N VIII A

THE HEAT OF MIXING OF MODERATELY DENSE GASES

UNIVERSITEIT TE LEIDEN
INSTITUUT-LORENTZ

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INSTITUUT-LORENTZ

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kast dissertaties

THE HEAT OF MIXING OF MODERATELY DENSE GASES

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 DONDERDAG 16 JUNI 1966
TE 14 UUR

DOOR

MAARTEN KNOESTER

GEBOREN TE 'S-GRAVENHAGE IN 1936

Promotoren:

PROF. DR. J. J. M. BEENAKKER
PROF. DR. K. W. TACONIS

Aan mijn ouders
Aan Jopie

Promotors
PROF. DR. J. J. M. [illegible]
PROF. DR. [illegible]

STELLINGEN

I

De in dit proefschrift beschreven calorimeter kan door middel van enkele eenvoudige wijzingen geschikt gemaakt worden voor metingen van de soortelijke warmte van gassen bij constante druk.

Dit proefschrift, p. 5.

II

Het verdient aanbeveling bij het tabelleren van thermodynamische grootheden van gassen en bij de discussie van hun nauwkeurigheid, duidelijk onderscheid te maken tussen het deel dat niet van de moleculaire wisselwerking afhangt en het zogenaamde residuele deel.

III

Voor het bepalen van temperaturen tussen 5 en 14°K met een gasthermometer is het van belang nieuwe metingen te verrichten van de tweede viriaalcoëfficiënt van helium.

IV

Wang Chang, Uhlenbeck en De Boer berekenen voor een gas met meer-atomige moleculen de volumeviscositeit. De conclusie dat deze nul is is in het limietgeval dat inelastische botsingen kunnen worden verwaarloosd, is onvoldoende geargumenteerd.

Wang Chang, C. S., Uhlenbeck, G. E. en De Boer, J., Studies in statistical mechanics (North-Holland Publishing Company, Amsterdam, 1964) Vol. II, Part C.

V

De door Doll en Wiedemann gegeven uitdrukking voor het rendement van de Meissner heliumliquefactor is niet juist.

Doll, R. en Wiedemann, W., Linde Berichte aus Technik und Wissenschaft **11** (1961) 14.

VI

Ten onrechte stellen Scott, Stapleton en Wainstein in enige gevallen van paramagnetische resonantie de lijnverbreding $\langle \delta H^2 \rangle$ ten gevolge van de nucleaire dipolen onafhankelijk van de oriëntatie van het veld ten opzichte van het kristal.

Scott, P. L., Stapleton, H. J. en Wainstein, C., Phys. Rev. **137A** (1965) 71.

VII

De wijze waarop Kip het electrische veld betrekt in de invoering van magnetohydrodynamische golven bevat principiële onjuistheden.

Kip, A. F., Fundamentals of Electricity and Magnetism (Mc Graw-Hill Book Company, Inc., New York, 1962) p. 356.

VIII

Om een inzicht te krijgen in de resultaten van een theorie voor de transportgrootheden van meer-atomige moleculen, dient men de nadruk te leggen op de mate waarin de afwijking van het gedrag van bolvormige moleculen correct beschreven wordt. Dit is niet het geval in de discussie van Dahler en medewerkers en Mason en medewerkers.

Condiff, D. W., Wei-Kao Lu en Dahler, J. S., J. chem. Phys. **42** (1965) 3445.
Dahler, J. S. en Sather, N. F., J. chem. Phys. **43** (1965) 1750.
Mason, E. A. en Monchick, L., J. chem. Phys. **36** (1962) 1622.

IX

Het onderwijs in de fysica aan studenten van de medische faculteit dient niet alleen in het eerste jaar, maar ook later in het curriculum te worden gegeven en in nauwere relatie te worden gebracht met de overige vakken.

X

Bij het onderzoek van de relatie tussen structuur en chemische samenstelling van cellen en weefsels biedt de door Lowry aangegeven ultramicrochemische techniek meer mogelijkheden dan microspectrofotometrie van de structuur in situ.

XI

Uit oogpunt van verkeersveiligheid is de gangbare wijze waarop straatnamen worden aangegeven, onvoldoende.

Het in dit proefschrift beschreven onderzoek werd uitgevoerd als onderdeel van het programma van de Werkgemeenschap voor Molecuulfysica van de Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.) met financiële steun van de Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.) en van de Staatsmijnen in Limburg.

Teneinde te voldoen aan het verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een overzicht van mijn studie.

Na beëindiging van mijn middelbare-schoolopleiding in 1954 aan de 1e Christelijke H.B.S. (thans Christelijk Lyceum Populierstraat geheten) te 's-Gravenhage begon ik mijn studie aan de Rijksuniversiteit te Leiden. In 1958 legde ik hier het candidaatsexamen in de natuur- en wiskunde met bijvak sterrenkunde af. Daarna werd ik in de gelegenheid gesteld ervaring in de experimentele natuurkunde op te doen op het Kamerlingh Onnes Laboratorium in de werkgroep voor molecuulfysica. De leiding van deze groep berustte aanvankelijk bij Prof. Dr. A. van Itterbeek, werd vervolgens overgenomen door Prof. Dr. K. W. Taconis en is thans in handen van Prof. Dr. J. J. M. Beenakker. Tot begin 1961 assisteerde ik Dr. H. F. P. Knaap bij metingen aan de waterstof-isotopen in de gas- en vloeistoffase. Daarna heb ik mij bezig gehouden met de in dit proefschrift beschreven onderzoekingen van de mengwarmte van gassen. In oktober 1961 legde ik het doctoraal examen in de experimentele natuurkunde af. Sindsdien was ik als wetenschappelijk medewerker in dienst van de Stichting voor Fundamenteel Onderzoek der Materie. Vanaf 1960 heb ik geassisteerd op het practicum voor prae-candidaten.

De werkzaamheden op het Kamerlingh Onnes Laboratorium werden van februari 1964 tot juni 1965 onderbroken in verband met de militaire dienstplicht; het grootste deel van dit tijdvak werd doorgebracht op de afdeling Fysica van het Medisch-Biologisch Laboratorium der Rijksverdedigingsorganisatie T.N.O. te Rijswijk.

Verschillende leden van de vaste staf van het Kamerlingh Onnes Laboratorium hebben technische assistentie verleend bij het in dit proefschrift beschreven onderzoek. Met name zijn hier vermeld de heren E. S. Prins en J. P. Hemerik, die de gebruikte calorimeter hebben geconstrueerd. Dr. H. F. P. Knaap was zo welwillend om het manuscript te lezen en van kritische opmerkingen te voorzien. Dr. R. A. Aziz en Dr. D. A. Curtis ben ik dank verschuldigd voor het corrigeren van het Engels.

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CONTENTS

CHAPTER I. *Excess enthalpies of gaseous mixtures of hydrogen, nitrogen and argon between* 150 *and* 293°*K and at pressures up to* 130 *atm* . . . 1

1. Introduction 1
2. Apparatus 4
3. Experimental method 6
4. Experimental results for the binary systems 10
5. Discussion 13
6. The system 2:1:1 H_2–N_2–A 20

CHAPTER II. *Corresponding states treatment for the excess enthalpy of moderately dense gaseous mixtures* 22

1. Introduction 22
2. Liquid theories 25
3. Results 28
4. Discussion 31

SAMENVATTING (*Summary in Dutch*) 36

Chapter I

EXCESS ENTHALPIES OF GASEOUS MIXTURES OF HYDROGEN, NITROGEN AND ARGON BETWEEN 150 AND 293°K AND AT PRESSURES UP TO 130 ATM

Synopsis

In order to collect data on the excess enthalpy of gaseous mixtures, a calorimeter of the flow-type was constructed with which direct measurements on the heat of mixing could be performed. The apparatus was used for the binary mixtures H_2–N_2, H_2–A and N_2–A at various compositions and for the ternary mixture 2 : 1 : 1 H_2–N_2–A. Measurements on these mixtures were done in a temperature range between 150 and 293°K and at pressures between 30 and 130 atm. The results of the measurements are reported. At low density the pressure and concentration dependence of the excess enthalpy is in accordance with the binary collision behaviour. The often very large excess enthalpies appearing at higher densities in the temperature range not far from the critical temperature of one of the components (*e.g.* at 169°K the excess enthalpy of a 1 : 1 H_2–A mixture at 100 atm amounts to more than 1000 J/mole $\approx 1.5\,RT$) are qualitatively explained by considering the change in the molecular interaction behaviour of the nearly critical gas (in our example A) when mixing it with an almost ideal gas (H_2).

1. *Introduction.* For most of the pure gases of a simple molecular structure, such as H_2, N_2 and A, a large number of data on the thermodynamic properties is available (for a survey see *e.g.*, the compilations of Din[43]) and the Nat. Bur. Stand.[44])[45])). The tabulated thermodynamic data are nearly always based on measurements on the equation of state. In some cases also measurements on the Joule-Thomson effect were performed, from which the enthalpy could be obtained.

Till now the gaseous mixtures were studied along the same lines. The results for these multi-component systems, however, are for obvious reasons far less complete. In table I a survey is given of the existing work, as far as known to us, that has been performed on gaseous binary mixtures of H_2, He, CH_4, Ne, N_2, CO, O_2, A and Xe. Only those publications have been referred to, which contain data for pressures higher than 40 atm.

A common feature of the methods usually applied, is that the total value of a property like the molar volume or the molar enthalpy of a mixture is

TABLE I

Literature on mixing properties of binary mixtures

mixture	conc.*)	temp. range °C	p_{max} atm	properties; method***)	ref.
H_2–He				comp.	1
H_2–CH_4	×	0/200	700	pVT; exp.	2
	×	−130/10**)	500**)	pVT; exp.	3
	×	−135/150**)	200**)	pVT; exp.	4
	×	− 35/40	100	J.T.; exp.	5
H_2–N_2	25% N_2	0/400	1000	pVT; exp.	6
	25% N_2	− 20/70	1000	pVT; exp.	7
	25% N_2	− 70/300	1400	pVT; th.	8
	×	0 en 20	200	pVT; exp.	9
	×	0/300	1000	pVT; exp.	10
	×	0/200	500	pVT; exp.	11
	×	0/200	700	pVT; exp.	2
	25% N_2	0/300	1000	pVT; th.	12
	25% N_2	− 50/200	1000	therm.; th., calc.	13
	25% N_2	0/150	340	pVT; exp.	14
	25% N_2	0/150	1000	therm.; th., calc.	15
	×	50/170	1000	pVT; exp.	16
	×	25/125	3000	pVT; exp.	17
	×	15	120	J.T.; exp.	18
	24% N_2	5/240**)	1000**)	therm.; calc.	19
	25% N_2	100	400	H; th.	20
				comp.	21
H_2–CO	×	25	170	pVT; exp.	22
	×	0 en 25	600	pVT; exp.	23
	48% CO	25	160	pVT; th.	24
	×	0/300	1000	pVT; th.	12
	×	25	160	pVT; th.	25
				comp.	26
He–Ne	72.4% Ne	0/400	100	pVT; exp.	27
He–N_2	×	−140/0	500	pVT; exp.	28
	×	20**)	250**)	pVT; exp.	29
	×	−100/250	200	J.T.; exp.	30
	×	15	120	J.T.; exp.	18
	×	−140/40**)	500**)	therm.; th., calc.	31
	×	30	100	pVT; exp.	32
	×	30	120	pVT; exp.	33
He–A	×	−100/250	200	J.T.; exp.	34
CH_4–N_2	×	0/200	700	pVT; exp.	2
	×	0/300	1000	pVT; th.	12
	×	0/200	200	pVT; exp.	35
	10% N_2 30% N_2	−170/90**)	100**)	pVT; exp. therm.; calc.	36, 37
	×	0/200	200	pVT; th.	38
	57% N_2	0	90	pVT; th.	24
	×	− 75/125	100	J.T.; th.	39

TABLE I (*continued*)

mixture	conc.*)	temp. range °C	$p_{\max}$ atm	properties; method***)	ref.
	×	− 75/30**)	100**)	H; th.	40
	×	0	90	pVT; th.	25
N_2–O_2	×	15	120	J.T.; exp.	18
	×	0/300	1000	pVT; th.	12
N_2–A	×	−140/25	48	J.T.; exp.	41
	×	15	120	J.T.; exp.	18
O_2–A	50% A	25	125	pVT; exp.	42
	×	15	200	J.T.; exp.	18

*) × = data are reported for several compositions over the whole concentration range.

**) The Fahrenheit-scale for the temperature was used; the pressure was given in p.s.i. For the table the values were converted to degrees centigrade and atmospheres.

***) comp. = compilation.
pVT = data on the molar volume at pressure p and temperature T.
J.T. = data on the Joule-Thomson effect.
therm. = data on several thermodynamic properties.
H = data on the enthalpy.
exp. = determination by experiment.
th. = calculated from data on the components; in some cases: derived by extrapolation from lower density data of the mixture.
calc. = calculated from (pVT-)data on the mixture.

determined. These differ in many cases only by a small amount from the average properties of the components (cf. fig. 1). These small differences, however, are the essential properties, since they are the variations on mixing. They are known under the name of excess quantities, denoted by an upper index E. One of them is the heat of mixing or excess enthalpy H^{E}, being the amount of heat that must be supplied to the system at isothermal, isobaric mixing. For a binary mixture H^{E}, as a function of concentration, pressure and temperature is given by

$$\tilde{H}^{\mathrm{E}}(x_{\mathrm{A}}, p, T) = \tilde{H}_{\mathrm{m}}(x_{\mathrm{A}}, p, T) - \{x_{\mathrm{A}}\tilde{H}^{0}_{\mathrm{A}}(p, T) + x_{\mathrm{B}}\tilde{H}^{0}_{\mathrm{B}}(p, T)\}, \qquad (1)$$

where the indices m, A and B refer to the mixture and the two components respectively and x is the molar concentration ($x_{\mathrm{A}} + x_{\mathrm{B}} = 1$); the tilde denotes that molar quantities are considered and the upper index 0 refers to the pure components.

The experimental methods mentioned are not very suited for the determination of the variations on mixing, because of the high accuracy required in the results for mixture and components. As Beenakker and Coremans[46]) have discussed, it is for an investigation of mixing properties far more attractive to perform measurements on the variations directly. Measurements on the heat of mixing are moreover of direct use for technical purposes, as was emphasized by Ruhemann[47]. A program that comprises measurements of $\tilde{H}^{\mathrm{E}}$ and the similarly defined volume change on mixing $\tilde{V}^{\mathrm{E}}$, was started by the Kamerlingh Onnes Laboratory group for

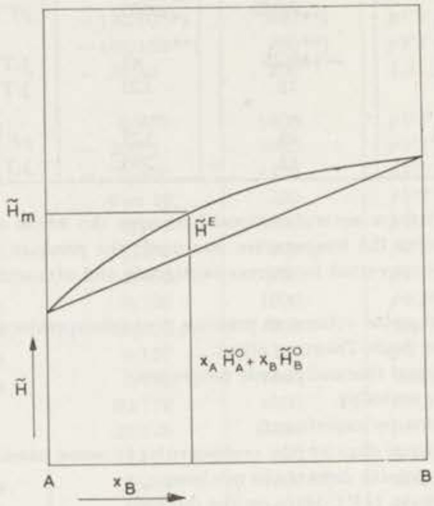

Fig. 1. $\tilde{H}^{\mathrm{E}}$ as the deviation from the ideal mixing behaviour.

