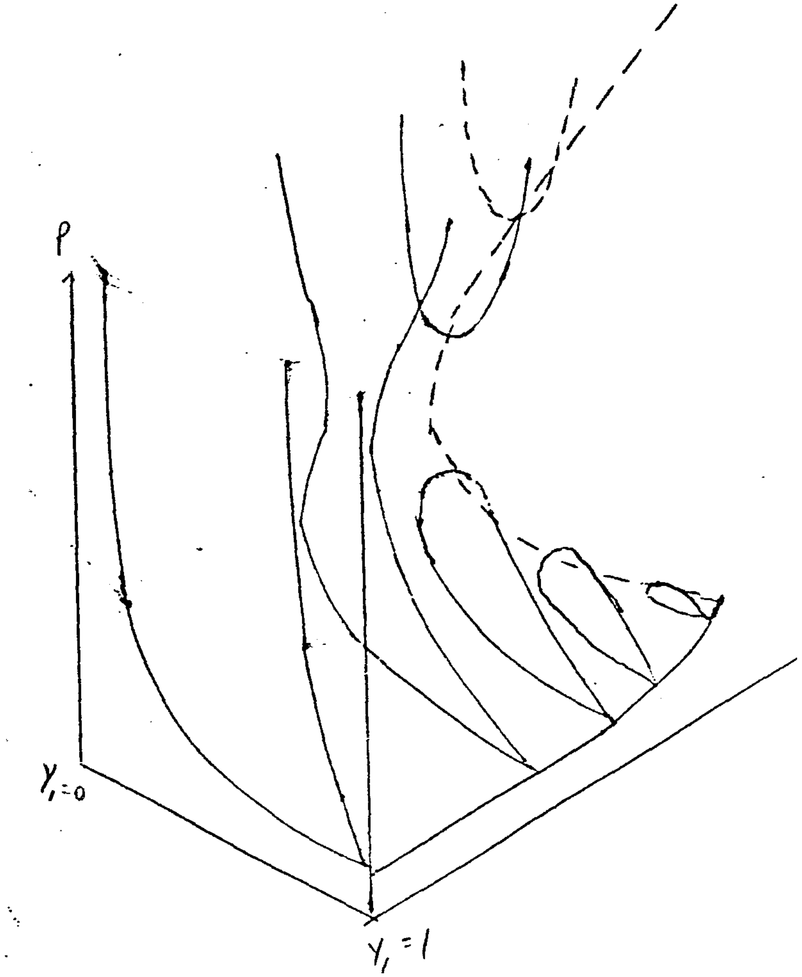


FIG 2

Dependence of the coexistent mole frac of the temperature and the pressure Ex: mixture of He-N_2 (Ref 22) mixture of hard spheres and hard spheres with attractive tails - or the second component is an ideal gas of zero molecular diameter and this case will be referred to as a mixture of poimts and hard spheres with attractive tails.

Chapter 2

Mixture of hard sheres and hard spheres with attractive tails

In a binary mixture, the over all intermolecular potential (attractive potential) can be expressed in the form:

$$U = y_1^2\, U_{11} + 2y_1y_2\, U_{12} + y_2^2\, U_{22} \tag{12}$$

where y_1 and y_2 are the mole fractions of the two components, U_{11} is the attractive potential between molecules of species 1, U_{22} is the attractive potential between molecules of species 2 and U_{12} is the attractive potential between molecules of species 1 and molecules of species 2.

Using the geometric mean combination rule :

$$U_{12}=\sqrt{U_{11}U_{12}} \tag{13}$$

The two perturbing potentials U_{11} and U_{22} are taken to have the depth ε and $\gamma\varepsilon$ respectively. In our model $\gamma=0$ so $U_{22}=0$ and $U_{12}=0$.

The perturbing potential of the mixture will be : $U= y_1^2 U_{11}$. The expression for the Helmholtz free energy of the mixture will be :

$$A_m = A_0 + (2\pi N^2/V) \int_0^\infty R^2\, U\, g_0(R)\,dR \tag{14}$$

where $g_0(R)$ belongs to the unperturbed system, so it is the same for both components.

The equation of state will be accordingly :

$$P_m v_0/NkT = P_0 v_0/NkT - (2\pi\sqrt{2}/X_m^2 T^*)\left(I_m - X_m \frac{\partial}{\partial X_m} I_m\right) \tag{15}$$

where :

$$I_m = \left(y_1^2 + 2y_1y_2\sqrt{\gamma} + y_2^2\,\gamma\right) I \tag{16}$$

where I is the integral defined by equation 7.

In our case, $I_m = y_1^2 I$, so for mixing at fixed pressure and temperature :

$$P^*/T^* = f(X_m) - a(X_m)y_1^2/T^* \tag{17}$$

where P^*, T^* and X_m are the reduced pressure, temperature and volume as defined earlier. Subscript m denotes the mixture. The separate equations of state for the two pure gases are :

1) $$P^*/T^* = f(X_1) - a(X_1)/T^* \tag{18}$$

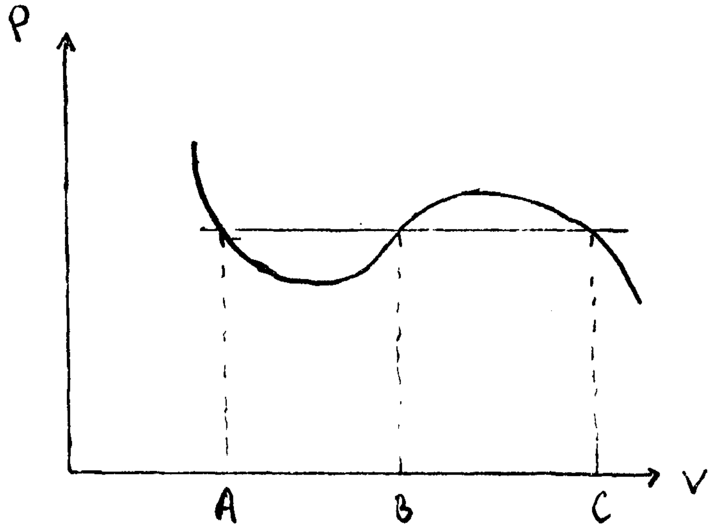
2) $$P^*/T^* = f(X_2) \tag{19}$$

where $f(X)$ and $a(X)$ are defined by equations 3 and 8, respectively.

Sets of compatible X_1, X_2 and X_m must be calculated in order to compute the excess functions of the mixture. The equations were solved numerically for different pressures and temperatures (See Appendix #1) and Table 1 shows some of the results.

When equation 18 was solved for pressures and temperatures below the critical point of pure gas 1, more than one solution was found for X_1. Actually, there were three solutions, corresponding to the Maxwell isotherm points (See for example Ref.12)

Fig 3



The point A represents the volume of the liquid phase, B is a non physical point and C represents the volume of the gaseous phase. Only one of A or C has physical meaning and the correct one can be chosen according to the fact that - from Gibbs phase rule - at fixed pressures lower than the vapor pressure at the given temperature of pure component 1, only the gaseous phase is present and at higher pressures the liquid phase is the only one present. In order to make the choice, it was necessary to estimate the vapor pressure of pure gas 1 at certain reduced temperatures below 1.41. The method of calculation and the results are described in Appendix #2.

Table 1

Sets of compatible X's for the mixture of hard spheres and hard spheres with tails

T*	X_1	X_2	X_m				
			$y_1=.1$	.3	.5	.7	.9
					P*=0.03475		
1.1	2.232	34.532	34.470	34.000	33.040	31.460	29.050
1.3	34.590	40.292	40.200	39.800	39.000	37.700	35.800
1.5	41.260	46.057	46.000	45.700	44.955	43.845	42.255
1.8	52.000	54.725	54.665	54.400	53.800	52.900	51.600
					P*=0.06950		
1.1	2.198	18.614	18.565	18.135	17.220	15.616	12.565
1.3	13.062	21.516	21.470	21.100	20.323	19.030	16.926
1.5	19.445	24.412	24.375	24.050	23.370	22.275	20.600
1.8	24.815	28.748	28.650	28.440	27.870	26.910	25.660
					P*=0.13900		
1.1	2.143	10.574	10.530	10.164	9.345	7.755	2.775
1.3	2.635	12.049	12.010	11.689	10.988	9.731	7.024
1.5	7.880	13.516	13.480	13.193	12.580	11.529	9.680
1.8	11.718	15.707	15.676	15.430	14.900	14.050	12.700
					P*=0.27800		
1.1	2.059	6.435	6.401	6.114	5.558	4.190	2.425
1.3	2.385	7.203	7.171	6.915	6.342	5.271	3.143
1.5	2.983	7.962	7.934	7.699	7.186	6.271	4.432
1.8	5.158	9.088	9.065	8.855	8.411	7.655	6.332

Table 1 (cont'd)

T^*	X_1	X_2	X_m				
			$y_1=.1$	.3	.5	.7	.9
			<u>$P^*=0.55600$</u>				
1.1	1.949	4.229	4.206	4.006	3.574	2.869	2.168
1.3	2.165	4.647	4.626	4.440	4.039	3.355	2.483
1.5	2.448	5.055	5.035	4.862	4.489	3.849	2.891
1.8	3.045	5.654	5.639	5.479	5.141	4.570	3.643
			<u>$P^*=1.11200$</u>				
1.1	1.816	2.911	2.975	2.855	2.606	2.266	1.930
1.3	1.961	3.232	3.218	3.090	2.860	2.505	2.118
1.5	2.122	3.464	3.450	3.338	3.105	2.745	2.122
1.8	2.403	3.799	3.788	3.681	3.460	2.989	2.280

Calculation of excess functions

An excess function is defined as the difference between the function for the real gas and the function for the ideal gas, under identical conditions.

The energy of a system is given by :

$$E_i = A_i - T\left(\frac{\partial}{\partial T}\right)_V A_i \tag{20}$$

and since both A_0 and the integral I from eq.14 are temperature independent, the excess energy of the mixture will be :

$$\frac{E_m^E}{RT} = -2\pi\sqrt{2}\, I(X_m)/T^*X_m \tag{21}$$

From eq.16, $I(X_m) = y_1^2\, I$, so :

$$E_m^E/RT = -y_1^2\, s(X_m)/T^* \tag{22}$$

where $s(X_m)$ is $I/X_m \times 2\pi\sqrt{2}$ and has the form:

$$s(X) = 7.0346/X + 7.273/X^2 + 1.249/X^3 - 6.088/X^4 - 4.98/X^5 \tag{23}$$

The energy of the pure hard spheres will be zero since A_0 does not depend on T*.

The excess energy of the pure gas 1 will be :

$$E_1^E/RT = -s(X_1)/T^* \tag{24}$$

So the excess energy of mixing which is the difference between the excess energy of the mixture and that of the pure components, will be :

$$\Delta E_m^E/RT = -y_1^2\, s(X_m) + y_1 s(X_1) \tag{25}$$

The excess entropy of a system over that of an ideal gas at the same pressure and temperature is defined by [24]:

$$S_1^E/R = \ln(X_1 P^*/T^*) - \int_{X_i}^{\infty} (P^*/T^* - 1/X_1)\, dX_1 + E^E/RT \tag{26}$$

Following the same way of calculation as for the energy:

$$\Delta S^E/R = \ln X_m - y_1 \ln X_1 - y_2 \ln X_2 - r(X_m) + y_1 r(X_1) + y_2 r(X_2) \tag{27}$$

The excess entropy of pure gas 2 is not zero so it had to be taken into consideration. r(X) comes from the integration of f(X)-1/X because the terms from a(X) cancel with the energy, having different signs. r(X) is given by :

$$r(X) = 2.9619/X + 2.7416/X^2 + 2.485/X^3 + 2.111/X^4 + 1.76/X^5 \tag{28}$$

The excess volume of mixing is :

$$\Delta V/v_0 = X_m - y_1X_1 - y_2X_2 \tag{29}$$

The excess enthalpy of mixing is :

$$\Delta H_m^E/RT = \Delta E_m^E/RT + \Delta\ (PV/RT-1) = \Delta E_m^E/RT + (\Delta V/v_0)P^*/T^* \tag{30}$$

The excess Gibbs free energy of mixing is :

$$\Delta G_m^E/RT = \Delta H_m^E/RT - \Delta S_m^E/R \tag{31}$$

All the excess functions described above are excess functions of formation of the mixture under isothermic and isobaric conditions.

Chapter 3

Mixture of points and hard spheres with attractive tails

The second case considered, is a mixture of molecules of an ideal gas - themselves exclude no volume, being "points" - and hard spheres with attractive tails. Calling the hard spheres with tails gas 1 and the points gas 2, we have the ratio of the radii : $R_2/R_1=0$.

For an ideal gas the equation of state is:

$$Pv_0/NkT = P^*/T^* = 1/X_2 \qquad (32)$$

where X_2 is the reduced volume.

The total volume of the mixture is V but the volume available to the points is $V-N_1\pi\sigma^3/6$. Recalling that we defined earlier $v_0= N\sigma^3/\sqrt{2}$, the reduced volume available to the points will be :

$$(V-N_1\pi\sigma^3/6)/v_0 = X-y_1\pi\sqrt{2}/6 \qquad (33)$$

If the partial pressure of the points in the system is P_2' :

$$P_2'(V-N_1\pi\sigma^3/6)/N_2kT = 1 \qquad (34)$$

$$P_2' = N_2kT/(V-N_1\pi\sigma^3/6) \qquad (34a)$$

$$P_2'v_0/NkT = y_2/(X_m-y_1\pi\sqrt{2}/6) \qquad (34b)$$

If we call P_1' the partial pressure of N_1 hard spheres with attractive tails, and as these exist in the whole volume of the mixture :

$$P_1'y_1v_0/N_1kT = f(X_m/y_1) - a(X_m/y_1)/T^* \qquad (35)$$

$$P_1'v_0/NkT \quad = f(X_m/y_1) - a(X_m/y_1)/T^* \qquad (35a)$$

The definition of X being $X=V/v_0$ and as we have only N_1 molecules of gas 1 , the variable has to be $V/\frac{N_1\sigma^3}{\sqrt{2}}$ which is X_m/y_1.

Thus, the equation of state of the mixture is:

$$P^*/T^* = Pv_0/NkT = v_0(\ P_1'+P_2')/NkT \tag{36}$$

$$P^*/T^* = \ y_2/(X_m-y_1\pi\sqrt{2}/6) + f(X_m/y_1) - a(X_m/y_1)/T^* \tag{36a}$$

Table 2 shows sets of compatible values for X_1, X_2 and X_m for various pressures and temperatures.

Calculation of excess functions

For pure gas 1 :

$$E^E/NkT = -2\pi\sqrt{2}I(X_1)/T^*X_1 \tag{37}$$

hence, for the mixture with N_1 molecules of species 1 :

$$E_m^E/NkT = -N_1\ 2\pi\sqrt{2}\ I(X_m/y_1)/T^*X_m/y_1 \tag{38}$$

$$E_m^E/NkT = -y_1\ s(X_m/y_1)/T^* + y_1\ s(X_1)/T^* \tag{39}$$

For the entropy we have the equation :

$$\begin{aligned} S_m^E/Nk = \ln(X_m(Pv_0)/NkT) - \int_0^\infty dX_m(\pi\sqrt{2}y_1y_2/6X_m(X_m-\pi\sqrt{2}y_1/2) \\ + f(X_m/y_1) - a(X_m/y_1)/T^*) + E_m^E/NkT \end{aligned} \tag{40}$$

$$S_m^E/Nk = \ln(X_m(P^*/T^*)) + (1-y_1)\ln(1-\pi\sqrt{2}/6y_1/X_m) - y_1r(X_m/y_1) \tag{40a}$$

For pure points the excess entropy is zero.

For pure gas 1 :

$$S_1^E/Nk = \ln(X_1(P^*/T^*)) - r(X_1) \tag{41}$$

So, as the excess entropy of mixing is the difference between the excess entropy of the mixture and that of the pure components,

$$\begin{aligned} \Delta S_m^E/Nk = \ln(X_m) - y_1\ln X_1 + (1-y_1)\ln(P^*/T^*)(1- \ \ 2y_1/6X_m)) + \\ y_1(r(X_1)-r(X_m/y_1)) \end{aligned} \tag{42}$$

here r(X) has the same meaning as in eq. 28.

For the excess volume :

$$\Delta V^E/v_0 = X_m - y_1X_1 - y_2X_2 \tag{43}$$

For the excess enthalpy :

$$\Delta H_m^E/NkT = \Delta E_m^E/NkT + P^*/T^* \; (\Delta V^E/v_0) \tag{44}$$

and for the Gibbs free energy :

$$\Delta G_m^E/NkT = \Delta H_m^E/NkT - \Delta S_m^E/Nk \tag{45}$$

When we solved the equation of state for this mixture, we found multiple solutions at low pressures and low temperatures for mole fractions of $y_1=.7$, .8 and .9 . We selected those solutions which proved to be correct in the sense that calculating the partial pressures of the pure components at the respective mole fraction, their sum proved to be equal to the pressure of the mixture.

Table 2

Sets of compatible X's for the mixture of points and hard spheres with tails

T*	X_1	X_2	X_m				
			y_1=.1	.3	.5	.7	.9
				P*=0.03475			
1.1	2.232	31.655	31.690	31.500	30.950	29.980	28.420
1.3	34.590	37.411	37.450	37.320	36.990	36.300	35.250
1.5	41.260	43.166	43.210	43.190	42.900	42.520	41.800
1.8	52.000	51.798	51.900	51.880	51.750	51.500	51.080
				P*=0.06950			
1.1	2.198	15.827	15.880	15.680	15.000	13.885	11.440
1.3	3.062	18.705	18.780	18.650	18.250	17.500	16.300
1.5	19.445	21.582	21.630	21.580	21.320	20.900	20.090
1.8	24.815	25.899	25.960	25.940	25.830	25.570	25.100
				P*=0.13900			
1.1	2.143	7.914	7.950	7.735	7.030	1.789	2.000
1.3	2.337	9.352	9.395	9.275	8.830	7.860	2.688
1.5	7.880	10.791	10.890	10.832	10.475	9.830	8.200
1.8	11.718	12.949	13.010	13.020	12.880	12.570	12.070
				P*=0.27800			
1.1	2.059	3.956	3.990	3.750	2.530	1.615	1.899
1.3	2.385	4.676	4.720	4.590	4.040	2.340	2.255
1.5	2.983	5.395	5.445	4.590	5.060	4.285	3.080
1.8	5.158	6.474	6.530	6.540	6.392	6.062	5.501

Table 2 (cont'd)

T*	X_1	X_2	X_m				
			y_1=.1	.3	.5	.7	.9
				P*=0.5560			
1.1	1.949	1.978	2.009	1.725	1.230	1.470	1.782
1.3	2.165	2.338	2.380	2.232	1.690	1.713	2.005
1.5	2.448	2.698	2.749	2.680	2.345	2.105	2.300
1.8	3.045	3.237	3.300	3.310	3.170	2.965	2.958
				P*=1.1120			
1.1	1.816	0.989	1.020	0.835	1.030	1.340	1.655
1.3	1.961	1.169	1.210	1.090	1.178	1.462	1.795
1.5	2.122	1.348	1.399	1.340	1.368	1.627	1.952
1.8	2.403	1.618	1.675	1.697	1.715	1.919	2.232

Chapter 4

Discussion of the results

Calculations were made, covering a range of temperatures from $T^*=0.65$ to about $T^*=2.6$ and a range of pressures from $.25\ P^*_{c1}$ to $20\ P^*_{c1}$ where P^*_{c1} is the reduced critical pressure of pure gas 1, that is 0.139.

Some results are shown in Tables 3 and 4.

The figures, from Fig 4 to Fig 35, show the dependence of the excess functions of mixing on the temperature at fixed pressure and fixed mole fraction, the dependence on pressure at fixed temperatures and fixed mole fractions and the dependence on the mole fraction at fixed pressures and temperatures, Some of the fixed temperatures used for the dependence on the pressure were $T^*=1.1$, 1.4, 1.8, and the mole fractions are $y_1=.3$ and .7. For the dependence on the mole fractions $T^*=1.2$ and 1.6 and $P^*=P^*_{c1}$ and $4P^*_{c1}$.were used and for the dependence on temperature, $y_1=.3$ and .7 and $P^*=.5\ P^*_{c1}$, P^*_{c1} and $8P^*_{c1}$.

As can be seen from the graphs, for hard spheres and hard spheres with tails, at low temperatures such as 1.1 and mole fraction $y_1=.7$, we find a decrease of the excess functions with the pressure, while at $y_1=.3$, except for the excess volume, they stay almost constant. At a temperature of 1.4 which is very near the critical temperature of pure gas 1, for both mole fractions we have at first a rise of the excess functions with the pressure, up to P^*_{c1} and then, they stay almost constant except for the volume which decreases rather abrubtly. At higher temperatures such as 1.8, we have almost the same behavior, only instead of staying almost constant, they increase slightly except for the volume which continue to decrease.

The large variations in excess volume for small changes in P* or T* can be explained by the fact that there is a phase transition from gas to liquid either in the mixture or in one of the components. For instance, between T*=1.4 and T*=1.5 at y_1=.7 and P*=P^*_{c1}, we notice a large change in the excess volume. This is normal, since pure gas 1 changes from liquid to gas (X=3.45 changes to X=7.88) and gas 2 and the mixture were already in gaseous state with very small changes in the reduced volumes. (from 12.78 to 13.51 and from 10.63 to 11.52 respectively). This comes from the fact that critical temperature of gas 1 lies between 1.4 and 1.5.

At high pressure, the excess volume increases slightly with T*. This could happen if the volume of the real mixture increases a little more with the temperature than the volume of an ideal mixture.

In the case of the mixture of points and hard spheres with attractive tails, under the same conditions, at low and medium temperatures(1.2 and 1.4), the excess functions present a maximum around or above P^*_{c1} and some of them such as the volume and the entropy decreases as much as to become negative at high pressures. Qualitatively, the same type of behavior is observed by Throop and Bearman[25] with the difference that their maxima are found at pressures twice or thrice as large as the critical pressure of one of the components. They calculate excess functions for Ar-Kr, using a Lennard-Jones potential and the Percus-Yevick equation. These gases do not differ among themselves very much in core size or depth of the attractive potential (the Lennard-Jones parameters for Ar and Kr are $119.8^{\circ}K$ and $171^{\circ}K$ respectively) yet the behavior of the excess functions is quite similar to that of the excess functions of our case of points and hard spheres with tails, that is, gases which differ very much both in core size and in attractive potential.

As far as the dependence on the temperature is concerned, at low pressures we find, for the mixture of hard spheres and hard spheres with attractive tails, a quite abrupt decrease of the excess functions with the temperature except for the excess volume which increases in the begining and then decreases. At high pressures, the excess energy and enthalpy decreases slightly, the excess entropy stays almost constant, and the excess volume, as mentined before, increases slightly.

For points and hard spheres with tails, at high pressures, all functions are almost constant and of very small size. The entropy and the volume are negative. For pressures around P^*_{c1} and $y_1=.3$, there is a rather abrupt decrease in energy from 1.1 to 1.5 and a smooth decrease in free energy from 1.1 to 1.8. The excess volume presents a slight peak around 1.4 and then decreases. At $y_1=.7$ all functions present a peak - energy and entropy at 1.2 and volume at 1.4 and they decrease to almost zero at 1.8. The free energy decreases monotonically from 1.1 to 1.8.

It is normal that the excess functions should decrease with the temperature, the higher is the temperature, the more a mixture becomes similar to a mixture of ideal gases.

With the mole fraction, at high pressures, energy and free energy have a maximum at y_1=.2 and entropy and volume have a minimum at y_1=.5. At $P^*=P^*_{c1}$, all excess functions have maxima around y_1=.5-.6, except for the volume which has a minimum at y_1=.7.

