THE HEAT OF MIXING AND THE LAW OF CORRESPONDING STATES FOR GASEOUS MIXTURES

B. VAN EIJNSBERGEN

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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 K. A. H. HIDDING, HOOGLERAAR IN DE FACULTEIT DER GODGELEERDHEID, TEN OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP WOENSDAG 5 OKTOBER 1966 TE 16 UUR

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BERT VAN EIJNSBERGEN

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Aan mijn moeder

Aan Mieneke

Het in dit proefschrift beschreven onderzoek werd uitgevoerd als onderdeel van het programma van de Werkgemeenschap voor Molecuulphysica 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.)

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

Na het afleggen van het H.B.S.-B examen in 1952 aan de Dalton H.B.S. (thans lyceum) te 's-Gravenhage, vervulde ik tot november 1954 mijn militaire dienstplicht als officier bij de Koninklijke Landmacht. In hetzelfde jaar begon ik mijn studie aan de Rijksuniversiteit te Leiden, waar ik in september 1959 het candidaatsexamen in de natuur- en wiskunde (a') aflegde. Mijn praktische opleiding genoot ik in het Kamerlingh Onnes Laboratorium, in de werkgroep K VII van de Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.). Het Leidse onderzoek van deze werkgroep stond onder leiding van Prof. Dr. K.W. Taconis, terwijl de dagelijkse leiding berustte bij Dr. J. Reuss, die ik assisteerde bij de constructie van een bellenvat. Nadat ik mijn doctoraal examen in de experimentele natuurkunde in juli 1963 had afgelegd, werd ik aangesteld als wetenschappelijke medewerker van de reeds genoemde Stichting F.O.M.

Sinds 1960 heb ik geassisteerd op het practicum voor precandidaten, terwijl ik vanaf 1964 als hoofdassistent het natuurkunde practicum voor medische studenten heb geleid.

De in dit proefschrift beschreven onderzoekingen werden aangevangen in oktober 1963 als onderdeel van het programma van de werkgroep molecuulphysica M II van de Stichting F.O.M.. De leiding van deze werkgroep berust bij Prof. Dr. K.W. Taconis en Prof. Dr. J.J.M. Beenakker.

Veel hulp en medewerking heb ik mogen ondervinden van de staf van het Kamerlingh Onnes Laboratorium. Met name zij vermeld de heer W.F. Tegelaar, die de in dit proefschrift voorkomende tekeningen heeft verzorgd. Dr. M. Knoester dank ik zeer voor de adviezen die ik, speciaal bij de aanvang van de experimenten, van hem mocht ontvangen. Dr. H.F.P. Knaap was zo vriendelijk het manuscript door te lezen en van kritische opmerkingen te voorzien. Veel dank ben ik verschuldigd aan Dr. R.A. Aziz voor het corrigeren van de Engelse tekst.

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CHAPTER 1

INTRODUCTION

In this chapter we will discuss the recently developed qualitative and quantitative approach to the thermodynamic behaviour of binary gaseous mixtures, particularly concerning the heat of mixing. Before going into this subject a short discussion is given on the enthalpy of pure gases and mixtures and, in connection with this, on the heat of mixing.

1.1 The enthalpy

The enthalpy $\tilde{H}$, also called the heat function, is defined as the sum of the internal energy $\tilde{U}$ and the product of pressure p and volume $\tilde{V}$:

$$\tilde{H} = \tilde{U} + p\tilde{V} \tag{1.1}$$

the tilde indicating that the molar quantity is considered. For many cases it is useful to introduce the molar residual enthalpy $\tilde{H}^{res}$. This property is the contribution to the enthalpy arising from the interactions of the molecules and is defined by the expression,

$$\tilde{H}(p,T) \equiv \tilde{H}(p=0,T) + \tilde{H}^{res}(p,T)\ . \tag{1.2}$$

For mixtures $\tilde{H}^{res}(p,T)$ is the relevant quantity, since the ideal mixing behaviour holds for the term $\tilde{H}(p=0,T)$. Furthermore the residual enthalpy is, in contrast to the total enthalpy, independent of the choice of a zero-point. For the molar residual enthalpy the following expression can be derived:

$$\tilde{H}^{res} = \int_0^p \{\tilde{V} - T\left(\frac{\partial\tilde{V}}{\partial T}\right)_p\}dp. \tag{1.3}$$

In the study of thermodynamic properties of mixtures it is useful to compare the molar enthalpy of a binary system $\tilde{H}_m$ with the linear combination of the enthalpies of the pure components $\tilde{H}^o_A$ and $\tilde{H}^o_B$, i.e. the ideal mixing term. The deviation from this linear combination is called the excess enthalpy:

$$\tilde{H}^E(p,T,x_A) \equiv \tilde{H}_m(p,T,x_A) - \{x_A\tilde{H}^o_A(p,T) + x_B\tilde{H}^o_B(p,T)\}\,, \qquad (1.4)$$

where x is the mole fraction, the subcripts m, A and B refer to the mixture and the gases A and B, respectively, and the superscript o indicates the pure state. $\tilde{H}^E(p,T,x_A)$ is the isobaric heat of mixing, i.e. the amount of heat that has to be supplied to ($\tilde{H}^E$ positive) or extracted from ($\tilde{H}^E$ negative) the system to keep the temperature constant on isobaric mixing. Since at zero pressure $\tilde{H}^E = 0$ one obtains by substituting eq. (1.2) into eq. (1.4)

$$\tilde{H}^E(p,T,x_A) = \tilde{H}^{res}_m(p,T,x_A) - \{x_A\tilde{H}^{o\ res}_A(p,T) + x_B\tilde{H}^{o\ res}_B(p,T)\} \qquad (1.5)$$

Finally, $\tilde{H}^E$ can be written in a form similar to (1.3):

$$\tilde{H}^E = \int_0^p \{\tilde{V}^E - T\left(\frac{\partial\tilde{V}^E}{\partial T}\right)_p\}dp \qquad (1.6)$$

where the molar volume change on mixing $\tilde{V}^E$ is defined in a way analogous to $\tilde{H}^E$ in formula (1.8).

1.2 Experiments on the excess enthalpy

Until recently the experiments on thermodynamic properties of gaseous mixtures were restricted to p-V-T determinations. Furthermore, very little experimental work had been done below room temperature. A survey of the experiments and calculations on thermodynamic properties of gaseous mixtures composed of simple molecules has been given by KNOESTER, TACONIS and BEENAKKER1). From the p-V-T data of a mixture the enthalpy $\tilde{H}_m$ can be derived with eq. (1.3). This has been done, for instance, for the system H_2-N_2 by MICHELS, DE GROOT and LUNBECK2) and for the system CH_4-N_2 by ELLINGTON, BLOOMER, EAKIN and GAMIN3). The first group derived the thermodynamic properties graphically from the p-V-T data, whereas the latter group represented the experimental data of the mixture by an equation of state, which then was used in the calculation of the desired properties. The accuracy of $\tilde{H}_m$ will be worse than that of the p-V-T data as a result of the derivative term $(\partial\tilde{V}_m/\partial T)_p$ in formula (1.3). Moreover, the heat of mixing is usually much smaller than the total enthalpy of the mixture $\tilde{H}_m$. This is shown in fig. 1.1, where $\tilde{H}^{res}$ is plotted against the mole fraction of argon x_A for the system CH_4-A at 201°K and 60 atm.

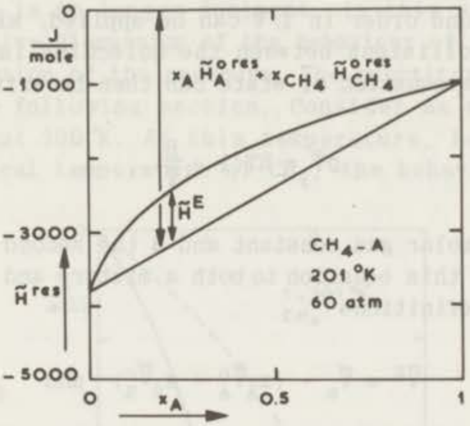


Fig. 1.1.

$\tilde{H}^E$ compared with the residual enthalpy of an ideal gaseous mixture $\tilde{H}_m^{res\ id}$.