Molecular Physics a few years ago. A general outline of the results was given earlier[48]. In this chapter[49] results for the heat of mixing are reported; for the volume change on mixing data will be published shortly[50].

The measurements on the heat of mixing are facilitated by the fact that in the gaseous state the excess enthalpies are mostly positive. So heat has to be supplied for compensating the cooling effect at mixing. Hence an isothermal flow-type calorimeter can be used for the measurements. Such an apparatus suited for measurements over a large temperature and pressure range is described in section 2. The further experimental procedure is explained in section 3. In section 4 a survey is given of the results obtained for the binary systems H_2–N_2, H_2–A and N_2–A. In section 5 a preliminary discussion follows. A more extensive discussion of the low temperature behaviour of $\tilde{H}^{\mathrm{E}}$ will be given in Chapter II[51]. Some information on the ternary system 2:1:1 H_2–N_2–A is given in section 6.

2. *Apparatus*. For the measurements of the heat of mixing a calorimeter of the flow-type was constructed. A diagram of the apparatus is shown in fig. 2. M is the mixing-chamber made of copper. The components for the gaseous mixture enter at the top of M and the mixture is removed at the bottom through stainless steel capillaries. The mixing is effected by the

continuous flow of gas through the mixing-chamber around the protruding disks of *M*, so that no mechanical mixing device is necessary. Heat can be supplied electrically to the calorimetric system. For this purpose a resistance wire is wound around *M*. To be sure that no heat radiates away from the relatively hot wire, *M* is surrounded by a copper shield which transports the radiated heat back to the mixing-chamber. In order to attain a sufficient thermal insulation, *M* is mounted in the vacuum vessel *V*, that is sealed on the cover *U* with an indium "O"-ring, compressed by the action of six brass bolts.

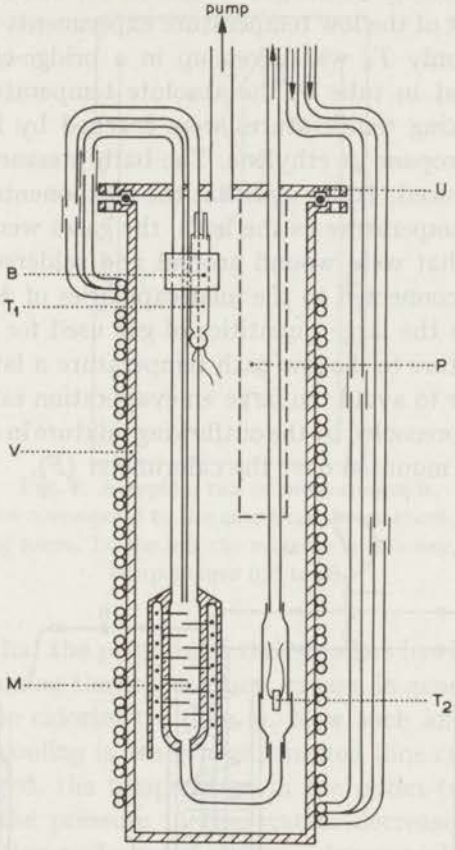

Fig. 2. Diagram of the calorimeter.

The temperatures of both the entering gases and the outflowing mixture were measured. At room temperature small glass-sealed thermistors T_1 and T_2 were used. T_1 was glued in a gap of the brass block *B*. T_2 was mounted in a block soldered on to the outlet-capillary about 5 cm from *M*. T_1 and T_2 were placed in a wheatstone-bridge, the unbalance of which was registered by a microvolt recorder (Micrograph, Kipp en Zonen). For the low temperatures special thermistors, type "midget disk", from the Keystone Carbon Company were used (see *e.g.*, Sachse[52]). In that case T_1 was mounted in a small He–filled copper tube, soldered with Wood's metal in the gap of B. T_2 was placed directly in the gas-stream in the outlet-tube, as is shown in the diagram. Part of the low temperature experiments was not performed differentially, but only T_2 was taken up in a bridge-circuit. With a Pt-thermometer, placed in tube P, the absolute temperature was measured.

The desired working temperatures were reached by immersing the apparatus in water, propane or ethylene. The bath pressure of the latter two liquids could be reduced. To be sure that the components to be mixed were both at the same temperature as the bath, the gases were led through long copper capillaries that were wound around and soldered on to V. At the point B they were connected to the inlet-capillaries of M.

For cooling down the large quantities of gas used for the measurements from room temperature to the low bath temperature a large amount of cold is required. In order to avoid too large an evaporation rate of the bath, the incoming gases are precooled by the outflowing mixture in a heat-exchanger*) (H in fig. 3) that is mounted over the calorimeter (F).

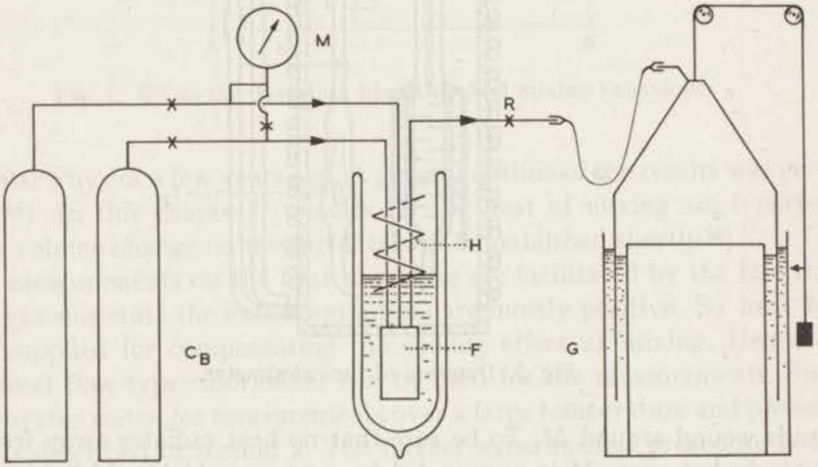

Fig. 3. A schematic diagram of the apparatus.

3. *Experimental method.* Two cylinders C_A and C_B (see fig. 3), with a volume of 3 or 10 l, contain the gases A and B that are to be mixed. At the start of the measurements, one of the cylinders, say C_A, being at a pressure about 5 atm higher than the other one, is opened. The gasflow through the apparatus is regulated by the valve R in the outlet-tube. The resistance of the calorimeter and its supply-capillaries is small enough to neglect the pressure drop over the system. This means that Joule-Kelvin effects cannot

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*) We thank Dr. Z. Dokoupil for the calculation of the dimensions of the heat-exchanger.

influence the measurements. The gasflow brings the calorimetric system to temperature equilibrium with the surrounding bath. The temperature at T_2, that is registered on the recorder, is then constant (line *a* in fig. 4).

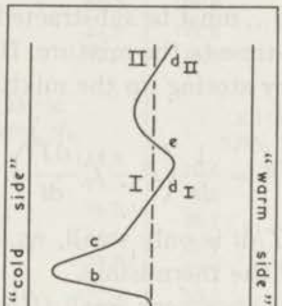

Fig. 4. A typical run of measurements.
Line *a* and its extension correspond to the case that the mixture is at the same temperature as the composing gases. To the left the mixture is at lower, to the right at higher temperature (cf. text).

At the moment that the pressure of the cylinders has become equal, C_B is also opened. The mixing that takes place, causes, in general, a cooling effect (positive $\tilde{H}^E$) in the calorimeter (line *b*). Now such an amount of heat is supplied, that this cooling is nearly compensated (line *c*). When the heating power is not changed, the temperature in the outlet-tube will slowly rise (line d_I), because the pressure in the system decreases gradually, which means a lower gas flux and almost always a lower molar excess enthalpy. At the intersection of line d_I with the extension of line *a* the cooling effect is compensated (measuring-point I). A second measurement is performed at a somewhat lower pressure by diminishing the heat supply by a small amount (line *e*); in the same way as for the first point compensation can be reached (line d_{II} and point II). In this way a set of data at various pressures can be obtained in a rather short time.

Occasionally the temperature at T_1 was checked. In the cases that a drift was observed, a correction was applied which never amounted to more than a few percent. When both T_1 and T_2 were placed in the wheatstone-bridge, such a correction was not necessary.

At compensation $\tilde{H}^E$ is equal to the quotient of the energy supplied per unit-time to the mixture, and the gas flux. With respect to the energy supply, a small complication arises from the fact that in the described way of measuring the temperature of the mixing-chamber is not strictly constant.

A small part of the applied power P, mostly less than 5%, is used for heating up the mixing-chamber including its shield and the outlet-tube up to the place of the thermometer. Therefore the amount $C\ \mathrm{d}T/\mathrm{d}t$, where C is the heat capacity of the mentioned parts and $\mathrm{d}T/\mathrm{d}t$ the temperature variation corresponding with d_{I}, d_{II}, ..., must be substracted from P in order to obtain the energy supply per unit-time to the mixture. If D is the gasflux (in moles per unit-time), measured by storing up the mixture in the small calibrated gasometer G, then

$$\tilde{H}^{\mathrm{E}} = \frac{1}{D}\left(P - C\frac{\mathrm{d}T}{\mathrm{d}t}\right). \tag{2}$$

It is obvious that, as $C\ \mathrm{d}T/\mathrm{d}t$ is only small, no strict demands need to be made on the calibration of the thermistors.

When the cooling effects were very small ($\tilde{H}^{\mathrm{E}}$ less than 10 J/mole), and in the rare cases that $\tilde{H}^{\mathrm{E}}$ turned out to be negative (for N_2–A), the excess enthalpies were determined by comparing the temperature changes at mixing with those when a known amount of heat was supplied to the mixture.

The conditions under which the mixing takes place are known: the temperature is given by the Pt-thermometer; the pressure is read on the manometer M, whose place of connection to the system, because of the low flow resistance, is not essential. The composition of the mixture is in first order determined by the ratio of the volumes V_{A} and V_{B} of the cylinders C_{A} and C_{B}, since these are always at the same pressure when emptying slowly during the measurements. A correction must be applied because of the unequal compressibilities of the gases in the cylinders, which give rise to a slight pressure dependence in the concentration for a given set of cylinders:

$$x_{\mathrm{A}} : x_{\mathrm{B}} = V_{\mathrm{A}}\left(\frac{\partial\rho_{\mathrm{A}}}{\partial p}\right)_T : V_{\mathrm{B}}\left(\frac{\partial\rho_{\mathrm{B}}}{\partial p}\right)_T. \tag{3}$$

It is clear that the pressure derivatives of the molar densities ρ must be taken at room temperature.

A few checks were performed to see if no undesirable effects occurred. A blank run, when mixing the same gases, gave a zero value for $\tilde{H}^{\mathrm{E}}$. When one gas was conducted through the apparatus, the temperature at T_2 was found to be independent of the flow-velocity. This indicates that the entering gases are definitely in temperature equilibrium with the bath. When heating the chamber, a stationary situation in the heat transfer from heater to gas was reached sufficiently soon after the start of the heat supply. In order to check if mixing was complete, the outlet-tube was replaced by a spiraled stainless steel capillary making further mixing possible. A third thermometer T_3 was mounted at the end of this spiral. T_3 turned out to be always at the same temperature as T_2. Furthermore a number of measurements was performed using flow velocities that varied by about a factor four. Within the experimental accuracy they gave the same results for $\tilde{H}^{\mathrm{E}}$.

TABLE II

The measured values of the excess enthalpy for H_2–N_2 mixtures

p atm	$\bar{H}^E$ J/mole	p atm	$\bar{H}^E$ J/mole	p atm	$\bar{H}^E$ J/mole	p atm	$\bar{H}^E$ J/mole
293°K		114.6	83.7	106.9	170	105.2	202
25% N_2		120.4	87.0	111.5	178	108.1	202
44.0	33.7	123.7	91.2	116.8	192	112.9	210
52.1	40.2					116.6	223
67.0	51.9	231°K		201°K			
78.1	61.2	$52^5\%$ N_2		$52^5\%$ N_2		170°K	
78.6	60.0	9.6	14.8	10.4	21.1	$52^5\%$ N_2	
79.8	61.9	12.8	19.3	11.8	24.0	7.8	20.1
79.8	62.3	16.9	26.0	26.7	58.3	15.5	43.3
82.0	63.4	20.1	31.6	28.1	60.4	23.4	70.8
93.4	72.3	23.6	36.5	37.9	85.8	24.3	73.3
104.9	79.1	37.5	59.7	50.8	121	26.6	71
105.3	78.7	42.0	69.5	51.6	117	29.8	87
114.4	85.1	46.4	78	53.0	124	33.9	103
115.9	84.5	51.0	86	55.3	127	36.8	121
120.1	84.6	53.2	91	56.6	133	37.2	119
		55.7	96	59.1	136	39.9	132
293°K		57.4	98	60.6	144	41.0	135
$52^5\%$ N_2		59.3	104	64.8	153	43.5	146
29.0	31.3	66.2	113	68.3	161	44.1	151
29.7	31.9	70.3	121	69.7	172	46.0	159
33.1	35.7	70.8	122	71.2	172	46.7	166
35.0	37.5	76.2	131	75.9	184	48.0	176
36.7	40.2	77.1	133	78.0	197	50.7	193
52.0	55.2	87.3	148	79.5	197	51.2	190
58.9	62.9	89.5	152	83.8	205	53.9	203
65.7	69.2	94.8	161	86.5	216	56.0	223
70.6	75.7	95.7	161	90.7	227	60.1	249
74.3	78.9	100.7	175	101.6	255	65.9	274
77.9	82.3	101.7	172	104.0	248	68.2	291
80.1	84.5	109.4	184	106.8	259	70.6	308
92.1	93.5	117.6	196	110.5	266	74.0	326
103.3	105	123.4	204	114.2	283	76.7	345
113.7	114					80.4	363
121.6	121	201°K				83.3	368
131.0	127	25% N_2		201°K		83.4	379
		29.4	43	78% N_2		86.4	395
		34.0	52	33.9	51	86.7	383
293°K		40.2	60	40.4	61	90.0	398
78% N_2		44.5	67	44.8	72	92.7	427
53.7	40.4	47.9	75	49.8	80	95.1	431
54.4	41.3	53.3	90	54.4	90	95.4	440
63.3	48.3	58.6	95	63.7	107	98.4	453
66.2	50.3	62.3	104	68.2	122	101.8	462
75.9	56.1	71.7	120	73.7	133	105.0	473
81.0	60.7	76.4	122	79.5	147	107.6	485
81.0	59.6	77.0	129	85.7	172	115.0	509
90.8	66.9	81.8	131	93.3	178	118.5	517
92.9	68.4	86.9	140	95.8	180	122.3	523
103.2	76.3	92.9	150	99.3	194	126.4	528
108.8	81.3	100.1	161	101.5	193	133.0	532