Table 3

Excess functions for the mixture of hard spheres and hard spheres with tails

$y_1=.1$ $P^*=0.03475$

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
1.1	0.39706	0.48515	3.17610	0.49740	0.01225
1.3	0.01473	0.01407	0.47820	0.02752	0.01344
1.5	0.01061	0.01046	0.42270	0.02040	0.00994
1.8	0.00694	0.00424	0.21250	0.01104	0.00680

$y_1=.1$ $P^*=0.06950$

1.1	0.40232	0.42117	1.59260	0.50295	0.08178
1.3	0.23035	0.31581	1.79940	0.32654	0.03000
1.5	0.02340	0.02441	0.45970	0.04470	0.02029
1.8	0.01500	0.01267	0.29530	0.02640	0.01372

$y_1=.1$ $P^*=0.13900$

1.1	0.41099	0.36042	0.79910	0.51197	0.15155
1.3	0.27356	0.29245	0.90240	0.37005	0.07760
1.5	0.06363	0.06966	0.52760	0.11252	0.04286
1.8	0.03366	0.03430	0.36790	0.06206	0.02776

$y_1=.1$ $P^*=0.27800$

1.1	0.42402	0.30509	0.40360	0.52692	0.22183
1.3	0.30424	0.25602	0.44980	0.40043	0.14442
1.5	0.20162	0.19377	0.46990	0.28871	0.09494
1.8	0.08610	0.08669	0.37000	0.14324	0.05655

Table 3 (cont'd)

		y_1=.1	P*=0.55600		
T*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
1.1	0.44418	0.25493	0.20500	0.54780	.0.29287
1.3	0.33511	0.22101	0.22720	0.43228	0.21127
1.5	0.25186	0.18501	0.24070	0.34108	0.15607
1.8	0.16119	0.13344	0.24590	0.23714	0.10371
		y_1=.1	P*=1.112		
1.1	0.46929	0.28236	0.17350	0.64469	0.36232
1.3	0.36733	0.18588	0.11310	0.46407	0.27819
1.5	0.29215	0.16341	0.12020	0.38126	0.21785
1.8	0.21095	0.13343	0.12860	0.29040	0.15697
		y_1=.3	P*=0.03475		
1.1	1.17948	1.44381	9.1643	1.46899	0.02518
1.3	0.03636	0.03636	1.21860	0.06836	0.03200
1.5	0.02551	0.02703	1.08210	0.05058	0.02355
1.8	0.01641	0.00993	0.49250	0.02592	0.01600
		y_1=.3	P*=0.06950		
1.1	1.18433	1.24208	4.44580	1.46522	0.22314
1.3	0.67475	0.93233	4.42050	0.94848	0.06811
1.5	0.05792	0.06148	1.12810	0.11019	0.04871
1.8	0.03641	0.03743	0.87190	0.07007	0.03264

Table 3 (cont'd)

T*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			y_1=.3	P*=0.13900	
1.1	1.19057	1.04481	2.11930	1.45837	0.41356
1.3	0.78999	0.85064	2.46420	1.05347	0.20283
1.5	0.16761	0.18863	1.36780	0.29436	0.10573
1.8	0.08462	0.08849	0.91970	0.15564	0.06716
			y_1=.3	P*=0.27800	
1.1	1.19949	0.85682	0.99180	1.45015	0.59333
1.3	0.85764	0.72520	1.15740	1.10515	0.37995
1.5	0.56270	0.54702	1.23070	0.79079	0.24377
1.8	0.22833	0.23413	0.94600	0.37443	0.14030
			y_1=.3	P*=0.55600	
1.1	1.20918	0.68136	0.46100	1.44219	0.76083
1.3	0.91326	0.59796	0.53760	1.14319	0.54523
1.5	0.68408	0.50343	0.58910	0.90244	0.39902
1.8	0.43187	0.35882	0.60770	0.61958	0.26076
			y_1=.3	P*=1.11200	
1.1	1.22402	0.58435	0.27250	1.49949	0.91514
1.3	0.96044	0.46633	0.23930	1.16513	0.69880
1.5	0.76503	0.42450	0.27660	0.97009	0.54559
1.8	0.55042	0.34557	0.30080	0.73625	0.39068

Table 3 (cont'd)

T*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
y_1=.5 P*=0.03475					
1.1	1.94497	2.38613	14.66250	2.40817	0.02204
1.3	0.04496	0.04752	1.55900	0.08663	0.03911
1.5	0.03158	0.03304	1.29650	0.06161	0.02858
1.8	0.01982	0.00900	0.43750	0.02826	0.01927
y_1=.5 P*=0.069500					
1.1	1.93136	2.02919	6.81400	2.36188	0.33269
1.3	1.09497	1.52547	7.22350	1.52448	0.08560
1.5	0.07464	0.08118	1.44150	0.14143	0.06026
1.8	0.04567	0.04744	1.07850	0.08731	0.03987
y_1=.5 P*=0.13900					
1.1	1.89818	1.66163	2.98650	2.27556	0.61394
1.3	1.25749	1.36289	3.64600	1.64734	0.28445
1.5	0.23597	0.27437	1.88200	0.41036	0.13600
1.8	0.11143	0.11919	1.18750	0.20313	0.08394
y_1=.5 P*=0.27800					
1.1	1.84150	1.32062	1.31100	2.17283	0.85221
1.3	1.31621	1.11226	1.54800	1.64725	0.53498
1.5	0.85479	0.84024	1.71350	1.17236	0.33212
1.8	0.32399	0.34106	1.28800	0.52292	0.18186

Table 3 (cont'd)

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			$y_1=.5$	$P^*=0.55600$	
1.1	1.74278	0.94549	0.48500	1.98793	1.04243
1.3	1.32796	0.85571	0.63300	1.42820	0.74299
1.5	0.99473	0.73022	0.73750	1.26809	0.53787
1.8	0.61881	0.51936	0.79150	0.86329	0.34393
			$y_1=.5$	$P^*=1.11200$	
1.1	1.65543	0.70418	0.24250	1.90058	1.19640
1.3	1.31468	0.62633	0.26350	1.54007	0.91374
1.5	1.05184	0.57115	0.31200	1.28314	0.71199
1.8	0.75641	0.47173	0.35900	0.97820	0.50646
			$y_1=.7$	$P^*=0.03475$	
1.1	2.68994	3.30600	19.54070	3.30725	0.00124
1.3	0.04053	0.04394	1.39940	0.07703	0.03400
1.5	0.02791	0.02985	1.14590	0.05446	0.02461
1.8	0.01675	0.00196	0.08250	0.01834	0.01638
			$y_1=.7$	$P^*=0.06950$	
1.1	2.62769	2.76012	8.49320	3.16431	0.40419
1.3	1.48397	2.08537	9.43850	2.04167	0.07752
1.5	0 .06988	0.07868	1.33990	0.13196	0.05328
1.8	0 .04095	0.04165	0.91510	0.07628	0.03463

Table 3 (cont'd)

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			y_1=.7	P*=0.13900	
1.1	2.46537	2.12530	3.08270	2.85491	0.72961
1.3	1.64754	1.79266	4.27180	2.10430	0.31163
1.5	0.25430	0.30795	1.95820	0.43756	0.12780
1.8	0.10782	0.12013	1.13530	0.19549	0.07536
			y_1=.7	P*=0.27800	
1.1	2.12626	1.39915	0.81820	2.33304	0.93389
1.3	1.58871	1.31873	1.44060	1.89677	0.57805
1.5	1.03111	1.02119	1.79430	1.36366	0.34247
1.8	0.35218	0.38298	1.31800	0.55574	0.17275
			y_1=.7	P*=0.55600	
1.1	1.78350	0.86187	0.23600	1.90278	1.04092
1.3	1.42199	0.86589	0.44540	1.61248	0.74660
1.5	1.08800	0.78094	0.61890	1.31741	0.53647
1.8	0.67281	0.56831	0.74230	0.90210	0.33379
			y_1=.7	P*=1.11200	
1.1	1.56287	0.57189	0.12150	1.68570	1.11380
1.3	1.27703	0.55856	0.16270	1.41620	0.85764
1.5	1.04094	0.53420	0.22040	1.20433	0.67013
1.8	0.75933	0.46369	0.29020	0.93861	0.47492

Table 3 (cont'd)

T*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			y_1=.9 P*=0.03475		
1.1	3.40609	4.19163	23.58890	4.15129	-0.04035
1.3	0.01904	0.02090	0.63980	0.03614	0.01524
1.5	0.01276	0.01382	0.51530	0.02470	0.01088
1.8	0.00926	0.00975	0.42590	0.01796	0.00822
			y_1=.9 P*=0.069500		
1.1	3.20721	3.33845	8.72540	3.75850	0.42005
1.3	1.82201	2.58324	12.01860	2.46454	0.03717
1.5	0.03496	0.04096	0.65830	0.06546	0.02451
1.8	0.01932	0.02126	0.45170	0.03676	0.01550
			y_1=.9 P*=0.13900		
1.1	1.25171	0.67713	-0.21110	1.22503	0.54790
1.3	1.78975	1.50850	3.44700	2.15837	0.24755
1.5	0.17171	0.22020	1.23640	0.28629	0.06609
1.8	0.05715	0.06665	0.58310	0.10218	0.03553
			y_1=.9 P*=0.27800		
1.1	0.99084	0.44088	-0.71600	0.97275	0.53187
1.3	0.98659	0.68086	0.27620	1.04565	0.36479
1.5	0.82009	0.78279	0.95110	0.99636	0.21357
1.8	0.23631	0.26625	0.78100	0.35694	0.09068

Table 3 (cont'd)

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			$y_1=.9$ $P^*=0.55600$		
1.1	0.82806	0.30020	-0.00900	0.82351	0.52331
1.3	0.72615	0.36391	0.06980	0.75601	0.39210
1.5	0.61632	0.39516	0.18230	0.68390	0.28874
1.8	0.41638	0.34317	0.33710	0.52050	0.17733
			$y_1=.9$ $P^*=1.11200$		
1.1	0.69049	0.17187	0.00450	0.69504	0.52317
1.3	0.60335	0.21808	0.02990	0.62893	0.41086
1.5	0.27870	-0.17383	-0.13420	0.17921	0.35304

Table 4

Excess functions for the mixture of points and hard spheres with tails

T*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
y_1=.1 P*=0.03475					
1.1	0.39695	0.48504	2.97730	0.49101	0.00597
1.3	0.01466	0.01513	0.32110	0.02325	0.01023
1.5	0.01056	0.01066	0.23460	0.01600	0.00534
1.8	0.00691	0.00512	0.06180	0.00810	0.00298
y_1=.1 P*=0.069500					
1.1	0.40191	0.42203	1.41590	0.49147	0.06933
1.3	0.03488	0.03956	0.41550	0.05709	0.01753
1.5	0.02323	0.02415	0.26170	0.03536	0.01121
1.8	0.01490	0.01530	0.16940	0.02144	0.00614
y_1=.1 P*=0.13900					
1.1	0.40952	0.36009	0.61310	0.48699	0.12690
1.3	0.27363	0.29214	0.71470	0.34905	0.05691
1.5	0.06300	0.06772	0.32010	0.09366	0.02494
1.8	0.03329	0.03465	0.18410	0.04751	0.01385
y_1=.1 P*=0.27800					
1.1	0.42009	0.30270	0.22370	0.47662	0.17392
1.3	0.30117	0.25552	0.27310	0.35957	0.10405
1.5	0.19953	0.19338	0.29120	0.25350	0.06012
1.8	0.08483	0.08624	0.18760	0.11380	0.02756

Table 4 (cont'd)

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			$y_1=.1$ $P^*=0.55600$		
1.1	0.42958	0.24618	0.03390	0.44672	0.20054
1.3	0.32567	0.21714	0.05930	0.35103	0.13389
1.5	0.24538	0.18434	0.07600	0.27355	0.08921
1.8	0.15717	0.13439	0.08220	0.18257	0.04818
			$y_1=.1$ $P^*=1.11200$		
1.1	0.42869	0.18555	-0.05170	0.37646	0.19091
1.3	0.34072	0.17434	-0.03820	0.30806	0.13373
1.5	0.27365	0.15986	-0.02640	0.25409	0.09423
1.8	0.19923	0.13179	-0.02150	0.18596	0.05416
			$y_1=.3$ $P^*=0.03475$		
1.1	1.18048	1.44250	8.67190	1.45240	0.00993
1.3	0.03518	0.03612	0.75530	0.05537	0.01925
1.5	0.02511	0.02632	0.59580	0.03892	0.01260
1.8	0.01618	0.00963	0.02140	0.01659	0.00695
			$y_1=.3$ $P^*=0.06950$		
1.1	1.18045	1.23775	3.94170	1.42950	0.19175
1.3	0.08678	0.09625	0.96650	0.13845	0.04220
1.5	0.05639	0.05939	0.63910	0.08600	0.02661

Table 4 (cont'd)

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			$y_1=.3$ $P^*=0.13900$		
1.1	1.17559	1.02413	1.55230	1.37175	0.34762
1.3	0.78110	0.83883	1.93810	0.98833	0.14950
1.5	0.16204	0.18604	0.91430	0.24677	0.06073
1.8	0.08129	0.08475	0.44030	0.11529	0.03054
			$y_1=.3$ $P^*=0.27800$		
1.1	1.14331	0.78324	0.36310	1.23508	0.45184
1.3	0.82533	0.68536	0.60130	0.95391	0.26855
1.5	0.54194	0.52196	0.70960	0.67345	0.15149
1.8	0.21637	0.22113	0.46080	0.28754	0.06641
			$y_1=.3$ $P^*=0.55600$		
1.1	0.99548	0.42272	-0.24430	0.87200	0.44928
1.3	0.79949	0.46620	-0.05410	0.77635	0.31015
1.5	0.61338	0.42571	0.05700	0.63451	0.20881
1.8	0.39187	0.32034	0.13060	0.43221	0.11187
			$y_1=.3$ $P^*=1.1120$		
1.1	0.56803	-0.09429	-0.40210	0.16184	0.25613
1.3	0.59780	0.11478	-0.31660	0.32718	0.21240
1.5	0.54192	0.20258	-0.24020	0.36398	0.16140
1.8	0.42687	0.23390	-0.15650	0.33026	0.09636

Table 4 (cont'd)

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			$y_1=.5$ $P^*=0.03475$		
1.1	1.94236	2.38200	14.00700	2.38485	0.00285
1.3	0.04348	0.04658	0.98950	0.06993	0.02335
1.5	0.03060	0.03134	0.68700	0.04652	0.01518
1.8	0.01926	0.00809	-0.14900	0.01648	0.00829
			$y_1=.5$ $P^*=0.06950$		
1.1	1.91954	2.00687	5.98750	2.29784	0.29097
1.3	0.11264	0.12698	1.24750	0.17934	0.05235
1.5	0.07071	0.07561	0.80650	0.10808	0.03347
1.8	0.04346	0.04429	0.47300	0.06172	0.01744
			$y_1=.5$ $P^*=0.13900$		
1.1	1.84407	1.58031	2.00150	2.09698	0.51667
1.3	1.23005	1.32218	2.83650	1.53334	0.21116
1.5	0.21940	0.24836	1.13950	0.32499	0.07663
1.8	0.10267	0.10756	0.54650	0.14487	0.03731
			$y_1=.5$ $P^*=0.27800$		
1.1	1.42213	0.71004	-0.47750	1.30145	0.59142
1.3	1.18642	0.93297	0.59800	1.31430	0.38133
1.5	0.78598	0.74746	0.87100	0.94741	0.19995
1.8	0.28922	0.29554	0.57600	0.37818	0.08265

Table 4 (cont'd)

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			$y_1=.5$ $P^*=0.55600$		
1.1	0.53177	-0.20445	-0.73350	0.16102	0.36546
1.3	0.71150	0.15528	-0.56150	0.47135	0.31607
1.5	0.70611	0.38761	-0.22800	0.62160	0.23399
1.8	0.48830	0.36803	0.02900	0.49726	0.12922
			$y_1=.5$ $P^*=1.11200$		
1.1	0.30745	-0.17222	-0.37250	-0.06911	0.10311
1.3	0.35975	-0.07845	-0.38700	0.02872	0.10716
1.5	0.39414	0.02495	-0.36700	0.12207	0.09712
1.8	0.38519	0.13596	-0.29550	0.20263	0.06667
			$y_1=.7$ $P^*=0.03475$		
1.1	2.68578	3.29968	18.92140	3.28352	-0.01616
1.3	0.03829	0.04131	0.86370	0.06138	0.02007
1.5	0.02660	0.02960	0.68820	0.04254	0.01294
1.8	0.01595	0.00052	-0.43940	0.00747	0.00695
			$y_1=.7$ $P^*=0.06950$		
1.1	2.60422	2.72160	7.59830	3.08429	0.36269
1.3	0.10661	0.12315	1.17850	0.16962	0.04647
1.5	0.06408	0.07362	0.81390	0.10180	0.02817
1.8	0.03784	0.03955	0.42980	0.05444	0.01489

Table 4 (cont'd)

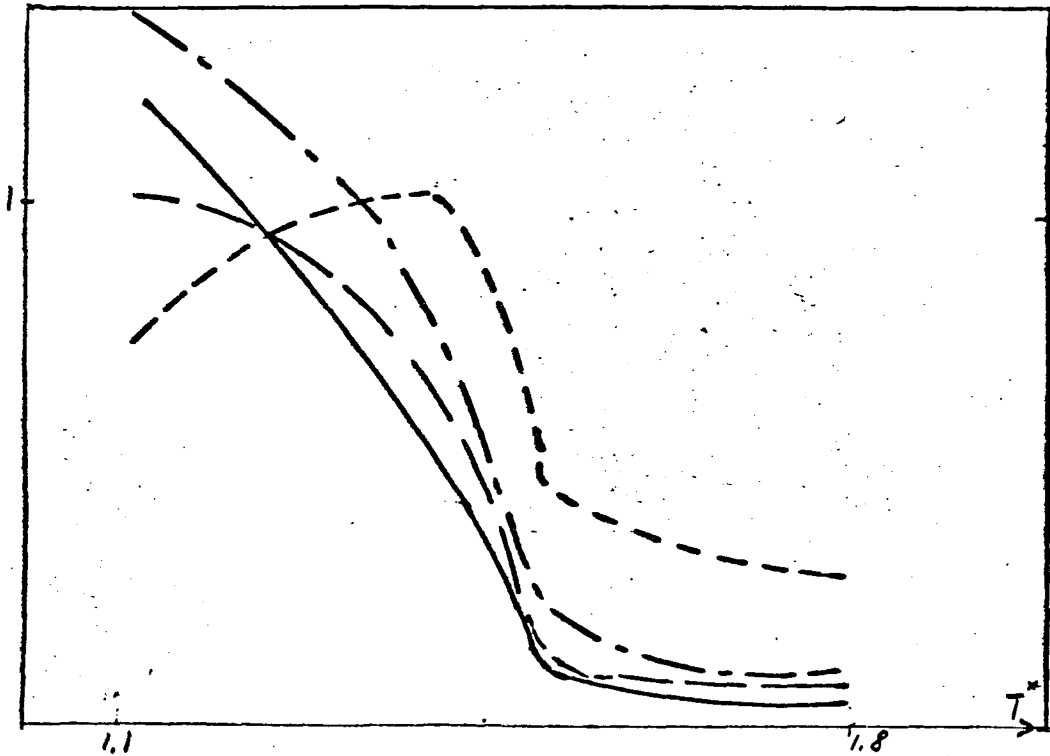
T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			y_1=.7 P*=0.13900		
1.1	0.53732	-0.26917	-0.08430	0.27394	0.54312
1.3	1.58055	1.68988	3.20990	1.92376	0.23388
1.5	0.22052	0.25049	1.07670	0.32030	0.06981
1.8	0.09316	0.09865	0.49070	0.13105	0.03240
			y_1=.7 P*=0.27800		
1.1	0.36641	-0.25239	-1.01310	0.11037	0.36276
1.3	0.72129	0.24709	-0.67920	0.57604	0.32896
1.5	0.83107	0.74715	0.57840	0.93827	0.19112
1.8	0.28245	0.28769	0.50920	0.36109	0.07340
			y_1=.7 P*=0.55600		
1.1	0.25123	-0.18326	-0.48770	0.00472	0.18798
1.3	0.32003	-0.07535	-0.50390	0.10452	0.17987
1.5	0.39733	0.08727	-0.47690	0.17230	0.16956
1.8	0.38461	0.24389	-0.13760	0.34210	0.09821
			y_1=.7 P*=1.11200		
1.1	0.18150	-0.06906	-0.22790	-0.04872	0.02034
1.4	0.20262	-0.03485	-0.26070	-0.00430	0.03055
1.6	0.21590	0.00384	-0.26410	0.03248	0.02864
1.8	0.22469	0.04895	-0.24850	0.07128	0.02233

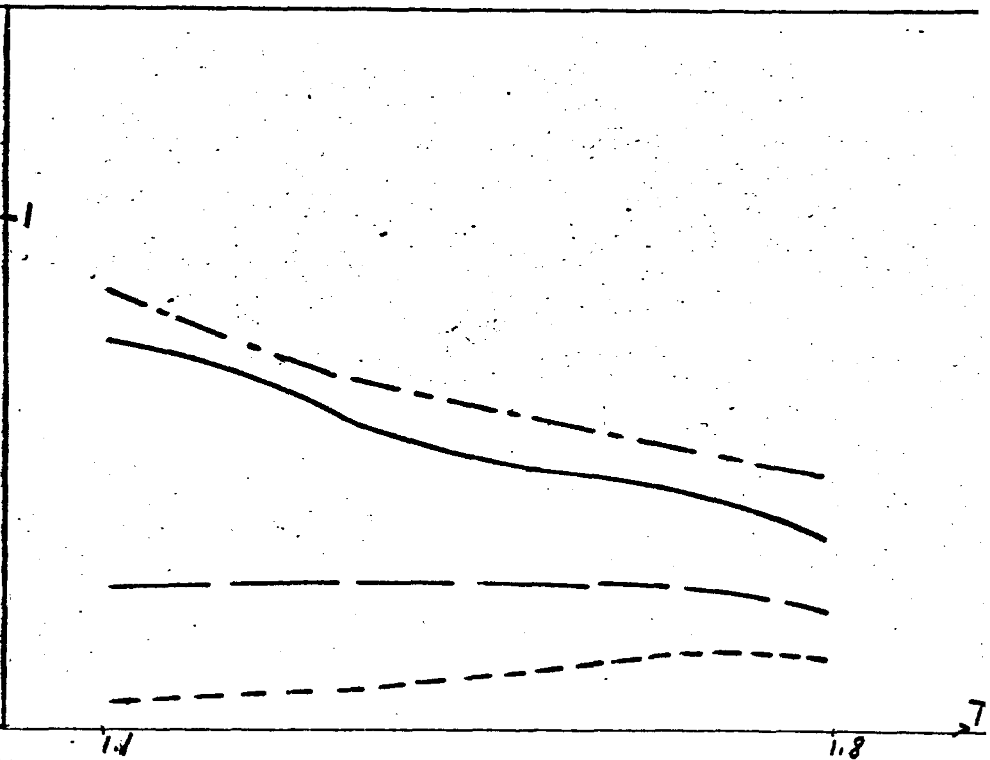
Table 4 (cont'd)

T*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			y_1=.9 P*=0.03475		
1.1	3.40252	4.18554	23.24580	4.13688	-0.04866
1.3	0.01738	0.01863	0.37790	0.02748	0.00885
1.5	0.01196	0.01441	0.34940	0.02006	0.00565
1.8	0.00588	-0.01433	-0.89980	-0.01149	0.00284
			y_1=.9 P*=0.069500		
1.3	0.05562	0.06937	0.65950	0.09088	0.02151
1.5	0.03078	0.03818	0.43130	0.05077	0.01259
1.7	0.01392	0.02101	0.22300	0.02904	0.00802
1.8	0.01686	0.01717	0.17660	0.02368	0.00651
			y_1=.9 P*=0.13900		
1.1	0.15032	-0.11682	-0.72010	0.05932	0.17614
1.3	0.346606	0.12226	-0.61870	0.27990	0.15765
1.5	0.090160	0.05747	0.02890	0.09283	0.03537
1.8	0.044220	0.04740	0.22890	0.06189	0.01449
			y_1=.9 P*=0.27800		
1.1	0.10437	-0.09743	-0.34970	0.01599	0.11342
1.3	0.15707	-0.02623	-0.34140	0.08406	0.11029
1.5	0.28315	0.17159	-0.14420	0.25643	0.08485
1.8	0.14511	0.14418	0.21140	0.17776	0.03358

