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SOME THERMODYNAMIC PROPERTIES OF BINARY GASEOUS SYSTEMS: VOLUME CHANGE ON MIXING AND PHASE SEPARATION

RIJKS UNIVERSITEIT TE LEIDEN
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kast dissertaties

SOME THERMODYNAMIC PROPERTIES OF BINARY GASEOUS SYSTEMS: VOLUME CHANGE ON MIXING AND PHASE SEPARATION

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WISKUNDE EN NATUURWETENSCHAPPEN AAN DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS DR. J. DANKMEIJER, HOOGLERAAR IN DE FACULTEIT DER GENEESKUNDE, TEN OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP WOENSDAG 22 JUNI 1966 TE 16 UUR

DOOR

PIETER ZANDBERGEN

GEBOREN TE NOORDWIJKERHOUT IN 1931

KONINKLIJKE DRUKKERIJ VAN DE GARDE N.V., ZALTBOMMEL

Promotor: PROF. DR. J. J. M. BEENAKKER

Aan mijn ouders
Aan mijn vrouw

Promotor: PROF. DR. J. J. M. BEENAKKER

STELLINGEN

I

Bij de vaststelling van de temperatuur van het tripelpunt van evenwichtswaterstof als vast punt in een nieuwe internationale temperatuurschaal is het van belang ook gebruik te maken van de relatie tussen de verzadigde dampspanning en de temperatuur, zoals deze langs thermodynamische weg uit gemeten thermische en calorische grootheden van evenwichtswaterstof is te berekenen.

II

De dichtheid van de verzadigde damp van helium boven het normale kookpunt kan worden afgeleid zowel uit de door Edwards en Woodbury gemeten brekingsindex als uit de gemeten schijnbare verdampingswarmte van helium en de T_{58}-temperatuurschaal. De op de tweede manier verkregen resultaten zijn meer betrouwbaar dan de resultaten van Edwards en Woodbury.

Edwards, M. H. and Woodbury, W. C., Phys. Rev. **129** (1963) 1911.

III

Het is wenselijk het gedrag van de weerstand van koolthermometers beneden 0.3°K te toetsen aan de boven die temperatuur gebruikte semi-empirische formules.

Edelstein, A. S. and Mess, K. W., Physica **31** (1965) 813.

Rafalowicz, J. and Sujak, B., Acta Phys. Pol. **25** (1964) 599.

Black Jr., W. C., Roach, W. R. and Wheatley, J. C., Rev. sci. Instr. **35** (1964) 587.

IV

De door Douglass gesuggereerde voortzetting van de vloeistof-gas overgangslijn boven het kritische punt is aan twijfel onderhevig.

Douglass Jr., D. H., Physics **1** (1965) 329.

V

De wijze, waarop in het boek van Herzfeld en Litovitz het gezamenlijk optreden van de zogenaamde klassieke absorptie met relaxatie absorptie wordt behandeld, is onvoldoende.

Herzfeld, K. F. en Litovitz, T. A., Absorption and dispersion of ultrasonic waves (Academic Press, New York) 1959.

VI

De in het "Leerboek der Natuurkunde" door Kronig gegeven vorm van de eerste wet van Maxwell, namelijk

$$\oint H_s \, ds = \iint \gamma E_n \, dS + \frac{d}{dt} \iint D_n \, dS$$

is uit didactisch oogpunt misleidend.

Kronig, R., Leerboek der Natuurkunde (Scheltema en Holkema, Amsterdam) 1966.

VII

In de organisch chemische research is men zich nog te weinig bewust van de mogelijkheden, die gesmolten zouten bieden als media voor organische reacties.

Sundermeyer, W., Angew. Chem. **77** (1965) 241.

VIII

De in de rubberindustrie algemeen gebruikte standaard-methoden voor het meten van de warmte ontwikkeling in rubber tengevolge van een mechanische trilling zijn ongeschikt voor een juiste onderlinge beoordeling van rubbermengsels.

ASTM-D623.

IX

De na-Stalinistische belletrie met betrekking tot de toestanden op het Russische platteland geeft een juister beeld van de moeilijkheden, waarmee economen en politici te kampen hebben in de agrarische sector, dan de politiek-economische beschouwingen, die op partijcongressen en andere conferenties worden gegeven.

X

Het is opvallend, dat van geen der voormannen van de socialistische beweging in Nederland – Domela Nieuwenhuis, Troelstra, Vliegen, Schaper en Wibaut – tot dusver een biografie is verschenen. Dit wijst op een tekort aan belangstelling voor de geschiedenis der politieke ontwikkeling in ons land.

[illegible]
Verlag 1959

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Ten einde te voldoen aan het verzoek van de Faculteit der Wis- en Natuurkunde volgt hier een beknopt overzicht van mijn studie.

Nadat ik in 1950, na het eindexamen H.B.S.B aan de Chr. H.B.S. te Den Haag te hebben afgelegd, mijn studie in de natuurkunde te Leiden was begonnen, legde ik in 1956 het candidaatsexamen A af. Mijn studie werd van 1952–1954 onderbroken ter vervulling van mijn militaire dienstplicht. Vervolgens deed ik in februari 1959 het doctoraal examen experimentele natuurkunde, na hiertoe de vereiste tentamina in de mechanica en de theoretische natuurkunde te hebben afgelegd.

Sinds december 1956 was ik werkzaam op het Kamerlingh Onnes Laboratorium als medewerker bij de werkgroep voor Molecuulphysica onder leiding van achtereenvolgens Prof. Dr. A. van Itterbeek, Prof. Dr. K. W. Taconis en Prof. Dr. J. J. M. Beenakker. Sinds 1957 heb ik geassisteerd op het practicum voor prae-candidaten. In 1961 werd ik tot wetenschappelijk ambtenaar benoemd.

Tot mijn doctoraal examen assisteerde ik Dr. J. M. J. Coremans bij metingen van de viscositeit van gassen. Aanvankelijk zette ik daarna dit onderzoek voort.

In 1963 ving ik een onderzoek aan van de volume verandering bij menging van gassen, hetgeen uiteindelijk resulteerde in dit proefschrift. De discussie van de resultaten vond plaats in samenwerking met Dr. H. F. P. Knaap.

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CHAPTER I

EXPERIMENTAL DETERMINATION OF THE VOLUME CHANGE ON MIXING FOR GASEOUS N_2–H_2, A–H_2 AND A–N_2 BETWEEN 170 AND 292°K UP TO 100 ATM.

Synopsis

A direct method is described for measuring the volume change on mixing of gases at constant pressure. Measurements were performed for the systems N_2–H_2, A–H_2 and A–N_2 at several concentrations between 170 and 292°K and at pressures between 3 and 100 atm.

1. *Introduction*. In the last years considerable progress has been made in the study of the thermodynamic properties of liquid mixtures, both theoretically and experimentally. For a large number of systems, quantities like heat of mixing, volume change on mixing and excess Gibbs free energy have been measured. In this respect a good deal of attention has been paid to systems, composed of simple molecules like H_2, D_2, N_2, A etc. Surveys are given by Parsonage and Staveley[1]), McGlashan[2]), and by White and Knobler[3]). Especially for these systems there has been important theoretical progress, based on a corresponding states treatment. Significant contributions have been reported by Prigogine[4]) and by Scott[5]). All this work is, however, virtually limited to liquid systems. Very little experimental work has been done on properties of gaseous mixtures at higher densities, not withstanding both their fundamental and technological importance. In our opinion the main reason for this lack of data is to be found in the way this problem was attacked. The classical approach to obtain thermodynamic data of gaseous mixtures is the same as the one used for pure gases, i.e. the performance of highly accurate pVT measurements. This type of work requires, as is well known, a rather complicated experimental set-up, combined with a great deal of experimental skill. Furthermore these measurements are very time-consuming. The extra parameter, given by the concentration, creates in the case of gaseous mixtures a problem that is nearly unsolvable along these lines.

At the moment, for most pure systems made up of simple molecules, thermodynamic properties are reasonably well known[6]). In this respect we mention the outstanding experimental work, performed in the Van der Waals laboratory and the impressive data-processing program of the National Bureau of Standards. This means that the value of most thermodynamic quantities can easily be obtained for an ideal mixture, i.e. a mixture, of which the volume varies linearly with the concentration. As a consequence the only relevant information, necessary to describe the behaviour of a real mixture, is the deviation from ideality, the excess property. Hence it seems worthwile to concentrate one's effort on a direct determination of the excess quantities, hoping that this will be the easier way to a knowledge, that enables a description of the behaviour of the real mixture.

With this philosophy the Kamerlingh Onnes Laboratory group for molecular physics started a few years ago a program for the determination of the thermodynamic properties of gaseous mixtures of simple molecules. Two problems were attacked at the same time; the heat of mixing and the volume change on mixing. The reason being, that the knowledge of these two quantities makes a complete thermodynamic description possible, without having to perform the measurements with excessive accuracy. It should of course have been possible, but not practical, to determine all thermodynamic properties, starting from the volume change on mixing at constant pressure, $\tilde{V}^E$, only. The accuracy needed in that case would, however, completely off-set the advantages of our direct approach. The situation in this respect is similar to the one, occurring in the study of liquid mixtures. From the point of view of theory a complete thermodynamic description is possible from a knowledge of G^E (vapour pressure and composition measurements). In practice, however, it is commendable to measure directly the heat of mixing. Another reason for a study of both $\tilde{H}^E$ and $\tilde{V}^E$ is that agreement with theory is in general more easily obtained in the case of $\tilde{H}^E$ than that of $\tilde{V}^E$. Hence for a theoretical description of the properties of the mixtures, a knowledge of both quantities is desirable.

In view of the experimental and theoretical state of affairs, the aim of our program was to measure $\tilde{H}^E$ and $\tilde{V}^E$ with an accuracy of a few percents. We started with the systems N_2–H_2, A–H_2 and A–N_2. This choice was the result of several considerations. We wanted to start with systems that would show rather large deviations from ideality. This was expected to be the case for a mixture of two components with widely different critical temperatures, in the pre-critical region of one of its components. Furthermore we preferred to work with inexpensive gases. The technological importance of the N_2–H_2 mixture, combined with these arguments decided the choice in favor of this system. A–H_2 was studied because it is expected that if non-sphericity is of little importance, this system will behave very similarly to that of N_2–H_2. This is so because the molecular interaction parameters are not too much different in both cases. Finally A–N_2 was chosen to study a mixture of rather similar molecules. We studied the aforementioned systems at several concentrations between 170 and 300°K and at pressures up to 100 atm.

This chapter will deal with the volume change on mixing. Work on heat of mixing is reported by Knoester, Taconis and Beenakker[7]) while a preliminary review of our program was given at the 1965 Purdue Thermophysical Properties Symposium[8]).

2. *Experimental Method.* In the past volume or pressure change on mixing measurements were only performed at pressures below 1 atm[9]). The higher pressures and the temperature range 170–300°K create some problems, that made in our case a different set-up necessary. In the systems under study $\tilde{V}^E$ is mostly positive, i.e. to keep the pressure on mixing constant, we have to increase the volume, or at constant volume the pressure increases on mixing. The most straight-forward way from the experimental point of view seems to be a determination of this pressure change. At pressures below 100 atm we preferred glass U-tube differential manometers, because of their simplicity combined with high sensivity. The draw-back of this method is the change in the dead volume of the U-tube of the manometer as a function of pressure-difference. To avoid this difficulty we have determined the amount of gas that has to be let out of the system to keep the pressure on mixing constant. The differential manometer serves now as a zero-point instrument. The amount of gas let out can easily be determined by using the ideal gas law from the measurement of the low pressure in a vessel of known volume at room temperature.

Fig. 1 shows a schematic diagram of the apparatus, which consists of the following parts:

a) The metal vessels V_1 and V_2 are filled with the gases to be mixed. The volumes of these vessels are calibrated by expansion of an ideal gas in a volume of known value.

b) A mixing arrangement. In the vessel V_1 a smoothly fitting plunger P is placed. This plunger can be moved up and down by a connecting rod, that leaves the high pressure part of the apparatus through an O-ring seal in the room temperature section. The gases in the vessels V_1 and V_2 are mixed by moving this plunger up and down after opening valves in the capillaries, that connect V_1 and V_2 and closing valves giving access to the differential manometry. To avoid dead spaces special attention is paid to have as small as possible the volumes of the connecting capillaries and the valves, e.g. the last ones are specially constructed for this purpose in our workshop. It may be noted that the corrections for the dead space never amount to more than around 3%.

c) Differential manometry and pressure reference system. To obtain an

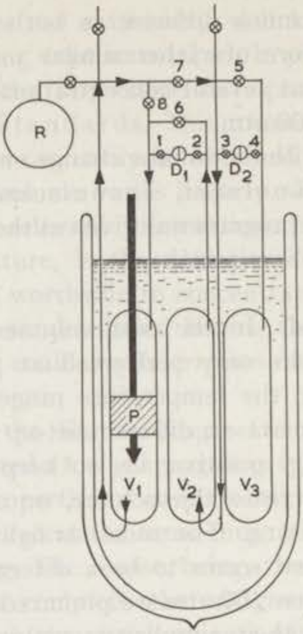

Fig. 1. A schematic diagram of the apparatus.

accuracy of say 2% in $\tilde{V}^E$ it is necessary to be able to detect pressure changes of the order of 1 part in 10^4 and this up to pressures of 100 atm. This requires not only the necessary sensitivity of the differential manometry but also a high degree of stability of the pressure in the system. The sensitivity of the manometry is easily obtained using oil or mercury U-tube differential manometers. These manometers are made of 2 mm internal and 10 mm external well annealed glass tubes. At the end of the tube a thin layer of platinum is chemically deposited and subsequently it is copper-electroplated. Connections with the rest of the apparatus were made by soft-soldering on this copper layer. This system works very well and seldom gives rise to leakage.

The pressure after mixing is compared with the initial pressure in a reference vessel, V_3, that is in good contact with V_1 and V_2. In this way pressure variations are balanced out and no long term pressure stability is required.

d) The constant temperature bath. The vessels V_1, V_2 and V_3 are placed in a Dewar that is filled with liquid propane and ethylene, boiling at their normal boiling point, to obtain respectively the temperatures 231.7 and 170.5°K. The necessary amount of stirring is obtained by a heater at the bottom of the cryostat, that produces a constant stream of vapour bubbles passing through the liquid. For the measurements at room temperature the Dewar is replaced by a normal waterthermostat.

e) To bring after mixing the pressure in V_1 and V_2 back to the original value, gas is vented in vessel R, that is placed in a thermostated waterbath. Depending on the expected volume change we used for R volumes of about 80, 1000 or 3000 cm^3. The volumes are calibrated by weighing with water. The pressure of the gas in R is measured with an oil or mercury manometer.

The normal procedure for a measurement is the following. The vessel V_1 is filled with gas A and V_2 and V_3 with gas B to the same pressure, as measured on the differential manometer D. Subsequently the valves 1, 2, 3, 4, 5 and 8 are closed the valves 6 and 7 are opened and gases A and B are mixed by moving plunger P up and down. We checked whether the mixing is complete by measuring with the manometer D_2 the pressure-changes after 5, 10, 15 and 20 strokes of the piston. After 10 strokes no further pressure changes were found. To be sure of complete mixing we mix with at least 20 strokes. After the mixing is completed D_2 is connected. The exact amount of gas that has to be let out to bring the pressure difference back to zero is determined by interpolation. The gas is let out in two steps, one at which the pressure difference is still slightly positive and one where this difference is slightly negative. In the very few cases studied where the pressure decreases on mixing, we obtained the volume change by extrapolation of two points with a slightly larger pressure decrease.

To be able to measure at different concentrations we used in combination with V_1, two vessel, V_2 and V_2', which volumes are half as large as the volume of V_1. By interchanging the position of the gases and by replacing V_2 by V_2' measurements at four concentrations can be performed.

In the earliest measurements at room temperature we used a slightly different set-up. The slit between the plunger and the cylinder is so small (of the order of one micron), that there is practically no gas leaking through the slit, even when there is an appreciable pressure difference over the slit. Having different gases above and below the piston, V_u and V_1, it is possible to perform the measurements without the use of a second vessel. The gases are now mixed by forcing them through a capillary, that connects V_u and V_1. The advantage of the method is that if one knows the volumes of V_u and V_1 as a function of the position of the piston, it is easily possible to perform measurements as a function of concentration. Damage of the plunger caused leakages along the slit and this method was abolished in favor of a separate second vessel in the later experiments at low temperatures. The values of the different volumes that are used are given in table I. The apparatus was

TABLE I

Values of the calibrated volumes in cm^3

	V_u	V_u'	V_1	V_1'	V_1	V_2	V_2'	R
Dead space	34.1	49.4	40.6	25.4	68.2	24.8	64.9	1082
					2.44	2.06	2.06	

checked by performing a blank run with the same gases in all vessels. After going through the mixing procedure we found no pressure change.