TABLE II (*continued*)

p atm	$\tilde{H}^E$ J/mole	p atm	$\tilde{H}^E$ J/mole	p atm	$\tilde{H}^E$ J/mole	p atm	$\tilde{H}^E$ J/mole
147°K		103.7	491	87.6	792	40.5	204
25% N_2		109.7	482	90.4	781	42.9	230
58.6	329	112.0	479	91.6	786	57.4	466
62.2	354			94.9	766	60.1	505
65.3	379	147°K		97.7	750	62.5	539
67.3	403	$52^5\%$ N_2		107.1	735	64.9	572
70.8	420	5.6	18.8	110.8	705	66.8	608
72.2	433	6.0	20.7	111.7	716	68.9	629
73.8	430	20.3	90.6	116.3	707	70.9	652
75.4	448	37.2	224	117.1	682	72.8	683
75.6	450	46.9	368	119.8	685	74.3	662
79.4	463	52.9	432	121.4	695	75.1	695
80.0	453	55.2	463	122.7	682	76.0	675
83.0	460	57.0	493	124.6	681	78.7	691
84.6	470	58.9	519	128.6	682	80.9	696
85.5	486	64.5	593	129.0	664	87.6	698
86.1	468	65.9	623	130.0	679	90.4	688
88.1	486	68.2	648	134.0	664	92.8	676
89.2	492	69.5	678			107.5	650
92.3	494	72.3	691	147°K		113.6	599
95.8	494	76.5	737	78% N_2			
98.6	498	79.3	754	34.6	162		
100.6	488	85.4	793	37.6	185		

4. *Experimental results for the binary systems.* The mixtures H_2–N_2, H_2–A and N_2–A were the binary systems for which the excess enthalpy was determined. For H_2–N_2 measurements were performed at the temperatures 293, 231, 201, 170 and 147°K. The lowest temperature was about 20°K above the critical temperature of N_2, so that we were sure that the whole mixing process took place in the gaseous state. For the mixtures containing argon the temperatures studied were 293, 231, 201 and 169°K (the critical temperature of A is 151°K). The pressure range under investigation was between about 30 and 130 atm. We have performed some measurements below 30 atm (for 47.5% H_2–52.5% N_2) in order to check whether the determined $\tilde{H}^E$-values tended to zero at zero pressure.

The results are reported in the tables II, III and IV. These tables represent the heat of mixing as a function of the pressure at fixed chosen values for temperature and composition. As, according to eq. (3), the composition of a mixture for a given set of gases and a given set of cylinders is slightly pressure dependent, the measured $\tilde{H}^E$-values had to undergo a small change to bring all the results of a series to the same value of the composition. For this interpolation procedure use was made of plots of $\tilde{H}^E/4x(1-x)$ *vs.* x(cf. section 5).

A main source of error in the results is formed by temperature instabilities of the bath. A variation ΔT in the bath temperature is followed quickly by T_1, but the reaction of T_2 is much slower because of the large heat

TABLE III

The measured values of the excess enthalpy for H_2–A mixtures

p atm	$\bar{H}^E$ J/mole
293°K 26^5% A	
33.9	29.3
40.7	34.7
48.3	42.0
57.5	52.1
66.5	58.7
74.3	67.1
84.3	74.6
293°K 54% A	
18.6	20.6
22.2	24.1
26.0	27.8
29.4	32.2
37.6	42.2
42.1	48.2
46.1	53.0
52.3	59.9
56.9	66.5
63.9	74.5
69.7	80.5
72.8	86.0
78.2	93.8
78.4	92.2
83.7	99.5
85.7	103
89.5	110
293°K 79% A	
30.4	22.3
43.6	32.4
48.4	36.5
56.8	46.4
58.8	47.3
60.4	47.3
64.7	53.1
67.9	54.0
68.6	54.7
74.1	64.0
75.5	63.1
76.2	62.4
83.8	71.8
83.9	69.9
86.2	72.4
92.3	79.9
231°K 54% A	
32.2	48
35.5	58
40.3	67
44.9	80
49.4	92
55.5	100
60.6	114
66.2	128
69.7	138
73.2	151
76.9	162
82.4	178
87.8	192
92.2	202
96.3	208
99.7	219
105.0	235
109.0	250
113.8	265
118.2	285
120.8	290
125.4	301
130.3	316
201°K 26^5% A	
31.9	48
34.8	56
40.9	65
44.9	75
50.1	84
56.7	112
62.2	126
66.7	140
72.1	157
76.8	177
82.6	185
91.1	231
96.1	251
102.1	276
107.0	295
112.0	314
115.3	335
201°K 54% A	
37.0	82
40.2	95
44.6	106
47.8	121
51.2	132
55.0	155
59.2	174
64.2	193
68.3	209
71.3	220
76.5	260
81.4	282
84.6	305
88.9	325
91.8	346
95.0	363
98.9	379
102.7	395
104.5	416
109.7	451
112.4	468
117.4	483
120.4	496
124.0	510
125.9	528
129.3	534
201°K 79% A	
36.1	69
41.4	81
45.7	97
50.3	112
54.8	127
59.3	143
66.2	168
70.4	189
75.0	212
79.8	229
83.3	246
88.7	266
90.9	299
95.6	327
100.9	354
107.0	380
111.3	412
117.0	434
120.2	450
124.2	472
169°K 26^5% A	
35.6	94
39.8	112
44.1	131
47.6	155
50.6	174
53.7	194
70.0	357
73.0	393
75.6	417
89.6	556
92.5	585
95.1	607
109.2	659
114.6	667
119.2	682
169°K 54% A	
45.3	220
48.8	252
51.7	285
54.5	319
58.1	350
69.7	555
71.3	589
79.7	761
81.2	787
94.0	989
95.8	1003
108.0	1043
109.1	1058
120.2	1052
124.6	1029
125.1	1061
129.3	1029
169°K 79% A	
43.9	163
46.9	193
49.8	224
54.2	250
67.0	467
82.6	812
83.5	795
85.5	859
87.6	901
94.8	958
99.0	973
100.6	992
101.1	957
107.0	953
120.7	967
125.2	952
126.6	973

capacity of the mixing-chamber. Therefore we may assume that ΔT causes a possible uncontrolled heat or cold supply per mole gas equal to $\{x_A \tilde{C}_{p,A} + x_B \tilde{C}_{p,B}\} \Delta T$, where $\tilde{C}_{p,A}$ and $\tilde{C}_{p,B}$ are the molar heat capacities of the components. ΔT can amount to 0.05°K at room temperature and 0.1°K at the lower temperatures. The amounts of heat corresponding to these

TABLE IV

The measured values of the excess enthalpy for N_2–A mixtures

p atm	$\tilde{H}^E$ J/mole	p atm	$\tilde{H}^E$ J/mole	p atm	$\tilde{H}^E$ J/mole	p atm	$\tilde{H}^E$ J/mole
293°K		48	2	169°K		169°K	
52% A		78	7	52% A		78% A	
90	−3	103	22	20	0	42.3	3
109	−3	127	39	38	3	50.9	12
				46.2	3	56.4	22
231°K		169°K		53.6	12	61.8	40
52% A		25% A		64.8	44	65.4	58
30	0	43.5	3	66.6	57	70.3	71
70	0	57.5	16	72.5	88	74.3	92
98	1	62.5	25	79.6	136	77.1	109
120	5	67.0	43	82.2	154	80.5	126
		74.3	70	84.9	168	83.5	136
201°K		80.8	101	86.5	177	86.3	148
52% A		86.3	116	90.5	179	91.7	145
23	0	94.2	138	95.2	176	116.7	94
33	0	110.8	105	111.7	136		
		121.1	88	116.2	127		
				123.6	113		

temperature changes, and so the errors to be expected in $\tilde{H}^E$, vary from about 1 or 2 J/mole for room temperature to values between 5 and 10 J/mole for H_2–N_2 at 147°K in the pressure region where $\tilde{H}^E$ passes through its maximum.

Other sources of error are formed by impurities in the gases used and inaccuracies in the determination of the gasflux D. With the type of impurities to be expected deviations at most of the order of the concentration of the impurities will be caused: *i.e.* smaller than 1%. Also in the gasflux a deviation of 1% may be expected. Hence both effects cause an uncertainty of 2%.

Combining all sources of error, the total possible error in the results depends on pressure, temperature and type of mixture, while the possible relative error in large heats of mixing will be less than in the small excess enthalpies. On the whole one can say that the errors in $\tilde{H}^E$, with the exception of values below 100 J/mole at the lower temperatures, may be expected to be less than 5%. For the very small excess enthalpies ($\tilde{H}^E < 10$ J/mole) and the negative values the sign rather than the value is reliable.

5. *Discussion.* For discussion of the behaviour of the heat of mixing it is useful to introduce residual enthalpies:

$$\tilde{H}^{\mathrm{res}}(p, T) = \tilde{H}(p, T) - \tilde{H}(p = 0, T) = \int_0^p \left\{\tilde{V} - T\left(\frac{\partial \tilde{V}}{\partial T}\right)_p\right\} \mathrm{d}p. \tag{4}$$

An obvious advantage of the residual values is that they are independent of the choice of a zero-point. For the spherical or nearly spherical molecules like H_2, N_2 and A, configurational quantities can be defined as well. The differences between both types of quantities are the perfect gas (defined by $p\tilde{V} = RT$; $R = 8.31$ J/mole °K) values of the configurational properties (cf. Rowlinson[53]); for the enthalpy one has

$$\tilde{H}^{\mathrm{res}} = \tilde{H}^{\mathrm{conf}} - RT. \tag{5}$$

In this case the residual quantities are the contributions to the thermodynamic properties from the non-perfect gas behaviour. $\tilde{H}^{\mathrm{E}}$ is then the variation of $\tilde{H}^{\mathrm{res}}$ on mixing:

$$\tilde{H}^{\mathrm{E}}(x_{\mathrm{A}}, p, T) = \tilde{H}^{\mathrm{res}}_{\mathrm{m}}(x_{\mathrm{A}}, p, T) - \{x_{\mathrm{A}}\tilde{H}^{0\,\mathrm{res}}_{\mathrm{A}}(p, T) + x_{\mathrm{B}}\tilde{H}^{0\,\mathrm{res}}_{\mathrm{B}}(p, T)\}. \tag{6}$$

Considering the low density region, we start with relation (4) for both the mixture and the components. Applying the definitions for $\tilde{H}^{\mathrm{E}}$ and $\tilde{V}^{\mathrm{E}}$ – the latter analogous to eq. (1) for $\tilde{H}^{\mathrm{E}}$:

$$\tilde{V}^{\mathrm{E}} = \tilde{V}_{\mathrm{m}} - \{x_{\mathrm{A}}\tilde{V}^0_{\mathrm{A}} + x_{\mathrm{B}}\tilde{V}^0_{\mathrm{B}}\}, \tag{7}$$

one arrives at the expression

$$\tilde{H}^{\mathrm{E}} = \int_0^p \left\{\tilde{V}^{\mathrm{E}} - T\left(\frac{\partial \tilde{V}^{\mathrm{E}}}{\partial T}\right)_{x,\,p}\right\} \mathrm{d}p. \tag{8}$$

Using the Kamerlingh Onnes equation of state

$$p\tilde{V} = RT\left(1 + \frac{B}{\tilde{V}} + \frac{C}{\tilde{V}^2} + \ldots\right) \tag{9}$$

for mixture and components, one can verify that for sufficiently low density $\tilde{V}^{\mathrm{E}} = B^{\mathrm{E}}$, where

$$B^{\mathrm{E}} = B_{\mathrm{m}} - \{x_{\mathrm{A}}B_{\mathrm{AA}} + x_{\mathrm{B}}B_{\mathrm{BB}}\} \tag{10}$$

is the excess second virial coefficient. The mixture virial coefficient B_{m} is composed of the contributions of the three kinds of interaction:

$$B_{\mathrm{m}} = x_{\mathrm{A}}^2 B_{\mathrm{AA}} + 2x_{\mathrm{A}}x_{\mathrm{B}}B_{\mathrm{AB}} + x_{\mathrm{B}}^2 B_{\mathrm{BB}} \tag{11}$$

where B_{AB} is the second virial coefficient due to the interaction of the molecules A and B. Substituting eq. (11) in (10), one has $B^{\mathrm{E}} = 2x_{\mathrm{A}}x_{\mathrm{B}}E$,

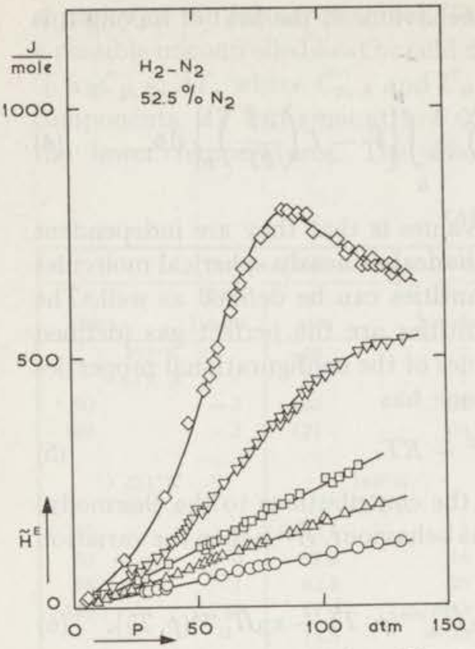

Fig. 5. The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the mixture 47.5% H_2–52.5% N_2 at (from below) 293, 231, 201, 170 and 147°K.

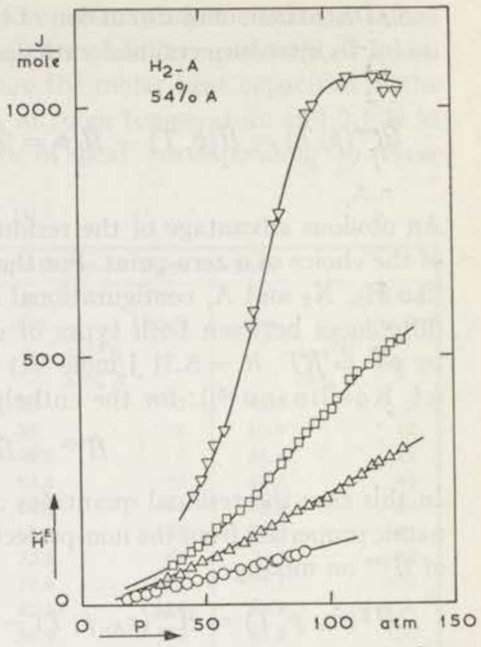

Fig. 6. The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the mixture 46% H_2–54% A at (from below) 293, 231, 201 and 169°K.