Table 4 (cont'd)

T^*	$\Delta E^E/RT$	$\Delta S^E/R$	$\Delta V^E/v_0$	$\Delta H^E/RT$	$\Delta G^E/RT$
			y_1=.9 P*=0.55600		
1.1	0.06918	-0.07003	-0.16990	-0.01670	0.05333
1.3	0.09970	-0.02904	-0.17730	0.02387	0.05291
1.5	0.11610	0.00376	-0.17300	0.05198	0.04822
1.8	0.13268	0.06538	-0.10620	0.09988	0.03449
			y_1=.9 P*=1.11200		
1.1	0.05548	-0.01973	-0.07830	-0.02362	-0.00389
1.3	0 .06258	-0.01157	-0.08680	-0.01161	-0.00005
1.5	0 .06716	-0.00293	-0.09260	-0.00144	0.00149
1.8	0 .07265	0.01491	-0.09250	0.01555	0.00064





Mixture of hard spheres and hard spheres with attractive tails: Excess functions vs T*

Fig 4

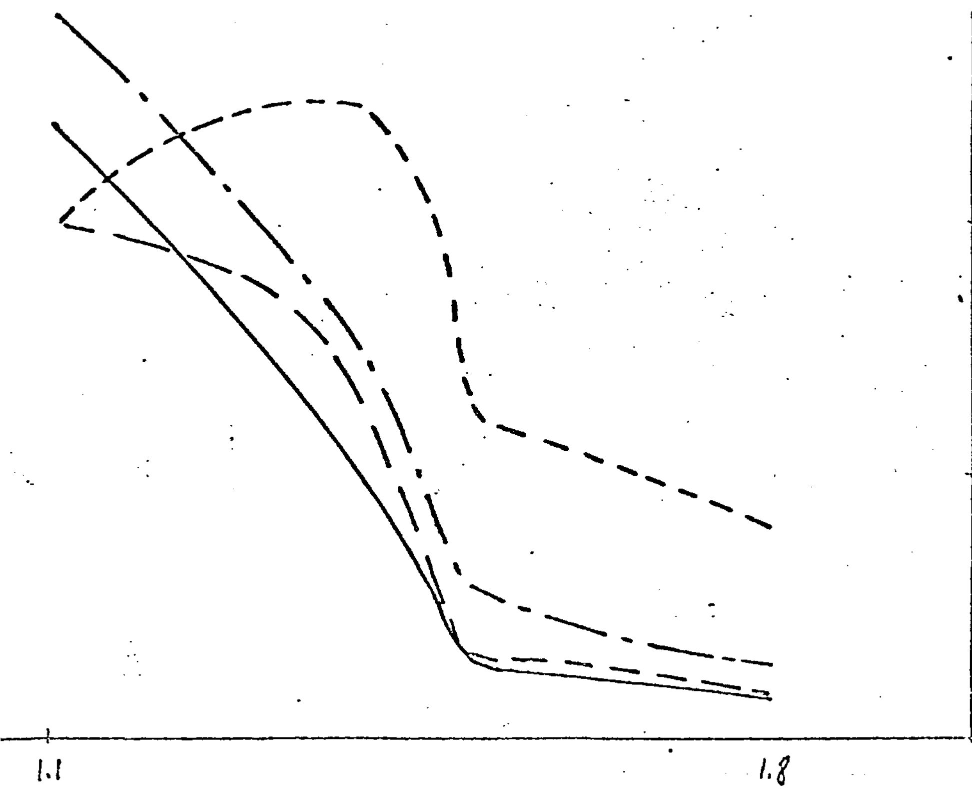
$y_1 = .7$ $P^* = P^*_{c1}$

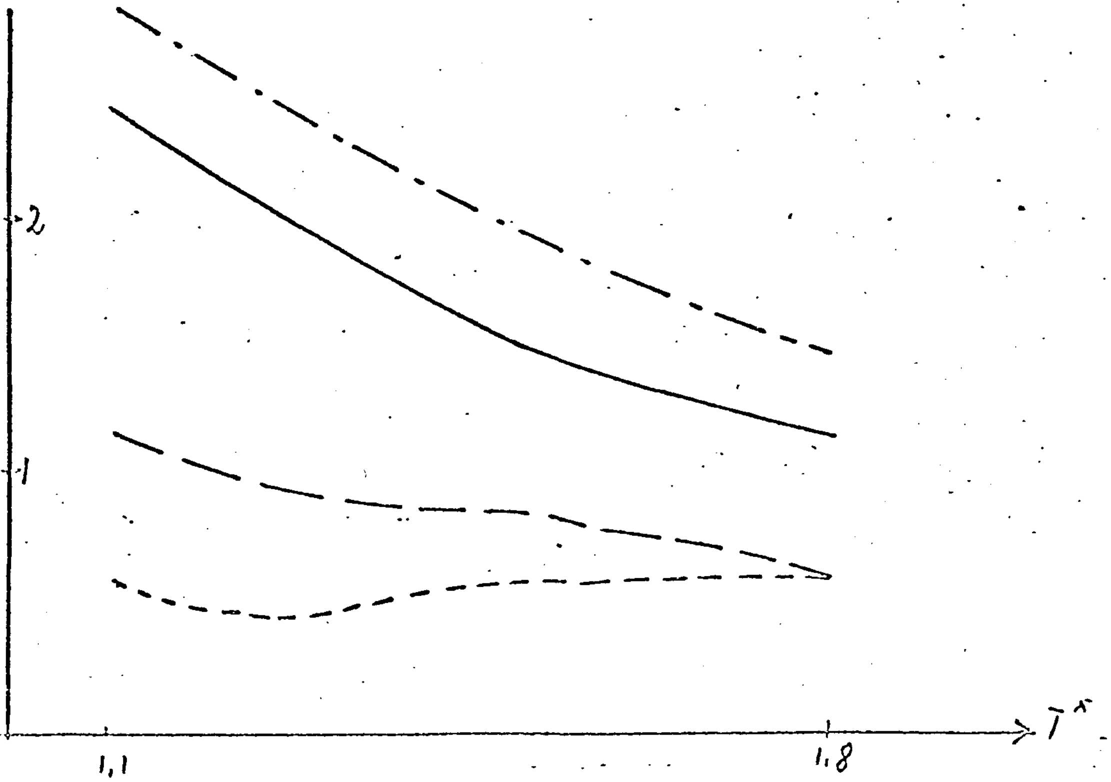
$\Delta E^E/RT$ ——— $\Delta S^E/R$ — — —

Fig 5

$y_1 = .7$ $P^* = 8P^*_{c1}$

$\Delta V^E/v_o$ ----- $\Delta H^E/RT$ — · —





Mixture of hard spheres and hard spheres with attractive tails: Excess functions vs T*

Fig. 6.

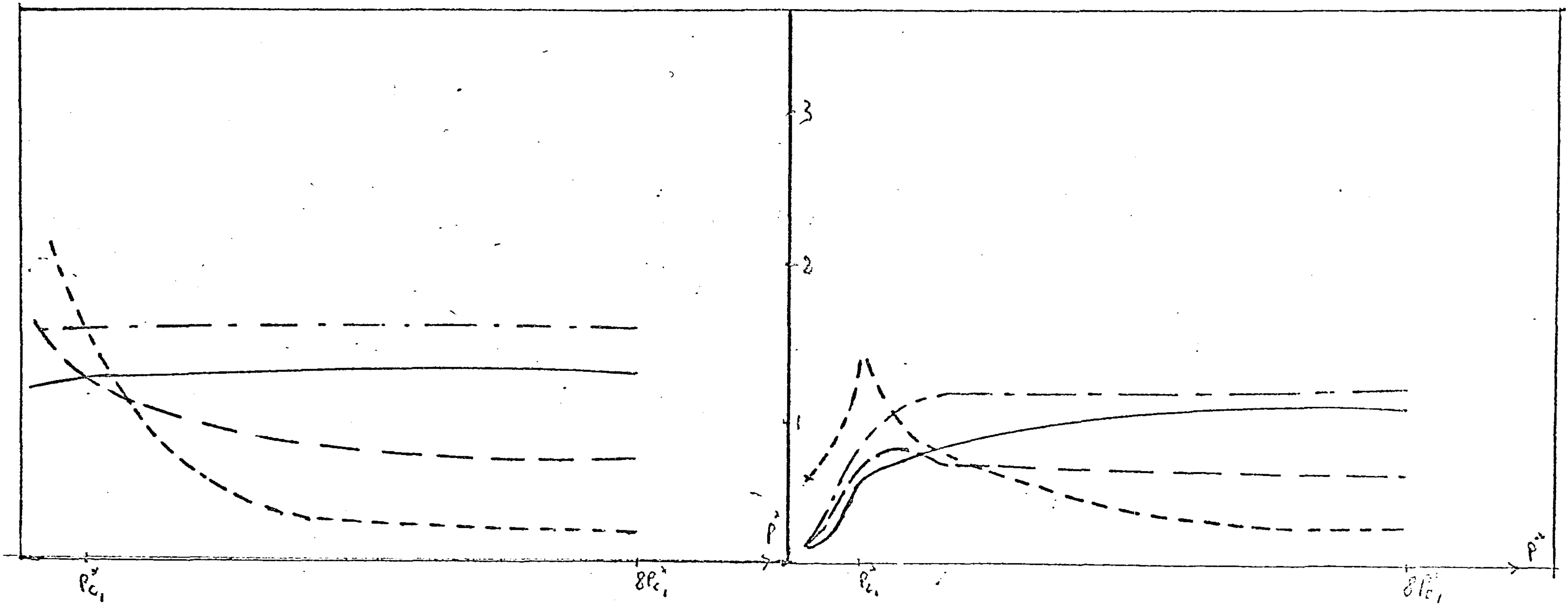
$y_1=.3$ $P^*=P^*_{c1} \times 8$

$\Delta E^E/RT$ ——— $\Delta S^E/R$ ——— ———

Fig 7

$y_1=.3$ $P^*=P^*_{c1}$

$\Delta V^E/v_0$ - - - - $\Delta H^E/RT$ —. ———



Mixture of hard spheres and hard spheres With tails : excess functions vs P*

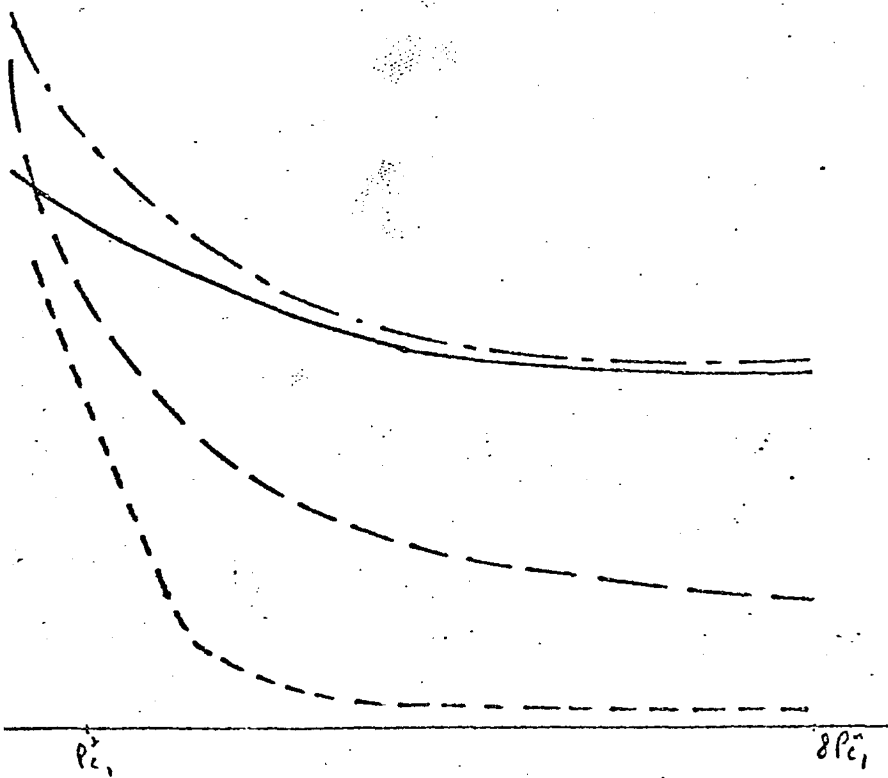
Fig 8

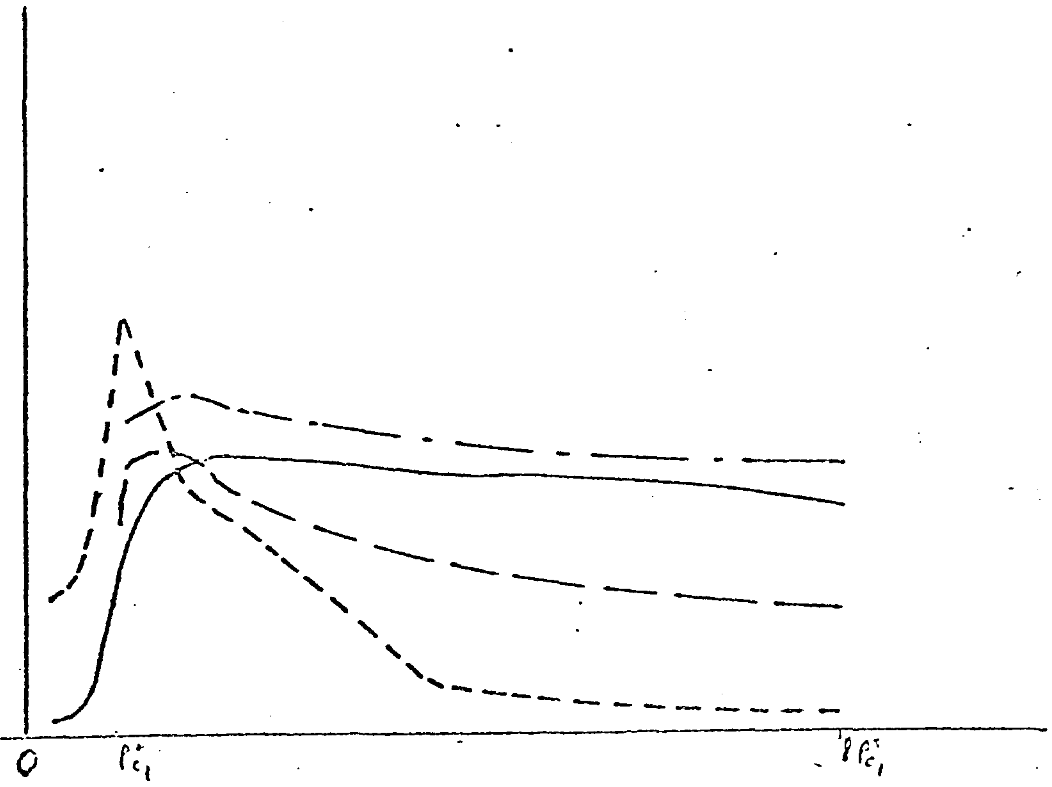
y_1=.3 T*=1.1

Fig 9

y_1=.3 T*=1.4

$\Delta E^E/RT$ ———— $\Delta S^E/R$ — — $.5\Delta V^E/v_0$ - - - - $\Delta H^E/RT$ —·—





Mixture of hard spheres and hard spheres with attractive tails : Excess functions vs P*

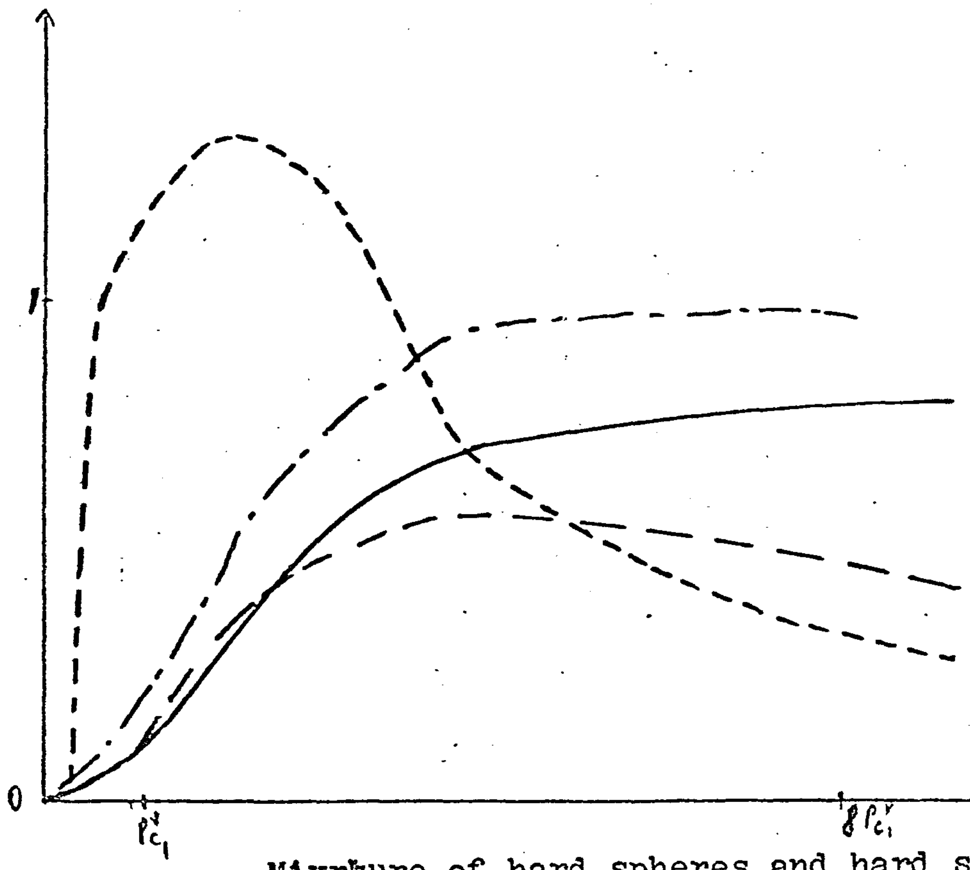
Fig 10

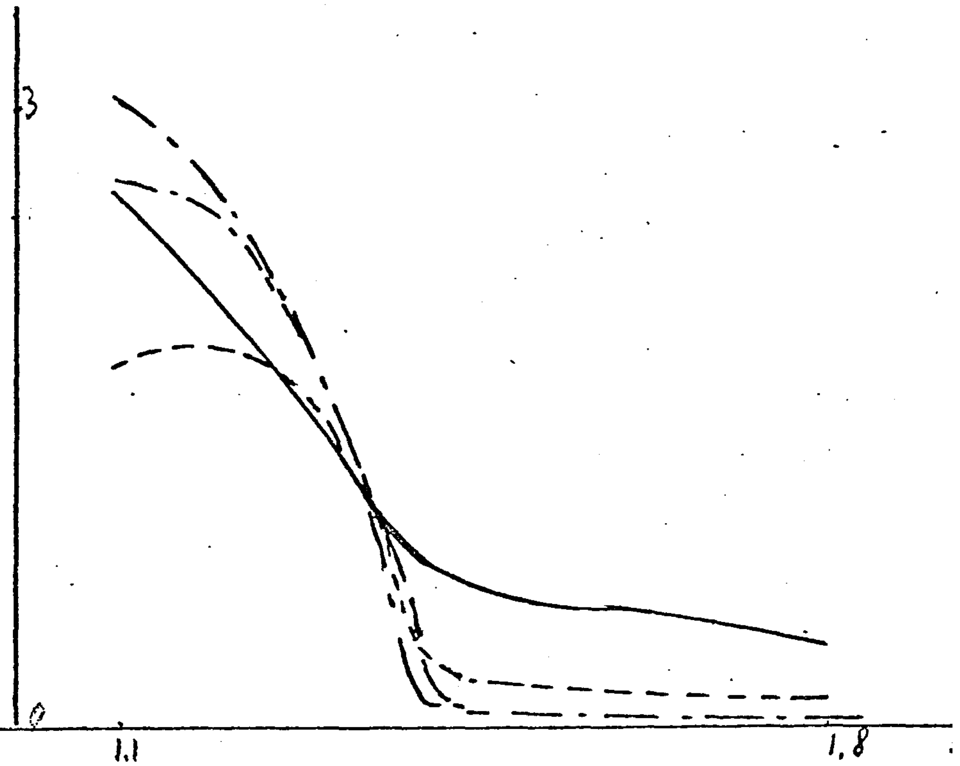
$y_1=.7$ $T^*=1.1$

Fig 11

$y_1=.7$ $T^*=1.4$

$\Delta E^E/RT$ —— $\Delta S^E/R$ — — $.5\,\Delta V^E/V_c$ - - - $\Delta H^E/RT$ —·—





Mixrhure of hard spheres and hard spheres with tails

$\Delta E^E/RT$ ____ $\Delta S^E/R$ — — $\Delta H^E/RT$ _ . _ .