3. *Experimental results*. To obtain the values of volume variation per mole of the mixture we proceed in the following way. Before the mixing we have in vessel V_1 at pressure p and temperature T, N_A mole of gas A and in vessel V_2, under the same condition of pressure and temperature, N_B mole of gas B. Thus we have

$$V_1 + V_2 = N_A \tilde{V}^0_A + N_B \tilde{V}^0_B \tag{1}$$

where $\tilde{V}^0_A$ and $\tilde{V}^0_B$ are the molar volumes of the pure components A and B respectively. The tilda denotes molar quantities. After mixing and re-establishment of the pressure p by letting out ΔN mole of the mixture in R we have

$$V_1 + V_2 = (N_A + N_B - \Delta N)\, \tilde{V}_m = N_A \tilde{V}^0_A + N_B \tilde{V}^0_B \tag{2}$$

where $\tilde{V}_m$ is the molar volume of the mixture. Rewriting eq. (2) and substituting the mole-fractions x_A and x_B we find

$$\frac{\Delta N}{N_A + N_B} = \frac{\tilde{V}_m - x_A \tilde{V}^0_A - x_B \tilde{V}^0_B}{\tilde{V}_m} = \frac{\tilde{V}^E}{\tilde{V}^m} \tag{3}$$

where the excess volume, $\tilde{V}^E$, is defined as

$$\tilde{V}^E = \tilde{V}_m - x_A \tilde{V}^0_A - x_B \tilde{V}^0_B. \tag{4}$$

Combining eqs. (3) and (4) we obtain for $\tilde{V}^E$

$$\tilde{V}^E = \frac{\Delta N}{N_A + N_B - \Delta N}\,(x_A \tilde{V}^0_A + x_B \tilde{V}^0_B) \tag{5}$$

ΔN can be calculated from the pressure and the temperature of the gas in R and the volume of R. N_A and N_B are calculated from the calibrated volumes of the vessels V_1 and V_2, the pressure p and the temperature T of gases A and B, using the known equations of state for the pure components[6]).

In the tables II, III and IV the results are given for the mixtures N_2–H_2, A–H_2 and A–N_2. As can be seen $\tilde{V}^E$ is not given at fixed concentrations. This is caused by the fact, that in the range of pressure and temperature where the measurements are performed, H_2, N_2 and A are no longer behaving as a perfect gas. As a consequence the number of moles is no longer proportional to the volumes. This results in a variation of the concentration, depending on the working pressure and temperature. In our case this effect is small at room-temperature, but becomes rather large at lower temperature, as is clear from the tables II, III and IV. This is illustrated in fig. 2 and the table V for three arrangements, *a*, *b* and *c*, of the vessels for the mixture

TABLE II

Results for the mixture N_2–H_2							
Temperature and combination of vessels	p atm	mole fraction H_2	$N_{N_2}+N_{H_2}$ mole	$\Delta N \times 10^4$ mole	$\tilde{V}_m^{id}$ cm^3/mole	$\tilde{V}^E$ cm^3/mole	$\frac{\tilde{V}^E}{4x(1-x)}$ cm^3/mole
T = 170.5°K	5.40	0.268	0.0373	1.05^{0}	2561	7.36	9.38
H_2 in V_2	10.05	0.264	0.0703	3.63^{0}	1361	7.26	9.35
N_2 in V_1	14.6	0.260	0.104	7.92^{5}	922	7.29	9.48
	25.2	0.250	0.185	26.2^{0}	517	7.62	10.2
	40.2	0.236	0.310	81.2^{0}	308	8.51	11.8
	50.4	0.226	0.401	137.^{0}	238	8.61	12.3
	60.9	0.217	0.500	219.^{0}	191	8.93	13.1
	69.7	0.210	0.588	293.^{0}	161	8.71	13.2
	79.6^{5}	0.204	0.687	382.^{5}	139	8.36	12.9
	92.1	0.198	0.807	455.^{5}	118	7.21	11.4
T = 170.5°K	3.00	0.510	0.0292	0.526	4643	8.54	8.54
H_2 in V_1	5.00	0.508	0.0488	1.48^{5}	2778	8.65	8.65
N_2 in V_2'	9.15	0.503	0.0900	5.32^{0}	1507	9.12	9.12
	12.05	0.502	0.118	9.47^{5}	1146	9.42	9.42
	16.3	0.496	0.163	17.9^{0}	833	9.43	9.43
	23.1	0.486	0.232	39.0^{0}	584	10.2	10.2
	27.7^{5}	0.481	0.283	57.9^{0}	480	10.2	10.2
	39.9	0.465	0.416	133.^{0}	326	11.0	11.0
	50.8	0.450	0.542	236.^{5}	250	11.6	11.7
	60.4	0.439	0.655	355.^{0}	207	12.1	12.2
	70.5	0.427	0.781	503.^{0}	174	12.2	12.4
	75.6	0.422	0.844	576.^{5}	161	12.0	12.3
	80.3^{5}	0.417	0.903	644.^{5}	150	11.7	12.1
	90.7	0.410	1.02	789.^{0}	132	11.2	11.6
T = 170.5°K	7.48	0.722	0.0513	1.94^{5}	1864	7.29	9.07
H_2 in V_1	14.75	0.715	0.102	7.79^{0}	739	7.44	9.13
N_2 in V_2	25.3	0.705	0.176	23.9^{0}	543	7.69	9.24
	32.7	0.698	0.228	43.7^{0}	418	8.38	9.93
	40.4	0.687	0.285	71.4^{0}	335	8.82	10.3
	56.9^{5}	0.670	0.406	157.^{5}	235	9.72	11.0
	65.0^{5}	0.662	0.467	212.^{5}	204	9.99	11.2
	75.3^{5}	0.651	0.545	286.^{0}	175	9.95	11.0
	84.9^{5}	0.644	0.616	345.^{5}	155	9.45	10.3
	92.9^{5}	0.639	0.674	397.^{5}	142	9.11	9.87
T = 205.7°K	6.5	0.270	0.0374	0.767	2572	5.47	6.94
H_2 in V_2	12.0^{5}	0.265	0.0698	2.67^{5}	1378	5.48	7.03
N_2 in V_1	15.9	0.266	0.0919	4.61^{5}	1046	5.45	6.98
	25.7	0.261	0.151	12.1^{0}	637	5.31	6.89
	39.5	0.254	0.236	28.1^{5}	408	5.08	6.70
	55.0	0.246	0.333	57.2^{0}	289	5.20	7.00
	75.3	0.239	0.463	111.^{5}	207	5.26	7.23
	91.6	0.235	0.569	168.^{5}	169	5.30	7.38

TABLE II (*continued*)

Temperature and combination of vessels	p atm	mole fraction H_2	$N_{N_2}+N_{H_2}$ mole	$\Delta N \times 10^4$ mole	$\bar{V}_{\mathrm{m}}^{\mathrm{id}}$ cm^3/mole	$\bar{V}^{\mathrm{E}}$ cm^3/mole	$\frac{\bar{V}^{\mathrm{E}}}{4x(1-x)}$ cm^3/mole
T = 205.7°K	6.1	0.724	0.0347	0.585	2768	4.82	6.03
H_2 in V_1	15.1	0.720	0.0861	3.68^5	1117	4.96	6.14
N_2 in V_2	24.7	0.715	0.150	9.72^0	683	4.91	6.02
	40.0	0.707	0.228	26.3^0	422	5.08	6.13
	40.6	0.706	0.232	26.7^0	415	5.01	6.04
	55.2	0.699	0.313	52.7^5	307	5.42	6.44
	55.6	0.699	0.316	50.0^0	364	5.06	6.01
	75.6	0.690	0.428	96.3^5	224	5.33	6.23
	90.7	0.686	0.513	$134.^5$	187	5.21	6.04
T = 231.7°K	9.5	0.271	0.0485	0.976	1990	4.16	5.27
H_2 in V_2	14.1	0.269	0.0804	2.13^0	1333	4.08	5.19
N_2 in V_1	15.7	0.268	0.0804	2.70^0	1200	4.20	5.35
	20.8	0.267	0.107	4.75^5	903	4.18	5.34
	29.9	0.264	0.155	9.90^0	624	4.17	5.36
	39.9	0.262	0.207	17.4^5	467	4.12	5.33
	59.6	0.255	0.311	38.7^0	310	4.04	5.31
	79.0	0.251	0.416	65.6^5	232	3.85	5.13
	97.0	0.247	0.511	98.7^5	189	3.86	5.19
T = 231.7°K	10.2	0.509	0.0735	2.11^0	1859	5.49	5.49
H_2 in V_1	15.3	0.507	0.108	4.79^0	1264	5.77	5.77
N_2 in V_2'	20.2	0.505	0.146	8.35^0	939	5.56	5.56
	31.6	0.501	0.229	20.0^0	598	5.41	5.41
	45.4^5	0.495	0.329	41.7^5	415	5.47	5.47
	59.9	0.489	0.433	71.8^5	315	5.45	5.45
	72.9^5	0.485	0.528	$104.^5$	259	5.35	5.35
	93.6	0.479	0.675	$168.^0$	202	5.30	5.31
T = 231.7°K	6.2^5	0.724	0.0317	0.431	3043	4.30	5.38
H_2 in V_1	10.6	0.723	0.0539	1.23^5	1792	4.27	5.33
N_2 in V_2	14.9	0.721	0.0754	2.48^0	1280	4.38	5.46
	21.8	0.719	0.110	5.07^5	876	4.21	5.20
	25.1^5	0.718	0.127	6.74^5	759	4.20	5.18
	31.8	0.716	0.161	10.7^0	601	4.18	5.14
	42.9^5	0.712	0.216	19.1^0	443	4.09	5.07
	60.3	0.707	0.302	37.3^5	320	4.16	5.02
	79.2	0.702	0.395	62.4^0	244	4.07	4.86
	96.2	0.699	0.476	87.3^5	203	3.94	4.68
T = 292.6°K	15.0	0.253	0.0461	0.709	1598	2.46	3.25
H_2 in V_1'	30.0	0.248	0.0920	2.96^0	800	2.58	3.46
N_2 in V_u'	50.2	0.248	0.154	7.92^0	479	2.47	3.31
	65.2	0.246	0.200	13.0^5	369	2.43	3.27
	82.6	0.247	0.249	20.3^5	296	2.44	3.27
	99.0	0.244	0.299	26.7^0	246	2.21	3.00

TABLE II (*continued*)

Temperature and combination of vessels	p atm	mole fraction H_2	$N_{N_2}+N_{H_2}$ mole	$\Delta N \times 10^4$ mole	$\tilde{V}_m^{id}$ cm^3/mole	$\tilde{V}^E$ cm^3/mole	$\frac{\tilde{V}^E}{4x(1-x)}$ cm^3/mole
T = 292.6°K	19.9^5	0.462	0.0612	1.72^0	1205	3.39	3.41
H_2 in V_1	22.8	0.464	0.0702	2.23^5	1051	3.36	3.38
N_2 in V_u	30.1	0.457	0.0917	3.74^0	805	3.30	3.32
	50.2	0.457	0.153	10.1^5	482	3.22	3.24
	65.1	0.454	0.198	16.3^0	373	3.10	3.13
	80.6	0.453	0.243	24.5^0	303	3.09	3.11
	99.0	0.452	0.296	33.2^5	249	2.83	2.86
T = 292.6°K	15.0	0.531	0.0460	0.899	1603	3.14	3.15
H_2 in V_u	16.0	0.530	0.0491	1.09^0	1501	3.33	3.35
N_2 in V_1	30.0	0.525	0.0913	3.66^0	366	3.26	3.27
	50.2	0.524	0.153	9.91^0	991	3.16	3.17
	65.2	0.522	0.197	16.0^5	374	3.07	3.07
	80.4	0.520	0.242	23.6^0	305	3.01	3.01
	98.9	0.519	0.295	32.5^0	250	2.79	2.80
T = 292.6°K	15.0	0.742	0.0458	0.699	1607	2.46	3.21
H_2 in V_u'	30.0	0.738	0.0904	2.81^5	815	2.55	3.29
N_2 in V_1'	50.2	0.738	0.151	7.59^5	487	2.46	3.18
	65.1	0.736	0.195	12.0^5	378	2.36	3.03
	80.7	0.734	0.240	17.4^5	307	2.25	2.89
	99.0	0.733	0.291	24.4^0	253	2.15	2.74

TABLE III

Results for the mixture A–H_2

Temperature and combination of vessels	p atm	mole fraction H_2	$N_{H_2}+N_A$ mole	$\Delta N \times 10^4$ mole	$\tilde{V}_m^{id}$ cm^3/mole	$\tilde{V}^E$ cm^3/mole	$\frac{\tilde{V}^E}{4x(1-x)}$ cm^3/mole
T = 170.5°K	4.00	0.268	0.0277	0.536	3450	6.87	8.75
H_2 in V_2	5.00	0.267	0.0348	0.901	2750	7.34	93.8
A in V_1	5.1^5	0.267	0.0358	0.958	2675	7.38	9.43
	5.2	0.267	0.0361	0.994	2649	7.51	9.59
	6.17	0.265	0.0431	1.40^5	2219	7.46	9.57
	6.3	0.265	0.0440	1.45^0	2171	7.37	9.46
	12.95	0.259	0.0923	6.96^0	1036	8.08	10.5
	16.05	0.255	0.116	11.3^0	822	8.26	10.9
	19.50	0.251	0.143	17.5^0	668	8.48	11.3
	25.4^5	0.244	0.191	33.1^5	500	9.05	12.3
	29.1^5	0.240	0.223	45.2^0	429	9.10	12.5
	35.3^5	0.232	0.278	82.4^5	343	10.8	15.1
	45.5	0.213	0.386	$176.^0$	247	12.1	18.1
	54.8	0.195	0.502	$322.^5$	190	13.3	21.2
	65.0	0.172	0.668	$601.^5$	142	14.4	25.2
	70.2	0.161	0.770	$793.^5$	124	14.5	26.8
	80.1	0.146	0.961	125^5	98.8	15.1	30.2
	87.0	0.140	1.08	153^0	87.9	14.8	30.7
	94.8	0.137	1.19	154^5	79.5	12.0	25.3

TABLE III (*continued*)

Temperature and combination of vessels	p atm	mole fraction H_2	$N_{H_2}+N_A$ mole	$\Delta N\times 10^4$ mole	$\tilde{V}_{m}^{id}$ cm^3/mole	$\tilde{V}^{E}$ cm^3/mole	$\frac{\tilde{V}^{E}}{4x(1-x)}$ cm^3/mole
T = 170.5°K	3.12	0.726	0.0218	0.361	4353	7.48	9.40
H_2 in V_1	10.15	0.716	0.0699	3.79^{5}	1368	7.67	9.43
A in V_2	15.00	0.712	0.105	9.00^{5}	941	8.40	10.3
	24.9	0.699	0.174	27.4^{0}	548	8.98	10.7
	36.6	0.682	0.261	73.1^{0}	365	10.8	12.4
	50.3	0.649	0.373	$180.^{0}$	248	12.9	14.2
	60.5	0.618	0.466	$323.^{0}$	205	15.6	16.6
	75.3	0.565	0.629	$703.^{0}$	151	19.5	19.9
	83.3	0.547	0.711	$948.^{5}$	134	21.07	21.26
	95.2	0.535	0.821	$119^{5}.$	116	20·21	20.31
T = 170.5°K	2.07	0.509	0.0199	0.258	6811	9.02	9.02
H_2 in V_1	3.98	0.507	0.0389	0.998	3491	9.16	9.16
A in V_2'	5.98	0.505	0.0587	2.30^{0}	2308	9.25	9.27
	10.03	0.498	0.0994	6.98^{5}	1365	9.85	9.85
	12.14	0.498	0.120	10.5^{0}	1128	10.1	10.1
	20.1	0.485	0.204	34.1^{0}	666	11.6	11.6
	24.15	0.478	0.247	52.1^{0}	549	12.0	12.1
	25.0	0.478	0.257	60.1^{0}	527	12.8	12.9
	30.1	0.467	0.314	91.7^{5}	431	13.2	13.3
	40.1^{5}	0.447	0.436	$194.^{0}$	311	14.8	14.9
	50.8	0.418	0.584	$397.^{5}$	232	17.2	17.7
	60.2	0.388	0.740	$700.^{0}$	183	19.5	20.5
	70.0	0.352	0.941	122^{5}	144	21.8	23.9
	77.8	0.329	1.11	178^{0}	122	23.6	26.7
	83.0	0.321	1.21	221^{0}	112	25.2	28.9
	86.6	0.315	1.28	244^{5}	106	25.3	29.3
	90.3^{5}	0.312	1.34	260^{5}	101	24.5	28.6
T = 170.5°K	6.1	0.269	0.0351	0.577	2735	4.65	5.91
H_2 in V_2	10.0	0.267	0.0580	1.91^{0}	1658	5.66	7.24
A in V_1	15.1	0.264	0.0883	5.04^{5}	1088	6.45	8.31
	21.7	0.256	0.130	10.0^{0}	740	5.95	7.00
	22.7	0.259	0.135	12.5^{5}	713	6.92	9.02
T = 205.7°K	6.3	0.723	0.0360	0.800	2672	6.16	7.68
H_2 in V_1	7.2	0.722	0.0411	0.972	2342	5.74	7.15
A in V_2	9.8	0.720	0.0560	1.62^{5}	1716	5.16	6.40
	10.0	0.720	0.0571	1.89^{5}	1683	5.78	7.18
	13.7	0.717	0.0784	3.43^{5}	1227	5.58	6.87
	15.9	0.717	0.0908	4.66^{5}	1059	5.65	6.96
	25.1	0.710	0.144	11.8^{5}	668	5.72	6.94
T = 231.7°K	10.15	0.268	0.0505	1.24^{0}	1842	4.53	5.77
H_2 in V_2	15.5	0.266	0.0776	2.88^{5}	1208	4.51	5.77
A in V_1	25.2	0.262	0.127	7.95^{0}	732	4.60	5.95
	30.0^{5}	0.260	0.153	11.5^{0}	611	4.64	6.03
	34.8	0.259	0.178	14.9^{0}	525	4.44	5.79
	45.2	0.254	0.232	27.4^{5}	401	4.80	6.34
	57.7	0.247	0.302	46.2^{0}	309	4.80	6.45
	76.0	0.240	0.406	84.9^{5}	230	4.91	6.74
	91.8^{5}	0.234	0.497	$126.^{5}$	187	4.90	6.84