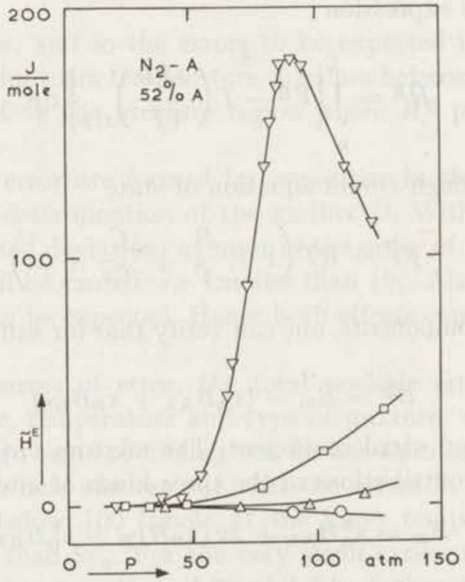

Fig. 7. The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the mixture 48% N_2–52% A at (from below) 293, 231, 201 and 169°K.

where $E = B_{AB} - \frac{1}{2}(B_{AA} + B_{BB})$. So for low densities, where $\tilde{V}^E = 2x_A x_B E$ and E is only a function of temperature, eq. (1) can be written as

$$\tilde{H}^E = 2x_A x_B p \left(E - T\frac{dE}{dT}\right) \tag{12}$$

an expression that is valid only when other then binary molecular interactions can be neglected.

The behaviour of the excess enthalpy as a function of the pressure is shown for the systems 47.5% H_2–52.5% N_2, 46%H_2–54% A and 48% N_2–52% A in the figs. 5, 6 and 7 respectively. The heat of mixing at room temperature seems for the first two systems to be rather well represented by a linear function of the pressure; the N_2–A curve at 293°K is deviating from linearity. For a good comparison we consider the quotients $\tilde{H}^E/p$. For the H_2–N_2 mixture up to 80 atm $\tilde{H}^E/p = 1.07 \pm 0.02$ J/mole atm. For H_2–A we find 1.15 ± 0.05. The $\tilde{H}^E/p$ value for N_2–A at 293°K, zero up to 40 atm, was at 80 atm about -0.03 J/mole atm.

The behaviour of $\tilde{H}^E$, for obvious reasons, deviates more from linearity in the pressure as temperature decreases. Especially for the lowest temperatures, only about 20°K above the critical values of the heavier components, the shape looks rather peculiar. The reason for this behaviour can be found in the pressure dependence of the enthalpy for nearly critical gases. We consider the molecular interactions in a mixture of an almost ideal gas and a gas with precritical behaviour as is the case in a H_2–N_2 mixture at 147°K. The energy due to H_2–H_2 and H_2–N_2 interactions is small compared with that of the N_2–N_2 interactions. When neglecting the first mentioned interactions, mixing N_2 and H_2 at constant pressure means an expansion of the nitrogen to its partial pressure*). The residual enthalpy before mixing is given by

$$x\tilde{H}^{0\,\mathrm{res}}_{N_2}(p, T) \tag{13}$$

where x is the molar N_2-concentration. After mixing, the partial pressure of the nitrogen determines the enthalpy:

$$x\tilde{H}^{0\,\mathrm{res}}_{N_2}(p_{\mathrm{part}}, T). \tag{14}$$

Hence

$$\tilde{H}^E(x, p, T) = x\{\tilde{H}^{0\,\mathrm{res}}_{N_2}(xp, T) - \tilde{H}^{0\,\mathrm{res}}_{N_2}(p, T)\}. \tag{15}$$

In fig. 8 half the vertical distance between the two curves is equal to the excess enthalpy of a 1:1 H_2–N_2 mixture at the given temperature, as it follows from this formula. The maximum of $\tilde{H}^E$ is caused by the rapid increase of the enthalpy of N_2 between 40 and 80 atm and the slow increase at higher pressure. In the figs. 9, 10 and 11 curves have been drawn for the ideal and the real enthalpy of H_2–N_2 (at 147°K) and H_2–A and N_2–A (both at 169°K) and for enthalpies of the pure components. The enthalpy values

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*) We express our thanks to Dr. P. J. Haringhuizen of the Staatsmijnen for his suggestions.

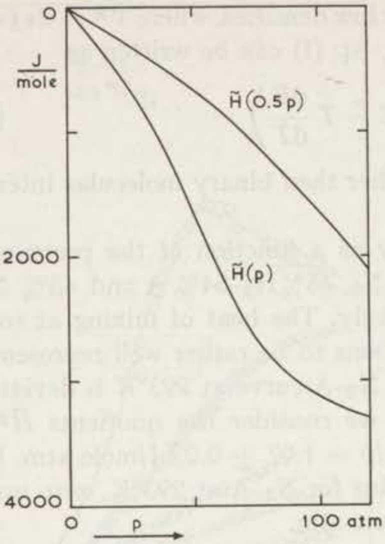

Fig. 8. The molar residual enthalpy, $\tilde{H}^{res}$, for N_2 at 147°K as a function of the pressure and half the pressure. $\tilde{H}^E$ corresponds approximately to half the vertical distance between the curves. This figure illustrates the low temperature behaviour of $\tilde{H}^E$ for 1:1 H_2–N_2.

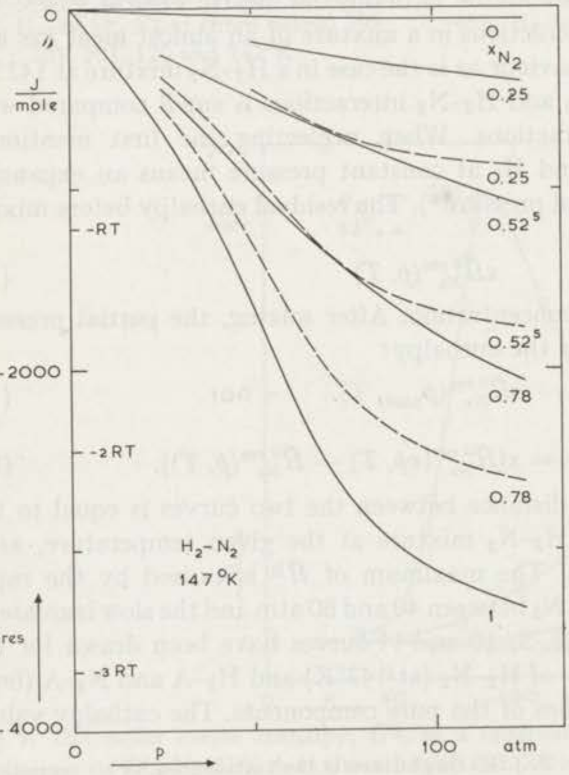

Fig. 9. The molar residual enthalpy, $\tilde{H}^{res}$, as a function of pressure for three H_2–N_2 mixtures at 147°K.
— — — — ideal enthalpy
———— real enthalpy

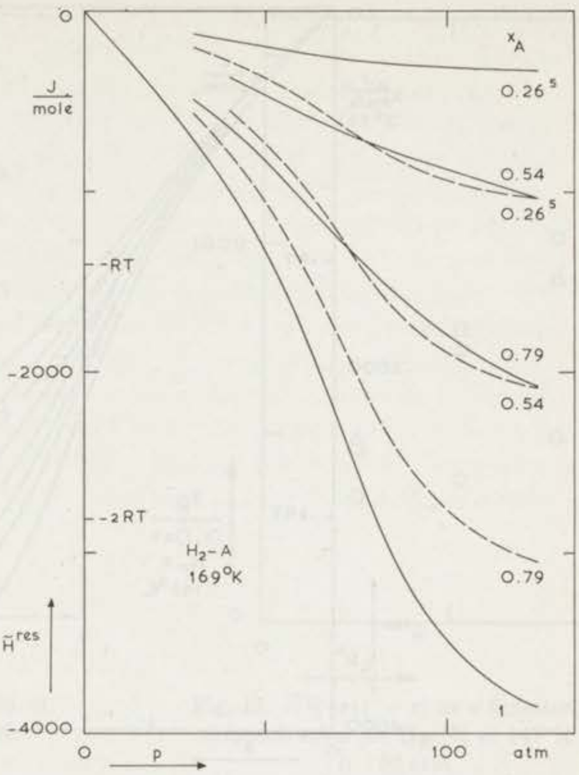

Fig. 10. The molar residual enthalpy, $\tilde{H}^{res}$, as a function of pressure for three H_2–A mixtures at 169°K. The curve for pure H_2 nearly coincides with the $\tilde{H}^{res} = 0$ axis.
— — — — ideal enthalpy
———— real enthalpy

for hydrogen are taken from Roder and Goodwin[54]), for nitrogen from Keesom, Bijl and Monté[55]) and for argon from Din[56]). In Chapter II[51]) the excess enthalpies at low temperatures will be discussed in more detail.

As to the concentration dependence of $\tilde{H}^E$, it follows from (12) that for low densities a straight horizontal line must be expected when $\tilde{H}^E/4x(1-x)$ is plotted as a function of the molar concentration x (see the figs. 12 and 13). We have divided $\tilde{H}^E$ by the product $4x(1-x)$ in order to make deviations from the expected parabolic behaviour of $\tilde{H}^E$ in the concentration more pronounced; the number 4 makes the quotient equal to $\tilde{H}^E$ for the 1:1 mixtures. Values for $\tilde{H}^E/4x(1-x)$ are given in the tables V and VI. At 50 atm and 293°K the difference between such values for the 1:3 and the 3:1 mixtures amounts to 5% for H_2–N_2 and 2% for H_2–A. For higher densities, it is sometimes possible to describe the relation between $\tilde{H}^E$ and x with $\tilde{H}^E/4x(1-x) = a + bx$, where a and b are functions of temperature and pressure. One obtains then $b > 0$, if x is the molar concentration of the heavier component. In the cases that it is impossible to relate $\tilde{H}^E$ and x in such a simple way, one can still notice that $\tilde{H}^E/4x(1-x)$ is larger for higher concentrations of the heavier component.

Concluding we can state that for low pressures at 293°K the behaviour

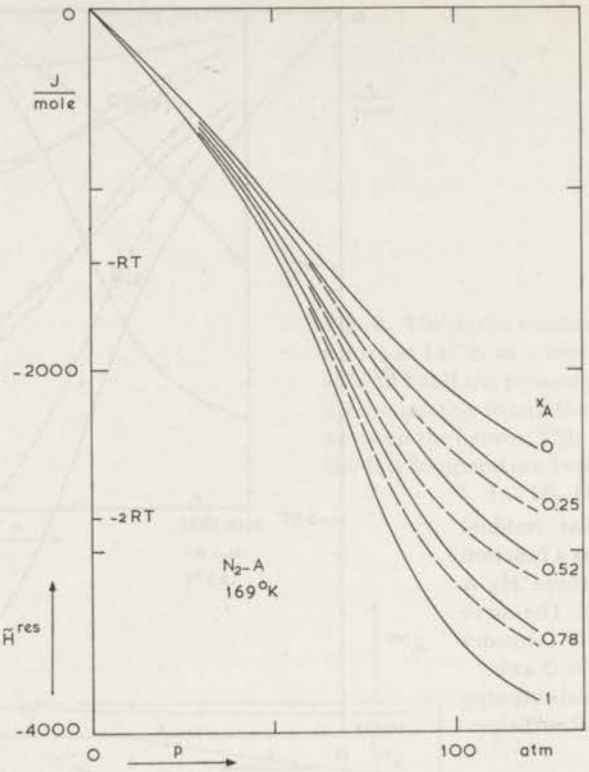

Fig. 11. The molar residual enthalpy, $\tilde{H}^{\text{res}}$, as a function of pressure for three N_2–A mixtures at 169°K.

— — — — ideal enthalpy

———— real enthalpy

TABLE V

$\tilde{H}^E/4x(1-x)$ in J/mole for H_2–N_2				
T °K	p atm	x_{N_2}		
		0.25	0.52^5	0.78
293	50	53	54	56
	80	82	84	87
	110	109	111	118
201	50	105	117	117
	80	173	199	213
	110	233	271	303
147	50	—	381	488
	80	460	777	1020
	110	480	722	911

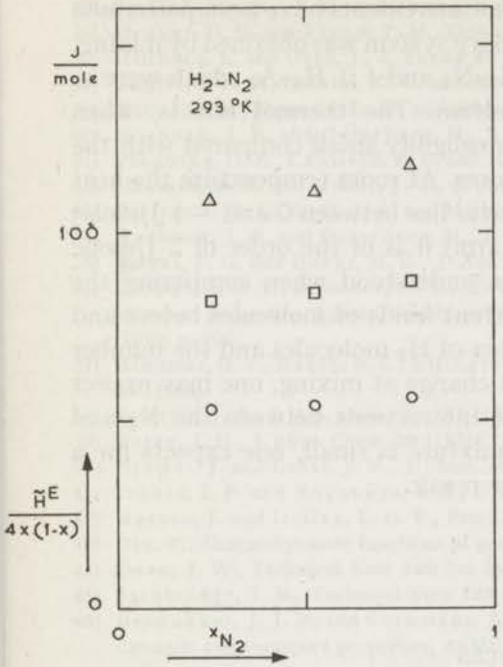

Fig. 12. $\tilde{H}^E/4x(1-x)$ as a function of concentration for H_2–N_2 at 293°K.
○ 50 atm
□ 80 atm
△ 110 atm

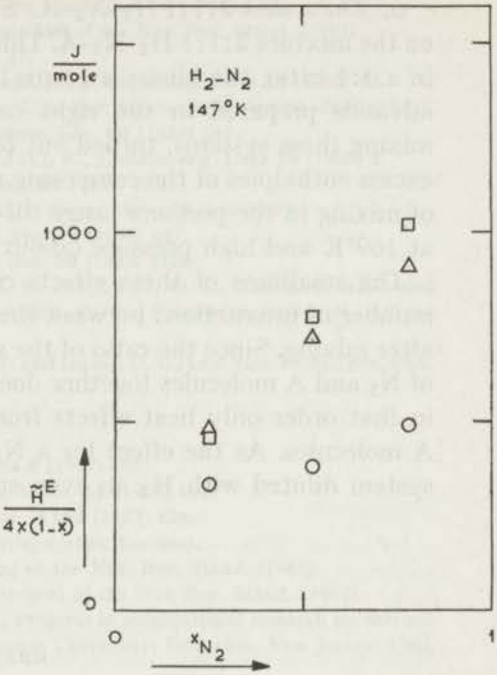

Fig. 13. $\tilde{H}^E/4x(1-x)$ as a function of concentration for H_2–N_2 at 147°K.
○ 50 atm
□ 80 atm
△ 110 atm

TABLE VI

$\tilde{H}^E/4x(1-x)$ in J/mole for H_2–A				
T	p	x_A		
°K	atm	0.26^5	0.54	0.79
293	50	56	57	57
	80	93	96	102
	110	—	—	—
201	50	112	127	167
	80	244	278	349
	110	392	453	602
169	50	216	267	324
	80	603	780	1130
	110	850	1063	1461

of $\tilde{H}^E$ is in accordance with the binary collision behaviour. At low temperature in the neighbourhood of the critical point of one of the components, it is the enthalpy behaviour of this component which mainly determines the behaviour of the excess enthalpy.