Fig 12

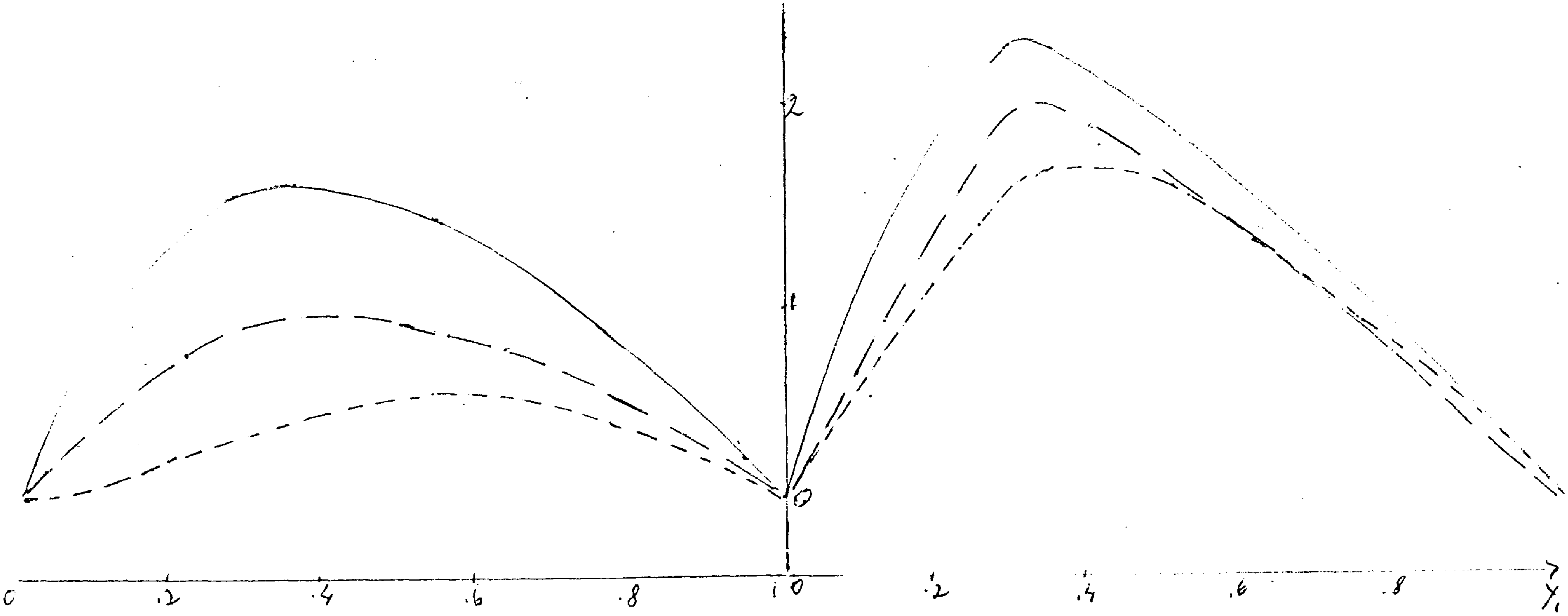
Excess functions vs Pressure , $T^*=1.8$ $y_1=.7$

$\Delta V^E/v_0$ -----

Fig 13

Excess functions vs T^* $P^*=.5\ P^*_{c1}$ $y_1=.7$

$.2\Delta V^E/v_0$ ----



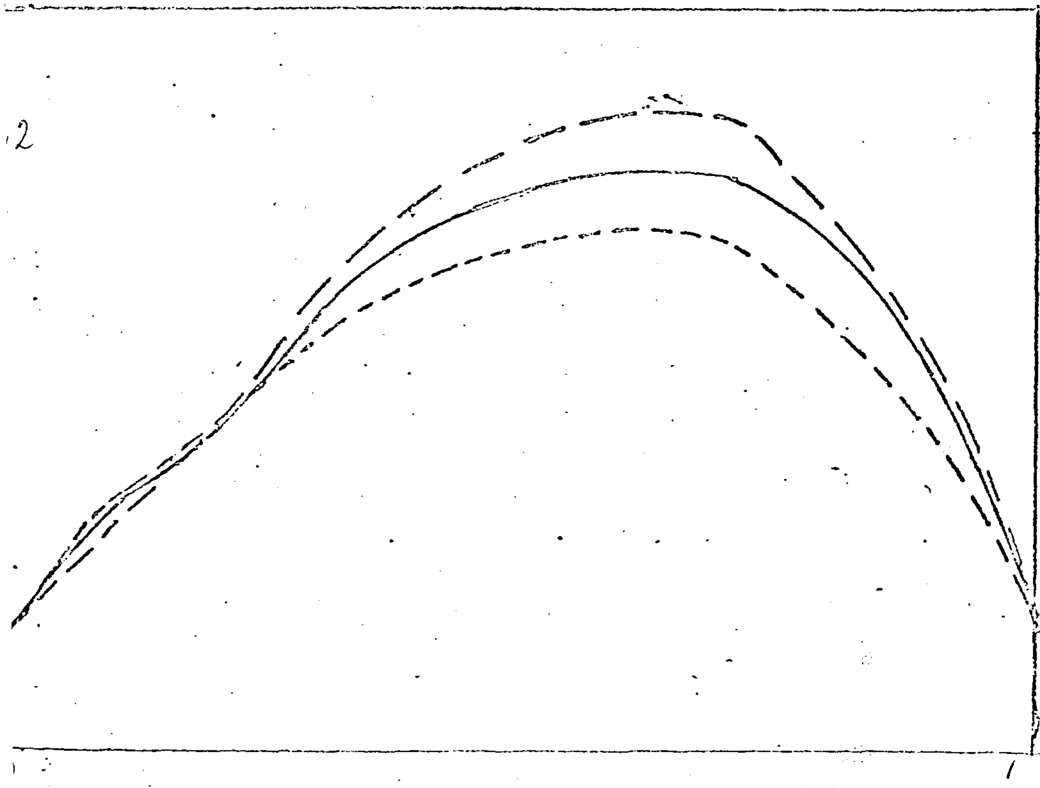
Mixture of hard spheres and hard spheres with tails :
Excess functions vs mole fraction

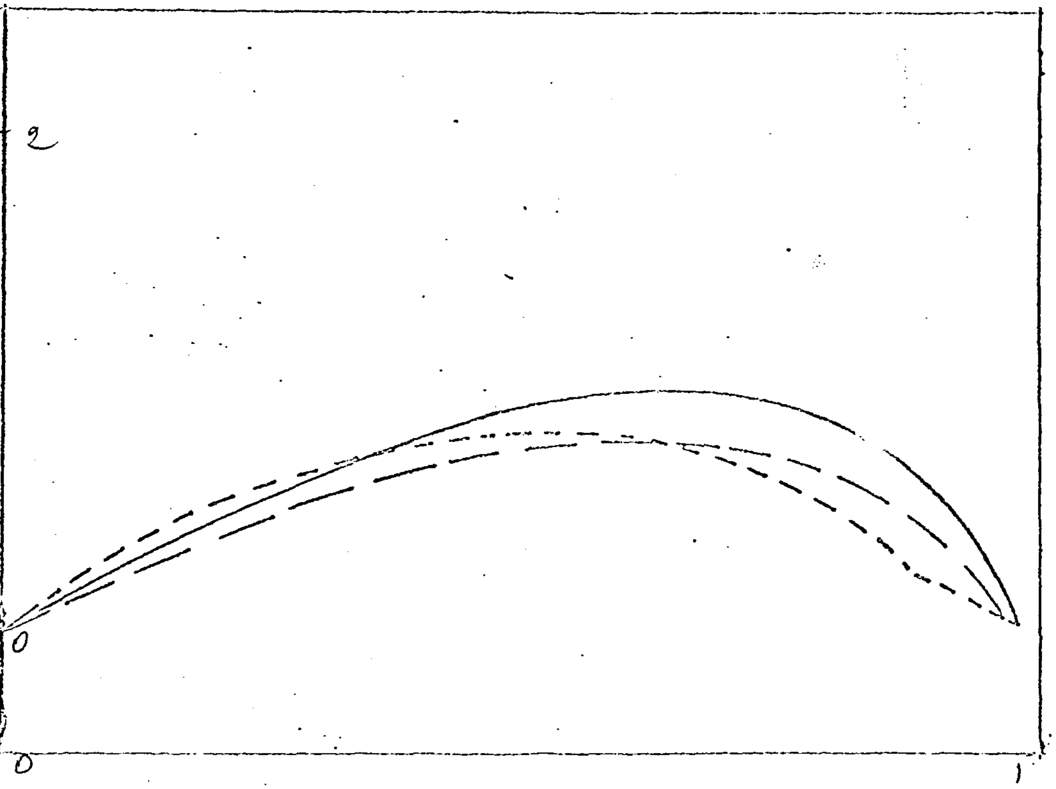
Fig 14 Fig 15

$\Delta V^E/v_0$ ---- $\Delta E^E/RT$ ___ $\Delta S^E/R$ — — $.5\Delta V^E/v_0$ -----

$T^*=1.2$ $P^*=4P^*_{cl}$

$T^*=1.2$ $P^*=P^*_{cl}$





Mixture of hard spheres and hard spheres with tails: Excess functions vs mole fraction

$\Delta E^E/RT$ ______

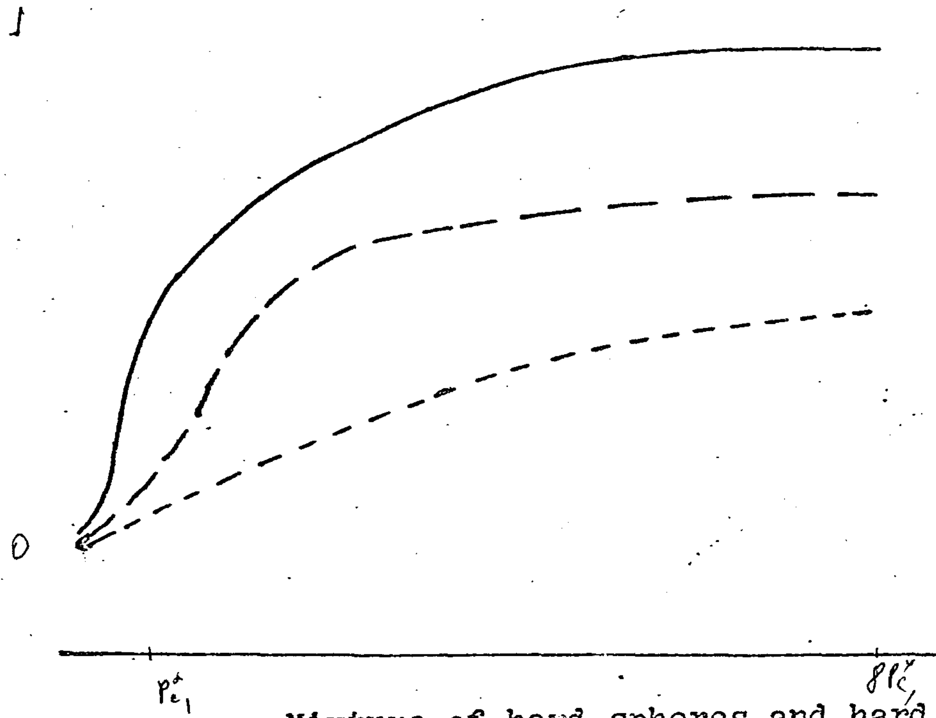
Fig 16

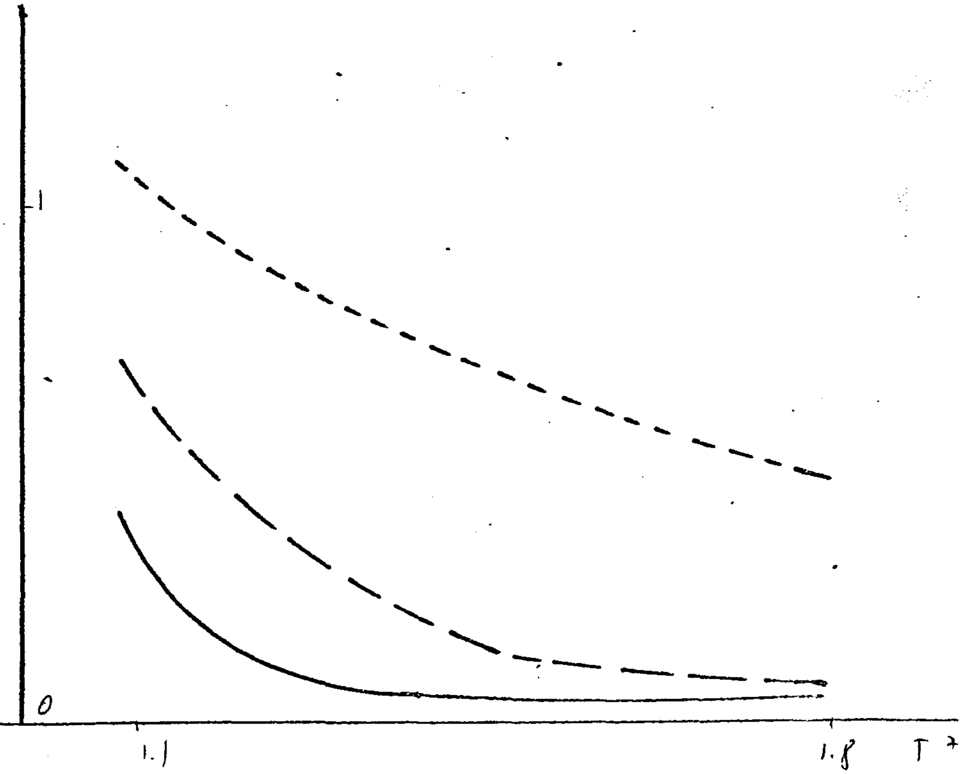
$T^*=1.6$ $P^*=P^*_{cl}$ .1 $\Delta V^E/v_0$ ......

$\Delta S^E/R$ - - - -

Fig 17

$T^*=1.6$ $P^*=4\ P^*_{cl}$ $\Delta V^E/v_0$ ......





Mixture of hard spheres and hard spheres with tails

Fig 18

$\Delta G^E/RT$ vs pressure $y_1 = .7$

$T^* = 1.2$ ———

$T^* = 1.4$ — —

$T^* = 1.8$ - - - -

Fig 19

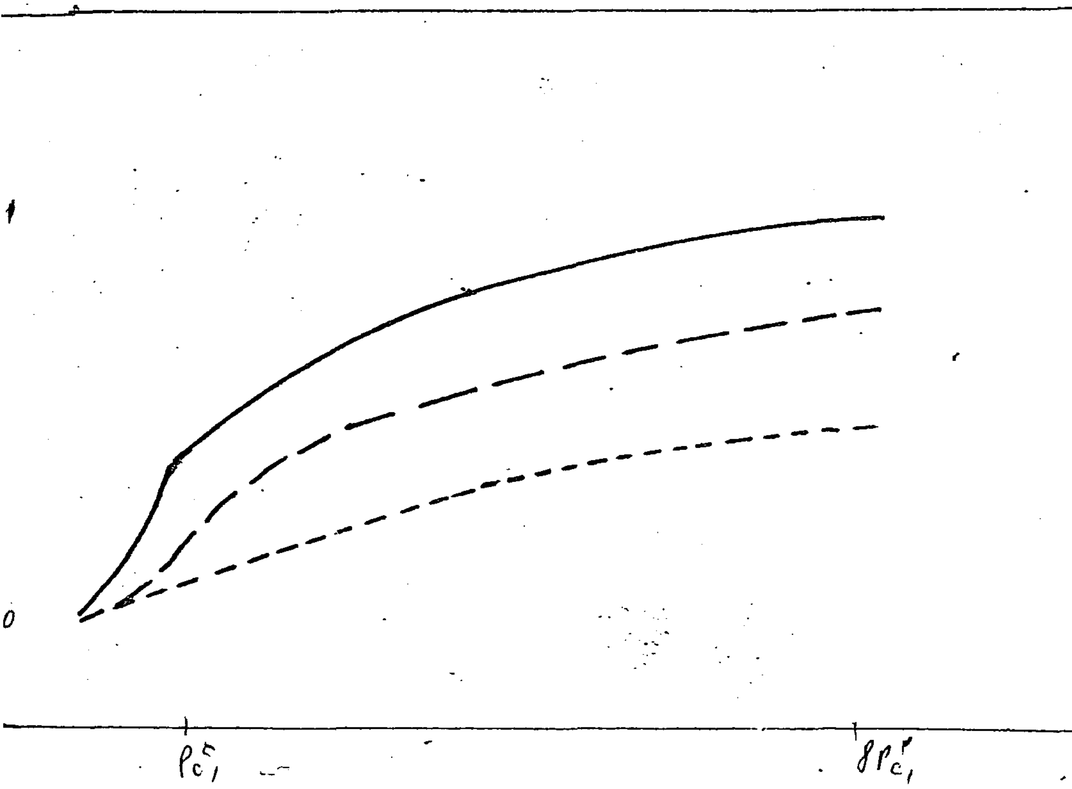
$\Delta G^E/RT$ vs T^*

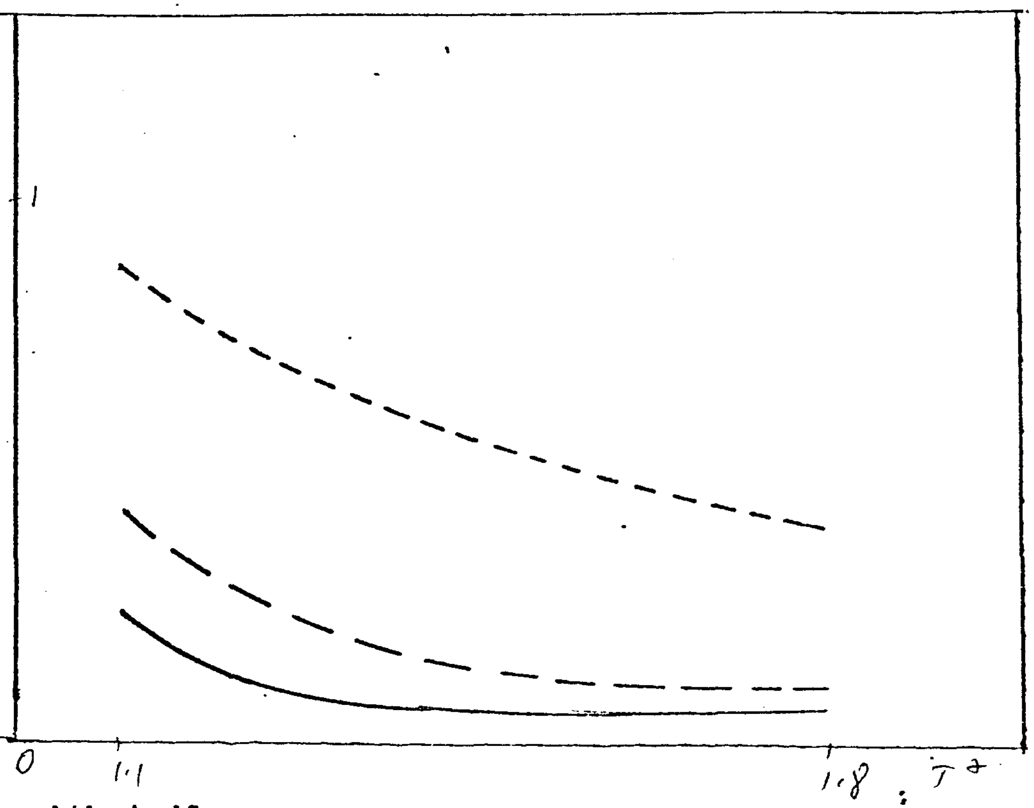
$y_1 = .7$

$P^* = .5P^*_{c1}$ ———

$P^* = P^*_{c1}$ — — —

$P^* = 8P^*_{c1}$ - - - -





Mixture of hard spheres and hard spheres with tails

Fig 20

$\Delta G^E/RT$ vs P^* $y_1 = .3$

$T^* = 1.2$ ———

$T^* = 1.4$ — —

$T^* = 1.8$ -----

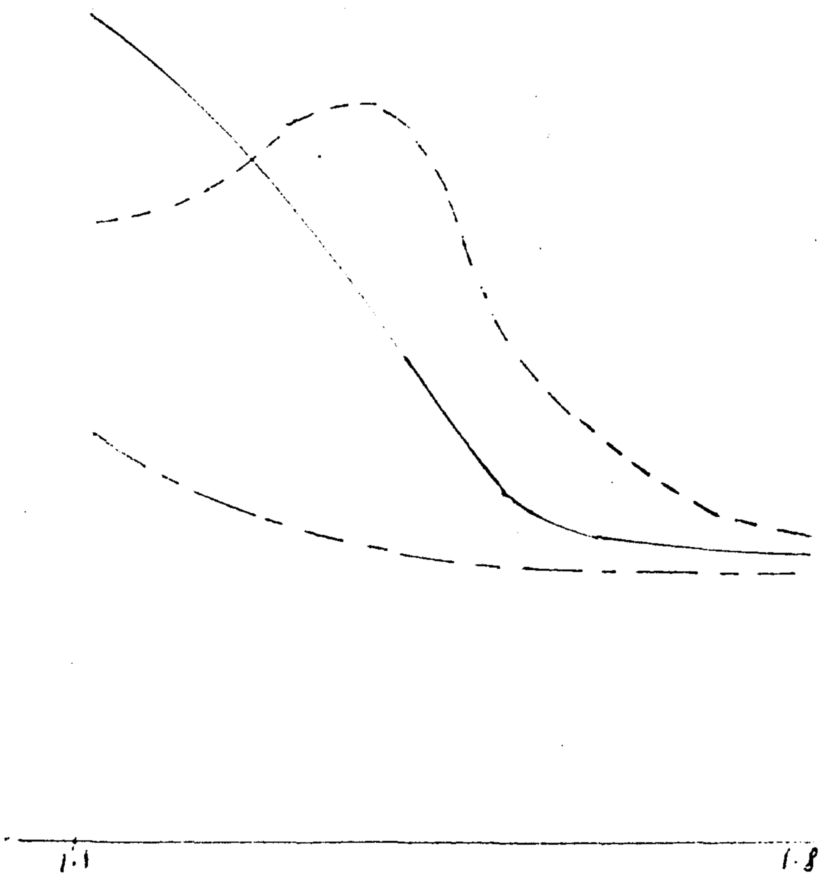
Fig 21

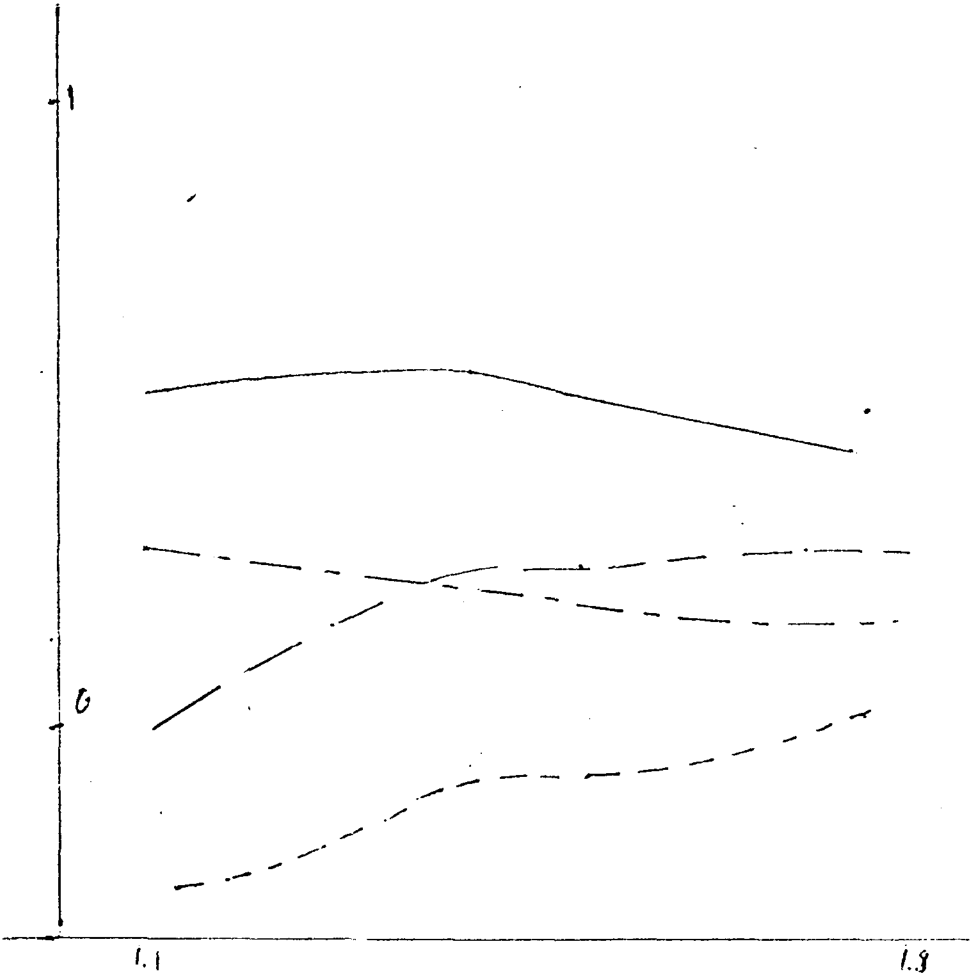
$\Delta G^E/RT$ vs T^* $y_1 = .3$

$P^* = .5\,P^*_{c1}$ ———

$P^* = P^*_{c1}$

P8 =8P* - - — —





Mixture of points and hard spheres with tails: Excess functions vs temperature

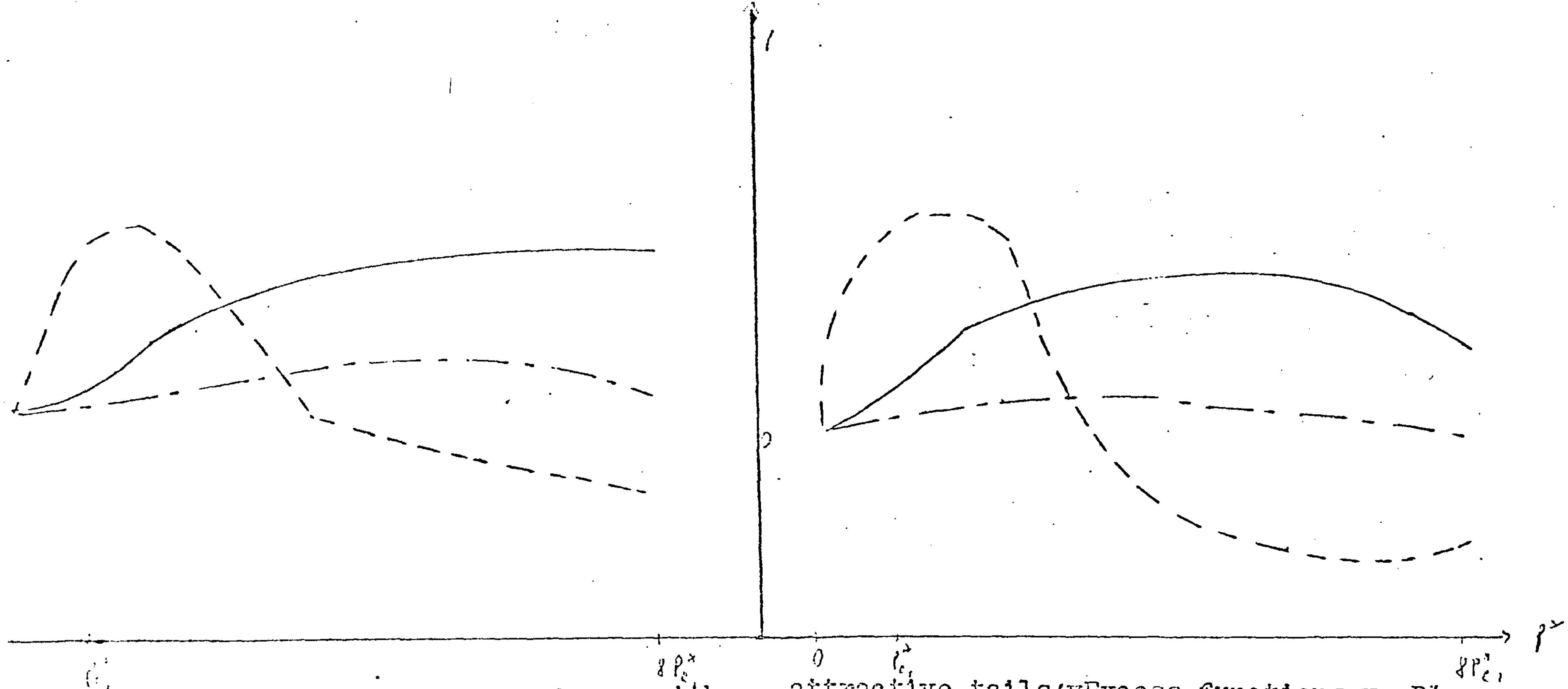
$\Delta E^E/RT$ ___ $\Delta V^E/v_0$ ----- $\Delta S^E/R$ — — $\Delta G^E/RT$ —·—