TABLE III (*continued*

Temperature and combination of vessels	p atm	mole fraction H_2	$N_{H_2}+N_A$ mole	$\Delta N\times 10^4$ mole	$\tilde{V}_\mathrm{m}^\mathrm{id}$ cm^3/mole	$\tilde{V}^\mathrm{E}$ cm^3/mole	$\dfrac{\tilde{V}^\mathrm{E}}{4x(1-x)}$ cm^3/mole
T = 231.7°K	12.1	0.505	0.0858	3.16^{0}	1552	5.73	5.73
H_2 in V_1	15.0	0.504	0.106	4.80^{5}	1257	5.72	5.72
A in V_2'	20.2	0.499	0.142	8.86^{5}	937	5.89	5.89
	25.3^{5}	0.497	0.180	14.3^{5}	739	5.94	5.94
	29.2	0.495	0.208	19.2^{0}	640	5.97	5.97
	35.4^{5}	0.493	0.254	29.7^{0}	525	6.21	6.21
	40.6	0.490	0.290	40.3^{5}	459	6.47	6.47
	49.4^{5}	0.485	0.355	61.2^{0}	375	6.56	6.56
	59.3	0.477	0.429	90.5^{0}	310	6.69	6.70
	69.6	0.471	0.507	$125.^{0}$	263	6.66	6.68
	80.1^{5}	0.466	0.586	$170.^{5}$	227	6.79	6.82
	92.1^{5}	0.459	0.679	$228.^{5}$	196	6.83	6.88
T = 231.7°K	11.6^{5}	0.719	0.0573	1.62^{5}	1624	4.61	5.71
H_2 in V_1	20.1^{5}	0.714	0.0978	4.84^{5}	951	4.73	5.80
A in V_2	30.4	0.712	0.149	10.9^{0}	623	4.57	5.57
	37.3	0.710	0.183	17.5^{0}	508	4.91	5.96
	46.5	0.704	0.227	27.7^{0}	409	5.04	6.05
	59.2	0.697	0.290	47.8^{0}	321	5.38	6.37
	70.0	0.692	0.343	67.4^{5}	271	5.44	6.36
	79.9^{5}	0.688	0.392	85.9^{5}	237	5.32	6.19
	92.7	0.682	0.454	$115.^{5}$	265	5.35	6.16
T = 292.6°K	5.0	0.255	0.0154	0.087	4787	2.70	3.56
H_2 in V_1'	17.9	0.249	0.0554	1.10^{0}	1331	2.65	3.35
A in V_u'	25.1^{5}	0.250	0.0778	2.26^{0}	947	2.76	3.67
	29.7^{5}	0.246	0.0921	3.15^{5}	800	2.75	3.70
	43.7	0.246	0.136	6.54^{0}	542	2.61	3.52
	57.2	0.242	0.179	12.3^{5}	412	2.87	3.92
	67.8	0.241	0.213	17.1^{5}	347	2.82	3.86
	85.0	0.237	0.267	26.7^{0}	276	2.87	3.85
	87.6	0.236	0.275	28.6^{0}	268	2.81	3.89
T = 292.6°K	15.0	0.461	0.0463	1.05^{5}	1595	3.65	3.67
H_2 in V_1	24.9	0.458	0.0770	2.97^{0}	958	3.71	3.73
A in V_u	34.9	0.456	0.108	5.55^{5}	686	3.56	3.59
	52.0	0.451	0.160	12.8^{0}	460	3.70	3.74
	68.8	0.446	0.212	22.3^{5}	348	3.70	3.74
	88.9	0.441	0.274	37.3^{5}	269	3.72	3.77
T = 292.6°K	6.6	0.528	0.0201	0.191	3667	3.48	3.49
H_2 in V_u	16.5	0.529	0.0507	1.27^{0}	1454	3.66	3.67
A in V_1	19.5	0.527	0.0601	1.74^{5}	1228	3.57	3.58
	20.0	0.527	0.0616	1.83^{5}	1197	3.57	3.58
	23.9	0.528	0.0737	2.62^{5}	1002	3.58	3.59
	25.8	0.526	0.0792	2.99^{0}	931	3.53	3.54
	35.9	0.523	0.110	5.96^{0}	670	3.64	3.65
	43.0	0.522	0.132	8.37^{0}	558	3.55	3.56
	55.1	0.516	0.169	13.4^{0}	437	3.50	3.50
	73.3	0.513	0.224	23.9^{5}	329	3.54	3.55
	88.6	0.509	0.271	34.0^{5}	273	3.47	3.47

TABLE III (*continued*)

Temperature and combination of vessels	p atm	mole fraction H_2	$N_{H_2}+N_A$ mole	$\Delta N \times 10^4$ mole	$\tilde{V}_m^{id}$ cm³/mole	$\tilde{V}^E$ cm³/mole	$\frac{\tilde{V}^E}{4x(1-x)}$ cm³/mole
T = 292.6°K	7.9	0.742	0.0241	0.206	3056	2.61	3.41
H_2 in V_u'	22.9^5	0.741	0.0705	1.77^0	1046	2.64	3.43
A in V_1'	24.5	0.739	0.0750	2.10^0	982	2.76	3.57
	26.9	0.738	0.0818	2.44^5	901	2.70	3.49
	27.9	0.737	0.0846	2.64^5	871	2.73	3.52
	38.3	0.736	0.116	4.88^5	689	2.67	3.44
	39.9	0.736	0.121	5.14^5	607	2.75	3.55
	39.9	0.736	0.121	5.47^5	607	2.59	3.33
	40.2	0.736	0.122	5.40^5	540	2.69	3.46
	43.1^5	0.735	0.131	5.99^0	562	2.58	3.32
	55.2	0.731	0.167	10.2^5	442	2.74	3.48
	69.8	0.729	0.210	16.4^0	351	2.75	3.48
	89.9	0.725	0.269	26.6^5	274	2.74	3.43

TABLE IV

Results for the mixture A–N_2

Temperature and combination of vessels	p atm	mole fraction N_2	$N_A+N_{N_2}$ mole	$\Delta N \times 10^4$ mole	$\tilde{V}_m^{id}$ cm³/mole	$\tilde{V}^E$ cm³/mole	$\frac{\tilde{V}^E}{4x(1-x)}$ cm³/mole
T = 170.5°K	15.2	0.268	0.112	0.071	855	0.056	0.071
N_2 in V_2	29.4	0.263	0.232	0.043	411	−0.008	−0.010
A in V_1	45.5	0.252	0.406	4.41^5	235	0.26	0.35
	59.4	0.233	0.606	32.2^5	157	0.86	1.20
	71.2	0.211	0.842	98.3^5	113	1.35	2.03
	78.9^5	0.201	1.00	$211.^0$	94.4	2.06	3.21
	85.2	0.196	1.12	$244.^5$	84.3	1.90	3.02
	91.9	0.194	1.24	$233.^0$	76.5	1.49	2.38
T = 170.5°K	7.48	0.513	0.0749	0.031	1807	−0.077	−0.077
N_2 in V'	14.95	0.509	0.154	0.148	875	−0.085	−0.085
A in V_2'	39.6^5	0.494	0.470	0.670	288	0.042	0.042
	51.7	0.478	0.670	16.9^0	202	0.52	0.52
	60.1^5	0.460	0.838	60.5^5	161	1.19	1.20
	69.8	0.433	1.07	$177.^0$	126	2.13	2.17
	76.8	0.419	1.25	$353.^5$	108	3.16	3.25
	83.0	0.411	1.40	$449.^0$	96.0	3.21	3.32
	88.2^5	0.407	1.52	$498.^5$	88.9	3.06	3.17
	93.7	0.466	1.64	$474.^0$	82.1	2.47	2.56
T = 170.5°K	10.02	0.725	0.0714	0.034	1338	−0.066	−0.083
N_2 in V_1	35.1	0.718	0.280	0.139	340	0.17	0.21
A in V_2	49.9^5	0.704	0.436	4.36^0	218	0.22	0.26
	57.3	0.692	0.525	20.7^0	181	0.73	0.86
	69.4	0.664	0.696	86.8^0	136	1.76	1.97
	74.1^5	0.654	0.769	$130.^5$	123	2.16	2.39
	82.3	0.643	0.887	$230.^0$	107	2.89	3.15
	86.9	0.639	0.949	$242.^5$	99.7	2.66	2.88
	94.3	0.638	1.05	$264.^5$	90.5	2.22	2.40

TABLE IV *(continued)*

Temperature and combination of vessels	p atm	mole fraction N_2	$N_A+N_{N_2}$ mole	$\Delta N\times10^4$ mole	$\tilde{V}_m^{id}$ cm³/mole	$\tilde{V}^E$ cm³/mole	$\frac{\tilde{V}^E}{4x(1-x)}$ cm³/mole
T = 231.7°K	17.1^5	0.272	0.0891	0.097	1084	−0.123	−0.155
N_2 in V_2	31.0	0.269	0.165	0.384	585	−0.141	−0.179
A in V_1	44.8^5	0.268	0.243	0.735	396	−0.124	−0.158
	66.2	0.263	0.371	1.61^5	260	−0.117	−0.151
	85.0	0.260	0.487	0.979	198	−0.041	−0.053
	94.4	0.257	0.548	1.59^5	176	−0.053	−0.069
T = 231.7°K	15.0^5	0.484	0.110	0.117	1237	−0.134	−0.134
N_2 in V_2'	30.0^5	0.481	0.225	0.504	607	−0.139	−0.139
A in V_1	46.1	0.479	0.352	1.37^0	388	−0.155	−0.155
	64.1	0.474	0.502	2.12^5	277	−0.120	−0.120
	85.1	0.468	0.682	3.70^5	200	−0.111	−0.111
T = 231.7°K	15.0	0.724	0.0776	0.080	1244	−0.134	−0.168
N_2 in V_1	45.3	0.721	0.242	0.804	398	−0.137	−0.170
A in V_2	69.9	0.715	0.384	1.81^5	251	−0.123	−0.151
	92.0	0.710	0.513	1.36^0	188	−0.052	−0.063
T = 292.6°K	30.8	0.253	0.0961	0.15	767	−0.12	−0.16
N_2 in V_1'	54.8^5	0.251	0.173	0.68	425	−0.17	−0.22
A in V_u'	84.9^5	0.247	0.271	1.44	272	−0.15	−0.20
T = 292.6°K	30.7	0.463	0.0956	0.27	772	−0.22	−0.22
N_2 in V_1	57.2	0.460	0.180	0.92	410	−0.21	−0.21
A in V_u	84.4	0.456	0.267	1.73	276	−0.18	−0.18
T = 292.6°K	31.2	0.530	0.0970	0.22	761	−0.17	−0.17
N_2 in V_u	51.8	0.528	0.162	0.52	454	−0.14	−0.15
A in V_1	52.3	0.528	0.164	0.54	450	−0.15	−0.15
	85.5	0.523	0.269	1.72	274	−0.18	−0.18
T = 292.6°K	30.4	0.742	0.0942	0.29	782	−0.24	−0.31
N_2 in V_u'	50.4	0.740	0.157	0.68	470	−0.20	−0.26
A in V_1'	84.2	0.737	0.263	1.11	281	−0.12	−0.15

TABLE V

The dependence of the concentration with pressures for three arrangements of the vessels for the mixture A–H_2 at 170.5°K

The vessel with A	The vessel with H_2	Pressure range in atm.	Concentration range in mole fraction H_2
V_1	V_2	4.00 – 94.8	0.268 – 0.137
V_2	V_1	3.12 – 95.2	0.726 – 0.535
V_2'	V_1	2.07 – 90.35	0.509 – 0.312

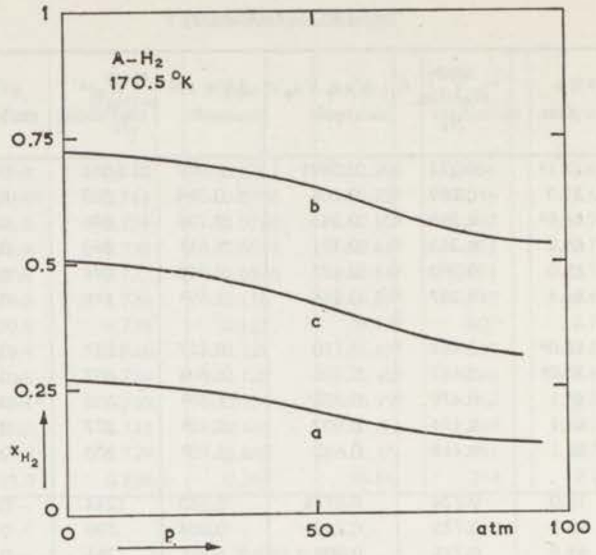

Fig. 2 The concentration as a function of pressure.

a. A in V_1 and H_2 in V_2; b. A in V_2 and H_2 in V_1; c. A in V_2' and H_2 in V_1.

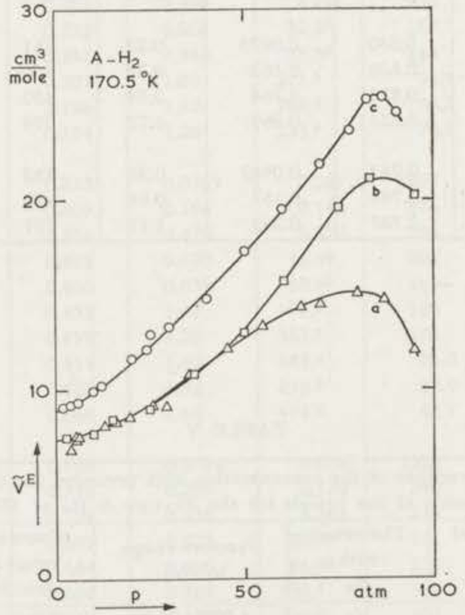

Fig. 3. $\tilde{V}^E$ as a function of pressure.

a. $x_{H_2} = 0.268–0.137$; b. $x_{H_2} = 0.726–0.535$; c. $x_{H_2} = 0.509–0.312$

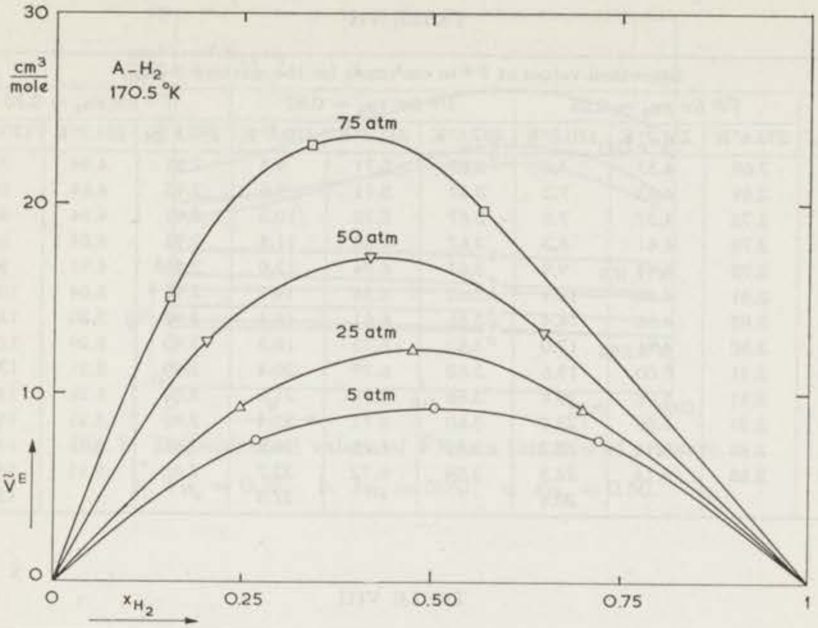

Fig. 4. $\tilde{V}^E$ as a function of concentration.