The straight line represents the molar residual enthalpy of an ideal mixture $\tilde{H}_m^{res\ id}$ and the curved line the molar residual enthalpy of the mixture $\tilde{H}_m^{res}$. Thus, the smallness of $\tilde{H}^E$ results in a further decrease of accuracy. These considerations lead to the idea of measuring the heat of mixing directly. Good accuracy in $\tilde{H}^E$ is very important for economical design of gas separation, gas purification and cryogenic processes, since uncertainties in enthalpy data usually lead to increased costs. This has been recognized earlier: in 1960 professor W.C. Edmister estimated the costs as a result of the "enthalpy ignorance" for the immediate future of the U.S.A., to be \$ 1,500,000 annually (cf. RUHEMANN[4]).

Hitherto experiments on the heat of mixing of the gaseous mixtures N_2-A, H_2-N_2 and H_2-A have been performed by KNOESTER et al.[1]. For the same mixtures the volume change on mixing V^E has been experimentally determined by ZANDBERGEN and BEENAKKER[5].
We will now consider the behaviour of the heat of mixing. In the discussion of the heat of mixing as a function of the density we

will make a distinction between mixtures at low and at high densities. This distinction is useful since at low densities the behaviour of the mixture can simply be derived by considering only binary collisions of the molecules. At high density the behaviour becomes more complicated. It turns out, however, that the behaviour of the gaseous mixtures can then be described satisfactorily with theories developed for liquid mixtures.

For lower densities a virial equation of state neglecting terms higher than second order in $1/\tilde{V}$ can be applied, since the effect of the binary collisions between the molecules is dominant. The Kamerlingh Onnes equation of state can then be written as

$$p\tilde{V} = RT\left(1 + \frac{B}{\tilde{V}}\right) , \tag{1.7}$$

where R is the molar gas constant and B the second virial coefficient. Applying this equation to both a mixture and its components and using the definitions

$$\begin{aligned} \tilde{V}^E &\equiv \tilde{V}_m - (x_A\tilde{V}^o_A + x_B\tilde{V}^o_B) \quad \text{and} \\ B^E &\equiv B_m - (x_A B_{AA} + x_B B_{BB}) \end{aligned} \tag{1.8}$$

one can derive,

$$\tilde{V}^E = B^E . \tag{1.9}$$

The mixture virial coefficient B_m is composed of the contributions of the three kinds of interaction of the molecules A and B,

$$B_m = x_A^2 B_{AA} + 2x_A x_B B_{AB} + x_B^2 B_{BB} . \tag{1.10}$$

With eq. (1.8) one gets

$$B^E = 2x_A x_B E ,$$

where

$$E \equiv B_{AB} - ½(B_{AA} + B_{BB}) .$$

Thus for low densities eq. (1.6) can be written as

$$\tilde{H}^E = 2x_Ax_Bp(E - T\frac{dE}{dT}) \qquad (1.11)$$

Since E is only a function of the temperature, the excess enthalpy $\tilde{H}^E$ is proportional to the pressure and parabolic in the mole fraction.

In mixtures of high density, the behaviour of the excess enthalpy cannot be described by eq. (1.11), since the effect of the binary collisions is no longer dominant. In this section we give only a qualitative discussion of the behaviour of the excess enthalpy as a function of the pressure. The quantitative discussion is given in the following section. Consider as an example the mixture He-CH_4 at 200°K. At this temperature, being only 10°K above the critical temperature of CH_4, the behaviour of CH_4 is

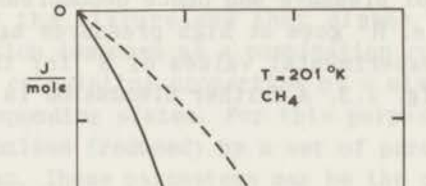


Fig. 1.2.

$\tilde{H}^{res}$ of pure CH_4.

——————— $\tilde{H}^{res}$ as a function of p

– – – – – – – – – – $\tilde{H}^{res}$ as a function of ½p nearly critical, whereas that of He is nearly ideal. On mixing the precritical state of methane is destroyed. If the contributions to the enthalpy of the He-He interaction and the He-CH_4 interaction are neglected, the mixing can be represented in the most simple way by an expansion of methane from its initial pressure p to its partial pressure $p_{CH_4} = x_{CH_4}\,p$. The molar excess enthalpy of a methane mixture with mole fraction x_{CH_4} becomes in that case:

$$\tilde{H}^E(x,p,T) = x_{CH_4}\{\tilde{H}^{res}_{CH_4}(x_{CH_4}p,T) - \tilde{H}^{res}_{CH_4}(p,T)\}. \qquad (1.12)$$

In fig. 1.2 this is illustrated for a 1:1 mixture. The difference between the two lines in the $\tilde{H}^{res}$-direction gives twice the molar excess enthalpy. In fig. 1.3 this excess enthalpy is plotted against p. The maximum in $\tilde{H}^E$ occurs because $\tilde{H}^{res}$ of methane becomes independent of pressure and hence decompression gives no effect on $\tilde{H}^{res}$, i.e. $\tilde{H}^E$ goes at high pressures again to zero. For comparison the experimental values of $\tilde{H}^E$ for the system He-CH_4 are plotted in fig. 1.3. A further discussion is given in section 2.5.

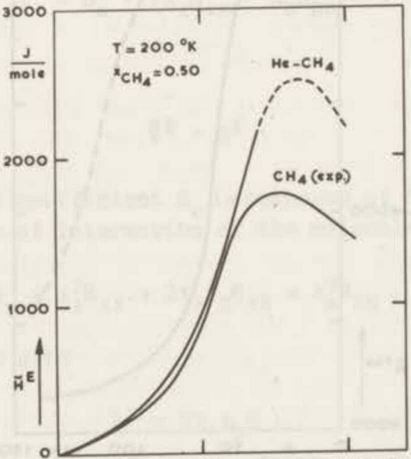


Fig. 1.3.

$\tilde{H}^E$ obtained from experiment for the system He-CH_4;
$\tilde{H}^E$ obtained from CH_4-expansion.

1.3 *Methods of calculating the excess enthalpy*

In the previous section a qualitative description is given of the behaviour of a mixture at high density. We will now examine some more quantitative approaches.
Theories of mixtures start from a knowledge of the properties of the pure components and are mainly based on equations of state or on a law of corresponding states.
Two of the best-known equations of state are the many-constants equation of BENEDICT, WEBB and RUBIN$^{6)}$ and the virial equation of KAMERLINGH ONNES$^{7)}$. With a suitable choice of constants these equations can give a description of the thermodynamic behaviour of pure gases. The constants of the equations of state are determined from experimental p-V-T data. To obtain a useful equation of state for mixtures, it is necessary to have a relation between the constants of the mixture and that of the pure components (such a prescription is known as a combination rule).
The other way of calculating properties of a mixture starts from the law of corresponding states. For this purpose the properties are made dimensionless (reduced) by a set of parameters characteristic for the gas. These parameters may be the critical pressure p_c, volume V_c and temperature T_c or the interaction parameters e.g. ϵ and σ from the Lennard-Jones potential (cf. form. (1.13)). Fluids of a simple molecular structure obey a law of corresponding states, i.e. that for instance the reduced enthalpy as a function of the reduced temperature and pressure of one gas equals the reduced enthalpy as a function of the same reduced temperature and pressure of another gas. If the mixture is assumed to obey the law of corresponding states, a reduced equation of state can be formed with variables reduced with the parameters of the mixture. Prescriptions can be found to obtain these parameters from those of the pure components. A survey of combination rules for the critical constants of a mixture (pseudo-critical constants) has been given by REID and LELAND$^{8)}$. PRIGOGINE$^{9)}$ and SCOTT$^{10)}$ have proposed rules for finding the parameters $<\epsilon>$ and $<\sigma>$ for liquid mixtures by an averaging procedure over the interaction of a molecule with its neighbours. The quantitative approach based on these "liquid" theories was successfully applied to gaseous mixtures by KNOESTER and BEENAKKER$^{11)}$. We will discuss the "liquid" theory in short.