6. *The system* 2:1:1 H_2–N_2–A. Some measurements have been performed on the mixture 2:1:1 H_2–N_2–A. This ternary system was obtained by mixing, in a 1:1 ratio, the binary systems 1:1 H_2–N_2 and 1:1 H_2–A, which were in advance prepared in the right composition. The thermal effects, when mixing these systems, turned out to be negligibly small compared with the excess enthalpies of the composing mixtures. At room temperature the heat of mixing in the pressure range till 130 atm lies between 0 and −1 J/mole; at 169°K and high pressure (about 100 atm) it is of the order of 2 J/mole.

The smallness of these effects can be understood when comparing the number of interactions between the different kinds of molecules before and after mixing. Since the ratio of the number of H_2 molecules and the number of N_2 and A molecules together does not change at mixing, one may expect in first order only heat effects from the interactions between the N_2 and A molecules. As the effect for a N_2–A mixture is small, one expects for a system diluted with H_2 an even smaller result.

REFERENCES

1) Drayer, D. E. and Flynn, T. M., Technical Note **109** of the Nat. Bur. Stand. (1961).
2) Krichevskii, I. R. and Levchenko, G. T., Acta Physico chim. (USSR) **14** (1941) 271.
3) Mueller, W. H., Leland, T. W. and Kobayashi, R., A.I. Ch. E. Journal **7** (1961) 267.
4) Solbrig, G. W. and Ellington, R. T., Chem. eng. Progress Symp. Ser. **59** (1963) 127.
5) Ayber, R., Private Communication, Max-Planck-Institut für Strömungsforschung, Göttingen, Germany.
6) Bartlett, E. P., Cupples, H. L. and Tremearne, T. H., J. Am. chem. Soc. **50** (1928) 1275.
7) Bartlett, E. P., Hetherington, H. C., Kvalnes, H. M. and Tremearne, T. H., J. Am. chem. Soc. **52** (1930) 1363.
8) Deming, W. E. and Shupe, L. E., J. Am. chem. Soc. **53** (1931) 860.
9) Verschoyle, T. T. H., Proc. roy. Soc. **A111** (1926) 552.
10) Wiebe, R. and Gaddy, V. L., J. Am. chem. Soc. **60** (1938) 2300.
11) Krichevskii, I. R. and Markov, V. P., Acta Physico chim. (USSR) **12** (1940) 59.
12) Krichevskii, I. R. and Kazarnovskii, Ya. S., Acta Physico chim. (USSR) **10** (1939) 217; J. phys. Chem. (USSR) **13** (1939) 378.
13) Krichevskii, I. R., Kazarnovskii, Ya, S. and Levchenko, G. T., J. phys. Chem. (USSR) **19** (1945) 314.
14) Michels, A. and Wassenaar, T., Appl. sci. Res. **A1** (1949) 258.
15) Michels, A., De Groot, S. R. and Lunbeck, R. J., Appl. sci. Res. **A1** (1949) 378.
16) Lialine, L., Hestermans, P. and Deffet, L., Proc. conf. on thermodynamic and transport properties of fluids 1957, London (1958) p. 43.
17) Bennett, C. O. and Dodge, B. F., Ind. eng. Chem. **44** (1952) 180.
18) Koeppe, W., Kältetechnik **11** (1959) 363.
19) Sage, B. H., Olds, R. H. and Lacey, W. N., Ind. eng. Chem. **40** (1948) 1453.
20) Dokoupil, Z., Proc. of the Meeting of Commission I of the Internat. Institute of Refrigeration, Eindhoven, The Netherlands (1960) p. 277.
21) Drayer, D. E. and Flynn, T. M., Technical Note **110** of the Nat. Bur. Stand. (1961).
22) Scott, G. A., Proc. roy. Soc. **A125** (1929) 330.
23) Townend, D. T. A. and Bhatt, L. A., Proc. roy. Soc. **A134** (1932) 502.
24) Gilliland, E. R., Ind. eng. Chem. **28** (1936) 212.

25) Su, G. J., Huang, P. H. and Chang, Y. M., J. Am. chem. Soc. **68** (1946) 1403.
26) Drayer, D. E. and Flynn, T. M., Technical Note **108** of the Nat. Bur. Stand. (1961).
27) Holborn, L. and Otto, J., Z. Physik **23** (1924) 77.
28) Canfield, F. B., Leland, T. W. and Kobayashi, R., J. chem. eng. Data **10** (1965) 92.
29) Miller, J. E., Brandt, L. W. and Stroud, L., U.S. Bur. Mines, Rept. Invest. 5845 (1961).
30) Roebuck, J. R. and Osterberg, H., J. Am. chem. Soc. **60** (1938) 341.
31) Pfenning, D. B., Canfield, F. B. and Kobayashi, R., J. chem. eng. Data **10** (1965) 9.
32) Kramer, G. M. and Miller, J. G., J. phys. Chem. **61** (1957) 785.
33) Pfefferle, W. C., Goff, J. A. and Miller, J. G., J. chem. Phys. **23** (1955) 509.
34) Roebuck, J. R. and Osterberg, H., J. chem. Phys. **8** (1940) 627.
35) Keyes, F. G. and Burks, H. G., J. Am. chem. Soc. **50** (1928) 1100.
36) Ellington, R. T., Bloomer, O. T., Eakin, B. E. and Gami, D. C., Thermodynamic and transport properties of gases, liquids and solids, ASME, Purdue University, Lafayette, Indiana (1959) p. 102.
37) Bloomer, O. T., Eakin, B. E., Ellington, R. T. and Gami, D. C., Inst. Gas Techn. Res. Bull. **21** (1955).
38) Beattie, J. A., J. Am. chem. Soc. **51** (1929) 19.
39) Perry, J. H., J. phys. Chem. **39** (1935) 1189.
40) Brewer, J. and Geist, J. M., J. chem. eng. Data **6** (1961) 405.
41) Ishkin, I. P. and Rogovaya, I. A., Zhur. Fiz. Khim. **31** (1957) 410.
42) Masson, I. and Dolley, L. G. F., Proc. roy. Soc. **A103** (1923) 524.
43) Din, F., Thermodynamic functions of gases (Butterworths, London).
44) Dean, J. W., Technical Note **120** (on hydrogen) of the Nat. Bur. Stand. (1961).
45) Strobridge, T. R., Technical Note **129** (on nitrogen) of the Nat. Bur. Stand. (1962).
46) Beenakker, J. J. M. and Coremans, J. M. J., Progress in international research on thermodynamic and transport properties, ASME, Princeton University, Princeton, New Jersey, 1962, p. 3.
47) Ruhemann, M., Cryogenics **1** (1960) 114; Proc. of the Meeting of Comm. I of the Int. Inst. of Refrigeration, Eindhoven, The Netherlands, 1960 p. 295.
48) Beenakker, J. J. M., Van Eijnsbergen, B., Knoester, M., Taconis, K. W. and Zandbergen, P., Advances in thermophysical properties at extreme temperatures and pressures, ASME, Purdue University, Lafayette, Indiana, 1965, p. 114.
49) Knoester, M., Taconis, K. W. and Beenakker, J. J. M., Commun. Kamerlingh Onnes Lab., Leiden No. 351a; Physica, to be published.
50) Zandbergen, P. and Beenakker, J. J. M., Commun. Leiden No. 351c; Physica, to be published.
51) Knoester, M. and Beenakker, J. J. M., Commun. Leiden No. 351b; Physica, to be published.
52) Sachse, H. B., Proc. of the Meeting of Comm. I of the Int. Inst. of Refrigeration, Delft, The Netherlands, 1958, p. 145.
53) Rowlinson, J. S., Liquids and liquid mixtures (Butterworths, London, 1959).
54) Roder, H. M. and Goodwin, R. D., Technical Note **130** of the Nat. Bur. Stand (1961).
55) Keesom, W. H., Bijl, A. and Monté, L. A. J., Commun. Leiden, Suppl. No. 108; Bull. Inst. int. Froid **23** (1942) Annexe No. 4.
56) Din, F., Thermodynamic functions of gases. Vol. 2 (Butterworths, London, 1956).

CHAPTER II

CORRESPONDING STATES TREATMENT FOR THE EXCESS ENTHALPY OF MODERATELY DENSE GASEOUS MIXTURES

Synopsis

A corresponding states treatment is applied to moderately dense gaseous mixtures using average potential models. Calculations on the excess enthalpy have been performed for H_2–N_2 at 147°K and for H_2–A and N_2–A at 169°K at pressures up to 130 atm. The results are compared with experimental data. The agreement obtained for large values of the excess enthalpies is good; for small values it is only qualitatively satisfactory.

1. *Introduction.* In the field of gaseous and liquid mixtures several theoretical approaches exist for predicting the thermodynamic properties on mixing from data for the pure components. We will examine here the importance of these approaches in the case of gaseous mixtures of moderately high density and especially for the heat of mixing or excess enthalpy H^E of such systems. H^E, as a function of composition, pressure and temperature, is defined as the variation of the enthalpy on isothermal, isobaric mixing; so, for a binary mixture of the gases A and B we have

$$\tilde{H}^E(x_A, p, T) = \tilde{H}_m(x_A, p, T) - \{x_A \tilde{H}^0_A(p, T) + x_B \tilde{H}^0_B(p, T)\}, \qquad (1)$$

where x is the molar concentration ($x_A + x_B = 1$), the tilde denotes that molar quantities are considered, and the superscript 0 refers to the pure components. In order to avoid difficulties on the choice of a zero-point, residual values of the enthalpy are introduced:

$$\tilde{H}^{res} = \tilde{H}(p, T) - \tilde{H}(p = 0, T) = \int_0^p \left\{\tilde{V} - T\left(\frac{\partial \tilde{V}}{\partial T}\right)_p\right\} dp, \qquad (2)$$

where $\tilde{V}$ is the molar volume. Since at zero-pressure $\tilde{H}^E = 0$, one can replace $\tilde{H}$ by $\tilde{H}^{res}$ in eq. (1). For a short survey of the existing approaches we shall divide them into two groups according to the starting point of each speculation.

In the first group one starts from the equation of state. In that case for mixtures and pure components, the same type of equation of state is used. For the pure components the coefficients of the equation of state are known from pVT measurements. For mixtures they are calculated by means of combination rules, which express the parameters of the mixture in terms of those of the pure components and of the concentration. Such rules have already been given by Van der Waals[1]). The thermodynamic properties of the mixture can then be derived from the equation of state so-obtained.

We will discuss this approach in the case of low densities where we have

$$p\tilde{V} = RT\left(1 + \frac{B}{\tilde{V}}\right). \tag{3}$$

As has been discussed in Chapter I[2]), one obtains then for the molar excess enthalpy of a binary mixture

$$\tilde{H}^{\mathrm{E}} = 2x_{\mathrm{A}}x_{\mathrm{B}}p\left(E - T\frac{\mathrm{d}E}{\mathrm{d}T}\right), \tag{4}$$

where

$$E = B_{\mathrm{AB}} - \tfrac{1}{2}(B_{\mathrm{AA}} + B_{\mathrm{BB}}). \tag{5}$$

In this expression the indices denote the molecular pair interaction. The usual assumption (see Guggenheim[3])) $B_{\mathrm{AB}} = \frac{1}{2}(B_{\mathrm{AA}} + B_{\mathrm{BB}})$ gives rise to $\tilde{H}^{\mathrm{E}} = 0$, which is in contradiction with experimental results. Other ad hoc assumptions are of course possible, but we will not pursue this point further.

There is also a more microscopic way of arriving at B_{AB} by using data for the pure components. For this purpose we consider the molecular pair interaction described by a simple potential *e.g.*, of the Lennard-Jones type:

$$\phi_{\mathrm{ij}}(r) = 4\varepsilon_{\mathrm{ij}}\left\{\left(\frac{\sigma_{\mathrm{ij}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{ij}}}{r}\right)^{6}\right\}. \tag{6}$$

The parameters for the A–B interaction are now found from those for the A–A interaction (component A) and the B–B interaction (component B) by using the microscopic combination rules:

$$\varepsilon_{\mathrm{AB}} = \sqrt{\varepsilon_{\mathrm{AA}}\varepsilon_{\mathrm{BB}}} \tag{7}$$

$$\sigma_{\mathrm{AB}} = \tfrac{1}{2}(\sigma_{\mathrm{AA}} + \sigma_{\mathrm{BB}}). \tag{8}$$

B_{AB} can be calculated with these parameters. The theoretical basis for the rules is rather weak, but they appear to work reasonably well.

To use the equation of state as a starting point for the higher density mixtures is, to say the least, doubtful because the assumptions to be made for the higher coefficients are very difficult to justify.

The other approach to mixing phenomena starts from a law of corresponding states that is assumed to be valid for the pure components. The mixture is described as a single fluid (or a combination of two fluids) that follows the same law. Again there are two levels at which one can make assumptions regarding the parameters for the mixture.

Remaining on the macroscopic level one can work with the critical parameters p_c and T_c and assume that the mixture can be described by means of pseudo-critical quantities $(p_c)_m$ and $(T_c)_m$. A rule for finding such parameters from the components is given by Kay4):

$$(p_c)_m = x_A(p_c)_A + x_B(p_c)_B \tag{9}$$

$$(T_c)_m = x_A(T_c)_A + x_B(T_c)_B. \tag{10}$$

More complicated variations of these rules have been reported; for a survey see Reid and Leland5). The drawback of this method is that such macroscopic rules are hard to verify. Attempts in this direction are not very convincing. Moreover the critical constants of gases like H_2 and He are influenced by quantum effects so that, for mixtures containing such a component, the parameters obtained are not representative at higher temperatures where quantum effects are much less important.

One can also go to the microscopic level and start from the molecular pair interaction. One uses again the law of corresponding states but now in terms of the parameters of the interaction potential *e.g.*, of the L.–J. (6–12) type of eq. (6). One treats the mixture as a single fluid which is characterized by a pair of effective parameters $\langle\varepsilon\rangle$ and $\langle\sigma\rangle$. The problem is now to make a sensible average for obtaining $\langle\varepsilon\rangle$ and $\langle\sigma\rangle$. Hecht6) finds the values of the parameters by requiring that the Lennard-Jones potential reproduce, over a given temperature range, the theoretical second virial coefficient of the mixture given by

$$B_m = x_A^2 B_{AA} + 2x_A x_B B_{AB} + x_B^2 B_{BB}. \tag{11}$$

The drawback of this approach is that it remains halfway between the macroscopic and the microscopic level, so it suffers from most of the weaknesses of the macroscopic one.