A–H_2 at 170.5°K. In figure 3 the calculated values of $\tilde{V}^E$ are plotted as a function of pressure for the three combinations of vessels (curves *a*, *b* and *c*). Combining the graphs 2 and 3 one can obtain at round values of p, say 5, 10, 15 etc. atm. values of $\tilde{V}^E$ at three different concentrations. Such results are plotted in fig. 4. To get the pressure dependence of $\tilde{V}^E$ at fixed concentrations we make cross-sections in fig. 4 at the mole fractions $x_{H_2} = 0.25$,

TABLE VI

Smoothed values of $\tilde{V}^E$ in cm³/mole for the mixture N_2–H_2

p	$\tilde{V}^E$ for $x_{H_2} = 0.25$			$\tilde{V}^E$ for $x_{H_2} = 0.50$			$\tilde{V}^E$ for $x_{H_2} = 0.70$		
atm	292.6°K	231.7°K	170.5°K	292.6°K	231.7°K	170.5°K	292.6°K	231.7°K	170.5°K
5	2.47	3.98	6.93	3.30	5.53	8.78	2.75	4.54	7.52
10	2.47	3.98	7.10	3.30	5.53	9.00	2.75	4.54	7.60
15	2.47	3.99	7.20	3.29	5.53	9.28	2.71	4.52	7.67
20	2.48	3.99	7.45	3.27	5.53	9.60	2.68	4.50	7.76
30	2.48	4.02	8.02	3.28	5.53	10.20	2.64	4.44	8.08
40	2.50	4.02	8.72	3.26	5.53	10.88	2.60	4.38	8.50
50	2.52	4.02	9.30	3.24	5.49	11.47	2.55	4.32	8.92
55	2.52	4.00	9.52	3.21	5.47	11.61	2.53	4.29	9.06
60	2.52	3.99	9.71	3.17	5.44	11.88	2.51	4.26	9.03
65	2.50	3.97	9.80	3.16	5.40	12.02	2.51	4.23	9.07
70	2.47	3.94	9.81	3.15	5.39	12.00	2.50	4.19	9.09
80	2.41	3.89	9.59	3.04	5.34	11.70	2.40	4.19	8.76
90	2.31	3.83	8.81	2.88	5.28	11.11	2.34	4.08	8.10
95	2.29	3.80	8.30	2.87	5.24	10.62	2.32	3.94	7.60
100	2.27			2.82			2.30		

TABLE VII

Smoothed values of $\tilde{V}^E$ in cm³/mole for the mixture A–H_2

p	$\tilde{V}^E$ for $x_{H_2} = 0.25$			$\tilde{V}^E$ for $x_{H_2} = 0.50$			$\tilde{V}^E$ for $x_{H_2} = 0.70$		
atm	292.6°K	231.7°K	170.5°K	292.6°K	231.7°K	170.5°K	292.6°K	231.7°K	170.5°K
5	2.69	4.33	7.2	3.67	5.71	9.3	2.95	4.84	7.9
10	2.69	4.33	7.3	3.67	5.71	9.6	2.95	4.84	8.0
15	2.72	4.37	7.8	3.67	5.75	10.3	2.95	4.84	8.2
20	2.75	4.41	8.3	3.67	5.80	11.4	2.95	4.84	8.55
30	2.75	4.49	9.9	3.67	6.04	13.0	2.95	4.91	9.2
40	2.81	4.65	12.1	3.63	6.38	14.7	2.91	5.04	10.3
50	2.85	4.88	14.4	3.66	6.61	16.4	2.92	5.20	11.5
60	2.90	4.91	17.0	3.63	6.73	18.3	2.90	5.29	12.5
70	2.91	5.00	19.6	3.60	6.79	20.4	2.90	5.31	13.8
75	2.91	5.05	20.8	3.60	6.78	21.6	2.89	5.26	14.1
80	2.91	5.09	22.0	3.60	6.77	22.4	2.88	5.21	14.2
85	2.88	5.11	23.2	3.55	6.75	22.8	2.86	5.16	14.2
90	2.85	5.14	22.3	3.50	6.72	22.7	2.85	5.11	14.2
95			20.8			21.4			13.8

TABLE VIII

Smoothed values of $\tilde{V}^E$ in cm³/mole for the mixture A–N_2

p	$\tilde{V}^E$ for $x_{N_2} = 0.20$		$\tilde{V}^E$ for $x_{N_2} = 0.50$		$\tilde{V}^E$ for $x_{N_2} = 0.70$	
atm	231.7°K	170.5°K	231.7°K	170.5°K	231.7°K	170.5°K
10	−0.13	0	−0.14	−0.07	−0.14	−0.05
15	−0.13	0	−0.14	−0.07	−0.14	−0.05
20	−0.13	0	−0.14	−0.07	−0.14	−0.05
30	−0.13	0	−0.14	−0.06	−0.14	−0.05
40	−0.13	0.05	−0.14	0.10	−0.14	0.06
45	−0.13	0.17	−0.14	0.25	−0.14	0.17
50	−0.13	0.35	−0.14	0.45	−0.13	0.40
60	−0.14	0.85	−0.14	1.11	−0.11	0.89
70	−0.13	1.51	−0.13	2.22	−0.10	1.64
75	−0.10	1.81	−0.12	2.89	−0.10	2.01
80	−0.08	2.00	−0.11	3.22	−0.10	2.43
85	−0.08	1.95	−0.10	3.21	−0.08	2.43
90	−0.07	1.66	−0.09	2.95	−0.06	2.22
95		1.26		2.42		1.95

0.5 and 0.7. The smoothed values of $\tilde{V}^E$ obtained in this way, are plotted in fig. 5. All the data given in the tables II, III and IV except the ones at 205.7°K, are treated in the same way as the of the A–H_2 data at 170.5°K. The final results are given in the tables VI, VII and VIII and are plotted in figs. 5, 6 and 7. The data at 205.7°K suffer from a rather low accuracy. These measurements were performed in a bath of liquid propane at reduced pressure. Temperature control under our experimental conditions appeared to be rather difficult. This resulted in an appreciable scattering of data.

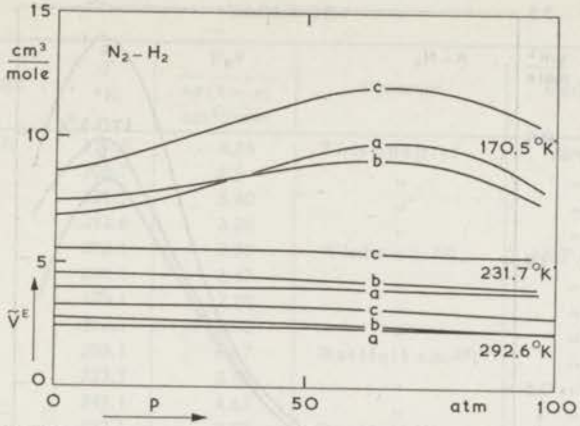

Fig. 5. The smoothed values of $\tilde{V}^E$ as a function of pressure.

a. $x_{H_2} = 0.25$; b. $x_{H_2} = 0.70$; c. $x_{H_2} = 0.50$.

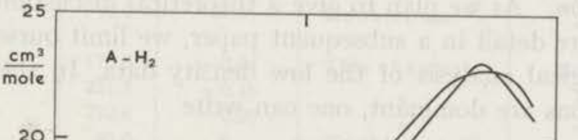

Fig. 6. The smoothed values of $\tilde{V}^E$ as a function of pressure.

a. $x_{H_2} = 0.25$; b. $x_{H_2} = 0.70$; c. $x_{H_2} = 0.50$.

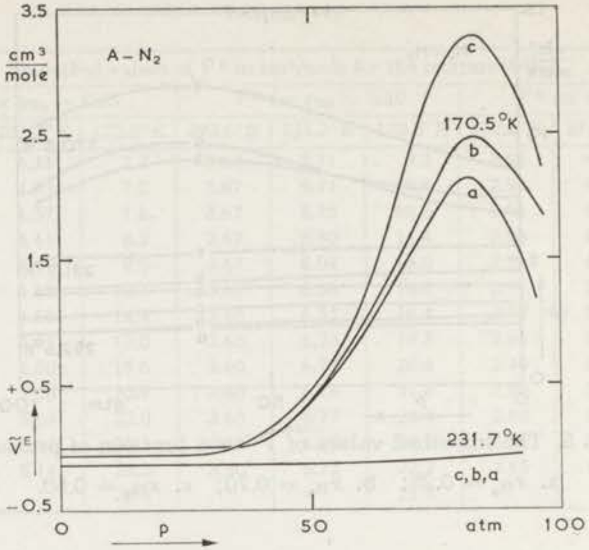

Fig. 7. The smoothed values of $\tilde{V}^{\mathrm{E}}$ as a function of pressure.
a. $x_{\mathrm{N}_2} = 0.20$; b. $x_{\mathrm{N}_2} = 0.70$; c. $x_{\mathrm{N}_2} = 0.50$.

4. *Discussion.* As we plan to give a theoretical discussion of the results for $\tilde{V}^{\mathrm{E}}$ in more detail in a subsequent paper, we limit ourselves here to a phenomenological analysis of the low density data. In the region where binary collisions are dominant, one can write

$$\tilde{V} = \frac{RT}{p}(1 + Bd) \tag{6}$$

Here B is the second virial coefficient and d is the molar density defined as $d = 1/\tilde{V}$. Denoting the second virial coefficients of the pure gases A and B and the mixture as B_{AA}, B_{BB} and B_{m} we get in the limit of low densities

$$\tilde{V}^{\mathrm{E}}_0 = B_{\mathrm{m}} - x_{\mathrm{A}}B_{\mathrm{AA}} - x_{\mathrm{B}}B_{\mathrm{BB}}. \tag{7}$$

The second virial coefficient of a binary mixture can be written as

$$B_{\mathrm{m}} = x_{\mathrm{A}}^2 B_{\mathrm{AA}} + 2x_{\mathrm{A}}x_{\mathrm{B}}B_{\mathrm{AB}} + x_{\mathrm{B}}^2 B_{\mathrm{BB}} \tag{8}$$

where B_{AB} is the second virial coefficient of a hypothetical gas with only A–B interactions. We define a quantity E by means of the expression

$$E = B_{\mathrm{AB}} - \tfrac{1}{2}(B_{\mathrm{AA}} + B_{\mathrm{BB}}). \tag{9}$$

By combining eqs. (7), (8) and (9) one obtains for $\tilde{V}^{\mathrm{E}}_0$

$$\tilde{V}^{\mathrm{E}}_0 = 2x_{\mathrm{A}}x_{\mathrm{B}}E. \tag{10}$$

At low densities $\tilde{V}^{\mathrm{E}}$ should be independent of pressure and parabolic as a function of concentration. This concentration dependence is clearly

TABLE IX

Mixture	T °K	$\frac{\tilde{V}_0^E}{4x(1-x)}$ cm³/mole	Observer	Method
N_2–H_2	170.5	8.84	This chapter	direct
	205.7	6.5	,,	,,
	231.7	5.40	,,	,,
	292.6	3.28	,,	,,
	273.1	3.95	Wiebe e.a. 10)	pVT data
	298.1	3.47	,,	,,
	323.1	2.70	,,	,,
	373.1	2.82	,,	,,
	203.1	6.67	Bartlett e.a. 12)	,,
	223.1	5.60	,,	,,
	248.1	4.67	,,	,,
	273.1	3.95	Bartlett 11)	,,
	293.1	4.00	,,	,,
	298.1	4.48	Edwards e.a. 13)	direct
	298.1	4.08	Lunbeck e.a. 14)	direct
	298.1	3.23	Michels e.a. 15)	pVT data
A–H_2	170.5	9.31	This chapter	direct
	205.7	7.15	,,	,,
	231.7	5.70	,,	,,
	292.6	3.59	,,	,,
	90.0	27.5	Knobler e.a. 16)	,,
A–N_2	170.5	−0.04	This chapter	direct
	231.7	−0.16	,,	,,
	292.6	−0.20	,,	,,
	90.0	0	Knobler e.a. 16)	,,

illustrated by the low pressure (5 atm.) curve in fig. 4. In the figs. 5, 6 and 7 one sees, that at room temperature $\tilde{V}^E$ is independent of pressure till about 50 atm. and till about 35 atm at 231.7°K. We determine $\tilde{V}_0^E$ from the figs, 5, 6 and 7 for all the temperatures, where measurements have been performed. The values of $\tilde{V}_0^E/4x(1-x)$ are generally equal within a few percents for the three concentrations of a mixture. In the fig. 8, 9 and 10 the average values of $\tilde{V}_0^E/4x(1-x)$ are plotted as a function of temperature. In these graphs and also in table IX the data from literature are given[10][11][12][13][14][15][16]. There is a rather good agreement between the results of the other authors and our experiments.

For the three mixtures N_2–H_2, A–H_2 and A–N_2 we calculate, using eqs. (9) and (10), B_{AB} as a function of temperature from the second virial coefficients of the pure gases and the values of E obtained experimentally (table X). For the B coefficients of H_2 and A we use the data of Michels *e.a.*[17][18][19] and for the B coefficients of N_2 the data of Hoover *e.a.*[20] Following a well known procedure, viz. plotting $\log|B_{AB}|$ versus $\log T$ and comparing this plot with the $\log|B^*|$ versus $\log T^*$ graph, we found that the

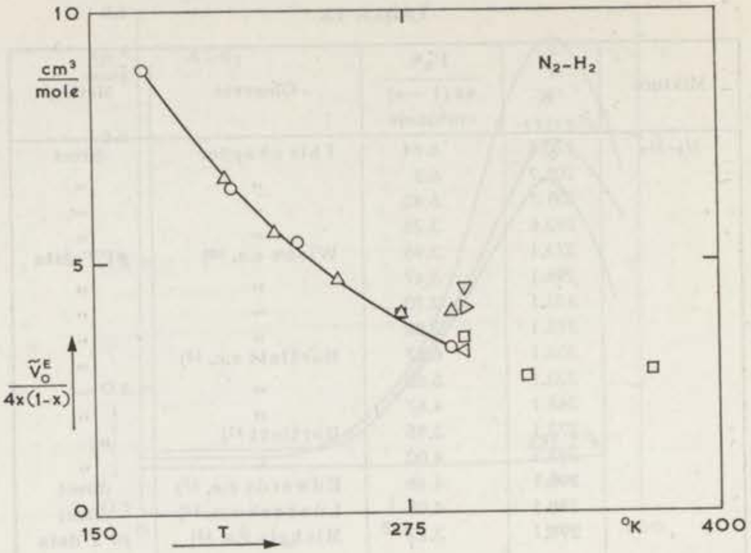

Fig. 8. $\frac{\tilde{V}_0^E}{4x(1-x)}$ as a function of temperature.

□ Wiebe e.a. [10])	▷ Lunbeck e.a. [14])
△ Bartlett e.a. [11 12])	◁ Michels e.a. [15])
▽ Edwards e.a. [13])	○ Our experiments

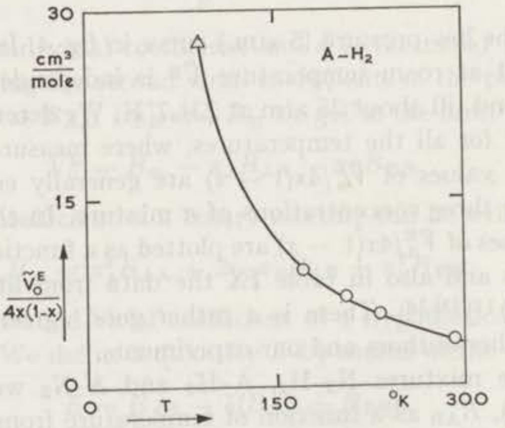

Fig. 9. $\frac{\tilde{V}_0^E}{4x(1-x)}$ as a function of temperature.

△ Knobler e.a. [16]) ○ Our experiments

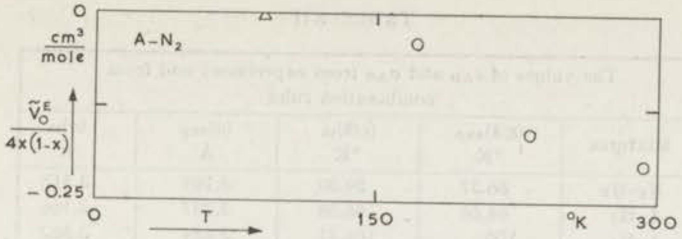

Fig. 10. $\dfrac{\tilde V_0^E}{4x(1-x)}$ as a function of temperature.

△ Knobler e.a. [16]) ○ Our experiments.

TABLE X

The calculated values of B_{AB} for the mixtures N_2–H_2, A–H_2, and A–N_2

T °K	$B_{N_2-H_2}$ cm³/mole	B_{A-H_2} cm³/mole	B_{A-N_2} cm³/mole
170	−5.04	−10.3	−60.5
180	−2.63	− 7.8	−53.5
190	−0.55	− 5.7	−47.4
200	1.15	− 4.0	−42.0
210	2.69	− 2.4	−37.2
220	4.08	− 0.9	−32.8
230	5.29	0.3	−29.0
240	6.25	1.5	−25.6
250	7.24	2.5	−22.5
260	8.24	3.5	−19.4
270	9.07	4.2	−16.8

data are consistent with a Lennard-Jones potential

$$\phi(r) = -4\varepsilon_{AB}\left\{\left(\frac{\sigma_{AB}}{r}\right)^6 - \left(\frac{\sigma_{AB}}{r}\right)^{12}\right\} \tag{11}$$

r is the distance between the centers of the molecules A and B, ε_{AB} is the energy of the depth of the potential well and σ_{AB} is the collision diameter. $B^* = B/2\pi N\sigma^3$ and $T^* = kT/\varepsilon$ are the reduced B coefficient and the reduced temperature respectively. B^* as a function of T^* is given in table I-B in the book of Hirschfelder, Curtiss and Bird[21]). From the shifts

TABLE XI

The molecular parameters from Hirschfelder e.a. [21])

Gas	ε/k °K	σ Å
H_2	37.00	2.928
N_2	95.05	3.698
A	119.8	3.405

TABLE XII

The values of ε_{AB} and σ_{AB} from experiment and from combination rules

Mixtures	$(\varepsilon/k)_{exp}$ °K	$(\varepsilon/k)_{th}$ °K	$(\sigma)_{exp}$ Å	$(\sigma)_{th}$ Å
N_2–H_2	56.37	59.30	3.169	3.313
A–H_2	66.68	66.58	3.037	3.166
A–N_2	100	106.71	3.684	3.552

along the B and T axes necessary to make the theoretical and experimental graphs, we obtain ε_{AB} and σ_{AB}. In table XI we give the values of ε and σ of the pure gases from Hirschfelder *e.a.*[21]) and in table XII we give the experimental values of ε_{AB} and σ_{AB}. For the purpose of comparison we note the values of ε_{AB} and σ_{AB} obtained from the usual combination rules

$$\varepsilon_{AB} = \sqrt{\varepsilon_{AA}\varepsilon_{BB}} \tag{12}$$

$$\sigma_{AB} = \tfrac{1}{2}(\sigma_{AA} + \sigma_{BB}). \tag{13}$$

The agreement is rather good.