The features underlying this theory are
a. The interaction potential is assumed to be of the form $\epsilon f(\sigma/r)$

for each of the pairs (A-A, A-B and B-B). Furthermore, as usual additivity of these potentials is assumed. For the potential the well-known Lennard-Jones (6-12) potential is chosen:

$$\phi_{ij}(r) = 4\epsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right\} \tag{1.13}$$

with parameters ϵ_{AA}, σ_{AA}, ϵ_{BB}, σ_{BB}, ϵ_{AB} and σ_{AB} for the interactions of the molecules A and B of a mixture. In this L.-J. potential, r is the intermolecular distance, σ_{ij} is a characteristic length ($\phi(\sigma) = 0$) and ϵ_{ij} is a characteristic energy.
For unlike pairs we assume the usual rules,

$$\sigma_{AB} = \tfrac{1}{2}(\sigma_{AA} + \sigma_{BB}) \quad \text{and} \tag{1.14}$$

$$\epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{\frac{1}{2}} \tag{1.15}$$

b. The same reduced equation of state is assumed to be valid for the pure components and the mixture.

Three "liquid" models, from which the parameters describing a mixture are obtained, will be discussed in brief.

A. "Single-liquid" model

The "single-liquid" model starts from the assumption that the mixture can be considered as a single liquid characterized by parameters $<\epsilon>$ and $<\sigma>$ determined by the average environment. The average potential $<\phi(r)>$ is assumed to be the sum of A-A, A-B and B-B interactions in the appropriate proportions, which can be represented by a L.-J.(6-12) potential. The average potential can then be written as a L.-J. potential with the average parameters:

$$<\epsilon> = \frac{(x_A^2\epsilon_{AA}\sigma_{AA}^6 + 2x_Ax_B\epsilon_{AB}\sigma_{AB}^6 + x_B^2\epsilon_{BB}\sigma_{BB}^6)^2}{x_A^2\epsilon_{AA}\sigma_{AA}^{12} + 2x_Ax_B\epsilon_{AB}\sigma_{AB}^{12} + x_B^2\epsilon_{BB}\sigma_{BB}^{12}} \tag{1.16}$$

$$<\sigma> = \left(\frac{x_A^2\epsilon_{AA}\sigma_{AA}^{12} + 2x_Ax_B\epsilon_{AB}\sigma_{AB}^{12} + x_B^2\epsilon_{BB}\sigma_{BB}^{12}}{x_A^2\epsilon_{AA}\sigma_{AA}^{6} + 2x_Ax_B\epsilon_{AB}\sigma_{AB}^{6} + x_B^2\epsilon_{BB}\sigma_{BB}^{6}}\right)^{1/6} \tag{1.17}$$

B. "Two-liquid" model (Prigogine's refined version II)

In the "single-liquid" model no distinction is made between the interactions of molecule A with neighbours and those of molecule

B with surrounding particles. In the "two-liquid" model, however, two hypothetical liquids are distinguished: one with molecules A interacting with molecules A and B (A-centered liquid) and one with molecules B interacting with molecules A and B (B-centered liquid). These two liquids are characterized by the average parameters $\langle\epsilon\rangle_A$, $\langle\sigma\rangle_A$ and $\langle\epsilon\rangle_B$, $\langle\sigma\rangle_B$, respectively. The mixture behaves as a weighted average of these liquids. The average potential of the A- and B- centered liquids can be written as a L.-J. potential with the average parameters:

$$\langle\epsilon\rangle_A = \frac{(x_A\epsilon_{AA}\sigma_{AA}^6 + x_B\epsilon_{AB}\sigma_{AB}^6)^2}{x_A\epsilon_{AA}\sigma_{AA}^{12} + x_B\epsilon_{AB}\sigma_{AB}^{12}} \tag{1.18}$$

$$\langle\sigma\rangle_A = \left(\frac{x_A\epsilon_{AA}\sigma_{AA}^{12} + x_B\epsilon_{AB}\sigma_{AB}^{12}}{x_A\epsilon_{AA}\sigma_{AA}^6 + x_B\epsilon_{AB}\sigma_{AB}^6}\right)^{1/6} \tag{1.19}$$

and $\langle\epsilon\rangle_B$ and $\langle\sigma\rangle_B$ similarly.

C "Three-liquid" model.

The "three-liquid" model distinguishes three isolated pair interactions A-A, A-B and B-B. This model is a low-density approach, since the pairs do not influence each other. The mixture is then regarded as made up of three independent "liquids" each with the set parameters ϵ_{AA}, σ_{AA}; ϵ_{BB}, σ_{BB} and ϵ_{AB}, σ_{AB}. The first two sets are the parameters of the pure components and the latter set is given by relations (1.14) and (1.15).

Examples of the relations between the average parameters and the mole fraction is given in four diagrams. In fig. 1.4 and fig. 1.5 the parameters $\langle\sigma\rangle$, calculated with the "single-" and "two-liquid" models, are plotted against the mole fraction of the heavier component for the systems CH_4-N_2 and He-CH_4, respectively. In figs. 1.6 and 1.7 the parameters $\langle\epsilon\rangle/k$ are plotted against the mole fraction for the same systems. These parameters are calculated by means of the relations (1.16), (1.17), (1.18) and (1.19). From these relations it follows that, for $x_A = 0$,

$$\langle\epsilon\rangle_A = \epsilon_{AB} \quad \text{and} \quad \langle\sigma\rangle_A = \sigma_{AB}$$

and for $x_B = 0$,

$$\langle\epsilon\rangle_B = \epsilon_{AB} \quad \text{and} \quad \langle\sigma\rangle_B = \sigma_{AB}$$

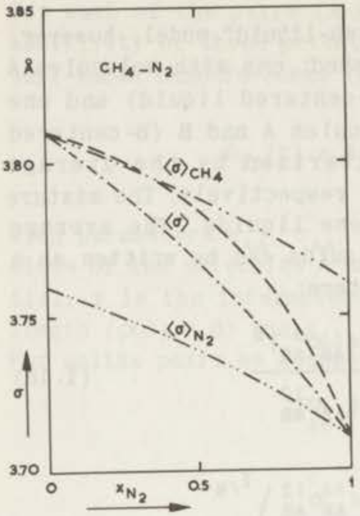


Fig. 1.4.

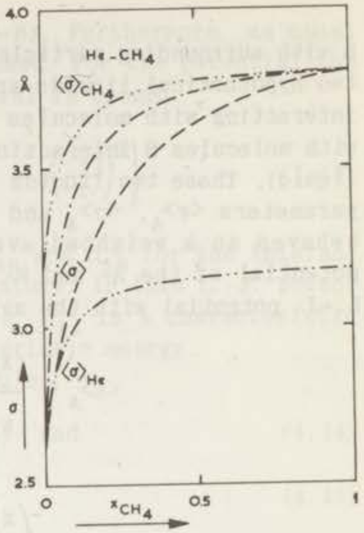


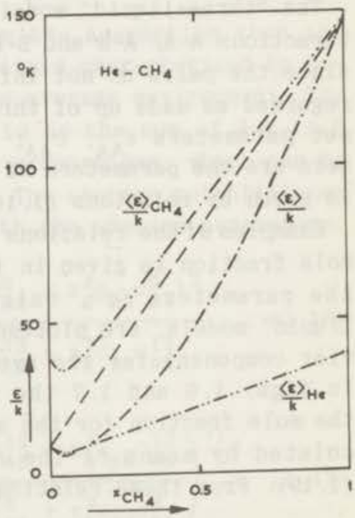
Fig. 1.5.

The calculated parameter σ as a function of the mole fraction.

— — — — — — the Kay-rules

—.—.—.— the "single-liquid" model

—..—..—..— the "two-liquid" model



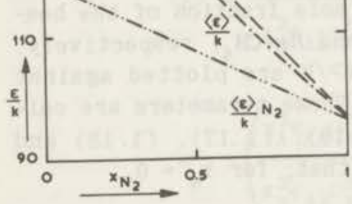


Fig. 1.6.

Fig. 1.7.

The calculated parameter ϵ/k as a function of the mole fraction.