A better treatment for liquid mixtures has been proposed by Prigogine7) and Scott8). Here $\langle\varepsilon\rangle$ and $\langle\sigma\rangle$ are obtained by an averaging procedure over the interaction of a molecule with its neighbours. These methods have not yet been applied to gaseous mixtures, probably because they have been developed from cell theories which are unrealistic for fluids at moderate density. Nevertheless it is worthwhile to apply them also in this case, because the only relevant condition appears to be that each molecule is always surrounded by a large enough number of neighbours that one can speak of an average interaction. Since experimental data on the heat of mixing are now available, the validity of the methods for such systems can be examined. In this chapter⁹) this will be done for the systems H_2–N_2, H_2–A and N_2–A.

The basic ideas of the theory, as far as they are important for our calculations are summarized in section 2. For a more general survey of the theories on liquid mixtures the reader is referred to *e.g.*, the study of Levelt and Cohen¹⁰) and the books of Prigogine⁷) and Rowlinson¹¹). In section 3 the results of the calculation of the excess enthalpy are given and compared with the experimental results on the heat of mixing reported in Chapter I²). Section 4 contains a discussion of the results. Preliminary results have been reported earlier¹²). Results of calculations on the related excess property viz the volume change on mixing, have been published by Zandbergen and Beenakker¹³).

2. *Liquid theories*. The features underlying the theory discussed here are (cf. Scott⁸)):

1) The intermolecular potential energy is assumed to be of the form $\phi(r) = \varepsilon f(\sigma/r)$ for each of the pairs present (A–A, A–B and B–B), where r is the distance between the molecular centers, σ is a characteristic length for each kind of interacting pair and ε a characteristic energy. The components A (A–A interactions) and B (B–B interactions) then conform to the same reduced equation of state with the reduced variables

$$T^* = \frac{kT}{\varepsilon}, \quad p^* = \frac{p\sigma^3}{\varepsilon}, \quad V^{0*} = \frac{\tilde{V}^0}{N\sigma^3}, \tag{12}$$

where k is Boltzmann's constant and N is Avogadro's number. This means that for both pure components the reduced residual enthalpy

$$H^{0\,\mathrm{res}\,*}(p^*, T^*) = \frac{\tilde{H}^{0\,\mathrm{res}}}{N\varepsilon} \tag{13}$$

is the same function of p^* and T^*.

2) The same reduced equation of state is assumed to be valid for the mixture. Three prescriptions will be discussed here for obtaining the effective parameters of the mixture. Following Scott⁸) we shall speak of the "single-", the "two-" and the "three-liquid" model. We will now treat these models in some detail.

a) The "single-liquid" model. In liquids and dense gases each molecule has at every moment a number of neighbours. When assuming additivity of forces, it seems reasonable to replace the sum of pair interactions by some average interaction depending on the mole fractions. In the "single-liquid" model one takes an average $\langle\phi(r)\rangle$ over all kinds of pairs in the system. The assumption of random mixing gives the relation

$$\langle\phi(r)\rangle = x_{\mathrm{A}}^2\phi_{\mathrm{AA}}(r) + 2x_{\mathrm{A}}x_{\mathrm{B}}\phi_{\mathrm{AB}}(r) + x_{\mathrm{B}}^2\phi_{\mathrm{BB}}(r), \tag{14}$$

where ϕ_{ij} stands for the interaction potential of the molecules i and j.

When for ϕ_{ij} the Lennard-Jones potential (eq. (6)) is used, one obtains from eq. (14) for $\langle\phi(r)\rangle$ also a function of the L.-J. type with the parameters

$$\langle\varepsilon\rangle = \frac{(x_A^2\varepsilon_{AA}\sigma_{AA}^6 + 2x_Ax_B\varepsilon_{AB}\sigma_{AB}^6 + x_B^2\varepsilon_{BB}\sigma_{BB}^6)^2}{x_A^2\varepsilon_{AA}\sigma_{AA}^{12} + 2x_Ax_B\varepsilon_{AB}\sigma_{AB}^{12} + x_B^2\varepsilon_{BB}\sigma_{BB}^{12}} \tag{15}$$

$$\langle\sigma\rangle = \left[\frac{x_A^2\varepsilon_{AA}\sigma_{AA}^{12} + 2x_Ax_B\varepsilon_{AB}\sigma_{AB}^{12} + x_B^2\varepsilon_{BB}\sigma_{BB}^{12}}{x_A^2\varepsilon_{AA}\sigma_{AA}^6 + 2x_Ax_B\varepsilon_{AB}\sigma_{AB}^6 + x_B^2\varepsilon_{BB}\sigma_{BB}^6}\right]^{\frac{1}{6}}. \tag{16}$$

Now the mixture is described – apart from Gibb's paradox entropy contribution – as a single fluid with these parameters.

The calculation of a thermodynamic property of the mixture, say the enthalpy, proceeds in the following way: One of the two components is chosen as a reference gas (denoted with index R). As this gas and the mixture are assumed to satisfy the same reduced equation of state, one obtains for the residual enthalpy

$$\frac{\tilde{H}_m^{res}}{N\langle\varepsilon\rangle}\left(\frac{p\langle\sigma\rangle^3}{\langle\varepsilon\rangle}, \frac{kT}{\langle\varepsilon\rangle}\right) = \frac{\tilde{H}_R^{0\,res}}{N\varepsilon_R}\left(\frac{p\sigma_R^3}{\varepsilon_R}, \frac{kT}{\varepsilon_R}\right) \tag{17}$$

Rewriting eq. (17) one obtains

$$\tilde{H}_m^{res}(x_A, p, T) = \frac{\langle\varepsilon\rangle}{\varepsilon_R}\,\tilde{H}_R^{0\,res}\left(\frac{\langle\varepsilon\rangle}{\varepsilon_R}\,\frac{\sigma_R^3}{\langle\sigma\rangle^3}\,p, \frac{\langle\varepsilon\rangle}{\varepsilon_R}\,T\right) \tag{18}$$

from which $\tilde{H}_m^{res}$ can be determined if $\tilde{H}_R^{0\,res}$ is known at the indicated values of pressure and temperature. The excess enthalpy or heat of mixing as defined by eqs. (1) and (2) follows by subtracting the ideal mixture residual enthalpy.

b) The "two-liquid" model. Whereas in the foregoing model the molecular potentials were averaged over all the binary interactions, it seems obvious to apply also a model in which the interactions of A-molecules with neighbours are distinguished from those of B-molecules with surrounding particles. So in the "two-liquid" model one considers the two average potentials $\langle\phi(r)\rangle$ and $\langle\phi(r)\rangle_B$. Under the same conditions as for the "single-liquid" model, one obtains

$$\langle\phi(r)\rangle_A = x_A\phi_{AA}(r) + x_B\phi_{AB}(r) \tag{19}$$

$$\langle\phi(r)\rangle_B = x_A\phi_{AB}(r) + x_B\phi_{BB}(r). \tag{20}$$

Again the L.-J. (6–12) type is used for the intermolecular potential and one obtains the same form for the average interaction but now with the parameters

$$\langle\varepsilon\rangle_A = \frac{(x_A\varepsilon_{AA}\sigma_{AA}^6 + x_B\varepsilon_{AB}\sigma_{AB}^6)^2}{x_A\varepsilon_{AA}\sigma_{AA}^{12} + x_B\varepsilon_{AB}\sigma_{AB}^{12}} \tag{21}$$

$$\langle\sigma\rangle_A = \left[\frac{x_A\varepsilon_{AA}\sigma_{AA}^{12} + x_B\varepsilon_{AB}\sigma_{AB}^{12}}{x_A\varepsilon_{AA}\sigma_{AA}^6 + x_B\varepsilon_{AB}\sigma_{AB}^6}\right]^{\frac{1}{6}} \tag{22}$$

and $\langle\varepsilon\rangle_{\rm B}$ and $\langle\sigma\rangle_{\rm B}$ similarly. In this way one describes the mixture as a system of two fluids, characterized by $\langle\varepsilon\rangle_{\rm A}$, $\langle\sigma\rangle_{\rm A}$ and $\langle\varepsilon\rangle_{\rm B}$, $\langle\sigma\rangle_{\rm B}$, respectively. The thermodynamic properties of the mixture are assumed to be the molar averages of the corresponding properties of these two "liquids". One has thus

$$\tilde{H}^{\rm res}_{\rm m} = x_{\rm A}\langle\tilde{H}^{\rm res}\rangle_{\rm A} + x_{\rm B}\langle\tilde{H}^{\rm res}\rangle_{\rm B} \tag{23}$$

where $\langle\tilde{H}^{\rm res}\rangle_{\rm A}$ is the residual enthalpy for a fluid characterized by $\langle\varepsilon\rangle_{\rm A}$ and $\langle\sigma\rangle_{\rm A}$. Its value is obtained from a reference fluid as in the case of the "single-liquid" model (see eqs. (17) and (18)). $\langle\tilde{H}^{\rm res}\rangle_{\rm B}$ is obtained similarly. For the heat of mixing one obtains using eqs. (1) and (2)

$$\tilde{H}^{\rm E} = x_{\rm A}\{\langle\tilde{H}^{\rm res}\rangle_{\rm A} - \tilde{H}^{0\,\rm res}_{\rm A}\} + x_{\rm B}\{\langle\tilde{H}^{\rm res}\rangle_{\rm B} - \tilde{H}^{0\,\rm res}_{\rm B}\}. \tag{24}$$

c) The "three-liquid" model. Since in a binary mixture three kinds of binary interactions are present, it is interesting to consider also the mixture as a system of three fluids, each characterized by one kind of pair interaction. In fact this is rigorously true for a low density system where other than binary collisions can be neglected. The residual enthalpy of a binary system is then given by

$$\tilde{H}^{\rm res}_{\rm m} = x^2_{\rm A}\tilde{H}^{0\,\rm res}_{\rm A} + 2x_{\rm A}x_{\rm B}\tilde{H}^{\rm res}_{\rm AB} + x^2_{\rm B}\tilde{H}^{0\,\rm res}_{\rm B} \tag{25}$$

where $\tilde{H}^{\rm res}_{\rm AB}$ is the residual enthalpy of a gas with the mixed interaction, characterized by the parameters $\varepsilon_{\rm AB}$ and $\sigma_{\rm AB}$. For the excess enthalpy one obtains using the definition given in eqs. (1) and (2)

$$\tilde{H}^{\rm E} = 2x_{\rm A}x_{\rm B}\{\tilde{H}^{\rm res}_{\rm AB} - \tfrac{1}{2}(\tilde{H}^{0\,\rm res}_{\rm A} + \tilde{H}^{0\,\rm res}_{\rm B})\}. \tag{26}$$

For this model $\tilde{H}^{\rm E}$ is parabolic in the concentration. For exploratory calculations it has the great advantage of computational simplicity.

For the calculation of the parameters of the "single-liquid" and the "two-liquid" model and for the application in the "three-liquid" model the interaction parameters $\varepsilon_{\rm AA}$, $\varepsilon_{\rm AB}$, $\varepsilon_{\rm BB}$, $\sigma_{\rm AA}$, $\sigma_{\rm BB}$ and $\sigma_{\rm AB}$ are necessary. The parameters of the pure components were taken from the compilation of Hirschfelder, Curtiss and Bird[14]). These values are given in table I. For $\varepsilon_{\rm AB}$ and $\sigma_{\rm AB}$ no accurate data are available and hence we applied the usual combination rules (7) and (8). (In an earlier publication[12]), $\sigma_{\rm AB} = \sqrt{\sigma_{\rm AA}\sigma_{\rm BB}}$ was used because the equations for the "average" parameters become

TABLE I

Parameters of the L.-J. (6–12) pot.

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

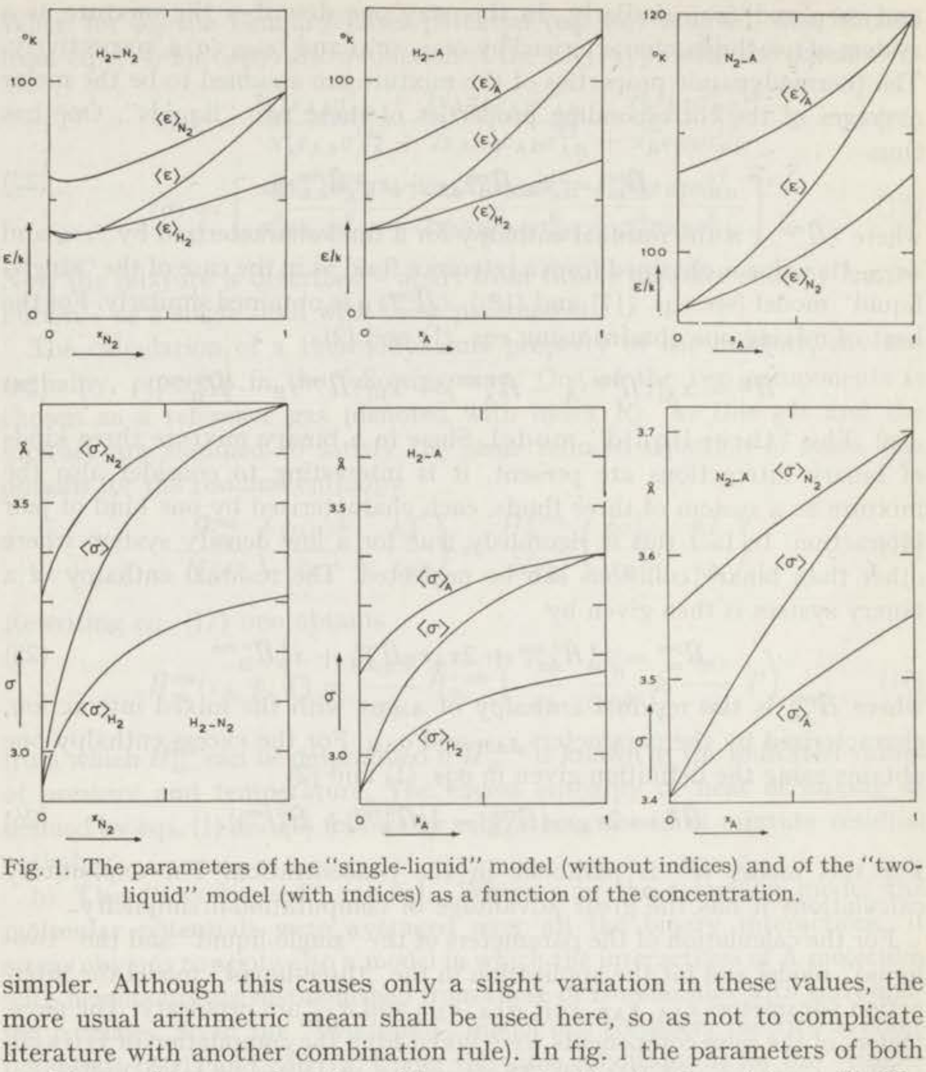

Fig. 1. The parameters of the "single-liquid" model (without indices) and of the "two-liquid" model (with indices) as a function of the concentration.

simpler. Although this causes only a slight variation in these values, the more usual arithmetic mean shall be used here, so as not to complicate literature with another combination rule). In fig. 1 the parameters of both models are given as a function of the concentration for the mixtures H_2–N_2, H_2–A and N_2–A.