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CHAPTER II

THEORETICAL DETERMINATION OF THE VOLUME CHANGE ON MIXING FOR GASEOUS N_2–H_2, A–H_2 AND A–N_2 AT 170°K UP TO 100 ATM

Synopsis

In chapter I we described a direct method to measure the volume change on mixing of gases at constant pressure. The results of the measurements on three mixtures, N_2–H_2, A–H_2 and A–N_2 were given. In this chapter we apply to these systems the ideas of Prigogine and of Scott for liquid solutions. We calculated the excess volume for three different models. Comparison of experimental and theoretical values of the volume change on mixing shows that there is always a good qualitative agreement. Quantitatively the results are reasonable for the systems N_2–H_2 and A–H_2, but poor for A–N_2.

1. *Introduction.* In chapter I[1]) we described the measurements, that were performed on three gaseous mixtures N_2–H_2, A–H_2 and A–N_2, to determine the volume change on mixing at constant pressure, $\tilde{V}^{\mathrm{E}}$. The experiments were carried out between 170 and 292°K at pressures below 100 atm and at three concentrations. For the low density range, where the binary collisions prevail, we already gave a phenomenological description of $\tilde{V}^{\mathrm{E}}$ in terms of the second virial coefficient. In this chapter we will give a theoretical discussion of the behaviour of $\tilde{V}^{\mathrm{E}}$ at higher densities.

There are two ways to attack this problem for higher densities, starting either from the low density or from the liquid side. In the first case we try to extend the low density treatment by including more terms in a virial expansion of the equation of state or by using one of the proposed closed form equations of state, as e.g. the Beattie-Bridgman equation. To describe the mixture one needs to relate the constants in the equation of state of the mixtures to those of the pure components by means of so called combination rules. Though these rules have at least some physical basis for the second virial coefficient, one approaches a state of complete arbitrariness for the higher order coefficients, where these rules are only justified by the reasonable results, they give in certain cases. As a result it is rather incorrect to extrapolate them outside the temperature and pressure range where they have been tested. The second way is to start from the high density side by applying the existing corresponding state theory for liquid mixtures to moderately dense gases.

2. *Theory*. In view of the success obtained with the ideas of Prigogine[2] and of Scott[3] in the case of liquid mixtures, we extended their ideas to gaseous mixtures.

The basic assumptions for the corresponding state theory were formulated by Scott in the following way.

1) The intermolecular potential energy is assumed to be due to central forces only, and of the same form for all kinds of pairs, and may be written symbolically as $\phi(r) = \varepsilon f(\sigma/r)$, where r is the distance between molecular centers, ε, is the energy of a moleculair pair at its equilibrium distance, and σ is the collision diameter. Both liquid then conform to the same reduced equation of state, a function of the reduced temperature and reduced volume.

2. The same reduced equation of state is assumed for the solution and a prescription is given for obtaining appropriate averages for the energy and volume parameters in the solution.

For the gaseous mixtures we take for the interaction potential the Lennard-Jones potential:

$$\phi(r) = -4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right\} \tag{1}$$

with parameters ε_{AA}, σ_{AA}, ε_{BB}, σ_{BB}, and ε_{AB}, σ_{AB} for the A–A, B–B and A–B interactions, respectively. For the A–B interaction we use the combination rules

$$\varepsilon_{AB} = (\varepsilon_{AA}\varepsilon_{BB})^{\frac{1}{2}} \tag{2}$$

$$\sigma_{AB} = \tfrac{1}{2}(\sigma_{AA} + \sigma_{BB}). \tag{3}$$

With the aid of these molecular parameters, ε and σ, the temperature, volume and pressure can be expressed in reduced units

$$T^* = \frac{kT}{\varepsilon}, \quad \tilde{V}^* = \frac{\tilde{V}}{N\sigma^3} \quad \text{and} \quad p^* = \frac{p\sigma^3}{\varepsilon}. \tag{4}$$

There are three models that can be used to obtain the above mentioned average interaction parameters for the mixture.

1. The "single liquid" solution (Prigogine's crude approximation).

The mixture behaves-aside from the Gibbs paradox entropy contribution-as a liquid with an effective interaction, that is the average of the pair interactions,

$$\langle\phi(r)\rangle = x_A^2\phi_{AA}(r) + 2x_Ax_B\phi_{AB}(r) + x_B^2\phi_{BB}(r) \tag{5}$$

where x_{A} and x_{B} are the mole fractions. $\langle\phi(r)\rangle$ is now again a Lennard-Jones potential with parameters $\langle\varepsilon\rangle$ and $\langle\sigma\rangle$,

$$\langle\varepsilon\rangle = \frac{(x_{\mathrm{A}}^2\varepsilon_{\mathrm{AA}}\sigma_{\mathrm{AA}}^6 + 2x_{\mathrm{A}}x_{\mathrm{B}}\varepsilon_{\mathrm{AB}}\sigma_{\mathrm{AB}}^6 + x_{\mathrm{B}}^2\varepsilon_{\mathrm{BB}}\sigma_{\mathrm{BB}}^6)^2}{x_{\mathrm{A}}^2\varepsilon_{\mathrm{AA}}\sigma_{\mathrm{AA}}^{12} + 2x_{\mathrm{A}}x_{\mathrm{B}}\varepsilon_{\mathrm{AB}}\sigma_{\mathrm{AB}}^{12} + x_{\mathrm{B}}^2\varepsilon_{\mathrm{BB}}\sigma_{\mathrm{BB}}^{12}} \tag{6}$$

and

$$\langle\sigma\rangle = \left(\frac{x_{\mathrm{A}}^2\varepsilon_{\mathrm{AA}}\sigma_{\mathrm{AA}}^{12} + 2x_{\mathrm{A}}x_{\mathrm{B}}\varepsilon_{\mathrm{AB}}\sigma_{\mathrm{AB}}^{12} + x_{\mathrm{B}}^2\varepsilon_{\mathrm{BB}}\sigma_{\mathrm{BB}}^{12}}{x_{\mathrm{A}}^2\varepsilon_{\mathrm{AA}}\sigma_{\mathrm{AA}}^6 + 2x_{\mathrm{A}}x_{\mathrm{B}}\varepsilon_{\mathrm{AB}}\sigma_{\mathrm{AB}}^6 + x_{\mathrm{B}}^2\varepsilon_{\mathrm{BB}}\sigma_{\mathrm{BB}}^6}\right)^{\frac{1}{6}} \tag{7}$$

2. The "two liquid" solution (refined model). In this model one introduces two "hypothetical" liquids, an A and a B centered one. For the A centered liquid the effective interaction is found by summing up the pair interactions of A with its neighbours,

$$\langle\phi(r)\rangle_{\mathrm{A}} = x_{\mathrm{A}}\phi_{\mathrm{AA}}(r) + x_{\mathrm{B}}\phi_{\mathrm{AB}}(r) \tag{8}$$

and similarly for the B centered liquid $\langle\phi(r)\rangle_{\mathrm{A}}$ is again a Lennard-Jones potential with parameters $\langle\varepsilon\rangle_{\mathrm{A}}$ and $\langle\sigma\rangle_{\mathrm{A}}$,

$$\langle\varepsilon\rangle_{\mathrm{A}} = \frac{(x_{\mathrm{A}}\varepsilon_{\mathrm{AA}}\sigma_{\mathrm{AA}}^6 + x_{\mathrm{B}}\varepsilon_{\mathrm{AB}}\sigma_{\mathrm{AB}}^6)^2}{x_{\mathrm{A}}\varepsilon_{\mathrm{AA}}\sigma_{\mathrm{AA}}^{12} + x_{\mathrm{B}}\varepsilon_{\mathrm{AB}}\sigma_{\mathrm{AB}}^{12}} \tag{9}$$

$$\langle\sigma\rangle_{\mathrm{A}} = \left(\frac{x_{\mathrm{A}}\varepsilon_{\mathrm{AA}}\sigma_{\mathrm{AA}}^{12} + x_{\mathrm{B}}\varepsilon_{\mathrm{AB}}\sigma_{\mathrm{AB}}^{12}}{x_{\mathrm{A}}\varepsilon_{\mathrm{AA}}\sigma_{\mathrm{AA}}^6 + x_{\mathrm{B}}\varepsilon_{\mathrm{AB}}\sigma_{\mathrm{AB}}^6}\right)^{\frac{1}{6}} \tag{10}$$

while similar expressions can be written for the B centered liquid.

The mixture behaves as the weighted average of the A centered and B centered liquids (cf eq. 8).

3. The "three liquid" solution. The mixture consists of three "liquids" with no interaction between them. The parameters for each of the "liquids" are $\varepsilon_{\mathrm{AA}}$, σ_{AA}, $\varepsilon_{\mathrm{AB}}$, σ_{AB}, and $\varepsilon_{\mathrm{BB}}$, σ_{BB} for the A–A, the A–B and the B–B liquid, respectively. The properties of the mixture, e.g. $\tilde{V}_{\mathrm{m}}$ are given by:

$$\tilde{V}_{\mathrm{m}_{\mathrm{III}}} = x_{\mathrm{A}}^2\tilde{V}_{\mathrm{A}}^0 + 2x_{\mathrm{A}}x_{\mathrm{B}}\tilde{V}_{\mathrm{AB}} + x_{\mathrm{B}}^2\tilde{V}_{\mathrm{B}}^0 \tag{11}$$

where $\tilde{V}_{\mathrm{A}}^0$ and $\tilde{V}_{\mathrm{B}}^0$ are the molar volumes of pure A and B and $\tilde{V}_{\mathrm{AB}}$ is the corresponding quantity for a "hypothetical "liquid made up of molecules with a pair potential corresponding to the A–B interaction. This approach is exact at low densities, because it treats the interaction as the result of isolated pairs with the appropriate weights for pair interaction.

We shall now discuss how we can make use of these ideas for calculating the volume change on mixing of a gaseous mixture. We assume that at least for one of the components of the mixtures, say A, the molar volume is known as a function of pressure, p, and temperature, T. With the assumption that the pure gases and the mixture conform to the same reduced equation of state, we have for the molar volume in the "single liquid" mixture,

$$\tilde{V}_{m_I}(p, T) = \left(\frac{\langle\sigma\rangle}{\sigma_{AA}}\right)^3 \tilde{V}^0_A\left\{p\,\frac{\varepsilon_{AA}}{\langle\varepsilon\rangle}\left(\frac{\langle\sigma\rangle}{\sigma_{AA}}\right)^3,\; T\,\frac{\varepsilon_{AA}}{\langle\varepsilon\rangle}\right\} \tag{12}$$

The excess volume can then be calculated from:

$$\tilde{V}^E_I(p, T) = \tilde{V}_{m_I}(p, T) - x_A\tilde{V}^0_A(p, T) - x_B\tilde{V}^0_B(p, T). \tag{13}$$

The index I denotes $\tilde{V}^E$ as calculated with the "single liquid "model. We follow the same procedure for the molar volume in the "two-liquid" solution. The molar volume is:

$$\tilde{V}_{m_{II}}(p, T) = x_A\langle\tilde{V}\rangle_A + x_B\langle\tilde{V}\rangle_B \tag{14}$$

where $\langle\tilde{V}\rangle_A$ and $\langle\tilde{V}\rangle_B$ can be calculated from

$$\langle\tilde{V}\rangle_A = \left(\frac{\langle\sigma\rangle_A}{\sigma_{AA}}\right)^3 \tilde{V}^0_A\left\{p\,\frac{\varepsilon_{AA}}{\langle\varepsilon\rangle_A}\left(\frac{\langle\sigma\rangle_A}{\sigma_{AA}}\right)^3,\; T\,\frac{\varepsilon_{AA}}{\langle\varepsilon\rangle_A}\right\} \tag{15}$$

$$\langle\tilde{V}\rangle_B = \left(\frac{\langle\sigma\rangle_B}{\sigma_{AA}}\right)^3 \tilde{V}^0_A\left\{p\,\frac{\varepsilon_{AA}}{\langle\varepsilon\rangle_B}\left(\frac{\langle\sigma\rangle_B}{\sigma_{AA}}\right)^3,\; T\,\frac{\varepsilon_{AA}}{\langle\varepsilon\rangle_B}\right\} \tag{16}$$

the excess volume in the "two liquid" mixture is:

$$\tilde{V}^E_{II}(p, T) = \tilde{V}_{m_{II}}(p, T) - x_A\,\tilde{V}^0_A(p, T) - x_B\tilde{V}^0_B(p, T). \tag{17}$$

For the "three liquid" model the molar volume of the mixture is given by:

$$\tilde{V}_{m_{III}}(p, T) = x_A^2\tilde{V}^0_A(p, T) + 2x_Ax_B\tilde{V}_{AB}(p, T) + x_B^2\tilde{V}^0_B(p, T) \tag{18}$$

where

$$\tilde{V}_{AB}(p, T) = \left(\frac{\sigma_{AB}}{\sigma_{AA}}\right)^3 \tilde{V}^0_A\left\{p\,\frac{\varepsilon_{AA}}{\varepsilon_{AB}}\left(\frac{\sigma_{AB}}{\sigma_{AA}}\right)^3,\; T\,\frac{\varepsilon_{AA}}{\varepsilon_{AB}}\right\} \tag{19}$$

We obtain for $\tilde{V}^E_{III}$,

$$\begin{aligned}\tilde{V}^E_{III}(p, T) &= x_A^2\tilde{V}^0_A(p, T) + 2x_Ax_BV_{AB}(p, T) + x_B^2\tilde{V}^0_B(p, T) - x_A\tilde{V}^0_A(p, T)\\ &\quad - x_B\tilde{V}^0_B(p, T) = 2x_Ax_B\{\tilde{V}_{AB}(p, T) - \tfrac{1}{2}(\tilde{V}^0_A(p, T) + \tilde{V}^0_B(p, T))\}.\end{aligned} \tag{20}$$

Equation (20) shows that the excess volume, $\tilde{V}^E_{III}$, is a parabola as a function of the concentration.

3. *Results*. The molecular parameters of the pure gases ε and σ are taken from Hirschfelder, Curtiss and Bird[4]) and are tabulated in table I. Table II gives the molecular parameters of the mixture N_2–H_2 for the different models, as computed from the equations (6), (7), (9) and (10). Similar data for the mixtures A–H_2 and A–N_2 are given in the tables III and IV.

In the figures 1, 2, 3 and 4 we plotted the molecular parameters of the mixtures A–N_2 and A–H_2 as a function of concentration. The initial and the

TABLE I

Molecular parameters from Hirschfelder e.a. [4])

Gas	ε/k °K	σ Å
H_2	37.00	2.928
N_2	95.05	3.698
A	119.8	3.405

TABLE II

Molecular parameters for the mixture N_2–H_2

mole fraction H_2	$\langle\varepsilon/k\rangle$ °K	$\langle\sigma\rangle$ Å	$\langle\varepsilon/k\rangle_{H_2}$ °K	$\langle\varepsilon/k\rangle_{N_2}$ °K	$\langle\sigma\rangle_{H_2}$ Å	$\langle\sigma\rangle_{N_2}$ Å
0.25	72.12	3.639	51.31	82.84	3.286	3.669
0.50	53.08	3.548	43.71	71.25	3.243	3.662
0.70	41.12	3.424	38.36	63.06	3.182	3.557

TABLE III

Molecular parameters for the mixture A–H_2

mole fraction H_2	$\langle\varepsilon/k\rangle$ °K	$\langle\sigma\rangle$ Å	$\langle\varepsilon/k\rangle_{H_2}$ °K	$\langle\varepsilon/k\rangle_{A}$ °K	$\langle\sigma\rangle_{H_2}$ Å	$\langle\sigma\rangle_{A}$ Å
0.25	91.23	3.362	57.97	104.6	3.146	3.383
0.50	67.18	3.296	49.65	89.82	3.113	3.350
0.70	51.50	3.211	43.46	78.78	3.071	3.307

TABLE IV

Molecular parameters for the mixture A–N_2

mole fraction N_2	$\langle\varepsilon/k\rangle$ °K	$\langle\sigma\rangle$ Å	$\langle\varepsilon/k\rangle_{N_2}$ °K	$\langle\varepsilon/k\rangle_{A}$ °K	$\langle\sigma\rangle_{N_2}$ Å	$\langle\sigma\rangle_{A}$ Å
0.20	112.2	3.476	103.3	115.9	3.587	3.440
0.50	103.9	3.569	99.4	11.5	3.633	3.487
0.70	99.8	3.624	97.4	109.2	3.661	3.515

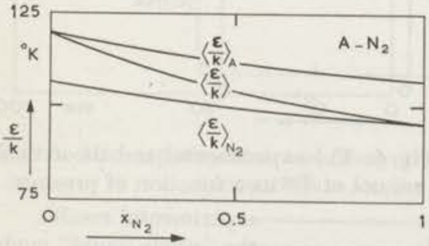

Fig. 1. The effective interaction parameter ε/k as a function of concentration.