— — — — — — the Kay-rules

—.—.—.— the "single-liquid" model

—..—..—..— the "two-liquid" model

In the beginning of this section T_c and p_c were also mentioned as reduction parameters. KAY$^{12)}$ has introduced combination rules for these critical constants, e.g.:

$$\langle p_c \rangle = x_A (p_c)_A + x_B (p_c)_B \qquad \text{and}$$

$$\langle T_c \rangle = x_A (T_c)_A + x_B (T_c)_B$$

Assuming that the law of corresponding states is valid for the mixture and its components, the Kay-rules can be expressed in intermolecular parameters by

$$\langle \sigma \rangle = \sigma_{AA} \sigma_{BB} \left(\frac{x_A \epsilon_A + x_B \epsilon_B}{x_A \epsilon_A \sigma_B^3 + x_B \epsilon_B \sigma_A^3} \right)^{1/3} \qquad \text{and}$$

$$\langle \epsilon \rangle = x_A \epsilon_{AA} + x_B \epsilon_{BB}$$

The last two relations are drawn as broken lines in figs. 1.4, 1.5 and 1.6, 1.7, respectively. The Kay-rules are a good approximation for the "single-liquid" model, if the mixture is composed of gases that have comparable values for both ϵ and σ, like CH_4-N_2 in figs. 1.4 and 1.6. For the system He-CH_4 in figs. 1.5 and 1.7, where the differences of the values for ϵ as well as for σ are large, deviations of the curves $\langle \epsilon \rangle$ and $\langle \sigma \rangle$ from the Kay-rules can be expected. Moreover one of the components of the latter mixture is He, for this gas the law of corresponding states shows deviations as a result of quantum effects. Therefore, in practice these rules cannot be applied for systems like He-CH_4.

1.4 The systems considered

The work described in this thesis concerns isobaric measurements of the heat of mixing as a function of pressure p, temperature T and mole fraction x of the gaseous mixtures CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 and He-A. The experiments are an extension of the research of KNOESTER et al.$^{1)}$, which dealt with mixtures composed of gases H_2, N_2 and A, of which only the last one has spherical molecules. We have added to these three gases CH_4, because of its spherical form and its industrial importance, and the noble gas He. The systems composed of these five gases are reported in table 1.I.

TABLE 1.I

The program performed of $\tilde{H}^E$ and $\tilde{V}^E$ determinations on binary mixtures

	H_2	He	CH_4	N_2	A
H_2					
He					
CH_4	X	X			
N_2	O		X		
A	O	X	X	O	

O { $\tilde{H}^E$ exp. KNOESTER, et al. 1)
{ $\tilde{V}^E$ exp. ZANDBERGEN, et al. 5)

X These $\tilde{H}^E$ experiments

These are the only systems for which the heat of mixing and volume change on mixing have been determined experimentally up till now. The following considerations underlie the choice of the systems.

Values calculated from the "liquid" theories shall be compared with the experimentally obtained values. These theories hold only for spherical non-polar molecules. Most of the gases chosen have spherical and non-polar molecules. The system He-A is interesting because of the large difference in size of the helium and argon molecules and since the mixture is composed of noble gases. The systems CH_4-N_2 and H_2-CH_4 consist of molecules of comparable size and interaction and of molecules with a large difference in size and interaction, respectively. The systems CH_4-N_2 and He-CH_4 are of great importance in industry, the first system for processes to separate N_2 from natural gas and the second one for the winning of helium. The system CH_4-A makes a mutual comparison of a number of methane mixtures possible. A short survey of the experiments and a theoretical discussion have already been given by BEENAKKER, VAN EIJNSBERGEN, KNOESTER, TACONIS and ZANDBERGEN 13).
In the first part of chapter 2 the heat of mixing apparatus and the method of measuring are described. Tabulated values and plots

of the heat of mixing as a function of pressure for temperatures between 170 and 293°K and at three compositions of the above mentioned mixtures are given and discussed in the final part of this chapter.

Chapter 3 deals with the calculation of the excess enthalpy of the five systems with the aid of the earlier mentioned "liquid" models and a comparison is made between the calculated values and the experimentally obtained values of the excess enthalpy.

Since the calculations of the excess enthalpy with the "liquid" models are based on the law of corresponding states it is interesting to know how far this law holds for the gases considered. This is checked for the gases A, N_2 and CH_4 in chapter 4, by comparing the reduced enthalpies as a function of reduced pressure and reduced temperature. Furthermore the compressibility factors of the gases A, CH_4, N_2 and Xe are compared.

While calculating excess enthalpies, we found that a handy survey of thermodynamic data of the most commonly used gases is lacking, a table reporting these data is inserted in chapter 5. The table gives the publications with thermodynamic properties for the gases normal-hydrogen, para-hydrogen, helium, methane, neon, nitrogen, carbon monoxyde, oxygen, argon and xenon.

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CHAPTER 2

MEASUREMENTS OF THE ISOBARIC HEAT OF MIXING FOR GASEOUS MIXTURES CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 AND He-A BETWEEN 170 AND 293°K AND AT PRESSURES UP TO 120 ATM.

2.1 Introduction

The determination of the heat of mixing, $\tilde{H}^E$, has been performed with the flow calorimeter constructed by KNOESTER, TACONIS and BEENAKKER. For a full description of the apparatus the reader is referred to their original paper[1]. In this apparatus the mixing takes place at constant pressure, hence one determines the isobaric heat of mixing. An important advantage of the calorimeter is the possibility of performing isothermal experiments, thus avoiding e.g. calibration problems of the thermometers. Another advantage of this type of calorimeter is the large series of measurements which can be done in a relatively short time. A disadvantage is the large amount of gas needed for a series of measurements. A series of $\tilde{H}^E$ determinations at one temperature and mole fraction over a pressure range of 100 atm. requires e.g. about 2 m^3 gas N.T.P.. As a result expensive gases like neon, xenon, etc. are not suitable for determinations in flow calorimeters without extensive provisions in connection with gas separation.

The systems considered here are the binary gaseous mixtures CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 and He-A. The heat of mixing of these systems is positive for the studied temperatures; this means that the gases cool upon mixing and that isothermal measurements are possible. The measurements of the heat of mixing of the systems have been performed at the temperatures 201, 231 and 293°K (for He-A mixture also at 169.5°K), at mole fractions of about 0.25, 0.50 and 0.75 and in a pressure range from 10 atm. up to 120 atm. The results of these measurements are represented in tables and graphs. This chapter is concluded with an examination of the sources of error in the measurements and with a discussion of the experimental results.

2.2 Description of the experimental set-up

The experimental determination of the heat of mixing runs essentially as follows. Two gases enter a mixing chamber, where the mixing takes place. To obtain an isothermal process a proper amount of heat is supplied to compensate the cooling upon mixing. The heat of mixing per mole of mixture can be calculated from this heat supply and the collected amount of gas.

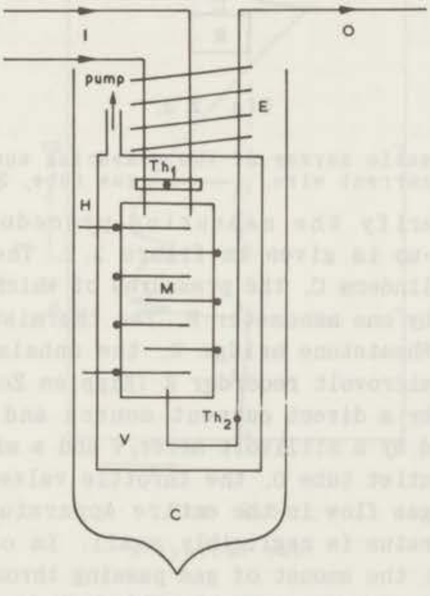

Fig. 2.1.

A schematic diagram of the heat of mixing apparatus.

A schematic diagram of the heat of mixing apparatus is given in figure 2.1. This calorimeter consists of a copper vessel, the mixing chamber M, which is enclosed in a vacuum can V. Both the inlet tubes I and the outlet tube O are spiralled together, forming the heat exchanger E. The entire apparatus, i.e. the vacuum can V and the heat exchanger E, is placed into the cryostat C, which is filled with a cooling liquid. Around M a resistance wire has been wound. This heater H is used to warm up the gas mixture in order to compensate for the cooling that occurs on mixing. The temperatures before and after mixing are measured with the thermistors Th_1 and Th_2 (Keystone Carbon Co), respectively.

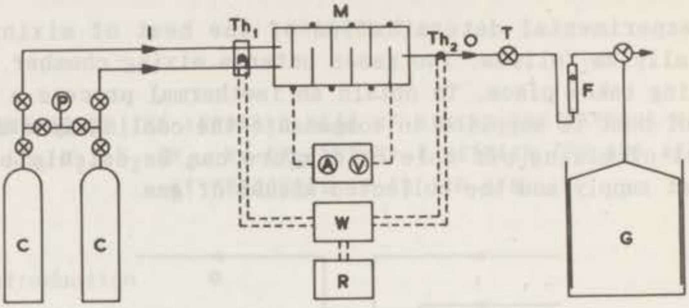

Fig. 2.2.