3. *Results.* Calculations of the heat of mixing were performed for three compositions of the systems H_2–N_2 at 147°K and H_2–A at 169°K and for one composition of the system N_2–A at 169°K. For each of these systems one of the components was chosen as a reference gas, since one may expect that then the corresponding states treatment is better than with an arbitrary gas. For the H_2–N_2 system nitrogen was taken as the reference gas and for H_2–A, argon. Hydrogen was not chosen for the following reason: the temperatures that are of importance in the mixture calculations become so low that quantum effects play an important role in the properties of H_2, whereas

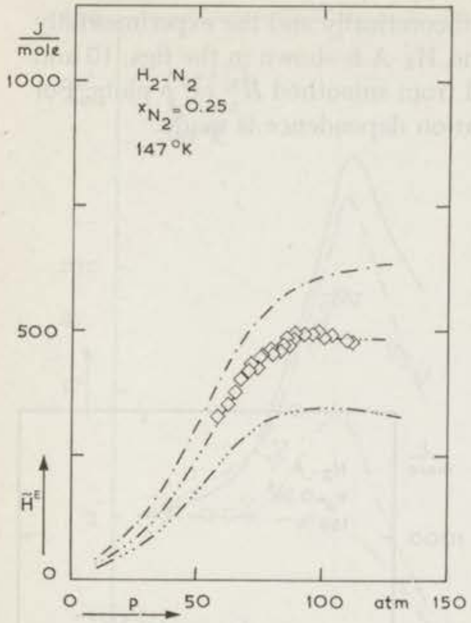

Fig. 2

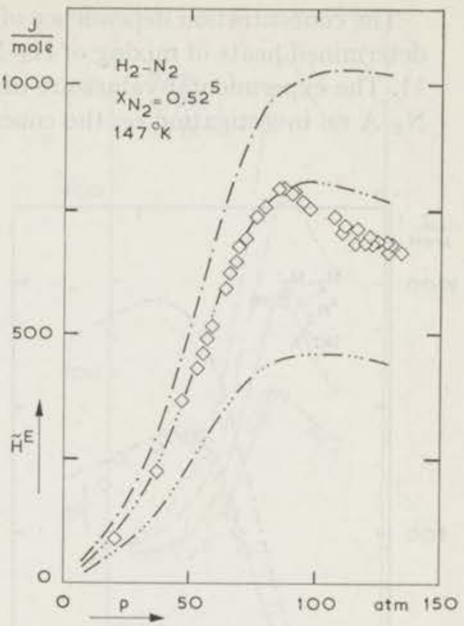

Fig. 3

Fig. 2. The excess enthalpy, $\tilde{H}^E$, as a function of the pressure for the system H_2–N_2 ($x_{N_2} = 0.25$) at 147°K.

—— . —— . —— calculated with "single-liquid" model.
—— .. —— .. —— calculated with "two-liquid" model.
——. . .——. . .—— calculated with "three-liquid" model.
The experimental points are from Chapter I [2]).

Fig. 3. $\tilde{H}^E$ *vs.* p for H_2–N_2 ($x_{N_2} = 0.52$[5])) at 147°K. See also the caption of fig. 2.

at the temperatures of the measurements these may be neglected both for the H_2–H_2 as well as for the H_2–N_2 and H_2–A interactions. The calculations for N_2–A were based on both components. The enthalpies of N_2 are taken from the H *vs.* log p isotherms of the diagram of Keesom, Bijl and Monté[15]). For A the tables of Michels, Lunbeck and Wolkers[16]) and those of Michels, Levelt and Wolkers[17]) are used. Values for the enthalpy of H_2 are derived from tables of Woolley, Scott and Brickwedde[18]). The results for the systems H_2–N_2 and H_2–A are shown in $\tilde{H}^E$ *vs.* p plots (see figs. 2–7, where also the concentrations are denoted). In these diagrams the experimentally determined values are also given. In figs. 8 and 9 we present the results obtained for the system N_2–A($x_A = 0.52$) with N_2 and A as reference gases respectively. In both figures an extra curve is drawn representing $\tilde{H}^E$ calculated for the "two-liquid" model, but now with nitrogen as reference for the N_2-centered "liquid" and argon for the A-centered "liquid".

The concentration dependence of the theoretically and the experimentally determined heats of mixing of H_2–N_2 and H_2–A is shown in the figs. 10 and 11. The experimental values are derived from smoothed $\tilde{H}^E$ *vs.* p plots. For N_2–A no investigation on the concentration dependence is made.

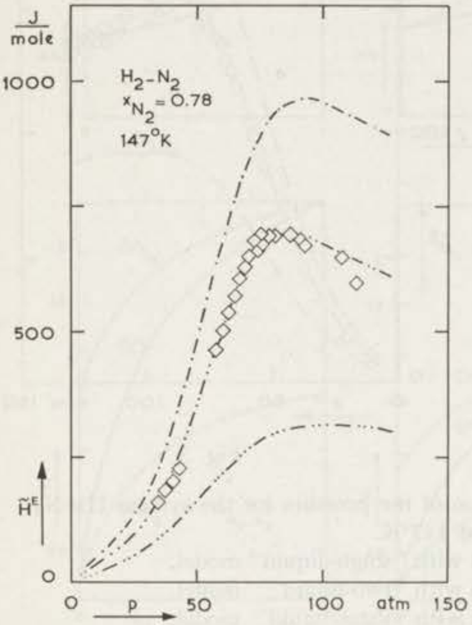

Fig. 4. $\tilde{H}^E$ *vs.* p for H_2–N_2 ($x_{N_2} = 0.78$) at 147°K. See also the caption of fig. 2.

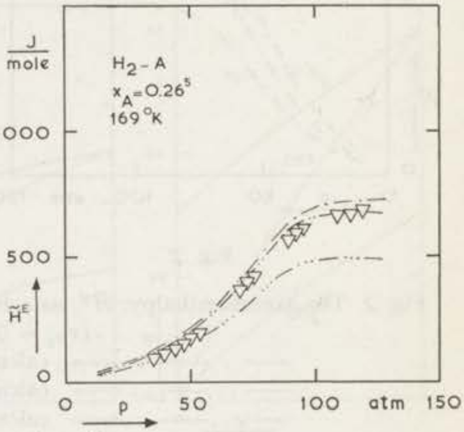

Fig. 5. $\tilde{H}^E$ *vs.* p for H_2–A ($x_A = 0.26^5$) at 169°K. See also the caption of fig. 2.

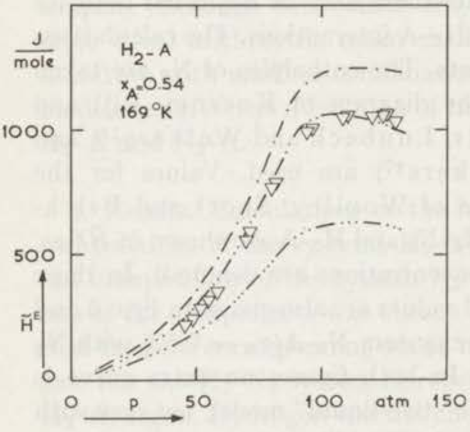

Fig. 6. $\tilde{H}^E$ *vs.* p for H_2–A ($x_A = 0.54$) at 169°K. See also the caption of fig. 2.

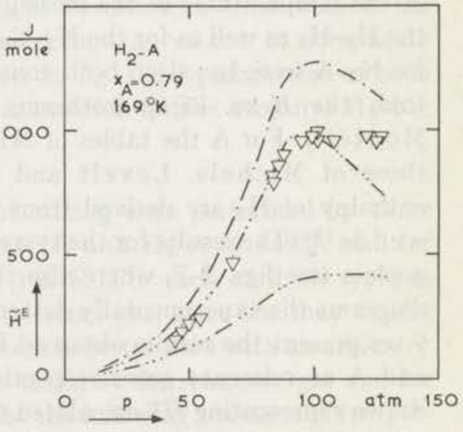

Fig. 7. $\tilde{H}^E$ *vs.* p for H_2–A ($x_A = 0.79$) at 169°K. See also the caption of fig. 2.

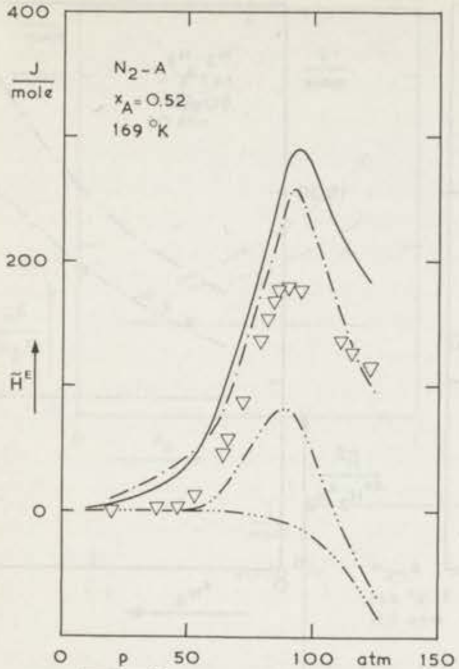

Fig. 8. $\tilde{H}^E$ *vs.* p for N_2–A ($x_A = 0.52$) at 169°K with N_2 as reference gas. For the drawn curve see text. See also the caption of fig. 2.

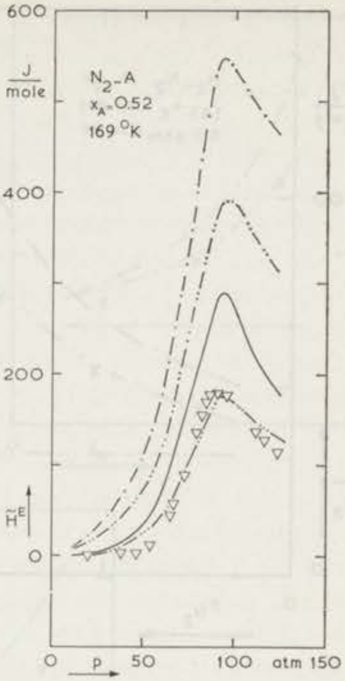

Fig. 9. $\tilde{H}^E$ *vs.* p for N_2–A ($x_A = 0.52$) at 169°K with A as reference gas. For the drawn curve see text. See also the caption of fig. 2.

4. *Discussion.* For discussion it is important to take into account the fact that the first two models applied differ essentially from the "three-liquid" model. The latter involves a typical low-density approach, based as it is on an isolated pair approximation whereas the first two are developed for dense fluids. So, for low enough densities one must expect that the "three-liquid" model gives the best fit with experimental data. This has already been treated in Chapter I[2]). In passing we mention that good agreement was indeed found at low densities.

For higher densities the "three-liquid" model is less suited, since it neglects other than binary collisions. The effects resulting from higher densities are, therefore, under-estimated. The "single-liquid" model, on the contrary, will be a better assumption at fairly high densities since it is characterized by a total loss of individuality of the molecules. In the "two-liquid" model two types of average interaction are distinguished. So the molecules have retained part of their individuality, whereas it is still essentially a high density approach. It is not surprising that the values of mixing properties obtained with this model lie between those based on the "single-liquid" and the "three-liquid" model. In case of liquid mixtures

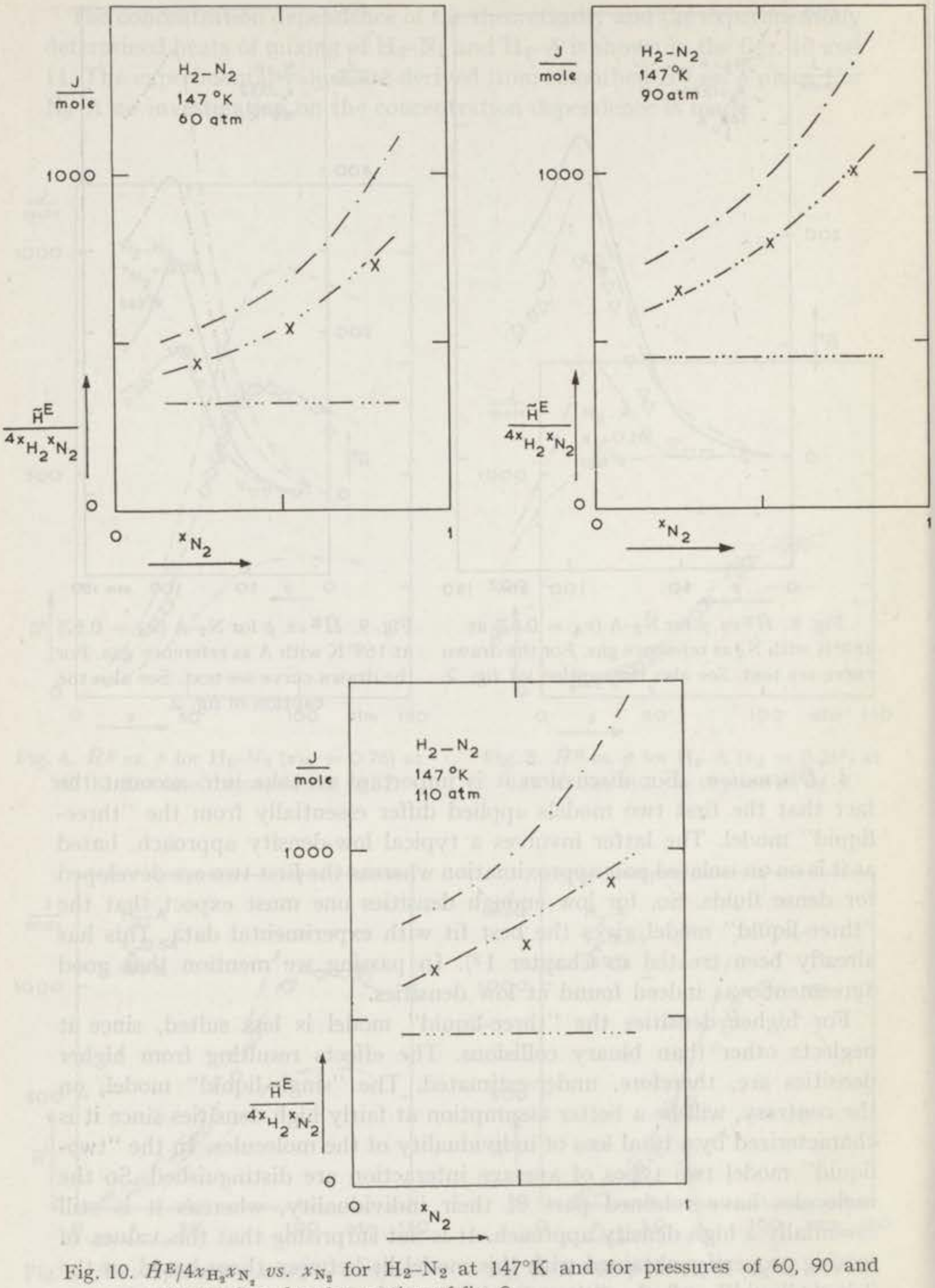

Fig. 10. $\tilde{H}^E/4x_{H_2}x_{N_2}$ *vs.* x_{N_2} for H_2–N_2 at 147°K and for pressures of 60, 90 and 110 atm. See also the caption of fig. 2.