Fig 22

$P^* = P^*_{cl}$ $y_1 = .3$

Fig 23

$P^* = 8P^*_{cl}$ $y_1 = .3$



Mixture of points and hard spheres with attractive tails; Excess functions vs P*

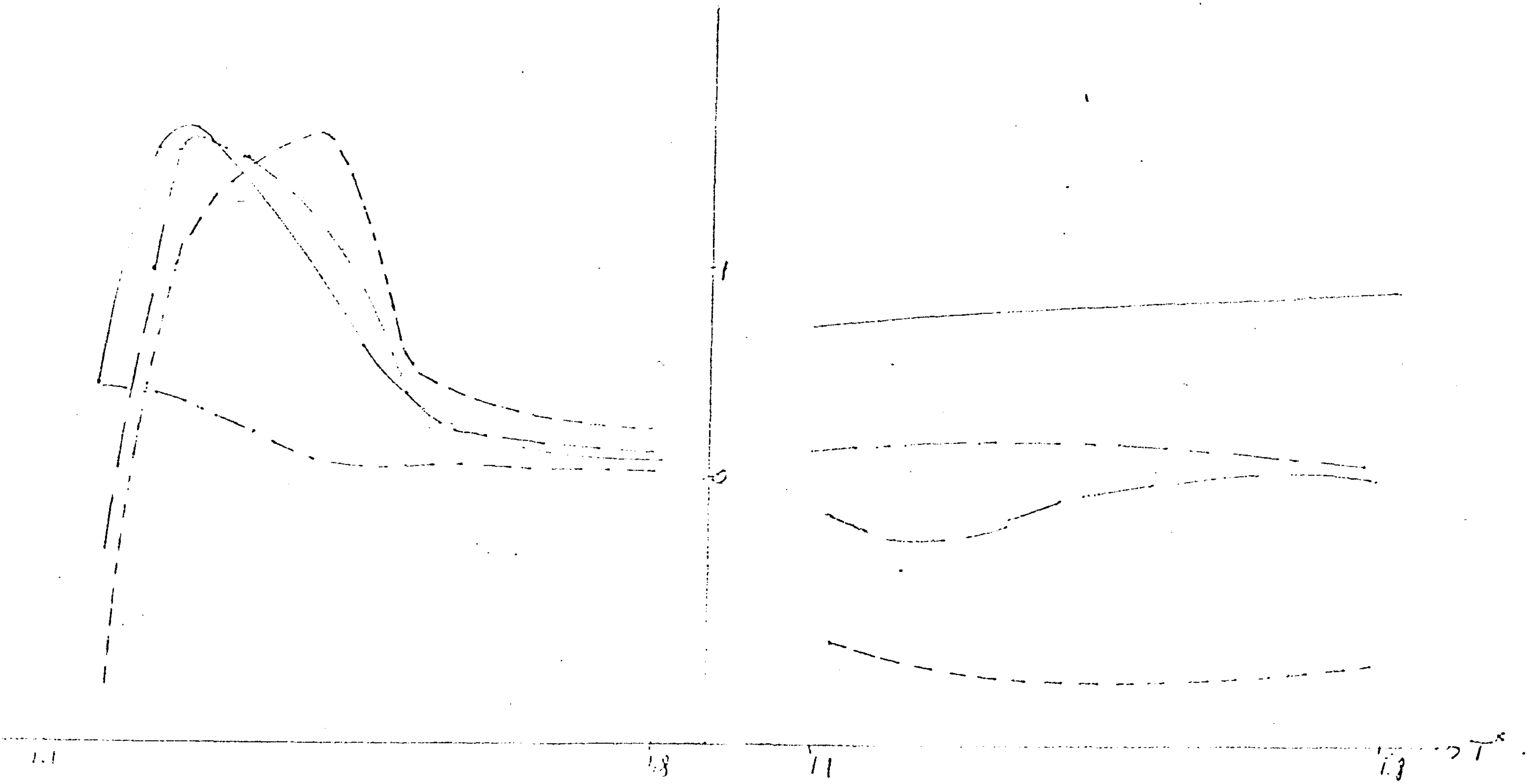
$\Delta E^E/RT$ ______ $\Delta V^E/v_0$ ---- $\Delta G^E/RT$ __.__.

Fig 25

$y_1=.3$ $T^*=1.8$

Fig 24

$y_1=.7$ $T^*=1.8$



Mixture of points and hard spheres with tails:

Excess functions vs T*

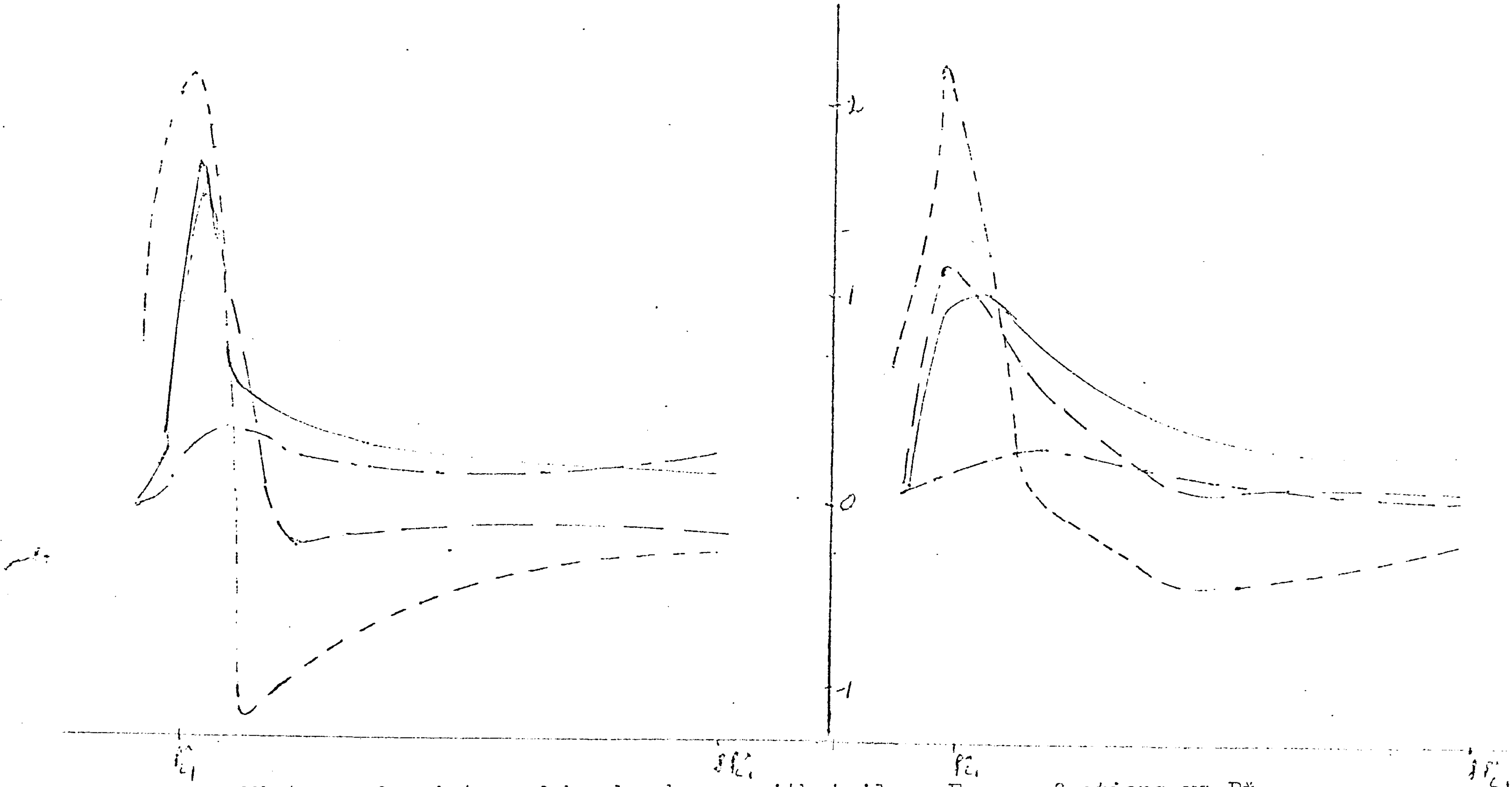
$\Delta E^E/RT$ ——— $\Delta V^E/v_0$ ---- $\Delta S^E/R$ — — $\Delta G^E/RT$ —·—

Fig 26

$y_1=.7$ $P^*=P^*_{c1}$

Fig 27

$y_1=.7$ $P^*=8P^*_{c1}$



Mixture of points and hard spheres with tails : Excess fuctions vs P*

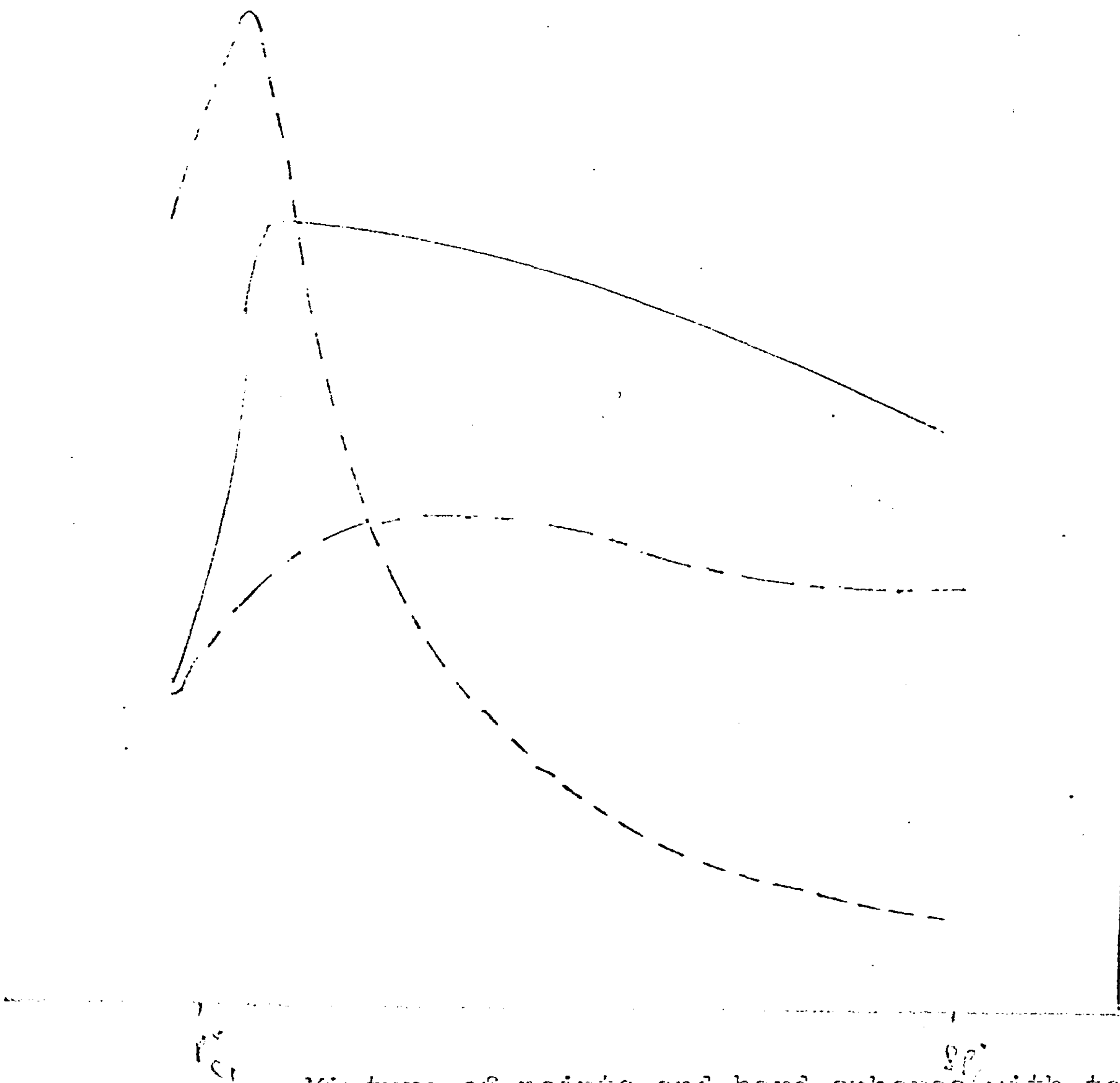
$\Delta E^E/RT$ ____ $\Delta S^E/R$ -- --- $\Delta V^E/v_0$ ----- $\Delta G^E/RT$ ---·---

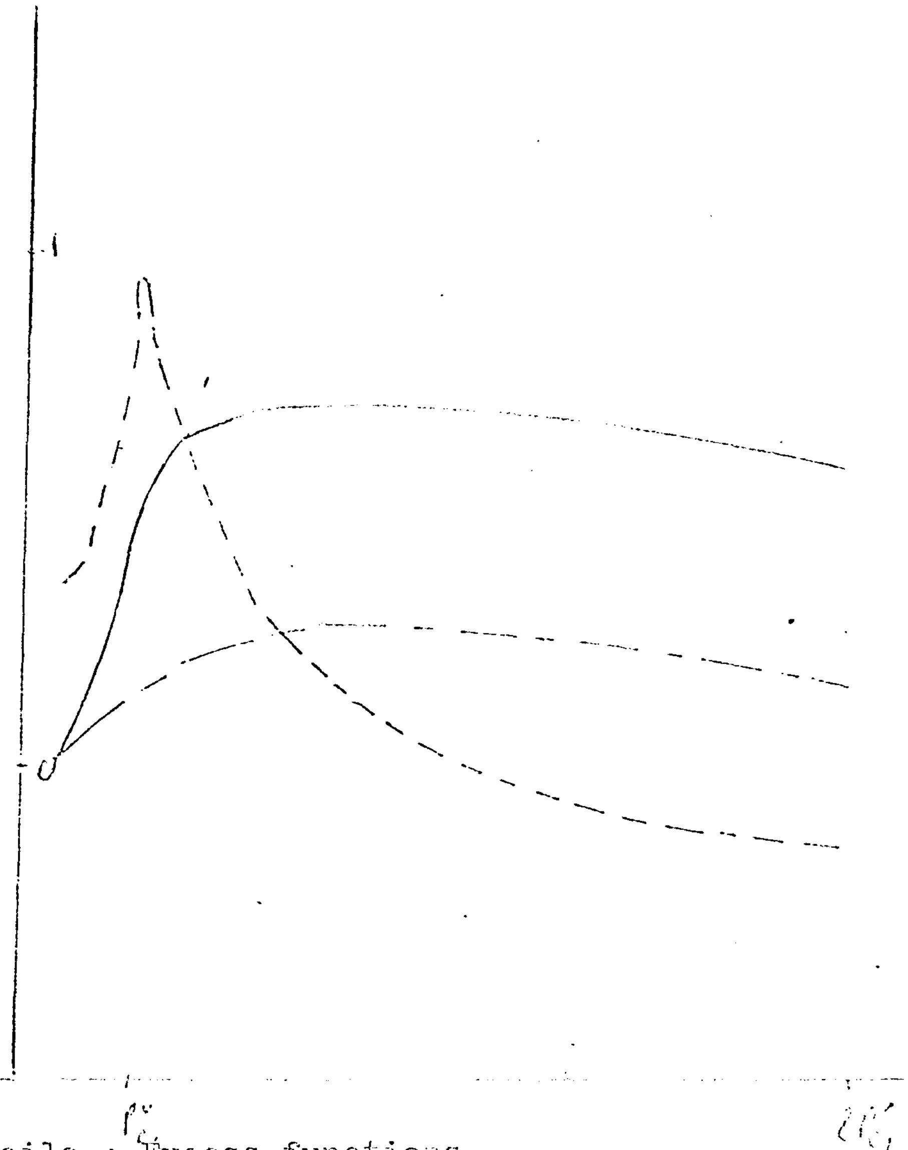
Fig 28

$y_1=.7$ $T^*=1.2$

Fig 29

$y_1=.7$ $T^*=1.4$





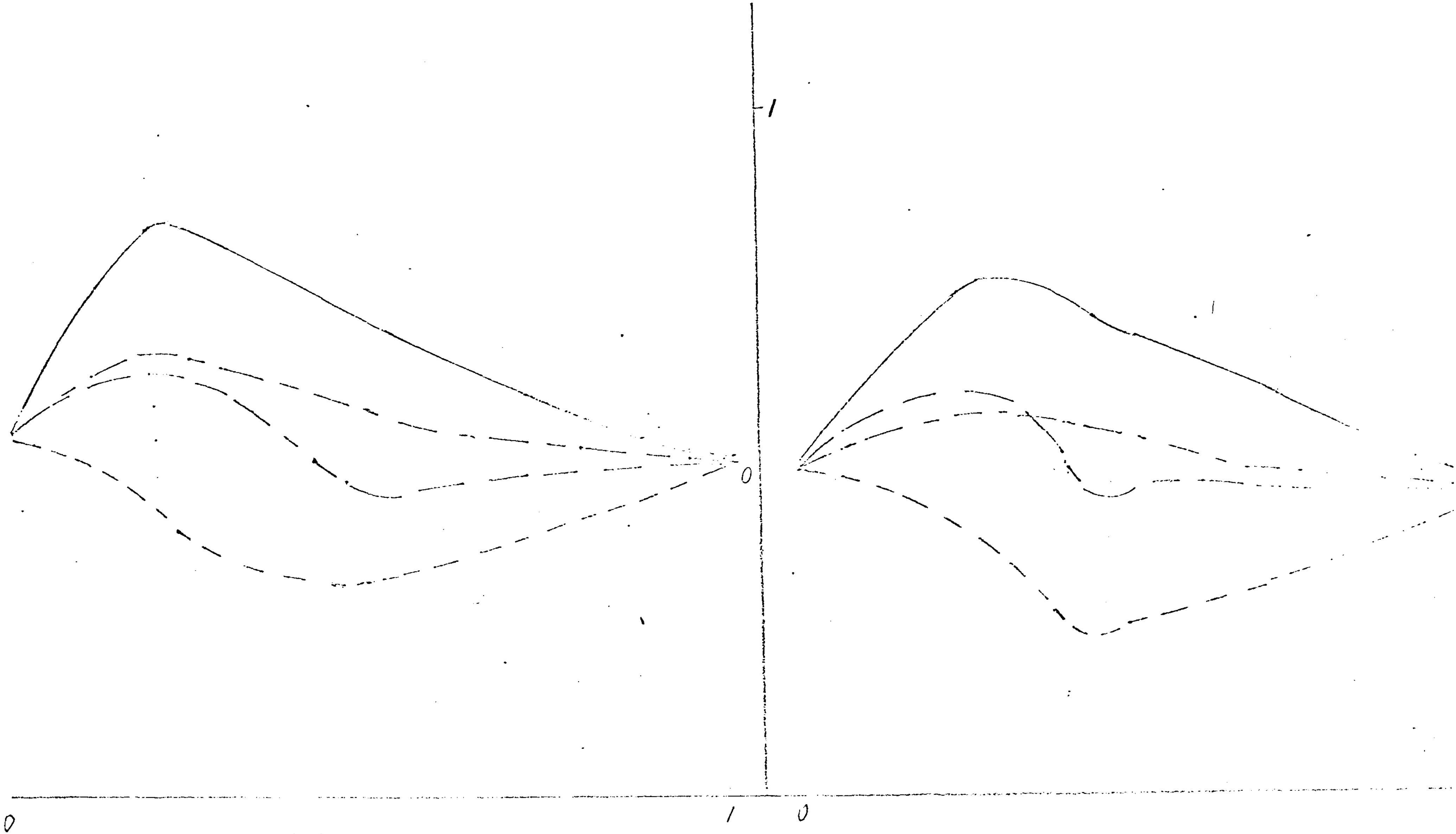
Mixture of points and hard spheres with tails : Excess functions vs P*

Fig 30 Fig 31

V^E/v_0 ----- E^E/RT ____ G^E/RT ---.--- $.5V^E/v_0$ ---

$y_1=.3$ $T^*=1.2$

$y_1=.3$ $T^*=1.4$



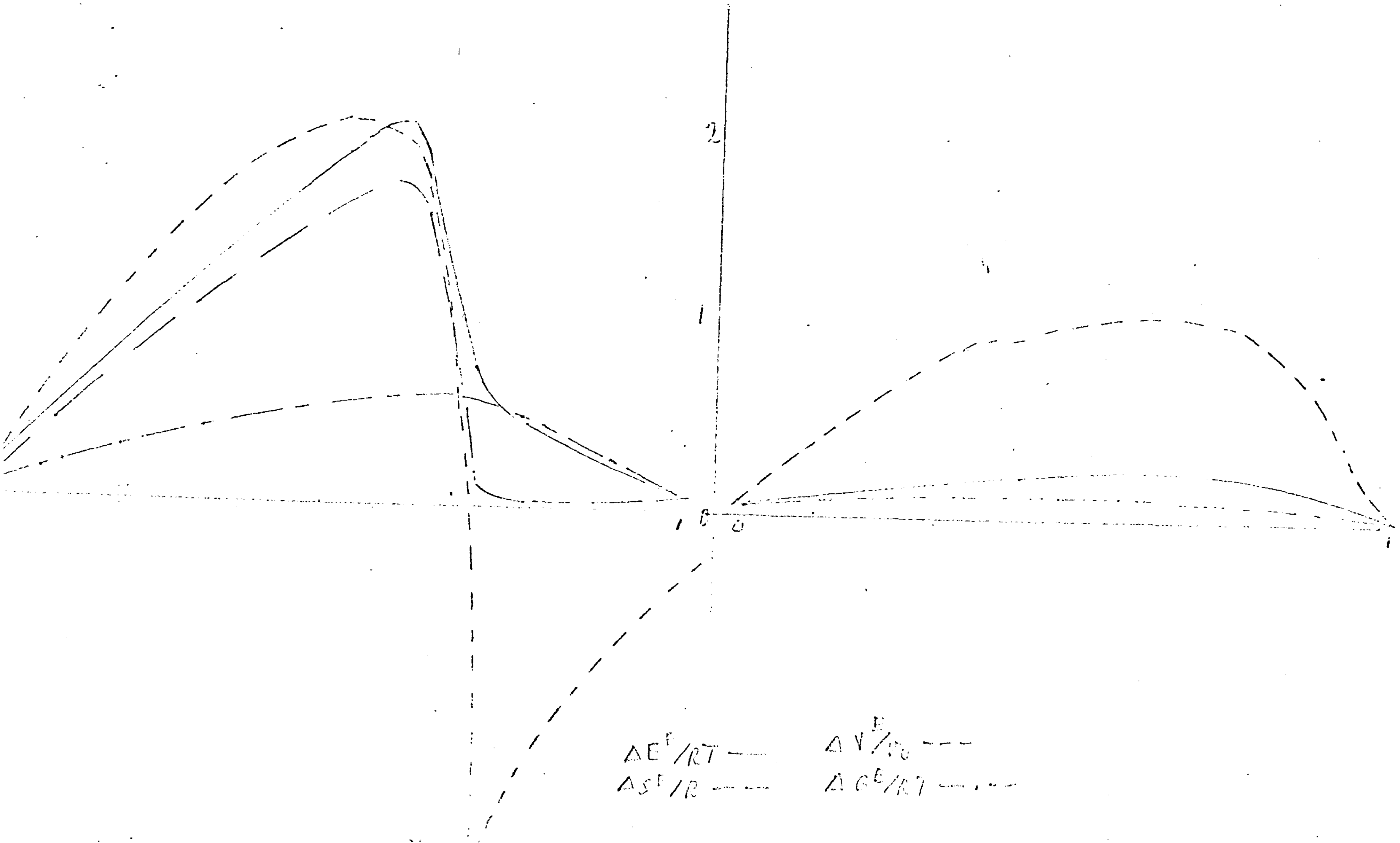
Mixture of points and hard spheres with tails: Excess functions vs mol mole fraction

Fig 32 $\Delta E^E/RT$ ——— $\Delta S^E/R$ ——— $\Delta V^E/v_0$ - - - - Fig 33

$\Delta G^E/RT$ —·—

$T^*=1.2$ $P^*=P^*_{c_1}$

$T^*=1.5$ $P^*=8P^*_{c_1}$



Mixture of points and hard spheres with tails:
Excess functions vs mole fraction

Fig 34
$T^*=1.1 \quad P^*=P^*_{c_1}$

Fig 35
$T^*=1.5 \quad P^*=8P^*_{c_1}$

Chapter 5

Phase transitions and critical lines

The critical temperature for a mixture is the temperature for which, at given pressure, the properties of two coexistent phases become identical. At temperatures below or above the critical (depending on the type of behavior of the system), there is a separation into two stable coexistent phases. For our model, critical temperatures were determined by plotting the Gibbs free energy of mixing for the system versus the composition and in all cases were of the upper consolute type.