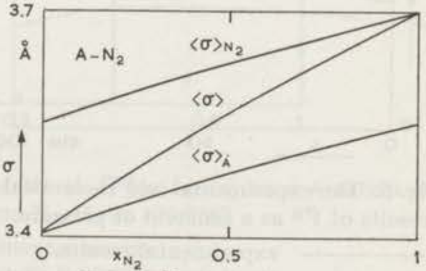

Fig. 2. The effective interaction parameter σ as a function of concentration.

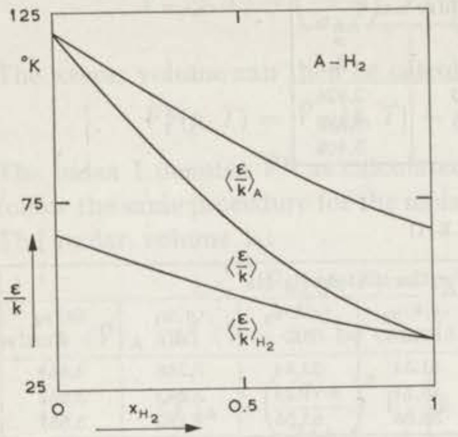

Fig. 3. The effective interaction parameter ε/k as a function of concentration.

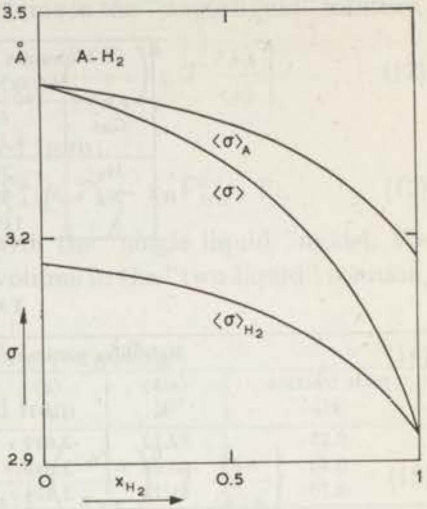

Fig. 4. The effective interaction parameter σ as a function of concentration.

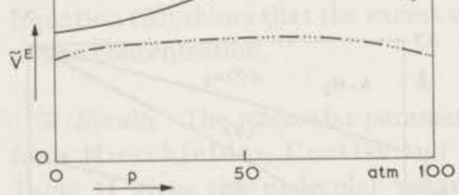

Fig. 5. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.

———— experimental results.

—— · —— the "single liquid" model.

—— ·· —— the "two liquid" model.

—— ··· —— the "three liquid" model.

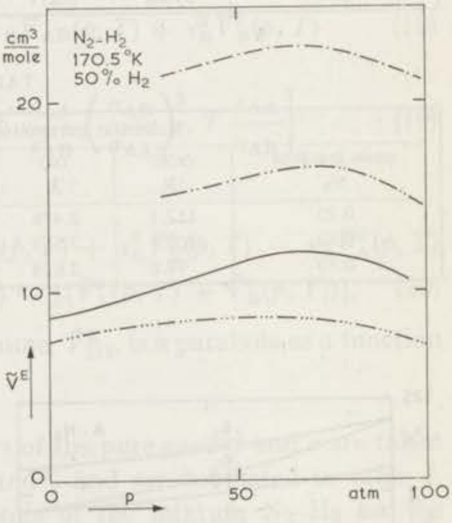

Fig. 6. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.

———— experimental results.

—— · —— the "single liquid" model.

—— ·· —— the "two liquid" model.

—— ··· —— the "three liquid" model.

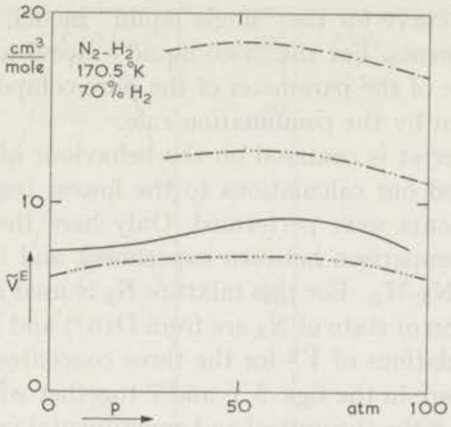

Fig. 7. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.

———— experimental results.
——— · ——— the "single liquid" model.
——— · · ——— the "two liquid" model.
——— · · · ——— the "three liquid" model.

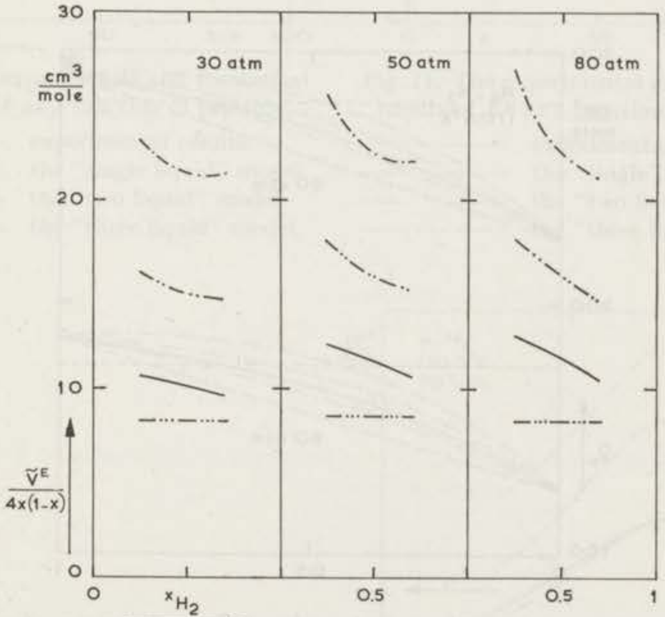

Fig. 8. The experimental and theoretical results of $\tilde{V}^E/4x(1-x)$ as a function of concentration for the system N_2–H_2 at 170.5°K.

———— experimental results.
——— · ——— the "single liquid" model.
——— · · ——— the "two liquid" model.
——— · · · ——— the "three liquid" model.

final points of the curve for the "single liquid" model, are the parameters of the pure components. For the "two liquid" model an end-point of the curve has the value of the parameter of the pure component, the other one has the value, given by the combination rule.

As our main interest is centered on the behaviour of mixtures of higher densities, we limited our calculations to the lowest temperature, 170.5°K, for which experiments were performed. Only here the densities are high enough to make comparison between experiment and theory.

The mixture N_2–H_2. For this mixture N_2 is used as the reference gas. Data of the equation of state of N_2 are from Din[5]) and Hilsenrath[6]). The results of our calculations of $\tilde{V}^E$ for the three concentrations are plotted as a function of pressure in the figs. 5, 6 and 7 together with the experimental data for $\tilde{V}^E$. In fig. 8 the theoretical and experimental values of $\tilde{V}^E/4x(1-x)$ are plotted as a function of concentration at 30, 50 and 80 atm. Finally the total molar volumes of the mixture, as calculated from the different models and as determined from the experiments are given as a function of concentration at 50 and 80 atm. in fig. 9.

The mixture A–H_2. Argon is used as the reference gas. Sources for the equation of state data of argon are Din[5]) and Hilsenrath[6]). The figs. 10,

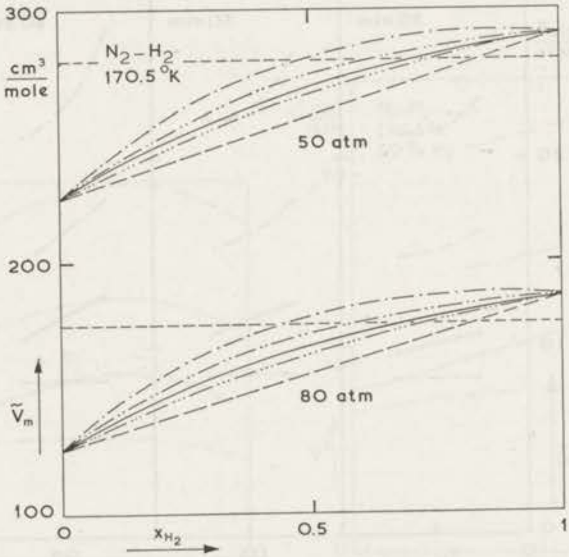

Fig. 9. The experimental and theoretical results of $\tilde{V}_M$ as a function of concentration

———————— experimental results.
- - - - - - - - - - - - - - perfect gas volume ($\tilde{V} = RT/p$)
— — — — — — ideal mixing.
———— . ———— the "single liquid" model.
———— .. ———— the "two liquid" model.
———— ... ———— the "three liquid" model.

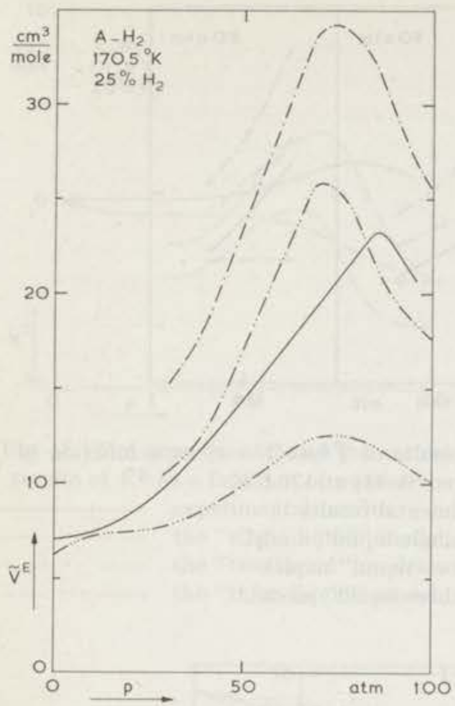

Fig. 10. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.

——————— experimental results.
—— · ——— the "single liquid" model.
—— ·· —— the "two liquid" model.
——— ··· —— the "three liquid" model.

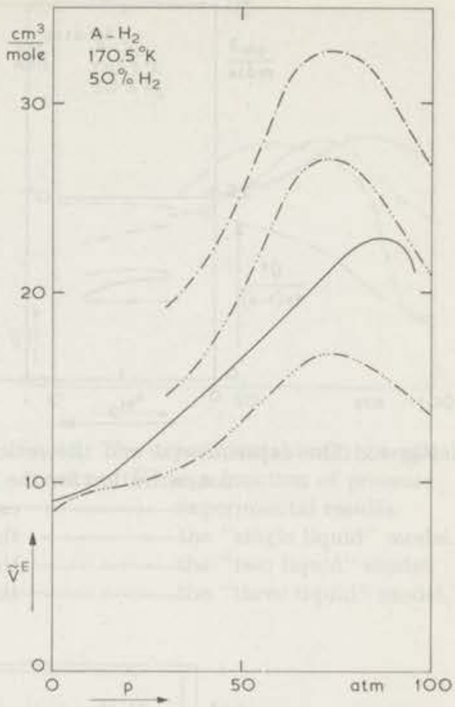

Fig. 11. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.

——————— experimental results.
—— · ——— the "single liquid" model.
—— ·· —— the "two liquid" model.
——— ··· —— the "three liquid" model.

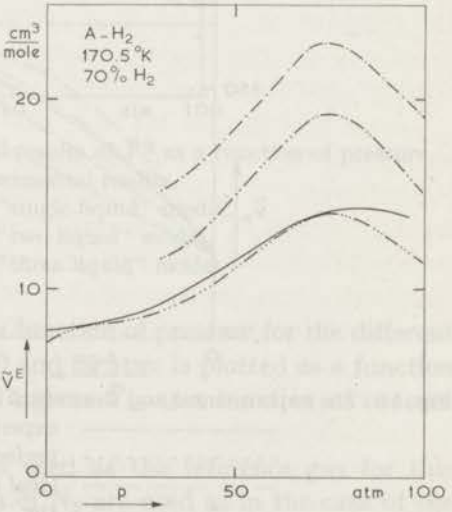

Fig. 12. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.

——————— experimental results.
—— · ——— the "single liquid" model.
—— ·· —— the "two liquid" model.
——— ··· —— the "three liquid" model.

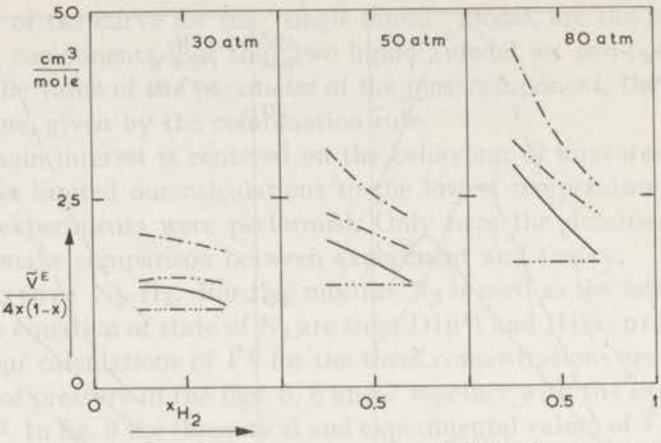

Fig. 13. The experimental and theoretical results of $\tilde{V}^E/4x(1-x)$ as a function of concentration for the system A–H_2 at 170.5°K.

———————— experimental results

——— . ——— the "single liquid" model.

——— . . ——— the "two liquid" model.

——— . . . ——— the "three liquid" model.

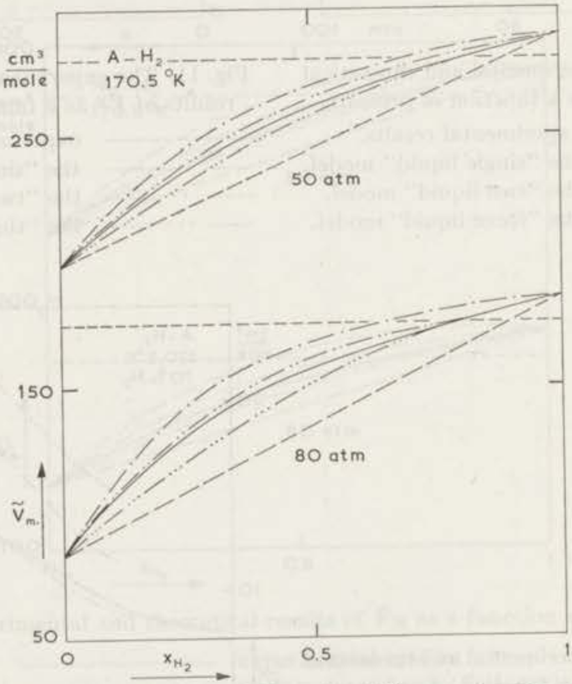

Fig. 14. The experimental and theoretical results of $\tilde{V}_M$ as a function of concentration.

———————— experimental results.

- - - - - - - - - - - - - perfect gas volume ($\tilde{V} = RT/p$).

— — — — — — ideal mixing.

——— . ——— the "single liquid" model.

——— . . ——— the "two liquid" model.

——— . . . ——— the "three liquid" model.

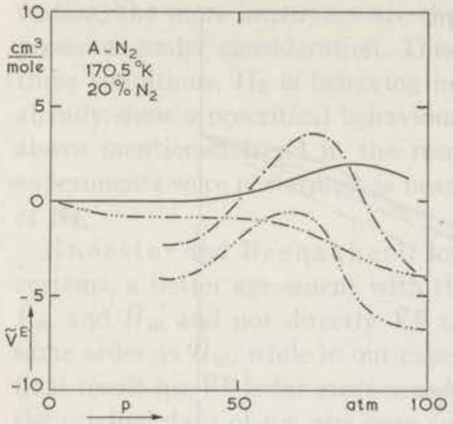

Fig. 15. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.
———— experimental results.
—— · —— the "single liquid" model.
—— ·· —— the "two liquid" model.
—— ··· —— the "three liquid" model.

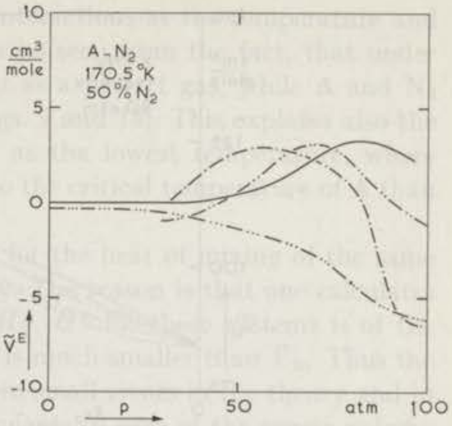

Fig. 16. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.
———— experimental results.
—— · —— the "single liquid" model.
—— ·· —— the "two liquid" model.
—— ··· —— the "three liquid" model.

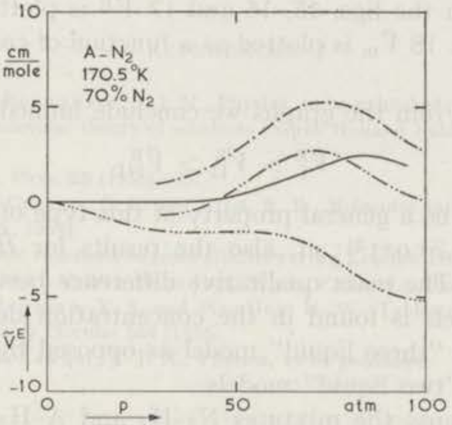

Fig. 17. The experimental and theoretical results of $\tilde{V}^E$ as a function of pressure.
———— experimental results.
—— · —— the "single liquid" model.
—— ·· —— the "two liquid" model.
—— ··· —— the "three liquid" model.

11 and 12 show the excess volumes as a function of pressure for the different concentrations. $\tilde{V}^E/4x(1-x)$ at 30, 50 and 80 atm. is plotted as a function of concentration in fig. 13, while fig. 14 gives $\tilde{V}_m$ as a function of concentration at 50 and 80 atm.