A schematic survey of the measuring equipment.
- - - current wire, ——— gas tube, ⊗ valve.

In order to clarify the measuring procedure a schematic experimental set-up is given in figure 2.2. The pure gases are stored in two cylinders C, the pressures of which can be compared with each other by one manometer P. The thermistors Th_1 and Th_2 are placed in a Wheatstone bridge W, the unbalance of which is registered by a microvolt recorder R (Kipp en Zonen, Delft). The heater H is fed by a direct current source and the electrical power is measured by a millivolt meter V and a milliammeter A. At the end of the outlet tube O, the throttle valve T regulates the velocity of the gas flow in the entire apparatus. The pressure drop in the apparatus is negligibly small. In order to measure the gas flux, i.e. the amount of gas passing through the apparatus per unit time, the mixture can be collected in the gasometer G. The flow meter F indicates roughly the flow velocity of the gas mixture. The temperatures 169.5 and 231°K are maintained by the liquids ethylene and propane respectively, boiling at atmospheric pressure. The temperature of 293°K is realised by using a water thermostat (Colora, Germany). Finally propane, boiling under a pressure of 16 cm Hg, maintains a temperature of 201°K. This pressure is controlled automatically, using a system described earlier$^{1)}$.

2.3 *Measuring method*

During the experimental run the temperature of the mixture which leaves the mixing chamber is registered by the thermistor Th_2 on the recorder R. Figure 2.3 represents an actual measuring run, where time t is plotted vertically and temperature T horizontally.

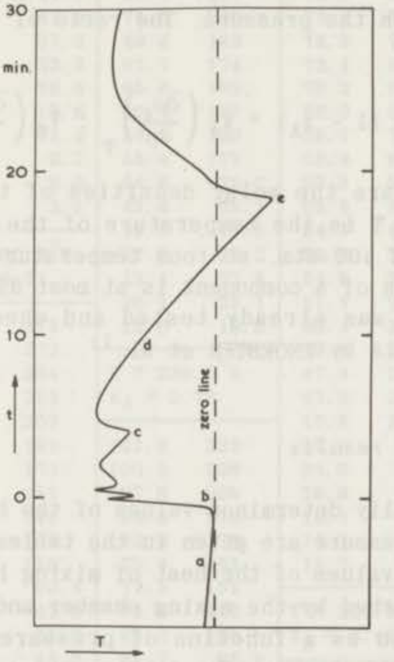

Fig. 2.3.

A typical run.

The temperature T of the flowing pure gas is registered by the recorder as a straight vertical line a in figure 2.3. At point b the cooling on mixing takes place. This effect is compensated for by supplying a constant heating power P. The temperature course is then represented by curve cde. At the intersection of the curve with the zero line the temperature of the mixture is equal to that of the incoming gases. A small part of the heating power is used to heat the mixing chamber. Its value is (dT/dt)C, where dT/dt is the slope of line d and C the heat capacity of the mixing chamber. Hence the molar heat of mixing becomes:

$$\tilde{H}^E(p, T, x) = \frac{1}{D}\left(P - \frac{dT}{dt}C\right), \qquad (2.1)$$

where D is the gas flux (in moles per unit time).

Since the gases leave the cylinders at equal pressure the volumes V_A and V_B of the cylinders C_A and C_B determine in first approximation the mole fractions of the mixture. Since, however, the gases have different compressibilities, the mole fractions depend slightly on the pressure. The ratio of the mole fractions at pressure p is

$$x_A : (1 - x_A) = V_A \left(\frac{\partial \rho_A}{\partial p}\right)_T : V_B \left(\frac{\partial \rho_B}{\partial p}\right)_T \qquad (2.2)$$

where ρ_A and ρ_B are the molar densities of the gases A and B, respectively and T is the temperature of the cylinders. Over a pressure range of 100 atm. at room temperature the variation of the mole fractions of a component is at most 8% (H_2-CH_4 system).

The apparatus was already tested and checked for possible undesirable effects by KNOESTER et al.[1].

2.4 *Experimental results*

The experimentally determined values of the heat of mixing as a function of the pressure are given in the tables 2.I, 2.II, 2.III, 2.IV and 2.V. The values of the heat of mixing have been corrected for the heat absorbed by the mixing chamber and for variations in the mole fraction as a function of pressure, as discussed in section 2.3 of this chapter. The tables give a complete survey of the experimentally determined $\tilde{H}^E$ values of the five systems CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 and He-A. The latter system has been investigated at 169.5, 201, 231 and 293°K and the other systems at 201, 231 and 293°K. The mole fractions are roughly 0.25, 0.50 and 0.75, the precise mole fraction is given in the tables. The experiments are performed at pressures varying from 10 to 120 atm. Note that each measured value of the excess enthalpy undergoes no other corrections than the two mentioned above. For the 1:1 composition graphs have been made in which $\tilde{H}^E$ is plotted against p for the five systems (cf. figs. 2.4, 2.5, 2.6, 2.7 and 2.8).

There are several possible sources of error in the experimental determination of the heat of mixing. We will discuss the most important ones.

TABLE 2.I

The experimental values of the molar excess enthalpy $\tilde{H}^E$ of the system CH_4-A

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	p atm	$\tilde{H}^E$ J/mole
T = 293.0°K		85.3	52.3	84.5	263	79.6	555	65.4	903
x_A = 0.21		77.2	47.0	82.8	250	78.3	610	55.1	471
		70.9	41.9	71.6	200	75.2	709	53.9	429
101.1	68.8	64.8	37.6	69.4	185	74.3	723	52.1	367
95.3	65.2	58.6	33.3	67.7	174	72.1	810	50.8	333
90.0	58.8	51.9	26.5	65.6	163	70.2	871	49.4	296
73.6	42.1	40.6	17.6	60.7	137	68.2	924	40.6	148
67.7	37.6	32.3	13.4	58.2	129	59.7	715	38.9	136
61.0	32.2	26.4	9.7	55.4	113	58.4	634	37.1	122
52.3	26.7	20.2	6.8	44.6	76.0	57.3	579	34.7	107
45.5	22.1	9.9	2.1	43.4	68.1	55.5	454	21.0	44.6
38.7	17.8			29.5	41.5	54.1	403	18.7	36.0
31.3	16.1	T = 230.5°K		27.0	31.2	52.8	353	16.6	29.1
30.8	14.3	x_A = 0.21		23.1	27.8	51.9	315	13.9	23.3
23.8	10.0			20.1	23.1	51.1	297		
16.0	6.2	106.8	275	16.6	18.0	50.1	269	T = 201.0°K	
7.6	2.5	102.3	272			49.2	252	x_A = 0.75	
		99.1	264	T = 230.5°K		47.3	214		
T = 293.0°K		95.7	253	x_A = 0.75		47.3	208	102.9	321
x_A = 0.48		83.5	209			45.8	175	98.6	345
		79.4	191	101.5	235	39.0	98.2	94.8	383
107.4	105.2	75.5	173	100.6	226	36.0	79.5	91.4	425
104.0	99.2	72.4	157	97.8	209	28.8	51.1	73.0	567
102.3	98.6	69.9	146	96.5	218	20.1	26.1	70.2	577
97.0	91.2	66.8	129	82.8	174	14.1	16.4	70.0	572
91.8	85.2	64.2	118	79.4	161	11.7	11.7	68.7	570
82.5	73.3	53.4	80.4	77.1	151			67.6	558
79.2	68.9	46.8	61.9	73.6	140	T = 201.0°K		66.6	556
76.4	66.3	43.5	51.7	65.3	108	x_A = 0.48		65.4	533
72.9	61.9	39.8	45.2	61.7	95.9			61.9	461
68.3	56.8	34.2	35.0	57.9	86.8	112.7	188	58.5	335
58.1	47.3	24.8	22.7	53.2	75.8	112.6	205	56.5	288
52.3	40.2	20.1	15.7	45.0	53.8	111.7	201	54.6	251
34.0	22.3	13.5	9.5	39.8	42.3	110.5	211	51.8	203
28.4	19.4	8.7	5.7	33.5	35.3	109.6	230	39.8	80.6
21.3	13.6			23.7	22.4	107.9	255	35.0	69.2
17.2	11.4	T = 230.5°K		17.8	15.3	105.8	280	32.5	54.0
15.0	11.7	x_A = 0.48		12.6	9.4	96.4	412	22.1	29.7
10.4	6.0			5.5	5.1	86.8	638	17.2	18.2
		98.5	356			85.6	685	14.5	13.6
T = 293.0°K		96.9	344	T = 201.0°K		84.7	711	7.6	8.3
x_A = 0.75		96.3	345	x_A = 0.21		72.9	945		
		94.2	328			69.8	963		
105.7	68.6	88.2	290	103.2	112	69.0	977		
99.3	64.6	87.4	295	100.7	128	67.7	981		
94.5	61.1	86.2	282	81.3	465	66.8	947		
90.0	56.6	85.0	276						