The Gibbs free energy of mixing is given by :

$$\Delta G^M/RT = \Delta G^E/RT + y_1 \ln y_1 + y_2 \ln y_2 \qquad (46)$$

where:

y_1 is the mole fraction of the less volatile component and $(y_1 \ln y_1 + y_2 \ln y_2)RT$ is the ideal Gibbs free energy of mixing.

For $y_1=0$ and $y_1=1$, ΔG^M is of course zero. For homogenous systems, $\Delta G^M/RT$ vs y_1 at constant P* and T* should be everywhere concave upwards, that is :

$$\left[\frac{\partial^2(\Delta G^M/RT)}{\partial y_1^2}\right]_{P,T} > 0 \qquad (47)$$

This is the condition for material stability, obtained from the fact that all spontaneous fluctuations in a system at equilibrium must lead to an increase in Gibbs free energy at given pressures and temperatures. When a convexity appears, this indicates separation into two phases and the value of the coexistent mole fractions is determined by the two points which have a common tangent. Indeed, this will insure the satisfaction of the equilibrium conditions:

$$\mu_1'' = \mu_1' \qquad \mu_2'' = \mu_2' \tag{48}$$

where μ_1' and μ_1'' are the chemical potential in phase 1 or 2.

$$\mu_1' = G'^{M} - y_2'\left(\frac{\partial G^{M'}}{\partial y_2}\right)_{P,T} = \mu_1'' = G^{M''} - y_2''\left[\frac{\partial G^{M''}}{\partial y_2}\right]_{P,T} \tag{49}$$

$$\mu_2' = G^{M'} - y_1'\left[\frac{\partial G^{M'}}{\partial y_1}\right]_{P,T} = \mu_2'' = G^{M''} - y_1''\left[\frac{\partial G^{M''}}{\partial y_1}\right]_{P,T} \tag{50}$$

Substracting the equations :

$$\left[\frac{\partial G^{M'}}{\partial y_1}\right]_{P,T} = \left[\frac{\partial G^{M''}}{\partial y_1}\right]_{P,T} \tag{51}$$

and by substitution :

$$(G^{M'} - G^{M''})/(y_1' - y_2'') = \left[\frac{\partial G^{M}}{\partial y_1}\right]_{P,T} \tag{52}$$

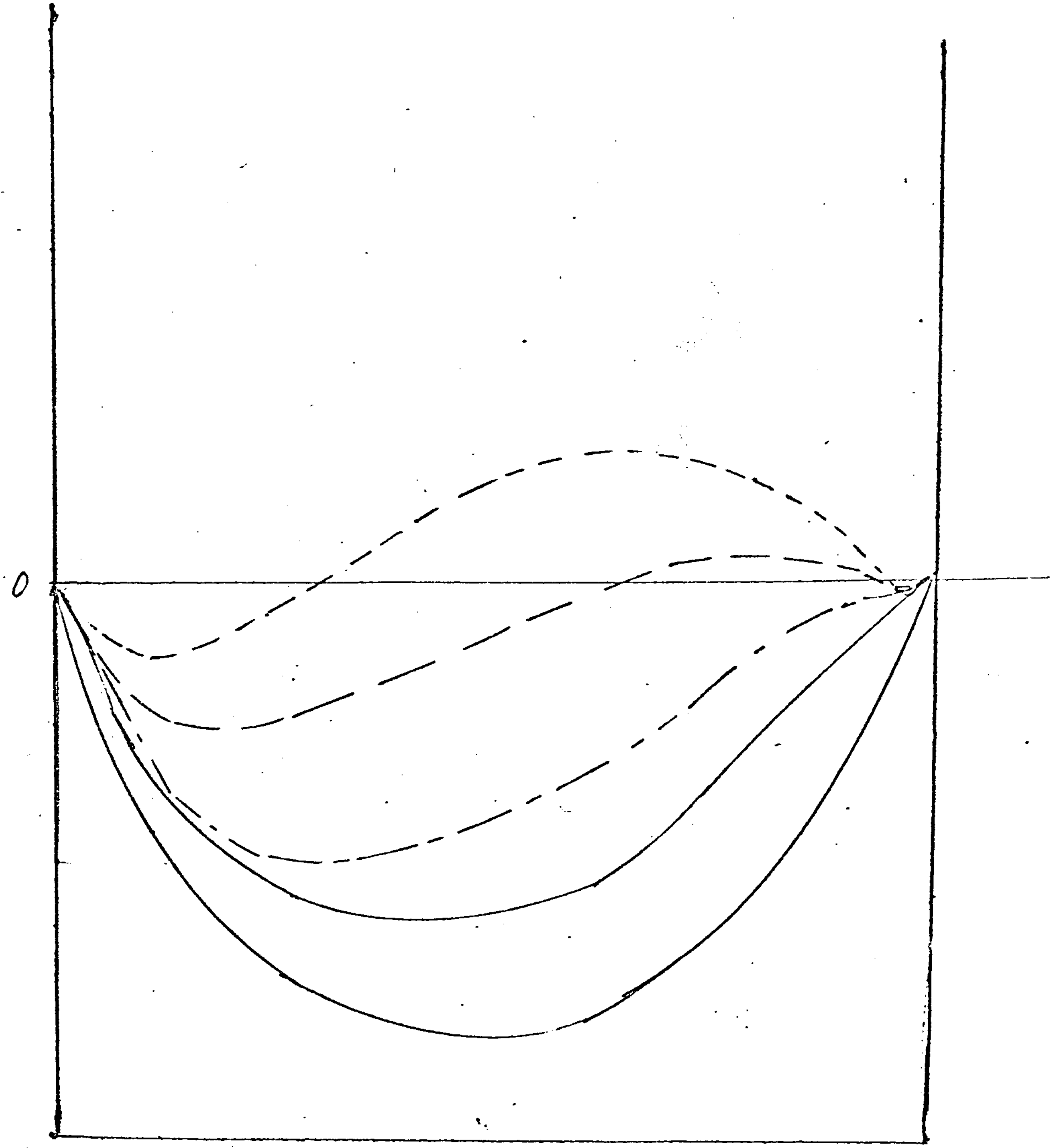
which is the equation of a tangent.

Instead of using G^M, we used ΔG^M which is:

$$\Delta G^M = G^M - y_1 G_1 - y_2 G_2 \tag{53}$$

This is perfectly legitimate since G_1 and G_2 do not depend on y_1 so the condition for critical point is satisfied.

The mixture will reach a critical point when the convexity desappears or, in other words, when the two points coincide. Fig 36 shows an example of phase separation for a binary mixture of hard spheres and hard spheres with attractive tails, at temperature $T^*=1.3$ and different pressures. Fig 37 shows the dependence of the coexistent mole fractions on T^* at a fixed pressure of $P^*=8P^*_{c1}$. The ordinate of the point where the two coexistent mole fractions coincide, will be the critical temperature at the given pressure. We plotted $\Delta G^M/RT$ for a wide range of pressures and temperatures and were able to determine in this way, for a given pressure, at what tem-



Mixture of hard spheres and hard spheres with tails

Fig 36

G^M/RT vs mole fraction

$P^*=P^*_{c1}$ and $P^*=P^*_{c1}x1.5$ ____

$P^*=2P^*_{c1}$ —·— $P^*=4P^*_{c1}$ — — $P^*=12P^*_{c1}$ ---

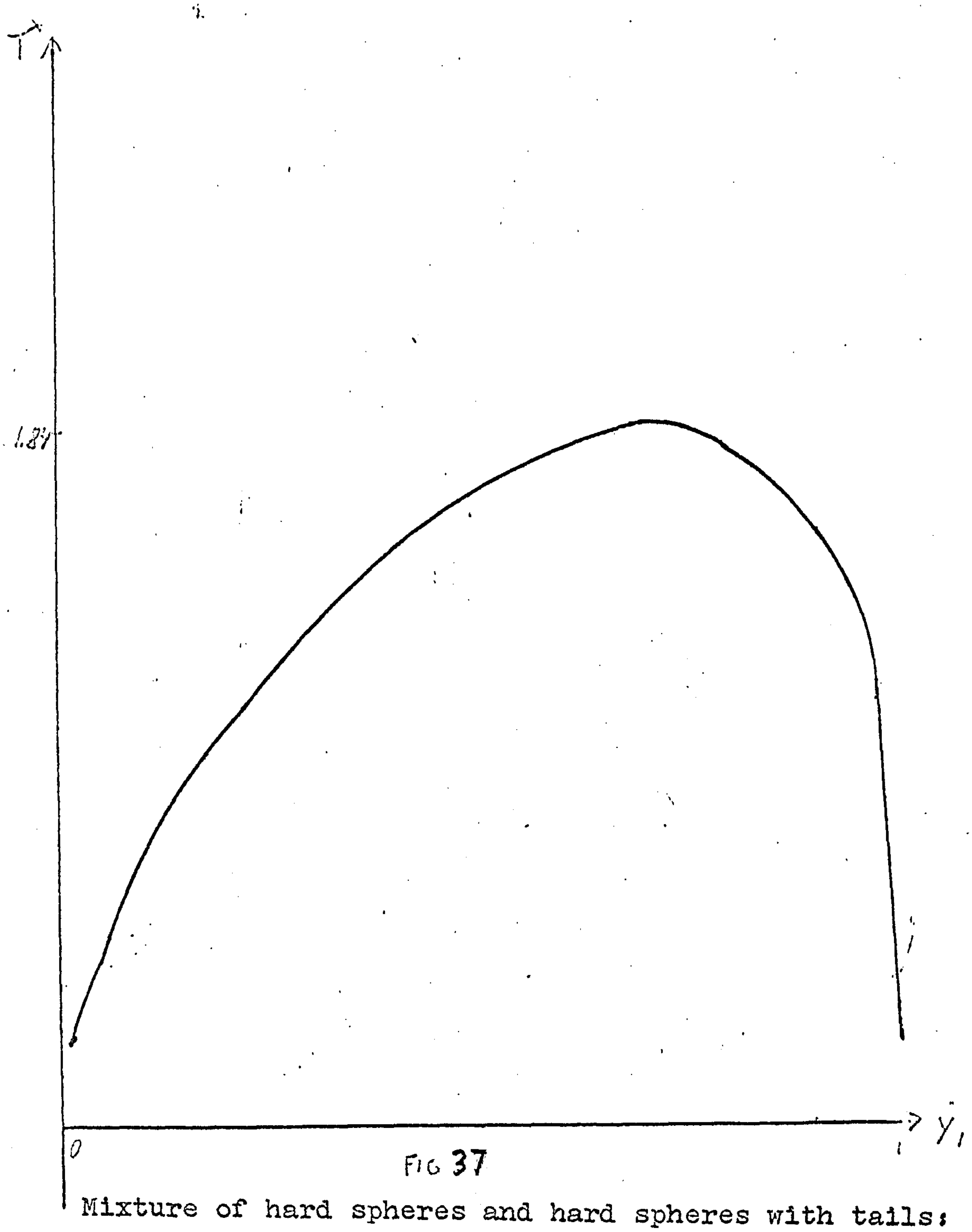


Fig 37

Mixture of hard spheres and hard spheres with tails:
Coexistent mole fractions vs T^* at $P^*=8P^*_{c1}$

perature there is no longer phase separation. We determined the mole fraction at this temperature which was the point of coincidence of the two previously coexistent mole fractions and called it "the critical mole fraction".

Before calculating critical points in the way described before, we tried to determine them from the two conditions [26]:

$$\frac{\partial^2(\Delta G^E/RT)}{\partial y_1^2} = -\frac{1}{y_1(1-y_1)} \quad ; \quad \frac{\partial^3(\Delta G^E/RT)}{\partial y_1^3} = \frac{-(2y_1-1)}{y_1^2(1-y_1)^2} \qquad (54)$$

In order to apply these conditions we attempted to fit $\Delta G^E/RT$ to the form:

$$\Delta G^E/RT = y_1(1-y_1)\left[A_0 + A_1(2y_1-1) + A_2(2y_1-1)^2\right] \qquad (55)$$

where A_0, A_1 and A_2 are functions of pressure and temperature. After some trial we reached the conclusion that this method is cumbersome and inaccurate.

Another idea which we considered was to calculate the Gibbs free energy for the mixture itself directly from eq. 1 and setting :

$$G^M/RT = A^M/RT + PV^M/RT \qquad (56)$$

and using:

$$A^M = \int -PdV \qquad (57)$$

This method seemed to be laborious and we prefered using the excess functions which were already calculated.

For the mixture of hard spheres and hard spheres with tails as expected, for temperatures below the critical temperature of pure gas 1, there is a phase separation at pressures greater than the vapor pressure of gas 1, at the given temperature. No loops are formed and no critical pressure exists at such temperatures up to the very high pressures so far calculated. In accord with Rowlinson[10], we do not believe these curves will ever close, no matter how high the pressure becomes. The behavior is definitely that of Fig 1 as it can be seen from Fig 38, which shows the dependence of the coexistent mole fractions with the pressure at fixed temperature. The coexistent mole fractions are plotted for pressures as high as $8P^*_{c1}$ at fixed temperatures of $T^*=1.1$, 1.2, 1.4, and 1.6.

Table 5 shows the critical points. As it can be seen, the critical temperature increases with the pressure almost linearly. The critical mole fraction is decreasing with the pressure, reaching a value of about $y_1=0.6$, for a pressure $P^*=20P^*_{c1}$. Actually, if we look at the value of X_m at high pressures, we see that they are almost constant with y_1. (For instance, at $P^*=14P^*_{c1}$, and $T^*=1.5$, the X_m for $y_1=.1$, .2, .3 are 2.70, 2.68 and 2.65 respectively) From equations 25, 27 and 31 it is clear that if X_m does not depend on y_1, the third derivative of $\Delta G^E/RT$ with y_1 will be zero, and thus, from equation 54, $y_{1c}=.5$. We expect that the y_{1c} from our equations will approach this value for extremely high pressures.

Again in accord with Rowlinson [10], we do not believe our higher temperature - higher pressure critical line will ever turn back to the zero temperature critical point of our more volatile component. As Rowlinson says, those who suggest that the critical line must go back are almost certainly wrong.[27,28] Indeed, a condition of material stability fixes the critical points in a two-component case, while the condition of mechanical stability determines the critical point for a one-component case. It does not seem to be an absolut thermodynamic requirement that such

Table 5

Critical points of a mixture of hard spheres and hard spheres with tails

P*	T* ± .005	y_1 ± .01
0.2085	1.44	.940
0.2780	1.51	.920
0.4170	1.56	.880
0.5560	1.64	.800
1.1120	1.84	.700
1.3900	1.94	.680
2.0850	2.10	.660
2.7800	2.22	.640

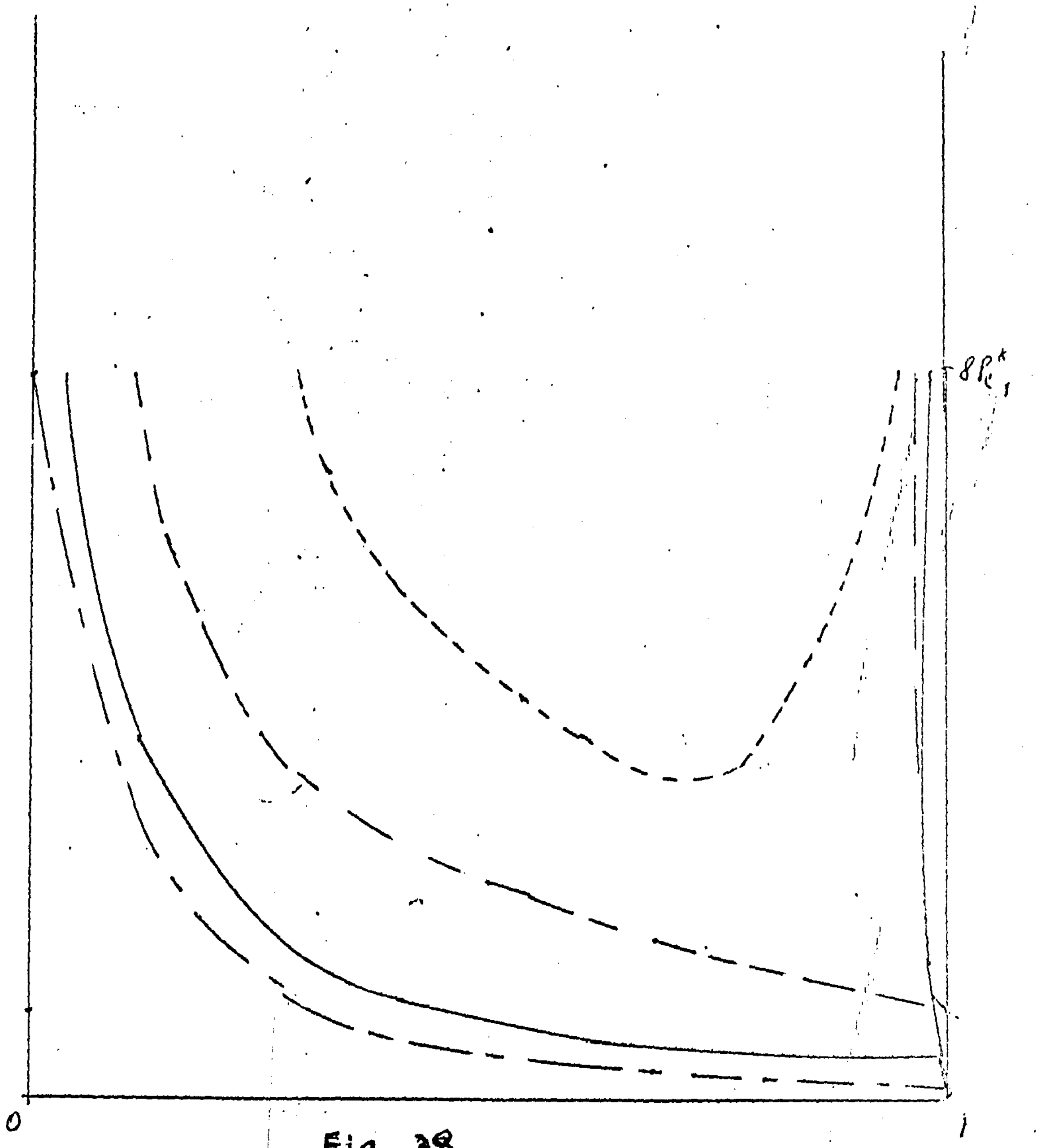


Fig. 38
Mixture of hard spheres and hard spheres with tails:
Coexistent mole fractions vs P^*
$T^*=1.1$ _ . _ . $T^*=1.4$ _ _ _
$T^*=1.2$ ____ $T^*=1.6$ ------

a critical line has to turn back continuously to the critical point of both or even either of the pure components.

Qualitatively, our results are in accord with the experimental work of De Swaan Arons and Diepen [21] for a mixture of He and Xe and with the theoretical predictions from a Prigogine type[29] "three liquid model" [30].

Quantitatively there is a discrepancy in the sense that we find a much larger increase in the critical temperature for a given pressure increment than it is found experimentally. It is true though, in the experimental case that the ratio of, for instance, Lennard-Jones well depth of Xe to that of He is only about 22, while in our model the more volatile component has zero-depth of energy well.

The comparison of T^*/T^*_{c1} vs P^*/P^*_{c1} from our model with the experimental one from [21] is shown in Fig 39.

Fig 40 and 41 show the dependence of the critical temperature on the pressure and on the mole fraction, respectively.