The mixture A–N_2. Nitrogen is used as the reference gas for this system. The same sources for the data of N_2 are used as in the case of the

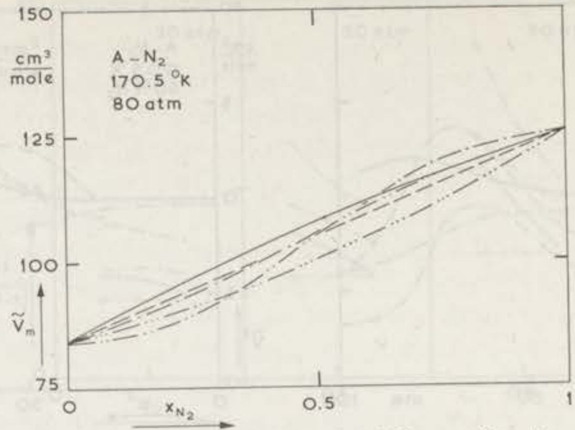

Fig. 18. The experimental and theoretical results of $\tilde{V}_m$ as a function of concentration.

———————— experimental results
— — — — — ideal mixing.
——— · ——— the "single liquid" model.
——— ·· ——— the "two liquid" model.
——— ··· ——— the "three liquid" model.

mixture N_2–H_2. In the figs. 15, 16 and 17 $\tilde{V}^E$ is plotted as a function of pressure and in fig. 18 $\tilde{V}_m$ is plotted as a function of concentration.

4. *Discussion*. From the graphs we conclude immediately that

$$\tilde{V}^E_I > \tilde{V}^E_{II} > \tilde{V}^E_{III}. \qquad (21)$$

This appears to be a general property of this type of treatment and was already found by Scott[3]; cf. also the results for $\tilde{H}^E$ as obtained by Knoester *e.a.*[7]) .The main qualitative difference between the results for the different models is found in the concentration dependence, which is symmetric for the "three liquid" model as opposed by the results for the "single" and the "two liquid" models.

Let us first discuss the mixtures N_2–H_2 and A–H_2. The experimental values of $\tilde{V}^E$ lie mostly in between the results for the "two" and the "three liquid" model. The pressure dependence is in general nearer to that predicted by the "two liquid" than by the "three liquid" model and the concentration dependence is asymmetric. Furthermore we see (figs. 5, 6, 7, 10, 11 and 12) that with increasing amount of A or N_2 the values of $\tilde{V}^E_{exp}$ come nearer to the "two liquid" model results, while with decreasing amount of A or N_2 the values of $\tilde{V}^E_{exp}$ come nearer to the "three liquid" model results. These tendencies are more pronounced in the results for the mixture A–H_2 than in these for N_2–H_2.

All these points to the fact that the "three liquid" model neglects the contribution of more than binary interactions. Higher the A or N_2 concentration, the more important are these interactions at the temperature and pressures under consideration. This can be seen from the fact, that under these conditions, H_2 is behaving nearly as a perfect gas, while A and N_2 already show a precritical behaviour (figs. 9 and 14). This explains also the above mentioned trend in the results, as the lowest temperature, where experiments were performed, is nearer to the critical temperature of A than of N_2.

Knoester and Beenakker7) found for the heat of mixing of the same systems, a better agreement with theory. The reason is that one calculates $\tilde{V}_m$ and $\tilde{H}_m$ and not directly $\tilde{V}^E$ and $\tilde{H}^E$. $\tilde{H}^E$ for these systems is of the same order as $\tilde{H}_m$, while in our case $\tilde{V}^E$ is much smaller than $\tilde{V}_m$. Thus the final result for $\tilde{V}^E$ is far more sensitive to small errors in the theory and in the original data of e.g. the pure components in case of the excess volume than in the case of the heat of mixing. This situation becomes even more pronounced in the system A–N_2, where $\tilde{V}^E_{exp}$ is much smaller as can be seen in the figs. 15, 16 and 17.

Considering the calculated molar volume instead of the excess volume we see that the agreement between experiment and theory is always within a few percents.

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CHAPTER III

THEORETICAL DETERMINATION OF THE FLUID-FLUID PHASE SEPARATION IN XE–HE

Synopsis

Using a corresponding states treatment, based on the average potential models introduced by Prigogine and Scott, the fluid-fluid phase separation in the system Xe–He is analysed. Agreement between experiment and theory is satisfactory. Predictions on phase separation for the system Kr–He are made.

1. *Introduction.* At the beginning of this century Van der Waals1) and Kamerlingh Onnes and Keesom2) predicted from the study of the free-energy surface of mixtures, that, under certain conditions, a phase separation could occur at temperatures well above the critical temperatures of both components. Kamerlingh Onnes and Keesom suggested the expression gas-gas equilibrium. To avoid the confusion3)4) to which this term gives rise, it is perhaps advisable to use the term fluid-fluid phase separation. The existence of this effect was verified in 1940 for the system NH_3–N_2 by Krichevskii5). Subsequently this behaviour was found in several other systems, mainly by the Russian group. A survey of these mixtures is given by Mage6) and by De Swaan Arons7).

At temperatures and pressures well below critical one finds liquid-gas equilibrium, characterized by a difference in density between the phases. At temperatures and pressures well above the critical conditions of the least volatile component one can find fluid-fluid phase separation, characterized by a difference in concentrations between both phases. In a certain region the phenomena overlap. Depending on the way in which the liquid-gas and the fluid-fluid equilibrium regions meet, one can distinguish two classes of systems:

a) The regions meet below the critical temperature of the least volatile component: e.g. systems with NH_3 as a component.

b) The critical point of the least volatile component is the meeting point: e.g., systems with helium as a component8)9).

The characteristic differences between the two classes are shown in the phase diagrams in the p, x, T space for A–NH_3 10) and Xe–He 7) (see figs. 1 and 2).

Most systems, showing fluid-fluid phase equilibrium, consist of rather complicated molecules, which makes a theoretical description unpromising.

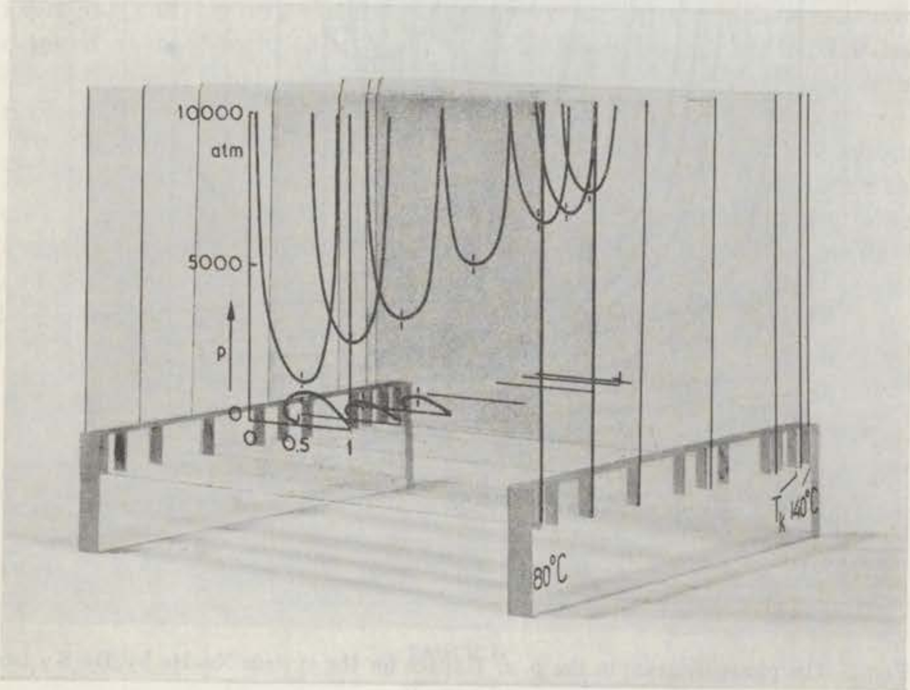

Fig. 1. The phase diagram in the p, x, T space for the system A–NH_3 by Tsiklis and Vasilev 10).

In 1963, however, De Swaan Arons and Diepen 7) 11) found phase separation of type b in Xe–He, a system that seems more suited for theoretical treatment.

In view of the success recently obtained in applying a corresponding states treatment of dense gaseous mixtures for the calculation of the thermodynamic properties of mixtures, as volume change on mixing 12) and heat of mixing 13), we will use this approach also for a description of the fluid-fluid phase separation in Xe–He.

2. *Theory and results*. To determine, whether phase separation will occur in a mixture, one can study its Gibbs free energy, $\tilde{G}_{\mathrm{m}}$, and look for an unstable region. The concentrations of the two phases, that are in equilibrium with each other, are then determined by a double tangent con-

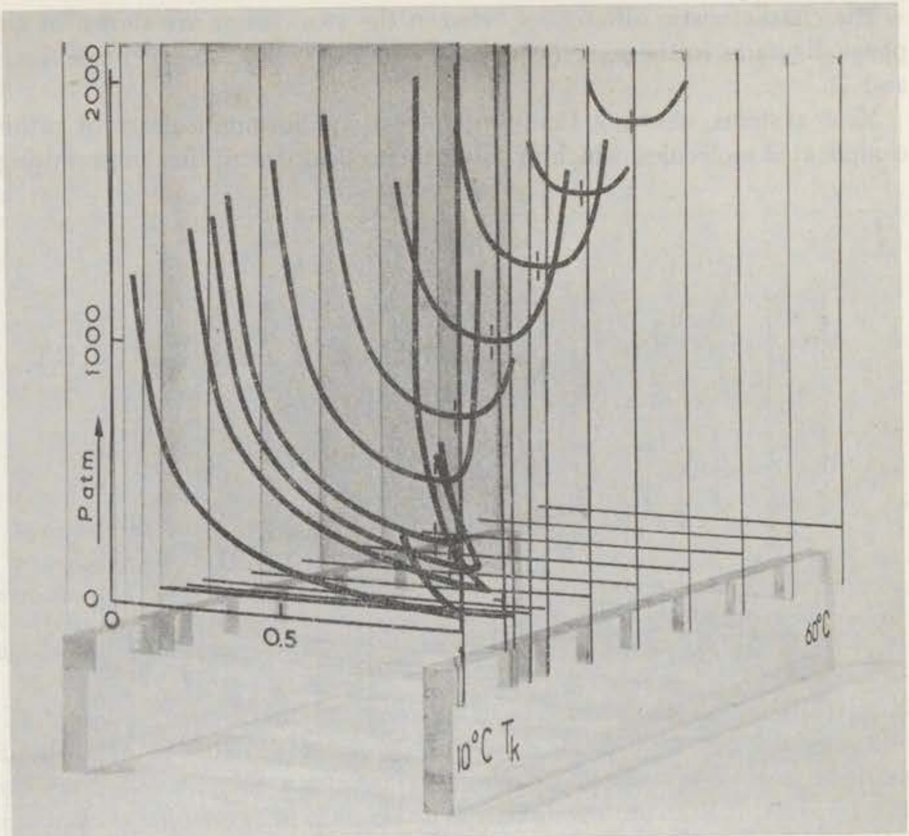

Fig. 2. The phase diagram in the p, x, T space for the system Xe–He by De Swaan Arons [7]).

struction. For convenience, however, we will study in stead of the behaviour of $\tilde{G}_{\mathrm{m}}$ the behaviour of the physically equivalent quantity $\Delta\tilde{G}$.

$$\Delta\tilde{G} = \tilde{G}_{\mathrm{m}} - x_{\mathrm{A}}\tilde{G}^{0}_{\mathrm{A}} - x_{\mathrm{B}}\tilde{G}^{0}_{\mathrm{B}} \tag{1}$$

where A and B denote the components and the superscript 0 indicates the pure state. Introducing residual quantities one gets:

$$\Delta\tilde{G} = (\tilde{G}^{\mathrm{id.}}_{\mathrm{m}} + \tilde{G}^{\mathrm{res.}}_{\mathrm{m}}) - x_{\mathrm{A}}(\tilde{G}^{0,\,\mathrm{id.}}_{\mathrm{A}} + \tilde{G}^{0,\,\mathrm{res.}}_{\mathrm{B}}) - x_{\mathrm{B}}(\tilde{G}^{0,\,\mathrm{id.}}_{\mathrm{B}} + \tilde{G}^{0,\,\mathrm{res.}}_{\mathrm{B}}) \tag{2}$$

or with

$$\tilde{G}^{\mathrm{id.}}_{\mathrm{m}} - x_{\mathrm{A}}\tilde{G}^{0,\,\mathrm{id.}}_{\mathrm{A}} - x_{\mathrm{B}}\tilde{G}^{0,\,\mathrm{id.}}_{\mathrm{B}} = RT(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) \tag{3}$$

one obtains

$$\Delta\tilde{G} = \tilde{G}^{\mathrm{res.}}_{\mathrm{m}} - x_{\mathrm{A}}\tilde{G}^{0,\,\mathrm{res.}}_{\mathrm{A}} - x_{\mathrm{B}}\tilde{G}^{0,\,\mathrm{res.}}_{\mathrm{B}} + RT(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) \tag{4}$$

where the superscript *id.* denotes the corresponding ideal gas value. In chapter II[12]) we described how one can calculate the molar volume of a mixture with the corresponding states theory. The basic idea of the method is, that one can derive the thermodynamic properties of a mixture from those of the pure components, using a corresponding states treatment and an effective interaction potential. This effective potential is obtained by averaging the three types of pair interactions present in the mixture. The averaging can be performed in three different ways, which are usually denoted as the "single", the "two" and the "three liquid" model. The last one is the most simple for actual calculations. For a detailed discussion the reader is referred to [14]) [15]).

We performed calculations with the "single liquid" model for the system Xe–He at 200 atm. and at temperatures of 300 and 310°K: i.e. above the critical temperature of Xe ($T_c = 289{,}7$°K, $P_c = 57.6$ atm.). In the tables I and II the molecular interaction parameters for the pure components[16]) and the effective parameters for the mixture are given for the "single" liquid model.

TABLE I

Molecular parameters from

Gas	ε/k °K	σ Å
He	10.22	2.556
A	119.8	3.405
Kr	171	3.60
Xe	221	4.100

TABLE II

Molecular parameters of the system Xe–He for the "single liquid" model

molefraction Xe	$\langle\varepsilon/k\rangle$ °K	$\langle\sigma\rangle$ Å
0.45	57.17	4.031
0.50	67.63	4.043
0.55	78.97	4.053
0.60	91.21	4.061
0.65	104.3	4.069
0.70	118.3	4.075
0.75	133.2	4.080
0.80	149.0	4.085
0.85	165.7	4.090
0.90	183.2	4.093
0.95	201.7	4.097

For the determination of $\tilde{G}_{\mathrm{m}}^{\mathrm{res.}}$ in eq. (4) from the corresponding states theory we would prefer to take one of the components of the system under consideration as a reference gas. Neither for Xe nor for He, however, sufficient data are available to permit calculations for the "single liquid" model over the whole concentration range, so that we had to make a compromise. For the low Xe concentrations ($0 < x < 0.1$) we used He as a reference gas and for the higher concentrations ($0.45 < x < 1$) we used N_2. For the intermediate concentrations ($0.1 < x < 0.45$) results were obtained by interpolation. For the calculations, based on He, we started with the expression:

$$\tilde{G}^{0,\,\text{res.}} = Bp \tag{5}$$

and we used for the second virial coefficient, B, Keesom's adopted values[17]). For N_2 the thermodynamic tables by Din[18]) were used.

As the Gibbs function for the pure components is not tabulated normally, we started from the tabulated values for enthalpy, $\tilde{H}$, and entropy, $\tilde{S}$. $\tilde{G}^{\text{res.}}$ is then obtained by

$$\tilde{G}^{0,\,\text{res.}}(p, T) = \tilde{H}^{0,\,\text{res.}}(p, T) - T\tilde{S}^{0,\,\text{res.}}(p, T) \tag{6}$$

where

$$\tilde{H}^{0,\,\text{res.}}(p, T) = \tilde{H}^{0}(p, T) - \tilde{H}^{0}(o, T) \tag{7}$$

and

$$\tilde{S}^{0,\,\text{res.}}(p, T) = \{\tilde{S}^{0}(p, T) + R \ln p\} - \{\tilde{S}^{0}(p, T) + R \ln p\}_{p=0} \tag{8}$$

Using the values of $\tilde{G}_{\text{m}}^{\text{res.}}$ thus obtained, $\Delta\tilde{G}$ can be calculated from eq. (4). In fig. 3 $\Delta\tilde{G}_{\text{I}}$, i.e. its value for the "single liquid" model, is plotted as a function of concentration. The common tangent determines the boundaries of the phase separation region. In fig. 4 we plotted the calculated T, x phase separation curve at a pressure of 200 atm., together with the experimental

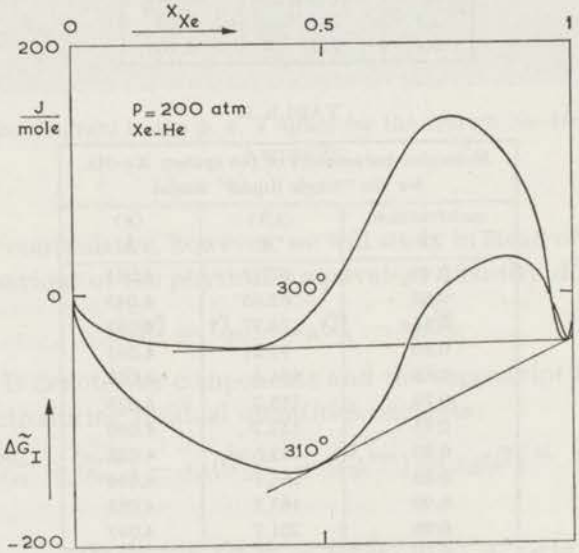

Fig. 3. $\Delta\tilde{G}_{\text{I}}$ as a function of concentration at 200 atm. for the system Xe–He.