TABLE 2.II

The experimental values of the molar excess enthalpy $\tilde{H}^E$ of the system CH_4-N_2

p atm	$\tilde{H}^E$ J/mole
$T = 293.1\ ^{\circ}K$ $x_{N_2} = 0.19$	
108.4	108
99.8	88.6
91.9	79.1
74.3	58.2
67.8	51.7
60.8	43.7
39.2	19.6
39.0	23.7
21.2	9.5
14.0	4.1
$T = 293.1\ ^{\circ}K$ $x_{N_2} = 0.44$	
108.7	144
104.3	135
99.3	128
92.2	117
87.8	110
86.2	101
80.9	92.6
75.5	83.5
72.9	81.3
66.7	71.7
59.4	61.2
45.7	40.7
38.8	32.7
31.4	23.6
25.2	18.1
17.7	10.0
$T = 293.1\ ^{\circ}K$ $x_{N_2} = 0.72$	
107.7	105
102.0	99.1
94.5	88.6
85.4	77.7
77.7	69.8
50.2	38.4
43.4	32.3
34.0	24.0
21.9	14.7
$T = 231.7\ ^{\circ}K$ $x_{N_2} = 0.19$	
108.8	430
104.6	401
99.2	372
85.8	288
82.9	269
79.2	243
75.8	222
59.7	133
54.8	105
49.6	84.3
44.0	65.0
32.8	37.0
25.7	25.3
18.4	16.1
$T = 231.7\ ^{\circ}K$ $x_{N_2} = 0.44$	
109.3	521
107.1	514
104.3	503
101.3	487
91.5	432
89.0	406
86.7	389
83.9	363
69.1	246
66.0	216
62.5	193
58.4	167
54.9	149
46.2	107
42.6	92.1
37.9	75.2
32.4	58.9
28.6	48.8
24.0	38.6
18.1	26.8
12.9	17.9
$T = 231.7\ ^{\circ}K$ $x_{N_2} = 0.72$	
104.3	339
101.1	328
98.0	314
93.7	297
90.4	276
77.9	214
73.6	189
68.9	167
64.3	145
60.3	125
51.0	93.4
45.5	77.4
39.4	60.9
31.6	45.3
25.5	32.6
17.5	21.9
$T = 201.2\ ^{\circ}K$ $x_{N_2} = 0.19$	
107.5	366
103.1	421
84.4	695
80.4	828
78.8	882
76.0	975
65.7	1303
63.9	1311
62.0	1241
56.5	789
55.1	668
53.7	574
52.4	496
50.6	415
49.1	355
44.4	221
41.9	176
39.0	142
36.4	117
33.0	92
$T = 201.2\ ^{\circ}K$ $x_{N_2} = 0.44$	
92.1	898
86.9	982
74.2	1218
72.1	1216
69.2	1196
68.8	1244
64.1	1165
61.1	1053
58.8	901
57.2	763
54.9	611
52.2	479
36.2	143
30.5	98
24.3	64.9
$T = 201.2\ ^{\circ}K$ $x_{N_2} = 0.72$	
105.3	563
103.8	572
101.5	593
83.6	705
81.6	710
76.3	749
62.4	714
60.4	649
58.7	585
57.1	509
55.7	440
53.5	365
51.9	310
49.2	256
41.6	142
37.8	107
33.5	81.4
29.4	61.4
24.6	43.5

TABLE 2.III

The experimental values of the molar excess enthalpy $\tilde{H}^E$ of the system H_2-CH_4

$T = 292.5\,^{\circ}K$, $x_{CH_4} = 0.27$

p atm	$\tilde{H}^E$ J/mole
114.9	292
109.5	295
104.8	280
99.8	258
99.5	267
94.7	255
87.7	232
82.8	224
78.5	204
72.3	188
65.8	173
62.7	161
60.2	150
55.6	140
49.9	129
46.4	117
44.8	117
41.3	100
38.7	96.6
33.2	80.7
24.4	59.7
23.9	56.4
19.5	46.1
16.3	40.7
11.2	30.4
10.2	27.9
8.1	22.1

$T = 292.5\,^{\circ}K$, $x_{CH_4} = 0.56$

p atm	$\tilde{H}^E$ J/mole
110.5	392
105.7	381
88.1	308
83.5	298
78.9	285
67.9	242
62.3	213
57.2	185
56.3	189
52.9	168
52.3	171
47.7	153
42.5	134
32.6	101
26.9	80.9
23.2	66.5
20.5	58.1
13.9	39.8
9.8	28.0

$T = 292.5\,^{\circ}K$, $x_{CH_4} = 0.81$

p atm	$\tilde{H}^E$ J/mole
110.1	307
108.0	293
107.4	290
78.4	192
73.5	179
65.1	147
57.1	127
55.6	122
52.6	113
46.1	97.4
35.2	71.0
27.7	53.7
16.8	21.4

$T = 230.6\,^{\circ}K$, $x_{CH_4} = 0.27$

p atm	$\tilde{H}^E$ J/mole
113.3	695
108.4	688
106.8	685
104.9	676
100.1	643
97.1	622
93.8	592
90.2	566
87.8	546
83.4	506
80.2	477
75.9	436
72.8	409
61.3	312
53.0	259
45.7	204
42.0	168
36.2	155
32.2	130
27.4	105
21.8	82.3
16.8	58.7
12.3	45.4
9.9	22.8

$T = 230.6\,^{\circ}K$, $x_{CH_4} = 0.56$

p atm	$\tilde{H}^E$ J/mole
119.7	1076
117.8	1145
116.5	1153
116.0	1129
114.6	1127
113.7	1126
113.0	1129
100.6	1033
98.4	1007
97.5	962
84.0	778
82.3	808
79.1	726
77.5	693
75.1	665
73.5	636
71.1	602
60.2	449
57.8	420
55.6	397
53.9	370
43.4	270
41.7	250
37.9	222
35.6	205
32.3	184
20.3	105
17.5	85.2
14.9	73.0
12.4	60.7

$T = 230.6\,^{\circ}K$, $x_{CH_4} = 0.81$

p atm	$\tilde{H}^E$ J/mole
119.9	1141
119.3	1137
117.8	1141
116.8	1143
114.3	1154
112.7	1159
110.7	1149
100.2	926
98.7	911
96.8	898
95.8	875
93.4	830
91.1	809
88.8	779
85.2	736
81.9	690
79.5	665
77.3	628
74.8	574
72.5	549
70.0	535
68.1	518
48.1	313
44.7	257
41.7	235
38.7	215
36.1	179
30.3	146
26.4	126
24.0	112
21.4	84.3
16.9	67.3
13.9	57.1

$T = 201.2\,^{\circ}K$, $x_{CH_4} = 0.28$

p atm	$\tilde{H}^E$ J/mole
60.3	854
58.3	769
56.8	692
54.4	612
38.2	284
34.9	235
31.6	201
28.6	169
24.6	142
22.1	118
18.8	95.3
13.8	68.2
9.6	54.3

$T = 201.2\,^{\circ}K$, $x_{CH_4} = 0.56$

p atm	$\tilde{H}^E$ J/mole
51.6	816
49.9	729
48.1	655
46.7	592
45.2	552
27.3	217
25.0	188
23.1	160
21.0	141
18.2	111
16.3	100
14.4	81.5

$T = 201.2\,^{\circ}K$, $x_{CH_4} = 0.81$

p atm	$\tilde{H}^E$ J/mole
58.1	1169
55.8	1000
53.9	872
51.7	724
50.5	611
47.9	542
38.8	309
35.7	259
32.7	219
28.3	182
25.5	145
23.9	131
20.6	98.6
16.3	74.9
12.4	50.7