For the mixture of points and hard spheres with attractive tails the case is seen to be entirely different. When we plotted the free energy vs mole fraction, for pressures starting with $.25P^*_{c1}$ we found phase separation only for temperatures below the critical temperature of pure gas 1. Applying the common tangent method as described earlier, we found loops for temperatures below T^*_{c1} and no phase separation for temperatures above T^*_{c1}, no matter how much we increased the pressure. Fig 42 shows these loops for temperatures of 1.1, 1.2 and 1.3 and for pressures as high as $P^*=3$. Raising the pressure to as much

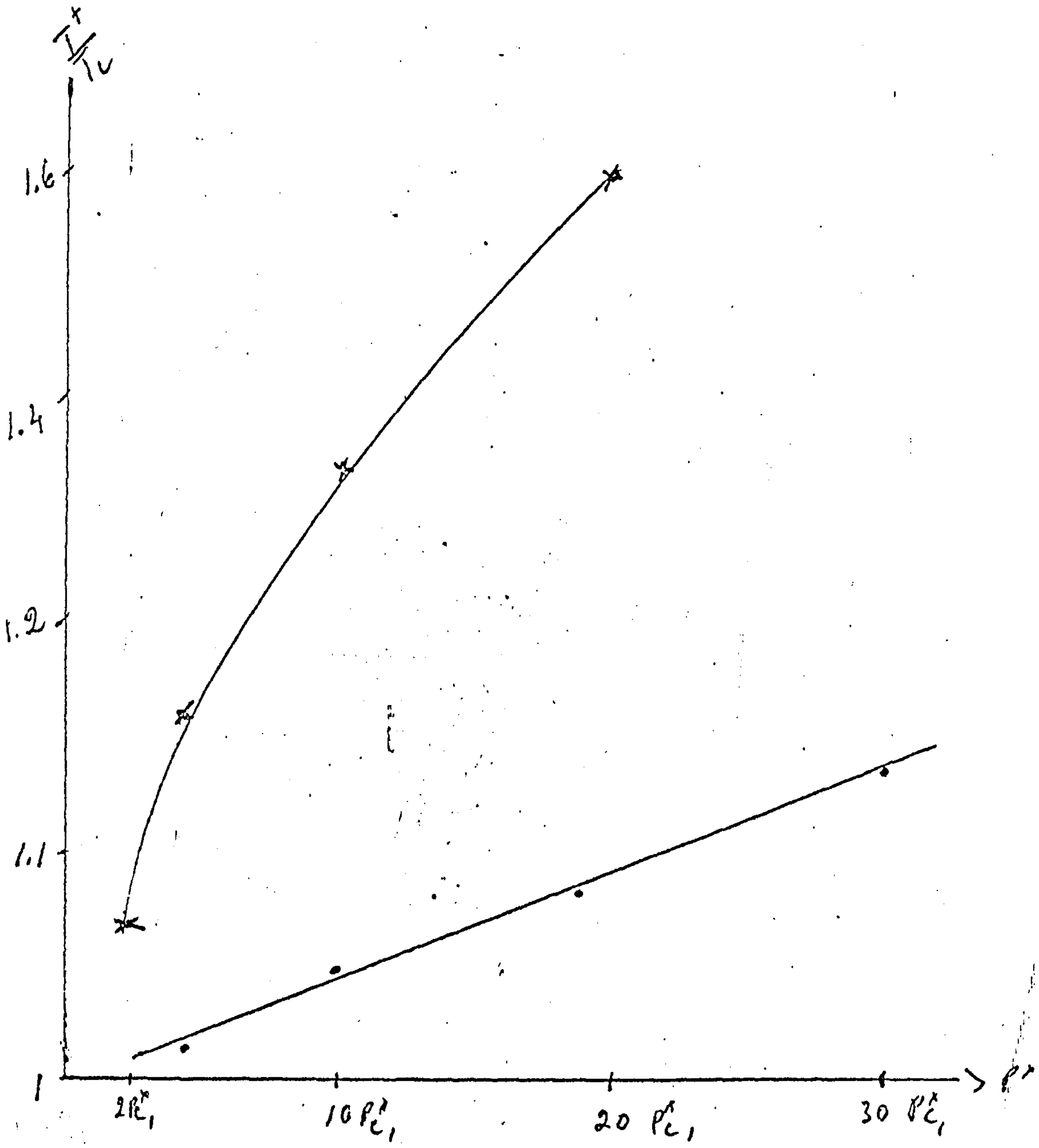


Fig 39

Mixture of hard spheres and hard spheres with tails:

T^*_c / T^*_{cl} vs P^* / P^*_{cl}

Our model: ×—×

Experimental(21) ●—●

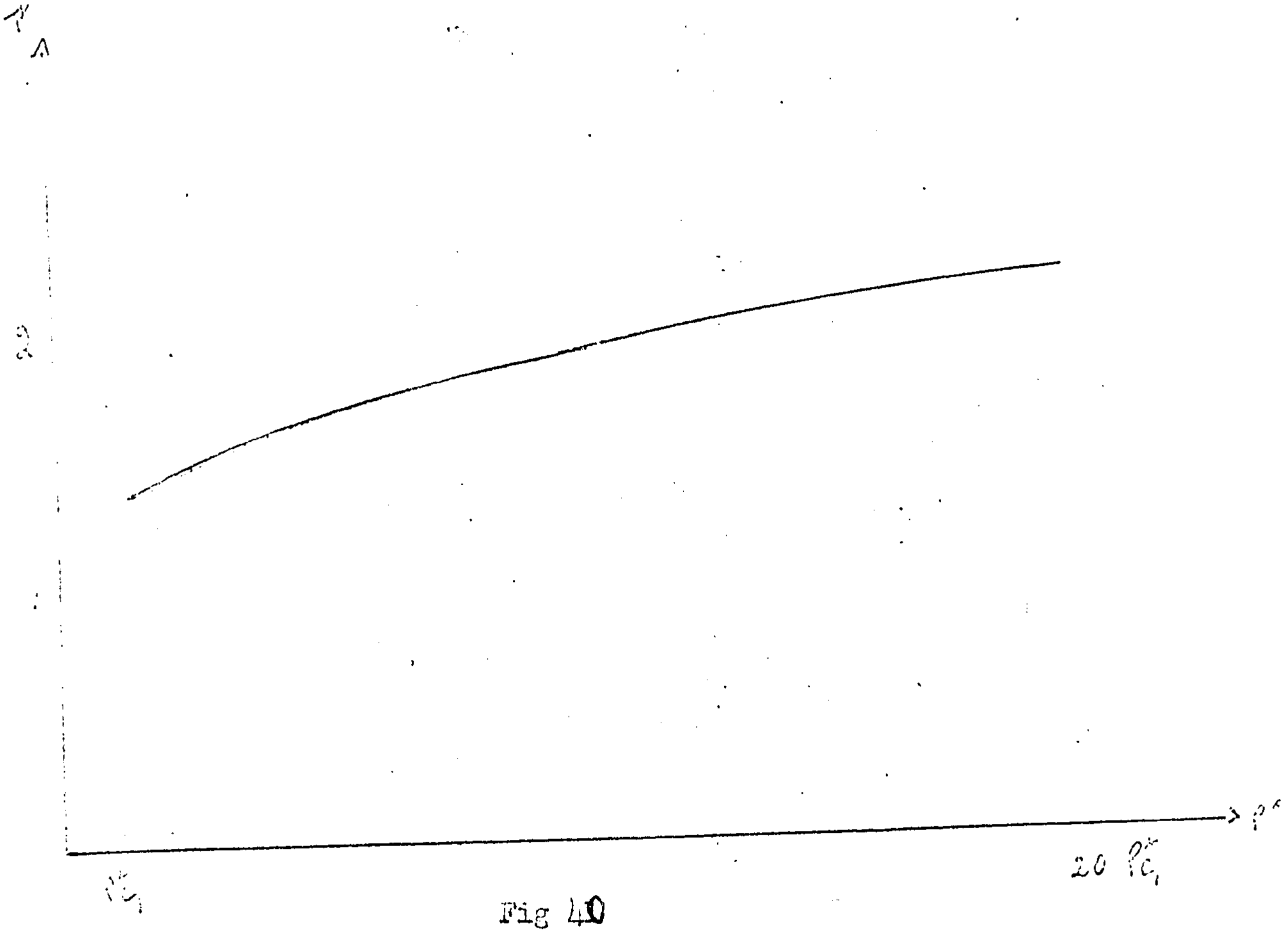


Fig 40
Mixture of hard spheres and hard spheres with tails:

Critical T* vs Critical P*

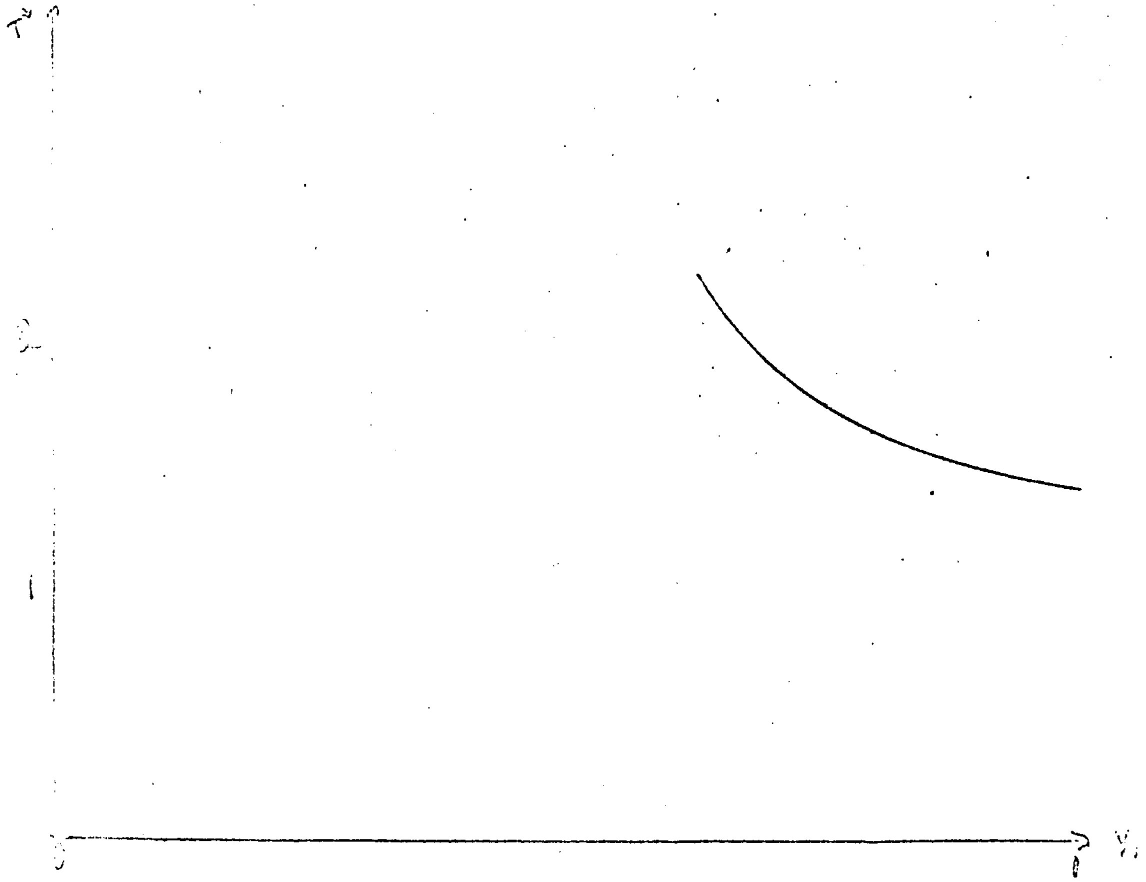


Fig 41
Critical T* vsc critical y_1

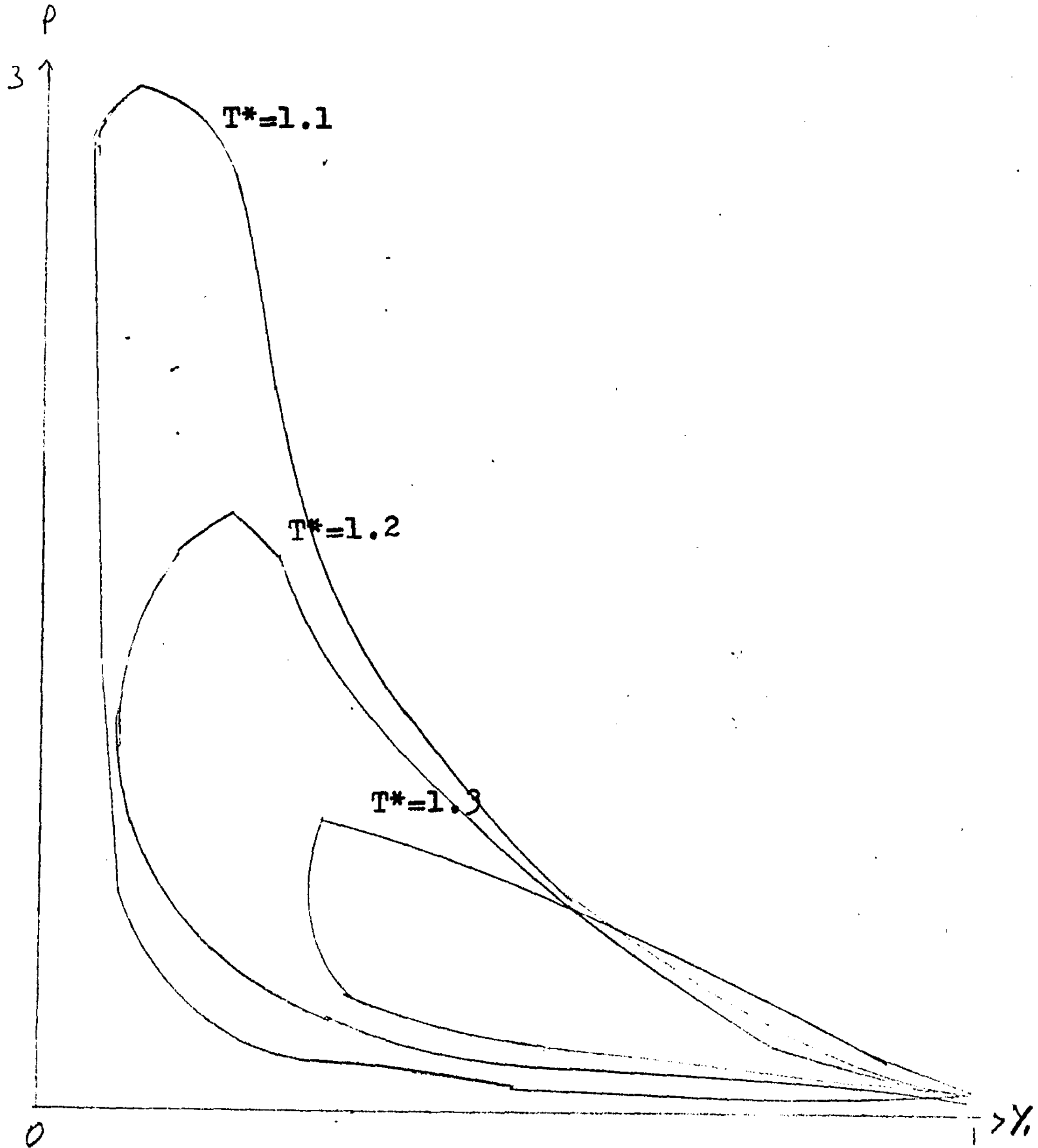


Fig 42
Mixture of points and hard spheres with tails:
Coexistent mole fractions vs pressure at fixed temperature

as 4, which is about 28 P^*_{c1}, and calculating G^M/RT for increments in the mole fraction as low as .01 between 0 and .1, we could not find any phase separation at pressures greater than 3, neither at low temperatures such as 1.1 nor at higher temperatures such as1.5 or 2. It is normal that not having found phase separation at lower temperatures, we could not find it at higher temperatures, since our case is an upper consolute critical temperature type. In order to calculate the excess free energy at high pressures and low temperatures, we had to use very small values for X_m and the AH approximation is valid only for values not much lower than 2. But the variable, as can be seen from the formulas is not X_m but X_m/y_1 which puts us in an appropriate range of values. However, if the reduced pressure would have been increased over 4 or the reduced temperature decreased below 1.1, this statement would not be true anymore. This is the reason why we did not extend the calculations to such pressures and temperatures.

We determined the critical points for various pressures and Table 6 shows the results.

As can be seen from Table 6, the critical temperature decreases with the increase of pressure and so does the critical mole fraction. Fig 43 and 44 show the dependence of the critical temperature on the pressure and the dependence of the critical mole fraction on the temperature, respectively.

The critical points determined are critical points for the gas-liquid phase, at temperatures below T^*_{c1}. The mixture of points and hard spheres with attractive tails does not seem to exhibit the phenomenon of gas-gas immiscibility.

Table 6

Critical points for the mixture of points and hard spheres with attractive tails

P^*	$T^* \pm .01$	$y_1 \pm .02$
0.278	1.39	0.68
0.556	1.36	0.54
1.112	1.28	0.30
1.390	1.26	0.24
3.000	1.10	0.11

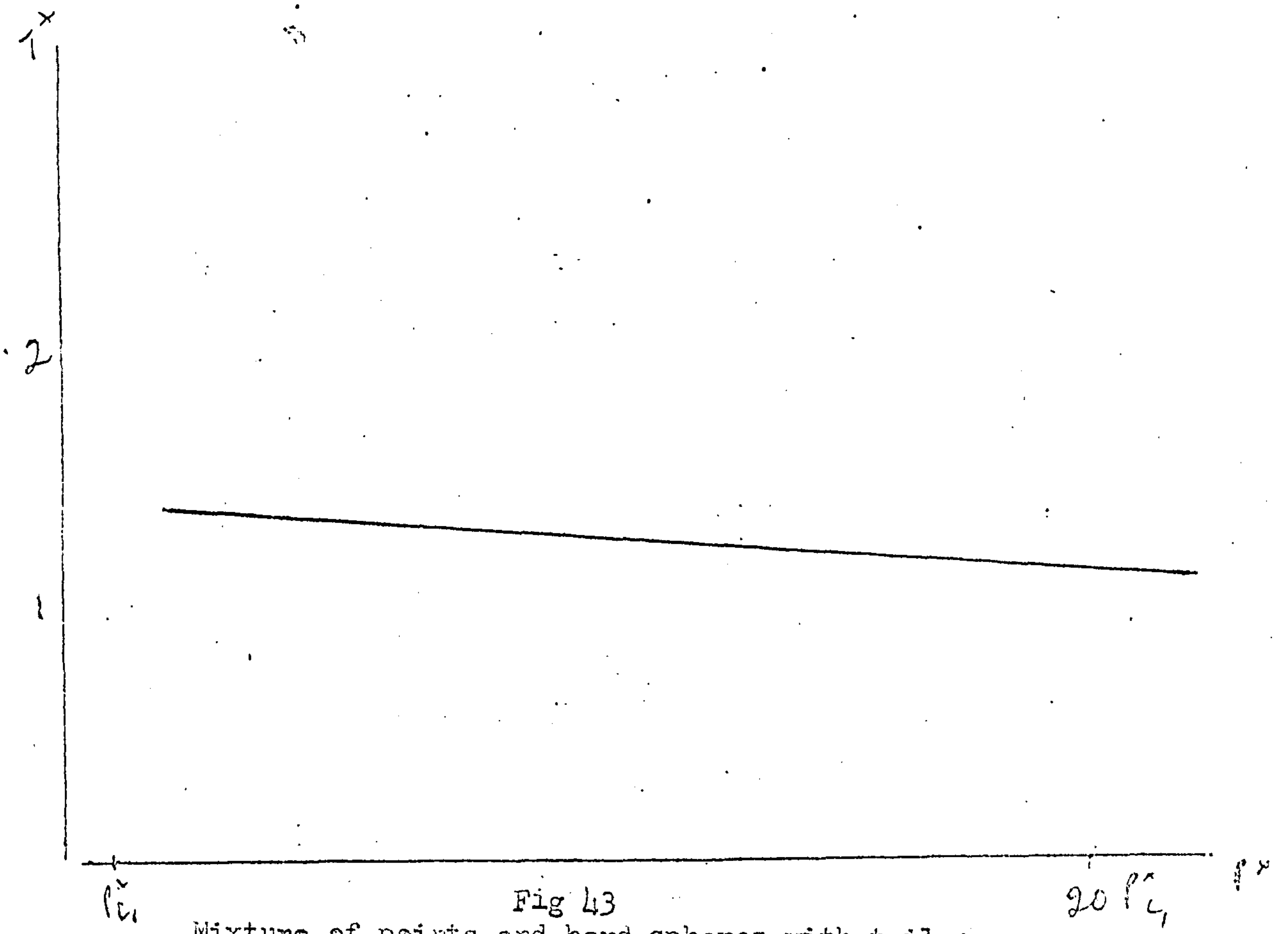


Fig 43
Mixture of points and hard spheres with tails:
Critical T* vs P*

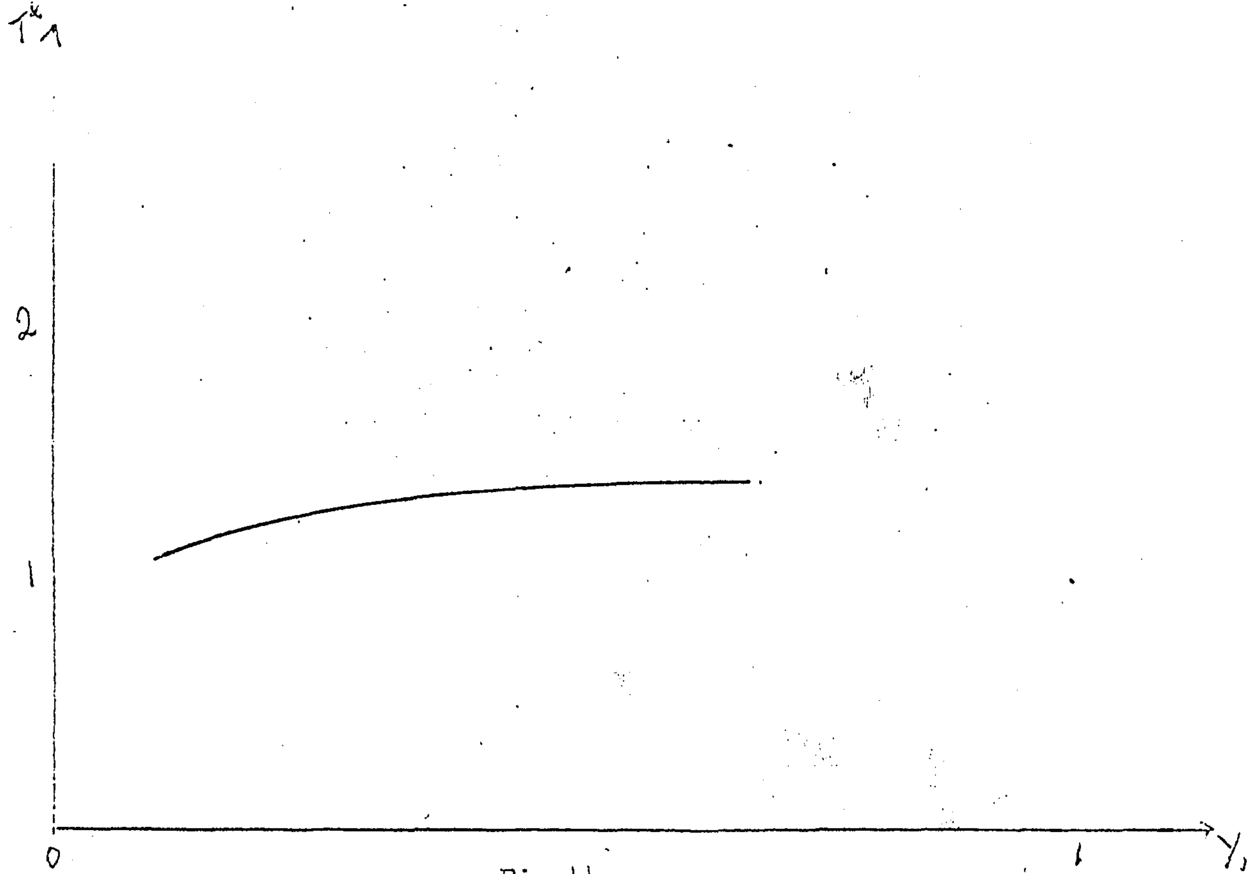


Fig 44
Mixture of points and hard spheres with tails
Critical T* vs critical y_1

The behavior of the mixture seems to be similar to an ordinary mixture of liquids, where the critical line goes from the critical point of one of the components to the zero temperature critical point of the other.