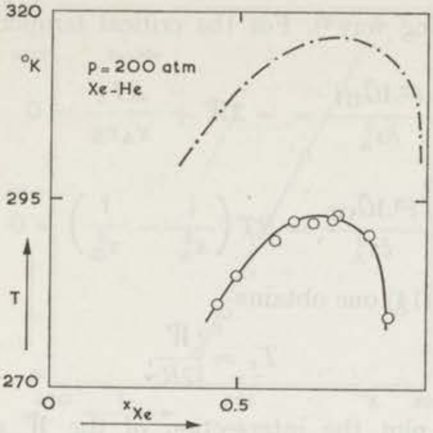

Fig. 4. Phase separation at 200 atm. for the system Xe–He.
— · — "single liquid" model.
——— measurements by De Swaan Arons [7])

data, obtained by De Swaan Arons [7]). The agreement is satisfactory. The maximum of the curve gives the upper critical solution temperature at this pressure.

As the calculations are much simpler for the "three liquid" model, we continued with this model. For this model one has for the residual Gibbs function of the mixture

$$\tilde{G}_{\mathrm{III}} = x_{\mathrm{A}}^2 \tilde{G}_{\mathrm{A}}^{0,\,\mathrm{res.}} + 2x_{\mathrm{A}}x_{\mathrm{B}}\tilde{G}_{\mathrm{AB}}^{\mathrm{res.}} + x_{\mathrm{B}}^2 \tilde{G}_{\mathrm{B}}^{0,\,\mathrm{res.}} \tag{9}$$

where $\tilde{G}_{\mathrm{AB}}^{\mathrm{res.}}$ is calculated with corresponding states from a reference gas using the parameters $\varepsilon_{\mathrm{AB}}$ and σ_{AB} obtained from

$$\varepsilon_{\mathrm{AB}} = \sqrt{\varepsilon_{\mathrm{AA}}\varepsilon_{\mathrm{BB}}} \tag{10}$$

and

$$\sigma_{\mathrm{AB}} = \tfrac{1}{2}(\sigma_{\mathrm{AA}} + \sigma_{\mathrm{BB}}). \tag{11}$$

For $\Delta\tilde{G}_{\mathrm{III}}$ we get:

$$\Delta\tilde{G}_{\mathrm{III}} = x_{\mathrm{A}}^2 \tilde{G}_{\mathrm{A}}^{0,\,\mathrm{res.}} + 2x_{\mathrm{A}}x_{\mathrm{B}}\tilde{G}_{\mathrm{AB}}^{0,\,\mathrm{res.}} + x_{\mathrm{B}}^2 \tilde{G}_{\mathrm{B}}^{0,\,\mathrm{res.}} - x_{\mathrm{A}}\tilde{G}_{\mathrm{A}}^{0,\,\mathrm{res.}} - x_{\mathrm{B}}\tilde{G}_{\mathrm{B}}^{0,\,\mathrm{res.}} + \\ + RT(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) = x_{\mathrm{A}}x_{\mathrm{B}}\tilde{W} + RT(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) \tag{12}$$

where

$$\tilde{W} = 2\{\tilde{G}_{\mathrm{AB}}^{\mathrm{res.}} - \tfrac{1}{2}(\tilde{G}_{\mathrm{A}}^{0,\,\mathrm{res.}} + \tilde{G}_{\mathrm{B}}^{0,\,\mathrm{res.}})\}. \tag{13}$$

It is clear from equation (12) that $\Delta\tilde{G}_{\mathrm{III}}$ is a parabola as a function of concentration. Using again N_2 as a reference gas, calculations were performed on the system Xe–He at pressures of 686 and 512 atm. Characteristic plots of $\Delta\tilde{G}_{\mathrm{III}}$ for this model are given in fig. 5 and 6.

One could of course determine the critical temperature of phase separation from such graphs. It is, however, more accurate to determine this temperature in the following way[8]). For the critical temperature one has using equation (12)

$$\frac{\partial^2 \Delta\tilde{G}_{\mathrm{III}}}{\partial x_{\mathrm{A}}^2} = -2\tilde{W} + \frac{RT_{\mathrm{c}}}{x_{\mathrm{A}}x_{\mathrm{B}}} = 0 \tag{13}$$

and

$$\frac{\partial^3 \Delta\tilde{G}_{\mathrm{III}}}{\partial x_{\mathrm{A}}^3} = RT\left(\frac{1}{x_{\mathrm{A}}^2} - \frac{1}{x_{\mathrm{B}}^2}\right) = 0 \tag{14}$$

From eqs. (13) and (14) one obtains

$$T_{\mathrm{c}} = \frac{\tilde{W}}{2R}. \tag{15}$$

In a $\tilde{W}$ versus T plot the intersection of the $\tilde{W}$ curve with the line RT determines T_{c} quite accurately. In fig. 7 a graph of p versus

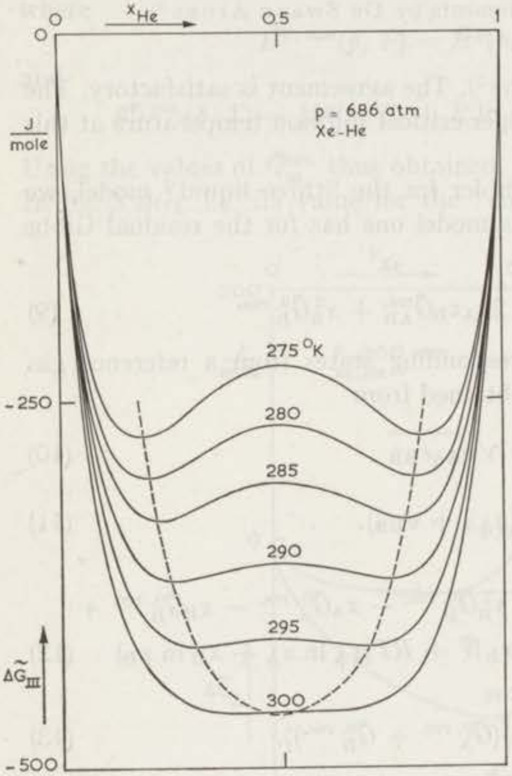

Fig. 5

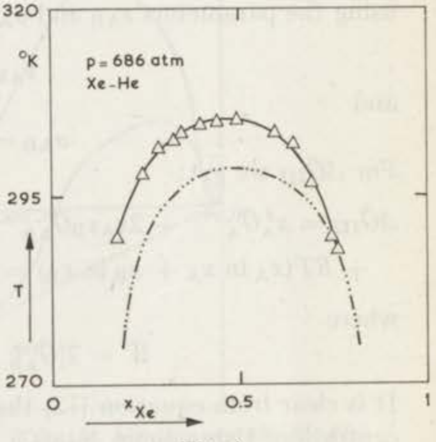

Fig. 6

Fig. 5. $\Delta\tilde{G}_{\mathrm{III}}$ as a function of concentration at 686 atm. for the system Xe–He.

Fig. 6. Phase separation at 686 atm. for the system Xe–He.

——— · · · ——— "three liquid" model

——————— measurements by De Swaan Arons [6])

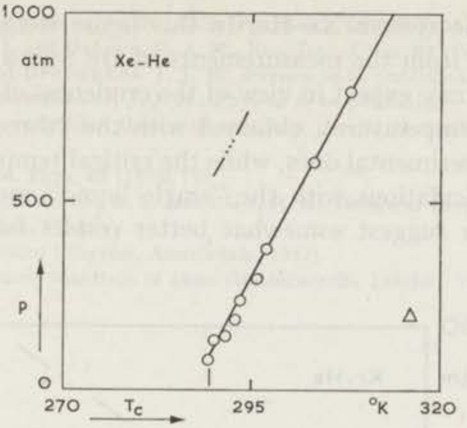

Fig. 7. The critical line of phase separation in Xe–He.

Δ "single liquid" model

——— · · · ——— "three liquid" model

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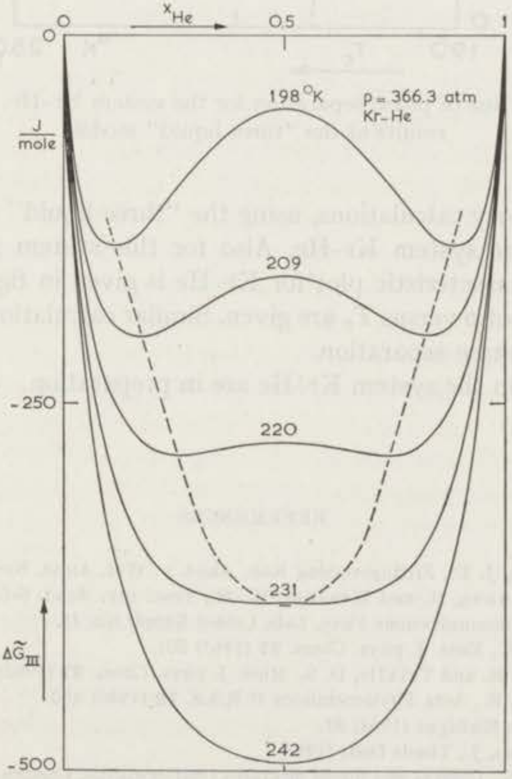

Fig. 8. $\Delta\tilde{G}_{III}$ as a function of concentration at 366.3 atm for the system Kr–He.

T_c is given for the system Xe–He. In this figure we also plotted the experimental values from the measurements of De Swaan Arons[7]). Agreement is what one may expect in view of the crudeness of this model. We see that the critical temperatures, obtained with the "three liquid" model are lower than the experimental ones, while the critical temperature at 200 atm. obtained from calculations with the "single liquid" model is higher. This type of behaviour suggest somewhat better results for the "two liquid" model.

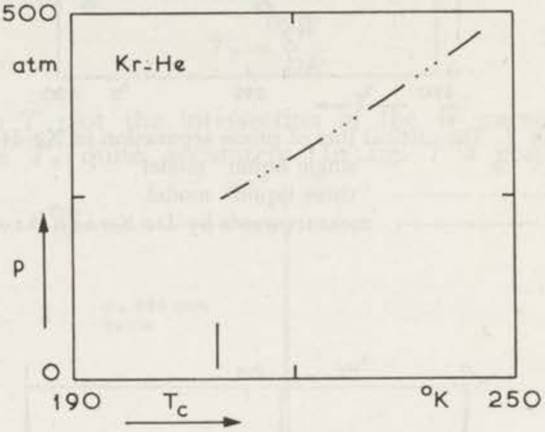

Fig. 9. The critical line of phase separation for the system Kr–He, predicted with the results of the "three liquid" model.

Some exploratory calculations, using the "three liquid" model have been performed for the system Kr–He. Also for this system phase separation was found. A characteristic plot for Kr–He is given in fig. 8. In fig. 9 the predicted values of p versus T_c are given. Similar calculations for the system A–He show no phase separation.

Experiments on the system Kr–He are in preparation.

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SAMENVATTING

In de laatste jaren is in de studie van de thermodynamische eigenschappen van vloeistofmengsels, zowel theoretisch als experimenteel, een aanzienlijke vooruitgang geboekt. Voor een groot aantal systemen bestaande uit eenvoudige moleculen zijn grootheden, als mengwarmte, volumeverandering bij menging en exces Gibbs vrije energie gemeten. De theoretische vooruitgang is vooral gebaseerd op het toepassen van de wet van overeenstemmende toestanden. Belangrijke bijdragen zijn geleverd door Prigogine en medewerkers en door Scott. Dit werk is echter beperkt tot vloeistofsystemen. Er is met name zeer weinig experimenteel werk verricht op het gebied van de eigenschappen van gasmengsels bij hogere dichtheden. Naar onze opvatting is de hoofdoorzaak voor dit gebrek aan gegevens te vinden in de manier, waarop dit probleem werd aangepakt. De klassieke benadering om thermodynamische gegevens van gasmengsels te verkrijgen is dezelfde als die, welke gebruikt wordt voor zuivere gassen, namelijk het uitvoeren van zeer nauwkeurige pVT metingen. Dit soort werk vereist, zoals bekend, een tamelijk gecompliceerde experimentele opstelling in combinatie met grote experimentele vaardigheid. Verder zijn de metingen erg tijdrovend. De extra parameter, gegeven door de concentratie, schept in het geval van gasmengsels een probleem, dat langs deze weg bijna onoplosbaar is.

Op dit ogenblik zijn voor de meeste gassen, bestaande uit eenvoudige moleculen, de thermodynamische grootheden redelijk goed bekend.

In dit opzicht noemen we het experimentele werk, dat in het Van der Waals laboratorium wordt verricht en het werk van het National Bureau of Standards. Dit betekent, dat de waarde van de meeste thermodynamische grootheden gemakkelijk kan worden berekend voor een ideaal mengsel, dat is een mengsel, waarvan de grootheid lineair varieert met de concentratie. Dus de extra informatie, nodig om het gedrag van een reëel mengsel te beschrijven is de afwijking van de idealiteit. Deze afwijking staat in de literatuur bekend als het exces van de betrokken grootheid. Dus lijkt het de moeite waard zich te concentreren op directe bepaling van dit exces, in de verwachting dat dit de gemakkelijkste weg zal zijn om kennis te verkrijgen, die nodig is voor een beschrijving van het gedrag van een reëel mengsel.

Met het oog op de experimentele en theoretische stand van zaken stelden wij ons tot doel $\tilde{V}^E$ te meten met een nauwkeurigheid van enkele procenten. Dit proefschrift beschrijft metingen aan de systemen N_2–H_2, A–H_2 en A–N_2. Deze keuze van gassen was het resultaat van verschillende overwegingen. Wij wilden beginnen met systemen, die grote afwijkingen van de idealiteit zouden vertonen. Wij verwachten namelijk, dat dit het geval zou zijn voor een mengsel met twee componenten, die ver uiteen liggende kritische temperaturen hebben, terwijl een van de componenten zich in het pre-kritisch gebied bevindt. Verder geven wij de voorkeur aan het werken met goedkope gassen. De technische betekenis van het systeem N_2–H_2 in combinatie met deze argumenten besliste de keus ten gunste van deze combinatie.

Het mengsel A–H_2 werd bestudeerd, omdat verwacht werd, dat indien de niet bolvormigheid van weinig invloed is, dit systeem zich op dezelfde manier zal gedragen als het systeem N_2–H_2. Ten einde een mengsel van tamelijk gelijke moleculen te bestuderen werd tenslotte A–N_2 gekozen.

In hoofdstuk I wordt een directe methode beschreven voor het meten van de volumeverandering bij mengen onder constante druk. Metingen aan bovengenoemde systemen werden uitgevoerd bij verschillende concentraties in het temperatuurgebied van 170 tot 292°K en bij drukken tot 100 atm.

In hoofdstuk II passen wij op de onderzochte systemen de ideeën van Prigogine en van Scott voor vloeistofmengsels toe. Wij berekenen het volume exces voor drie verschillende modellen. Vergelijking van experimentele en theoretische waarden van de volumeverandering bij mengen toont aan, dat er een goede kwalitatieve overeenstemming is. Kwantitatief zijn voor N_2–H_2 en A–H_2 de resultaten redelijk. Voor A–N_2 echter is de overeenstemming slecht.

Aan het begin van deze eeuw voorspelden Van der Waals en Kamerlingh Onnes en Keesom uit de studie van het vrije energie oppervlak van mengsels, dat, onder bepaalde voorwaarden, een fase scheiding kan optreden bij temperaturen boven de kritische temperaturen van beide componenten. Het bestaan van dit verschijnsel werd geverifieerd aan het systeem NH_3–N_2 en vervolgens werd dit gedrag ook voor verschillende andere systemen waargenomen.

De meeste systemen, die de fase scheiding vertonen, bestaan uit tamelijk gecompliceerde moleculen, hetgeen een theoretische beschrijving weinig aantrekkelijk maakt.

In 1963 vonden De Swaan Arons en Diepen echter fase scheiding in Xe–He, een systeem, dat meer geschikt lijkt voor een theoretische benadering.

In hoofdstuk III wordt met het oog op het succes, verkregen bij het toepassen van de wet van overeenstemmende toestanden op verdichte gasmengsels, deze theorie nu ook toegepast op de fase scheiding in Xe–He. De overeenstemming tussen experiment en theorie is bevredigend. Voor het systeem Kr–He wordt fase scheiding voorspeld.

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[illegible] van de wet van [illegible] op [illegible] [illegible], deze theorie is ook toegepast op de [illegible] [illegible]. De overeenstemming tussen experiment en theorie is bevredigend. Voor het systeem Re–Hg wordt een verklaring voorgesteld.

Acknowledgements. I like to thank Prof. Dr. K. W. Taconis for his continuous interest and Dr. H. P. R. Knaap for suggesting this research. From the technical staff of the laboratory I would like to thank particularly Mr. R. S. Pruis and Mr. S. P. L. Verdegaal for constructing the apparatus.