TABLE 2.IV

The experimental values of the molar excess enthalpy $\tilde{H}^E$ of the systems He-CH_4

p atm	$\tilde{H}^E$ J/mole
T = 293.1 °K	x_{CH_4} = 0.28
100.1	433
97.0	410
93.0	401
82.0	353
77.3	326
72.5	307
66.0	289
54.8	232
48.4	204
44.6	188
40.1	169
32.0	134
24.9	105
20.4	84.7
16.2	74.3
12.9	62.6
T = 293.1 °K	x_{CH_4} = 0.56
101.3	575
95.4	538
72.1	398
64.3	342
58.1	312
50.8	281
45.8	250
32.9	173
19.3	102
13.2	82.7
T = 293.1 °K	x_{CH_4} = 0.81
101.7	422

p atm	$\tilde{H}^E$ J/mole
98.7	409
96.0	391
87.8	350
85.0	340
82.0	328
79.4	309
71.3	280
68.6	265
66.4	252
58.6	218
54.8	207
51.3	190
46.8	172
43.3	156
40.8	139
32.8	117
29.6	100
25.3	83.0
22.5	72.6
T = 231.4 °K	x_{CH_4} = 0.28
100.2	927
96.9	888
91.1	768
88.9	728
88.1	789
85.9	681
85.3	723
83.9	653
69.3	506
67.5	460
63.7	448
61.8	422
53.5	321
50.4	302
46.4	279

p atm	$\tilde{H}^E$ J/mole
43.6	260
38.4	232
27.6	155
23.7	129
20.1	108
16.0	88.6
T = 231.4 °K	x_{CH_4} = 0.56
104.0	1331
97.0	1224
86.6	1037
83.8	994
80.8	970
71.3	784
68.9	740
65.3	672
61.5	630
53.9	538
50.2	495
46.1	420
43.0	386
35.6	308
30.9	247
28.0	216
24.8	185
T = 231.4 °K	x_{CH_4} = 0.81
107.5	1107
104.8	1114
100.7	1062
95.5	1038
93.9	1005
93.3	940
82.7	826

p atm	$\tilde{H}^E$ J/mole
81.5	798
79.7	785
77.9	750
76.6	725
75.9	714
74.5	696
71.7	643
69.3	627
57.5	452
54.0	399
51.1	367
48.9	336
45.8	308
43.4	281
33.5	201
30.0	171
26.5	145
22.7	119
19.9	103
T = 201.2 °K	x_{CH_4} = 0.28
68.6	1206
67.4	1163
65.2	1123
63.8	1073
52.5	659
50.1	593
47.7	541
44.8	461
37.0	339
34.6	312
32.5	281

p atm	$\tilde{H}^E$ J/mole
T = 201.2 °K	x_{CH_4} = 0.56
67.4	1961
65.0	1829
63.6	1724
61.3	1552
51.6	936
48.4	845
45.6	707
43.2	630
30.2	340
19.4	191
15.3	148
T = 201.2 °K	x_{CH_4} = 0.81
68.3	2039
67.6	1985
66.2	1972
52.3	907
51.3	849
50.0	787
48.5	705
30.6	260
28.5	246
26.0	215
24.2	190
22.0	165

TABLE 2.V

The experimental values of the molar excess enthalpy $\tilde{H}^E$ of the system He-A

p atm	$\tilde{H}^E$ J/mole
T = 293.0 °K, x_A = 0.26	
109.4	197
103.9	189
98.6	179
86.2	152
80.3	143
74.7	134
67.4	119
61.0	109
46.1	79.8
37.2	64.3
31.8	54.7
24.4	40.8
18.4	30.0
T = 293.0 °K, x_A = 0.54	
97.5	249
92.7	238
88.8	227
81.4	209
76.8	199
73.2	187
68.2	176
64.5	167
53.0	137
48.2	125
43.6	113
39.0	101
35.6	92.3
31.2	81.9
27.1	71.0
T = 293.0 °K, x_A = 0.79	
74.6	140
68.3	128
62.4	120
56.4	106
49.1	91.4
36.0	65.7
31.5	56.8
26.2	48.3
22.0	41.9
16.4	32.5
T = 231.0 °K, x_A = 0.26	
107.3	320
103.4	299
100.0	280
95.4	276
87.1	244
82.7	232
78.2	212
73.5	200
69.2	194
57.3	159
53.5	147
49.0	138
44.0	124
39.9	112
30.5	86.9
25.6	73.0
22.3	59.6
T = 231.0 °K, x_A = 0.54	
104.9	427
101.3	405
94.9	380
90.8	358
68.2	266
63.0	240
57.4	213
52.9	196
48.6	180
34.0	123
27.7	105
T = 231.0 °K, x_A = 0.79	
87.4	265
84.2	253
81.6	237
77.8	230
67.1	192
63.6	180
60.6	166
57.8	157
51.8	140
48.7	126
45.3	119
41.9	107
33.4	84.8
27.9	70.1
25.3	59.1
22.4	56.4
18.9	50.0
T = 201.1 °K, x_A = 0.26	
107.5	442
104.2	419
100.5	397
85.7	339
82.9	323
78.2	302
73.0	277
70.0	260
67.1	247
55.8	205
51.3	184
47.2	166
44.1	154
40.9	137
32.7	112
28.1	94.4
24.8	83.5
21.8	69.3
T = 201.1 °K, x_A = 0.54	
102.3	618
100.7	590
98.4	563
72.1	388
68.7	372
65.9	343
63.5	309
40.7	198
36.7	170
33.4	150
29.4	134
25.4	109
22.4	95
T = 201.1 °K, x_A = 0.79	
101.8	508
100.0	504
97.8	482
81.1	368
78.0	341
75.7	328
61.6	247
59.1	238
55.8	220
52.9	206
49.4	190
36.5	127
33.1	116
29.9	107
28.2	86
24.3	78
T = 169.6 °K, x_A = 0.26	
104.4	817
102.6	791
99.0	764
98.7	743
90.3	739
89.3	668
87.5	665
86.3	628
83.1	638
81.8	625
81.8	686
78.9	588
78.9	637
76.9	596
75.1	568
73.4	543
71.4	518
70.0	483
50.7	290
48.3	267
45.8	242
43.6	219
33.6	164
30.9	149
28.6	133
25.9	119
23.3	104
T = 169.6 °K, x_A = 0.54	
103.9	1191
102.7	1197
101.9	1186
86.3	1157
85.0	1084
84.2	1034
82.4	1011
68.8	757
68.1	765
67.0	730
65.9	719
65.1	686
64.1	656
61.5	591
58.7	542
52.8	460
50.9	430
47.9	394
45.5	355
43.3	326
29.4	195
25.8	158
22.9	131
T = 169.6 °K, x_A = 0.79	
100.5	1298
98.9	1293
97.0	1279
82.6	1060
81.1	1021
80.0	994
73.1	812
71.2	760
70.0	721
59.1	487
56.8	447
54.9	420
53.6	380
51.0	354
40.8	238
38.5	217
36.4	198
33.9	178
31.3	158
29.6	145

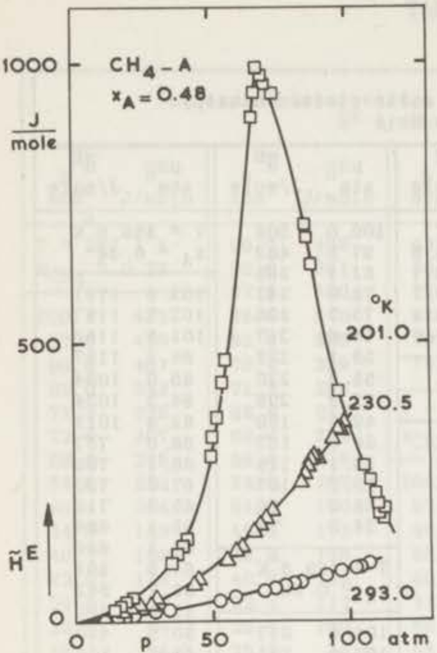

Fig. 2.4.

The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system CH_4-A.