The fact that the critical temperature is decreasing with the pressure is thermodynamically consistent in the model. As shown by Rowlinson [10], if we express a displacement along the critical line by :

$$\delta\left(\frac{\partial^2 G}{\partial y_1^2}\right) = \frac{\partial^3 G}{\partial^2 y_1 \partial P}(\partial P) + \frac{\partial^3 G}{\partial y_1^2 \partial T}(\partial T) + \frac{\partial^3 G}{\partial y_1^3}(\partial y_1) \qquad (58)$$

this has to be equal to zero, so that with :

$$\frac{\partial^3 G_c}{\partial y_1^3} = 0 \qquad \frac{\partial T_c}{\partial P_c} = -\frac{\partial^3 G_c}{\partial P \partial y_1^2} \Big/ \frac{\partial^3 G_c}{\partial T \partial y_1^2} = \frac{\partial^2 V_c}{\partial y_1^2} \Big/ \frac{\partial^2 S_c}{\partial y_1^2} \qquad (59)$$

The second derivative of the entropy with the mole fraction is always negative since:

$$\frac{\partial^2 S_c}{\partial y_1^2} = \frac{\partial^2(\Delta S_c^E)}{\partial y_1^2} - \frac{1}{y_1(1-y_1)} \qquad (60)$$

and $1/y_1(1-y_1)$ is always larger than the second derivative of the excess entropy of mixing as can be easily seen from Table4. The second derivative of the volume, which is the same as the second derivative of the excess volume of mixing is seen to be by simple substraction-type calculations, positive at pressures temperatures and mole fractions around the critical points.

Table 7 shows some examples. So, the derivative of the critical temperature with the pressure proves to be consistenly negative.

Table 7

y_1	$\Delta V^E/v_0$	$\partial(\Delta V^E/v_0)/\partial y_1$	$\partial^2(\Delta V^E/v_0)/\partial y_1^2$
		<u>$P^*=0.556$ $T^*=1.2$</u>	
.1	0.04780		
		-0.0390	
.2	0.00860		-0.11
		-0.1492	
.3	-0.14060		-0.16
		-0.3134	
.4	-0.45400		+0.07
		-0.2400	
.5	-0.69400		+0.19
		0.0530	
.6	-0.64100		+0.08
		0.1340	
.7	-0.50700		+0.03
		0.1610	
.8	-0.34600		+0.01
		0.1702	
.9	-0.17580		
		<u>$P^*=0.278$ $T^*=1.3$</u>	
.1	0.27300		
		0.2110	
.2	0.46400		-0.070
		0.1400	
.3	0.60100		-0.013
		0.1270	
.4	0.72800		-0.257
		-0.1300	
.5	0.59800		-0.289
		-0.4190	
.6	0.17900		-0.468
		-0.8580	
.7	-0.67900		+0.900
		0.5120	
.8	-0.62780		+0.230
		0.2870	
.9	-0.34100		

In summary then for the two types of mixtures investigated: the mixture of hard spheres and hard spheres with attractive tails and the mixture of points and hard spheres with attractive tails, it is found that the former case follows the pattern of monotonic increase of the locus of critical temperature with pressure, while the latter case shows decrease of critical temperature with pressure and does not exhibit the phenomenon of "gas-gas immiscibility".

Appendix 1

The X values were calculated solving the equation of state numerically by programming, using the following program, in Fortran 1V :

For the mixture of hard spheres and hard spheres with tails:

```
    Dimension T(n),y(m),G(m)
    Read 2,T(1).....T(n)
  2 Format (nF4.2)
    Read 3,y(1)......y(m)
   3Format(mF4.2)
    do 1 i=1,50
    do 1 j=1,100
    do 1 l=1,n
    do 5 k=1,m
    X=float(i) + .01*float(j)
    F=f(X)  from eq3
    A=a(X)  from eq9
  5 G(k)=F-(y(k)**2)*A/T(l)
  1 Print 4,X,G(k)
  4 Format(m+1 F9.5)
    End
  $Entry
```

For the mixture of points and hard spheres with tails, the same program was used with the difference that for G(k) eq 36a was used.

In these programs G(k) means P*/T*. From all the P*/T* calculated this way, we selected the value corresponding to the pressure and temperature for which we wanted to solve the equation and found the X corresponding to it.

Appendix 2

In order to calculate the vapor pressure of pure gas 1, for T*=1.1, 1.2 and 1.3, the following method was used:

The first derivative of the pressure with the volume is expanded around the critical point in a Taylor series:

$$-\left(\partial P/\partial V\right)_{T_c, V_c} = \alpha t + \beta \omega^2 + \gamma \omega^2 t + D \omega^3 + \cdots$$

Where:

$$\alpha = -\left(\frac{\partial^2 P}{\partial V \partial T}\right)_{\text{crit}} \qquad \gamma = -\left(\frac{\partial^3 P}{\partial^2 V \partial T}\right)_{\text{crit}}$$

$$\beta = -\frac{1}{2!}\left(\frac{\partial^3 P}{\partial V^3}\right)_{\text{crit}} \qquad \omega = V - V_c$$

$$D = -\frac{1}{3!}\left(\frac{\partial^4 P}{\partial V^4}\right)_{\text{crit}} \qquad t = T - T_c$$

From the expansion, two equations with two unknowns are set:

$$\frac{1}{2}\left(\frac{1}{\phi_1} + \frac{1}{\phi_3}\right) = 1 - \frac{3\alpha}{2\beta}\left(\frac{T - T_c}{\tilde{V}_c^2}\right)\left(2 + \zeta \tilde{V}_c\right)$$

$$\frac{1}{\phi_1} - \frac{1}{\phi_3} = -\frac{2}{\tilde{V}_c}\left(-\frac{3\alpha}{\beta}\left(T - T_c\right)\right)^{1/2}$$

Where: $\zeta = \frac{3D}{5\beta} - \frac{\gamma}{3\alpha}$ and $\phi_i = \frac{\tilde{V}_i}{\tilde{V}_c}$

All was calculated in reduced units which was legitimate because of the relations:

$$\frac{P^*}{T^*} = \frac{P v_0}{NKT} \qquad P^* = \frac{P \frac{N\sigma^3}{V_2}}{\varepsilon}$$

$$\frac{\partial P}{\partial V} = \frac{\left(\frac{N\varepsilon}{v_0}\right)\partial P^*}{v_0 \; \partial X} = \frac{N\varepsilon}{v_0^2}\left(\frac{\partial P^*}{\partial X}\right)$$

$$\alpha = -\frac{\partial^2 P}{\partial V \partial T} = -\left(\frac{NK}{v_0^2}\right)\frac{\partial^2 P^*}{\partial X \partial T^*}$$

$$\beta = -\frac{1}{2}\frac{N\varepsilon}{v_0^4}\frac{\partial^3 P^*}{\partial X^3} \qquad \frac{\alpha}{\beta} = -\frac{1}{2}\frac{K v_0^2}{\varepsilon}\frac{\frac{\partial^2 P^*}{\partial X \partial T^*}}{\frac{\partial^3 P}{\partial X^3}}$$

So in the first equation:

$$\frac{\mathcal{D}}{\beta} = \frac{\frac{\partial^4 \rho}{\partial y^4}}{\frac{\partial^3 \rho}{\partial y^3}} = \frac{v_0^4}{v_0^5} \frac{\frac{\partial^4 \rho^*}{\partial X^4}}{\frac{\partial^3 \rho^*}{\partial X^3}} \approx v_0^{-1} \frac{\frac{\partial^4 \rho^*}{\partial X^4}}{\frac{\partial^3 \rho^*}{\partial X^3}}$$

$$\frac{\gamma}{\alpha} \approx \frac{v_0^2}{v_0^3} \sim v_0^{-1} \qquad \tau \sim v_0^{-1}$$

$$\frac{\alpha}{\beta} \times \frac{(T^* - T_c^*)}{v_0^2 X_c^2} \frac{\varepsilon}{k} \times \left(2 + \frac{1}{v_0} \times v_0 X_c\right) \sim \frac{\cancel{k} v_0^2}{\cancel{\varepsilon}} \frac{(T^* - T_c^*)}{\cancel{v_0^2} X_c^2} \frac{\cancel{\varepsilon}}{\cancel{k}} (2 + X_c)$$

$$\sim \frac{T^* - T_c^*}{X_c^2} (2 + X_c)$$

For the second equation:

$$\frac{\alpha}{\beta} (T^* - T_c) \sim v_0^2$$

$$(v_0^2)^{1/2} \frac{1}{X_c v_0} \sim \frac{1}{X_c}$$

Results are shown in Table 8.

According to the results, the following values were selected for X_1 :

For T*=1.1:

at $P^*=0.25P^*_{c1}$ the liquid value was chosen

at $P^*=0.50P^*_{c1}$ only one solution was found, corresponding to the liquid phase.

For T*=1.2:

at $P^*=0.25P^*_{c1}$ the gaseous value was chosen

at $P^*=0.50P^*_{c1}$ the liquid value was chosen

For T*=1.3:

at both $P^*=0.25P^*_{c1}$ and $P^*=0.50P^*_{c1}$ the gaseous value was chosen.

Table 8

	α	β	γ	D	X_{Gas}	X_L	ρ^*/T^*
T*=1.1	0.1784	0.0092	-0.1292	-0.0103	32.07	2.26	.0276
T*=1.2	"	"	"	"	16.44	2.50	.0420
T*=1.3	"	"	"	"	9.43	2.91	.0720

Part 11

Phase separation temperatures in solid isotopic mixtures

It was experimentally found [31,32] that solid isotopic mixtures of He^3-He^4 and H_2-D_2 exhibit phase separation at certain low temperatures. Theoretically, the inherent cause of the separation is assumed to be due to the difference in zero-point motion of the two isotopes, which is manifested experimentally by the difference in molar volume [33,34,35]. An explanation suggested by Klemens and Maradudin [36] is that a light isotope has a tendency to minimize its excess zero-point energy by expanding the lattice and vice-versa for the heavy isotope. All theoretical models yeld a zero-point energy proportional to the mass as shown by Klemens e.a. [37]

The condition for phase-separation in a mixture is :

$$\frac{\partial^2 G}{\partial X_i^2} < 0 \qquad (1)$$

A study of the requirements for this inequality to occur, is made on a solid isotopic mixture of He^3-He^4 and on a mixture of H_2-D_2.

The Gibbs free energy of a system is :

$$G = E - TS + PV \qquad (2)$$

In a solid system, the Gibbs free energy is essentially equal to the Helmholtz free energy since PV can be neglected, so :

$$G = E - TS \qquad (3)$$

where of course T is the temperature, S is the entropy and E is the internal energy. In a solid mixture E can be expressed as a sum of the pair energies of interaction on its space lattice neglecting the Debye contributions to the energy at such low temperatures.

Following Kikuchi's method [38], and taking into consideration only nearest neighbor interactions, the energy can be expressed in the form :

$$E = \frac{Nz}{2} \left(y_{33}\varepsilon_{33} + 2y_{34}\varepsilon_{34} + y_{44}\varepsilon_{44} \right) \qquad (4)$$

where N is the total number of particles, z is the number of nearest neighbors, the division by two is made so as not to count the same pair twice, ε_{ij} is the energy of interaction between a particle of species i and a particle of species j and y_{ij} is the probability of existence of an ij pair.

Rigorously:

$$y_{33} = X_3 - y_{34} \qquad (5)$$

$$y_{44} = (1-X_3) - y_{34}$$

where X_3 and $(1-X_3)$ are the mole fractions of He^3 and He^4 respectively. In a random mixture, the Bragg-Williams approximation can be made :

$$y_{34} = X_3(1-X_3) \qquad (6)$$

It follows that:

$$y_{33} = X_3^2 \quad \text{and} \quad y_{44} = (1-X_3)^2 \qquad (7)$$

So the energy of the mixture can be written in the form:

$$E = \frac{Nz}{2} \left(X_3^2\varepsilon_{33} + 2X_3(1-X_3)\varepsilon_{34} + (1-X_3)^2\varepsilon_{44} \right) \qquad (8)$$

For pure He^3 :

$$E_3 = \frac{Nz}{2} X_3 \varepsilon_{33} \qquad (9)$$

For pure He^4 :

$$E_4 = \frac{Nz}{2} (1-X_3)\varepsilon_{44}$$

So the excess energy of mixing will be :

$$E^E = E - E_3 - E_4 = \frac{Nz}{2} X_3(1-X_3) \left(2\varepsilon_{34} - \varepsilon_{33} - \varepsilon_{44} \right) \qquad (10)$$

To calculate the entropy, again Kikuchi's method [38] is used : The probability of existence of a He^3 particle is X_3, and for He^4 is $(1-X_3)$

Applying Kikuchi's formula for the entropy:

$$S = kN\,(z-1)(X_3\ln X_3 + X_4\ln X_4) - z/2\,(y_{33}\ln y_{33} + 2y_{34}\ln y_{34} + y_{44}\ln y_{44}) \qquad (11)$$

Expressing y_{ij} by expressions 6 and 7, the entropy takes the form :

$$S = kN(\,-X_3\ln X_3 - X_4\ln X_4) \qquad (12)$$

since the other terms cancel .

This expression does not depend on z and is simply the entropy of mixing, which shows that the excess entropy is zero, as one expects for a random mixture.

This means that the expression for the Gibbs free energy will be :

$$\Delta G^E/RT = \frac{z}{2kT} X_3(1-X_3)\ (2\varepsilon_{34} - \varepsilon_{33} - \varepsilon_{44}) \qquad (13)$$

We call :

$$W(0) = (2\varepsilon_{34} - \varepsilon_{33} - \varepsilon_{44}) \qquad (14)$$

and : $c_2 = zW(0)/2k$ (15)

so the excess free energy takes the form :

$$\Delta G^E/R = c_2\, X_3(1-X_3)$$

This way it is proved that the solid isotopic mixture will be a regular solution since $\Delta G^E/RT$ is of the form characteristic to regular solutions. The second derivative of $\Delta G^E/RT$ with the mole fraction will be :

$$\frac{\partial^2(\frac{\Delta G^E}{RT})}{\partial X_3^2} = -\,c_2/T \qquad (16)$$

so in order to have a phase separation, c_2 has to be positive.

According to the theory of critical points as shown in Part 1, one of the conditions for critical point is :

$$\frac{\partial^2(\Delta G^E/RT)}{\partial X_3^2} = -\frac{1}{X_3(1-X_3)} \qquad (17)$$

In a regular solution, $X_c = 0.5$, so :

$1/X_3(1-X_3) = 4$; $c_2 = 2T_c$

In order to evaluate T_c of a mixture, c_2 has to be calculated.

The effective pair potentials are assumed to be of Lennard-Jones form :

$$\mathcal{E}_{ii} = 4\varepsilon\left(\frac{1}{\gamma^4 (v_i^*)^4} - \frac{1}{\gamma^2 (v_i^*)^2}\right) \tag{18}$$

where ε is the Lennard-Jones potential depth, $v_1^* = \tilde{v}_1/N\sigma^3$ with $\tilde{v}_1$ being the molar volume, $\gamma = a^3/v$ where v is the volume per particle in the given lattice. a is the distance between two nearest neighbors.

The average pair energy in a random mixture may be denoted by $\mathcal{E}_{Xi}$:

$$\mathcal{E}_{Xi} = 4\varepsilon\left(\frac{1}{\gamma^4 (v_m^*)^4} - \frac{1}{\gamma^2 (v_m^*)^2}\right) = 2X_i(1-X_i)\mathcal{E}_{ij} + X_i^2\mathcal{E}_{ii} + (1-X_i)^2\mathcal{E}_{jj} \tag{19}$$

where $\tilde{v}_m$ is the molar volume of the mixture, assumed given by :

$$\tilde{v}_m = X_i\tilde{v}_i + X_j\tilde{v}_j \tag{20}$$

When second nearest neighbor interactions are taken into consideration, :

$$c_2 = zW(0)/2k + z'W'(0)/2k \tag{21}$$

where z' is the number of second nearest neighbors of any site on the space lattice of the solid and W'(0) is :

$$W'(0) = (2\mathcal{E}'_{34} - \mathcal{E}'_{33} - \mathcal{E}'_{44}) \tag{22}$$

$\mathcal{E}'_{ii}$ is the potential which describes the interaction between a pair of second nearest neighbors and is equal to:

$$\mathcal{E}'_{ii} = 4\varepsilon\left(\frac{1}{(v_i^*)^4(\gamma')^4} - \frac{1}{(v_i^*)^2(\gamma')^2}\right) \tag{23}$$

where $\gamma' = a'^3/v$ and a' is the distance between second nearest neighbors. As it can easily be seen the only parameter which changes in going from first nearest neighbor interactions to second, are γ and z, since the volume of course remains constant. The γ, z, γ', z' and a' values were calculated as follows:
For a simple cubic lattice, the Miller indices for nearest neighbors are (1,0,0) and for second nearest neighbors are (1.1.0). By permutations, z is found to be 6 and z' is 12. In this case a is the edge of the cell so the volume per atom is a^3(one atom per cell). So $\gamma = a^3/a^3 = 1$. For second nearest neighbors $a' = a\sqrt{2}$ so $\gamma' = a^3 2\sqrt{2}/a^3 = 2\sqrt{2}$.

For a body centered lattice, the Miller indices are (1/2,1/2,1/2) and (1,0,0) which gives z=8 and z'=6. The cell edge is $2a/\sqrt{3}$ so the volume per atom is $4a^3/3\sqrt{3}$ (two atoms per cell). γ will be $a^3/4a^3/3\sqrt{3} = 3\sqrt{3}/4$. a' is just the cell edge, so $\gamma' = 2$.

For a face centered lattice, the Miller indices are (1/2,1/2,0) and (1,0,0) so z=12 and z'=6. a' is the cell edge so having 4 atoms per cell, $\gamma' = 4$. a is $a'\sqrt{2}/2$ so $\gamma = \sqrt{2}$.

Equation 19 becomes :

$$z\,\varepsilon_{xi} + z'\,\varepsilon'_{xi} = 4z\varepsilon\left(\frac{1}{\gamma^4 (v_m^*)^4} - \frac{1}{\gamma^2 (v_m^*)^2}\right) + 4z'\varepsilon\left(\frac{1}{(\gamma')^4 (v_m^*)^4} - \frac{1}{(\gamma')^2 (v_m^*)^2}\right)$$

$$= 2X_i(1-X_i)(z\,\varepsilon_{ij} + z'\,\varepsilon'_{ij}) + X_i^2(z\,\varepsilon_{ii} + z'\,\varepsilon'_{ii}) + (1-X_i)^2(z\,\varepsilon_{jj} + z'\,\varepsilon'_{jj}) \qquad (24)$$

Since there is some ambiguity depending on the X value chosen, the average of the limits of $zW(0) + z'W'(0)$ when $X_3 \to 0$ and $X_3 \to 1$, was chosen. This leads to the equation:

$$\frac{zW(0)+z'W'(0)}{4\varepsilon} =$$

$$\left[\frac{y^2(3+3y+y^2)}{(v_j^*)^2(1+y)^3}\,\frac{z}{\gamma}+\frac{z'}{\gamma'}\right] - \left[\frac{2y^2(5+10y+10y^2+5y^3+y^4)}{(v_j^*)^4(1+y)^5}\right]\left[\frac{z}{\gamma}+\frac{z'}{\gamma'}\right] \quad (25)$$

where $y = \frac{v_i^* - v_j^*}{v_j^*}$ with v_j^* standing generally for the reduced molar volume of the isotope with smaller molar volume.

The formulas could have been extended to 3rd or more nearest neughbors, but it is difficult to imagine a pair of atoms at such distances which would not have a different type of atom between them, much closer.

These equations were applied to a solid mixture of He^3-He^4 and to an isotopic mixture of H_2-D_2. The molar volumes used for He^3 and He^4 were 24.75 cm^3 and 20.75 cm^3, respectively,[39] which correspond to a pressure of 30 atm.

The Lennard-Jones parameters used for helium were [40]:

$\varepsilon/k = 8.5°K$ and $N\sigma^3 = 9.422$ cm^3/mole.

These values were determined by Hillier, Islam and Walkley as zero-point parameters. Considering the particles as spherical with no angular dependence of the potential, they calculate ε and σ from zero-point crystal data.

For D_2-H_2 the molar volumes are [41] 19.56 cm^3 and 22.65 cm^3 for D_2 and H_2 respectively, which are the volumes at zero pressure. The parameters used are [40]:

$\varepsilon/k = 32.6°K$ and $N\sigma^3 = 15.64$ cm^3/mole

Table 9 shows the results obtained.

Other calculations were made with the parameters :

$\varepsilon/k = 10.22°K$ and $N\sigma^3 = 10.06$ cm^3/mole, for helium,[42] which were calculated by De Boer using second virial coefficient data.

Table 10 presents the results of calculations using these parameters. As will be seen later, these give results further apart from the experimental ones. This is normal, since these are parameters of the gaseous state, and the former are zero-point parameters, more adequate for a solid mixture.

Edwards e.a.[31] have been able to fit their data for helium isotopes (obtained over a range of pressures from 27 to 36 atm, which variation is of no significance in deducing c_2 values in our model) to a regular mixture form with $c_2=0.76^\circ K$, that is, $T_c=0.38^\circ K$. Although it is known that at low pressures pure He^3 and He^4 have different crystal structures (bcc and hcp respectively), no evidence of a crystallographic transition was obtained in the experiments of Edwards e.a. and it is likely that their data represent separation between two bcc phases. For a common bcc lattice, our model gives for the nearest neighbor interactions only a value of $T_c=0.36^\circ K$ which seems to be in good agreement with the experimentally found value and with the value of $T_c=0.37^\circ K$ obtained by considering the atoms as independent oscillators [37]. When the second nearest neighbor interaction is introduced, this value is rised to $0.52^\circ K$ which still is qualitatively satisfactory.

For H_2-D_2, experiments have proved that a phase separation occurs around $T_c= 3^\circ K$.[32,43] Proton magnetic resonance studies of Gaines e.a.[44] indicate a T_c in the vicinity of $3^\circ K$. Kogan e.a.[45,46] made a claim to have found a separation at $16^\circ K$ but their data are refuted by a series of authors such as White[32], Simon[43] and Gaines[44]. White gives a value for T_c around $3^\circ K$.

Our value of 1.6 for c_2 which would indicate a temperature of separation of 0.8°K is below the experimental value but qualitatively in the right range, that is, below 3°K.

A further qualitative aspect of our model is that if y decreases or remains small with the increase in pressure, as it is the case, c_2 can fall towards zero and thus mutual solubility is predicted to increase with large pressure increments. In fact, for c_2 to be positive, taking equation 25 and neglecting powers of y beyond the second, we obtain the condition for phase separation :

$$v_1^* > \left(\frac{10}{3}\right)^{1/2} \left[\frac{\frac{z}{\gamma^4} + \frac{z'}{(\gamma')^4}}{\frac{z}{\gamma^2} + \frac{z'}{(\gamma')^2}}\right]^{1/2} \tag{26}$$

where v_1^* is the reduced molar volume of the isotope with larger molar volume.

It easily seen that for a sc lattice this condition is not satisfied for H_2-D_2 . For He^3-He^4 in order that c_2 would be positive, for sc v_1^* should be greater than 14 cm^3, for bcc, greater than 12 cm^3 and for fcc greater than 9 cm^3.

It is conceivable that at very high pressures the mechanism for phase separation would be entirely suppressed. Nevertheless phase separation would still be favored because of the otherwise small differential effects of the zero-point vibrational spectrum, as shown by Prigogine [47] and by Chester [48].

In summary, taking into account first and second order neighbor interactions, the phase separation temperatures calculated are qualitatively in the right range of experimental values, even though not quantitatively exact. It seems that introducing the second order interactions improves the value for the H_2-D_2 mixture by increasihg it, and in the case of He^3-He^4 mixture it makes the value to be further appart from the experimental value.

Table 9

Lattice	z	z'	γ	γ'	He^3-He^4		H$_2$-D$_2$	
					T_c (nearest neigh.)	T_c (total)	T_c (near. neigh.)	Tc (total)
sc	6	12	1	$2\sqrt{2}$	0.32°K	0.44°K	-	-
bcc	8	6	$\frac{3\sqrt{3}}{4}$	2	0.36°K	0.52°K	0 .32°K	0.32°K
fcc	12	6	$\sqrt{2}$	4	0.51°K	0.55°K	0 .64°K	0.80°K

Table 10

He^3-He^4

Lattice	T_c(nearest neighbors)	T_c(total)
sc	0.37°K	0.61°K
bcc	0.55°K	0.79°K
fcc	0.75°K	0.82°K

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