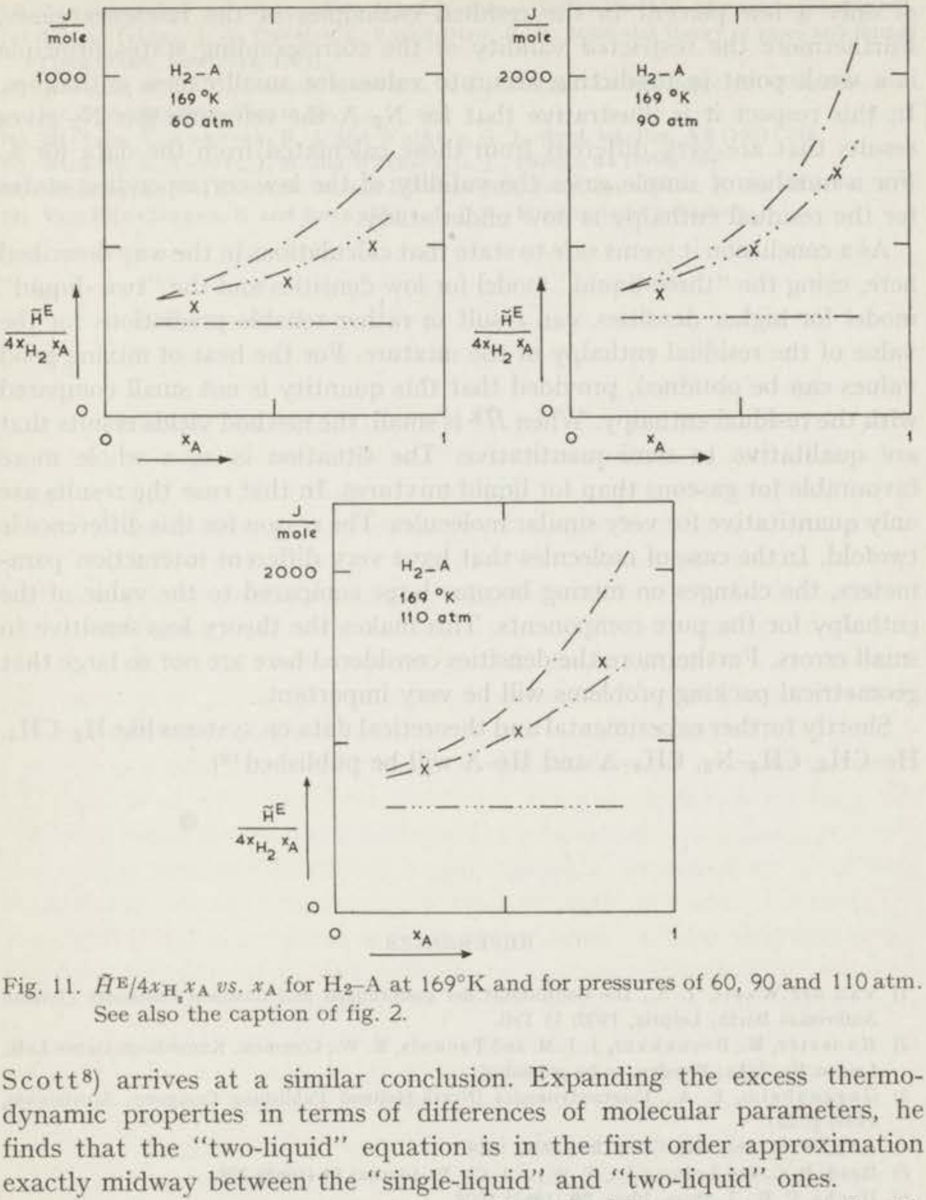

Fig. 11. $\tilde{H}^E/4x_{H_2}x_A$ *vs.* x_A for H_2–A at 169°K and for pressures of 60, 90 and 110 atm. See also the caption of fig. 2.

Scott[8]) arrives at a similar conclusion. Expanding the excess thermodynamic properties in terms of differences of molecular parameters, he finds that the "two-liquid" equation is in the first order approximation exactly midway between the "single-liquid" and "two-liquid" ones.

For the systems H_2–N_2 and H_2–A the "two-liquid" curves agree well with experimental data for moderately high densities. The curves for the "single-liquid" model are too high and those for the "three-liquid" model too low.

For the mixture N_2–A the small value of the excess enthalpy – small compared with the residual enthalpy of the system – creates difficulties. Although the shape of the theoretical curves (see figs. 8 and 9) is in rather good agreement with experimental data, the calculated values of the heat of mixing deviate considerably. Such discrepancies can be caused by errors of only a few percent in the residual enthalpies of the reference gases. Furthermore the restricted validity of the corresponding states principle is a weak point in predicting accurate values for small excess enthalpies. In this respect it is illustrative that for N_2–A the reference gas N_2 gives results that are very different from those calculated from the data for A. For a number of simple gases the validity of the law corresponding states for the residual enthalpy is now under study.

As a conclusion it seems safe to state that calculations in the way described here, using the "three-liquid" model for low densities and the "two -liquid" model for higher densities, can result in rather reliable predictions for the value of the residual enthalpy of the mixture. For the heat of mixing good values can be obtained, provided that this quantity is not small compared with the residual enthalpy. When $\tilde{H}^{\mathrm{E}}$ is small, the method yields results that are qualitative to semi-quantitative. The situation is as a whole more favourable for gaseous than for liquid mixtures. In that case the results are only quantitative for very similar molecules. The reason for this difference is twofold. In the case of molecules that have very different interaction parameters, the changes on mixing become large compared to the value of the enthalpy for the pure components. This makes the theory less sensitive to small errors. Furthermore the densities considered here are not so large that geometrical packing problems will be very important.

Shortly further experimental and theoretical data on systems like H_2–CH_4, He–CH_4, CH_4–N_2, CH_4–A and He–A will be published[19]).

REFERENCES

1) Van der Waals, J. N., Die Continuität der gasförmigen und flüssigen Zustándes (Johann Ambrosius Barth, Leipzig, 1900) II Teil.

2) Knoester, M., Beenakker, J. J. M. and Taconis, K. W., Commun. Kamerlingh Onnes Lab., Leiden No. 351a; Physica, to be published.

3) Guggenheim, E. A., Thermodynamics (North-Holland Publishing Company, Amsterdam, 1959) p. 221.

4) Kay, W. B., Ind. eng. Chem. **28** (1936) 1014.

5) Reid, R. C. and Leland Jr., T. W., A.I. Ch. E. Journal **11** (1965) 228.

6) Hecht, C. E., J. chem. Phys. **38** (1963) 1008.

7) Prigogine, I., The molecular theory of solutions (North-Holland Publishing Company, Amsterdam, 1957).

8) Scott, R. L., J. chem. Phys. **25** (1956) 163.

9) Knoester, M. and Beenakker, J. J. M., Commun. Leiden No. 351b; Physica, to be published.

10) Levelt, J. M. H. and Cohen, E. G. D., Studies in statistical mechanics (North-Holland Publishing Company, Amsterdam, 1964) Vol. II, Part B.

11) Rowlinson, J. S., Liquids and liquid mixtures (Butterworths, London, 1959).

12) Beenakker, J. J. M., Van Eijnsbergen, B., Knoester, M., Taconis, K. W. and Zandbergen, P., Advances in thermophysical properties at extreme temperatures and pressures, ASME, Purdue University, Lafayette, Indiana, 1965, p. 114.

13) Zandbergen, P. and Beenakker, J. J. M., Commun. Leiden No. 351d; Physica, to be published.

14) Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., Molecular theory of gases and liquids (John Wiley, New York, 1954).

15) Keesom, W. H., Bijl, A. and Monté, L. A. J., Commun. Leiden, Suppl. No. 108; Bull. Inst. int. Froid **23** (1942) Annexe No. 4.

16) Michels, A., Lunbeck, R. J. and Wolkers, G. J., Appl. sci. Res. **A2** (1951) 345.

17) Michels, A., Levelt, J. M. and Wolkers, G. J., Physica **24** (1958) 769.

18) Woolley, H. W., Scott, R. B. and Brickwedde, F. G., Bur. Stand. J. Res. **41** (1948) 379.

19) Van Eijnsbergen, B. and Beenakker, J. J. M., Physica, to be published.

SAMENVATTING

Bij de experimentele bepaling van thermodynamische grootheden van gasmengsels is tot nu toe gebruik gemaakt van methoden die niet essentieel verschillen van die welke zijn toegepast voor pure gassen. Voor de enthalpie houdt dit in, dat de meeste gegevens zijn gebaseerd op metingen betreffende de toestandsvergelijking en, in veel mindere mate, op metingen van het Joule-Thomson effect. Beide methoden zijn echter weinig aantrekkelijk en het aantal enthalpiegegevens van gasmengsels is dan ook beperkt. In sommige gevallen heeft men getracht hieraan tegemoet te komen door berekeningen uit te voeren gebaseerd op gegevens van de pure componenten. De daarbij gebruikte aannamen zijn echter in het algemeen theoretisch niet te rechtvaardigen en de betekenis van zulke berekeningen moet dan ook twijfelachtig worden genoemd.

Het is opmerkelijk dat men bij gasmengsels, in tegenstelling tot vloeistofmengsels, steeds voorbij is gegaan aan de betekenis van de mengwarmte. Dit is de hoeveelheid warmte die moet worden toegevoerd om gassen onder gelijk blijvende druk en temperatuur te doen mengen. De mengwarmte is daarmee gelijk aan de verandering van de enthalpie bij menging en wordt veelal aangeduid als „exces enthalpie" (H^E). Het is duidelijk dat, bij bekende enthalpieën van de componenten, de enthalpie van het mengsel direct volgt uit gegevens van de mengwarmte. In dit proefschrift wordt een onderzoek beschreven naar het gedrag van de mengwarmte van de systemen H_2–N_2, H_2–A, N_2–A en 2:1:1 H_2–N_2–A. De nadruk ligt hierbij op het gedrag van mengsels bij lage temperatuur (maar nog in de gasfase) en gematigd hoge druk (tot ca. 130 atm).

In hoofdstuk I wordt – nadat een literatuuroverzicht van de bestaande thermodynamische gegevens van gasmengsels gegeven is – de experimentele bepaling van de mengwarmte besproken. Voor de metingen is een calorimeter gebruikt waarin continu de te mengen gassen, die op gelijke temperatuur zijn gebracht, binnenstromen en daar mengen. De temperatuur van het uitstromende mengsel kan worden vergeleken met die van de binnenkomende componenten. In de hier besproken gevallen werd bijna steeds een afkoeling geconstateerd, die werd gecompenseerd door via een stookdraad warmte aan de mengruimte toe te voeren. Uit de hiervoor benodigde hoeveelheid warmte en de doorgestroomde hoeveelheid gas(mengsel) wordt vervolgens de mengwarmte uitgerekend. De mengwarmte van de reeds eerder genoemde systemen is op deze wijze bepaald bij temperaturen tussen ca. 150 en 300°K. Bij de hogere temperaturen constateert men dat in goede benadering voldaan is aan de evenredigheid van mengwarmte en druk, die een gevolg is van het binaire-botsingsgedrag van de moleculen. Bij de lagere temperaturen treden reeds bij lage druk grote afwijkingen van dit gedrag op. In vele gevallen wordt bij ca. 80 atm een maximum in de mengwarmte gevonden. De mengwarmte kan dan hoge waarden bereiken (voor een 1 : 1 H_2–N_2 mengsel van 80 atm vindt men 85 J/mole bij 293°K en 760 J/mole bij 147°K). Het blijkt dat een dergelijk gedrag verwacht kan worden, wanneer de temperatuur niet ver van de kritische temperatuur van één van de componenten is.

In hoofdstuk II is, m.b.v. de verkregen gegevens nagegaan in hoeverre mengseltheorieën in staat zijn bovengenoemd gedrag bij de lagere temperaturen te verklaren. In de inleiding van dit hoofdstuk worden een aantal mogelijke uitgangspunten besproken, waarna verder de discussie beperkt is tot een methode die zowel door Prigogine als door Scott voor vloeistofmengsels is ontwikkeld. Daar bij deze aanpak de belangrijkste voorwaarde is dat elk molecuul een aantal buren heeft waarmee het tegelijkertijd in wisselwerking is, is het aantrekkelijk op soortgelijke wijze te werk te gaan voor gasmengsels van gematigd hoge dichtheid. Men gaat er bij deze methode van uit dat men te maken heeft met ronde of bijna ronde moleculen met een interactiepotentiaal die voor elk molecuulpaar gekarakteriseerd wordt door slechts twee parameters: een lengte- en een energieparameter. Voor de pure gassen geldt in dat geval een wet van overeenstemmende toestanden, d.w.z. dat de thermodynamische grootheden, mits dimensieloos gemaakt (gereduceerd) met bovenstaande parameters, onder gelijkwaardige condities (gelijke gereduceerde temperatuur en druk) aan elkaar gelijk zijn. Voor het mengsel wordt nu dezelfde wet van overeenstemmende toestanden aangenomen, waarbij de parameters zijn verkregen uit een middeling over de interacties van een molecuul met zijn naaste buren. De enthalpie van het mengsel (en dus ook de mengwarmte) kan dan worden uitgerekend uitgaande van de enthalpiegegevens van één van de componenten. Op deze wijze zijn mengwarmtes berekend van de reeds eerder genoemde binaire systemen bij lage temperatuur. De overeenkomst met experimentele resultaten is bevredigend en soms zelfs verrassend goed. Dit houdt overigens nog niet in dat de mengwarmte van een systeem altijd zonder meer voorspeld kan worden. Alleen al onnauwkeurigheden in de enthalpiegegevens van de componenten kunnen, vooral voor kleine mengwarmtes, grote afwijkingen ten gevolge hebben.