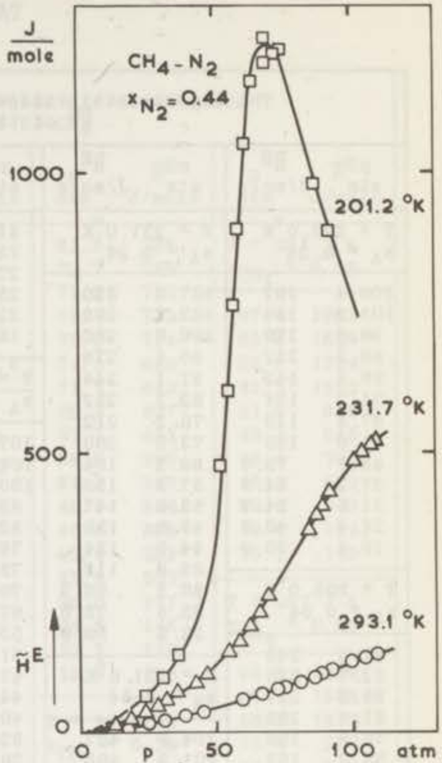

Fig. 2.5.

The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system CH_4-N_2.

a. In the pressure range to 80 atm. a bourdon manometer (Heise) with an accuracy of 0.1 atm. was used and from 80 to 150 atm. a bourdon manometer (Schaeffer and Budenberg) with an accuracy of 0.2 atm.. The error in the pressure corresponds to a maximum uncertainty of 0.5% at 293°K and 2.0% at 201°K in $\tilde{H}^E$.

b. The temperature of the cooling liquid was determined by a platinum resistance thermometer. The accuracy obtained was better than 0.05°K. The difference in the temperature of the cooling liquid, as a result of small differences in the barometric pressure at various runs, was at 293°K about 0.05°K and at lower temperatures less than 0.3°K. Normally the corrections for these variations will be negligibly small with the exception of the

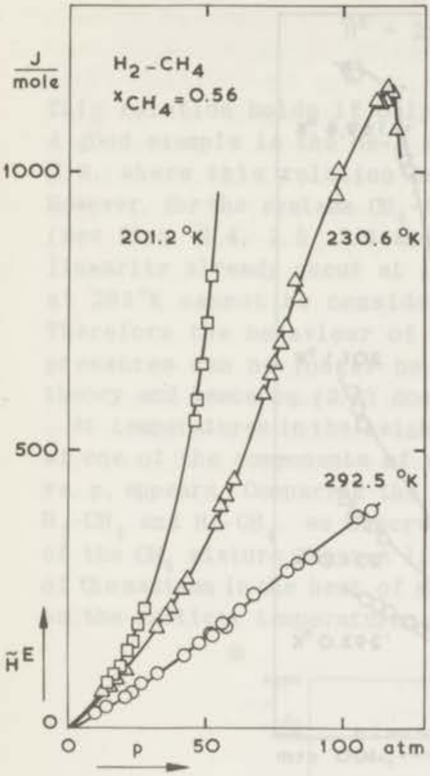

Fig. 2.6.

The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system H_2-CH_4.

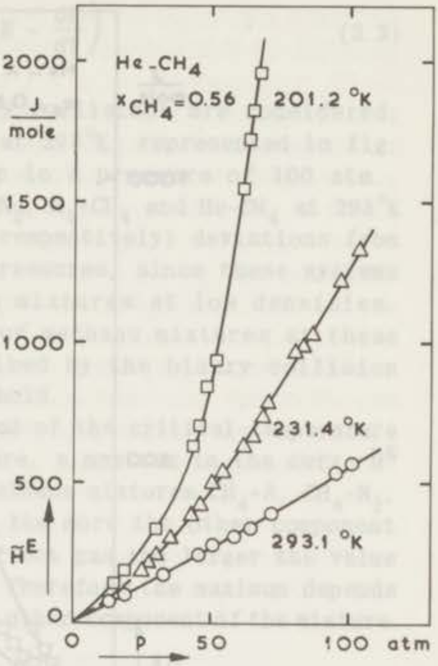

Fig. 2.7.

The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system He-CH_4.

measurements around the maximum in the heat of mixing where they are about 2%. In this region however, the temperature dependence of $\tilde{H}^E$ is not well known (cf. fig. 2.16), and for this reason no corrections were applied in this case either.

c. An average error in the determination of the gas flux of at most 1% results from the variation in room temperature, and the accuracy of the indication of the gasometer.

d. The heating power was determined within 1%.

e. The amount of impurities is less than 0.2% for the gases He, H_2 and N_2, about 0.2% for A and about 2% for CH_4. We accepted the impurity in the last gas, since methane of higher purity is expensive and these experiments require a large amount of gas.

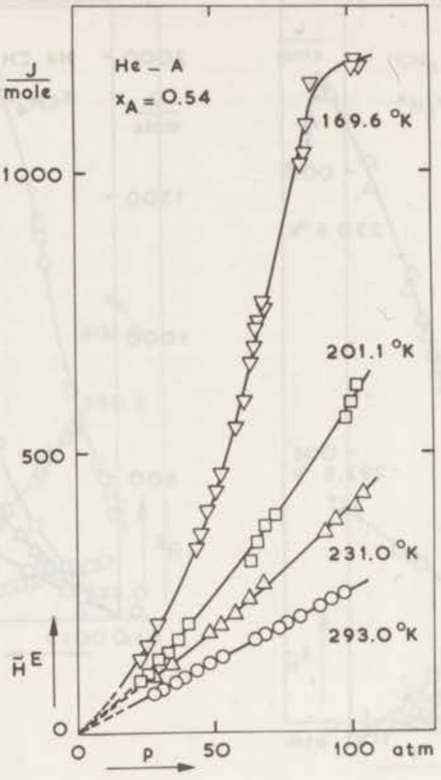

Fig. 2.8.

The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system He-A.

Fortunately the correction is small and will not exceed 2%. These accuracy considerations result in an average error in the molar excess enthalpy of 2 to 3% at 293°K and 3 to 4% at lower temperatures. This is in agreement with the scattering of the measured points in the graphs in figs. 2.4, 2.5, 2.6, 2.7 and 2.8.

2.5 *Discussion*

For mixtures at low densities, the excess enthalpy at constant temperature and mole fraction is proportional to the pressure as discussed in chapter 1. This follows from:

$$\tilde{H}^E = 2x_A x_B p \left(E - \frac{dE}{dT}\right) \qquad (2.3)$$

This relation holds if only binary collisions are considered. A good example is the He-A system at 293°K, represented in fig. 2.8, where this relation holds up to a pressure of 100 atm.. However, for the systems CH_4-A, CH_4-N_2, H_2-CH_4 and He-CH_4 at 293°K (see figs. 2.4, 2.5, 2.6 and 2.7, respectively) deviations from linearity already occur at lower pressures, since these systems at 293°K cannot be considered as mixtures at low densities. Therefore the behaviour of the four methane mixtures at these pressures can no longer be described by the binary collision theory and hence eq.(2.3) does not hold.

At temperatures in the neighbourhood of the critical temperature of one of the components of a mixture, a maximum in the curve $\tilde{H}^E$ vs. p, appears. Comparing the four methane mixtures CH_4-A, CH_4-N_2, H_2-CH_4 and He-CH_4, we observe that the more the other component of the CH_4 mixture behaves like a perfect gas the larger the value of the maximum in the heat of mixing. Therefore the maximum depends on the critical temperatures of the other component of the mixture.

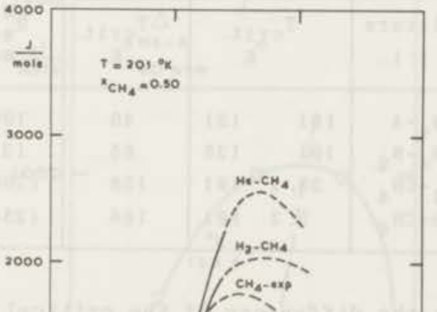

Fig. 2.9.

The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure. Experimental curves for the systems CH_4-A, CH_4-N_2, H_2-CH_4 and He-CH_4. Calculated curve obtained from CH_4-expansion.

In fig. 2.9 the curves of the experimental values of $\tilde{H}^E$ as a function of p are drawn for the systems CH_4-A, CH_4-N_2, H_2-CH_4 and He-CH_4 in a composition of 1:1 and at 201°K. The dotted line in this figure represents $\tilde{H}^E$ obtained from the CH_4-expansion as described in chapter 1. Starting from this expansion representation one would expect that the smaller the contribution to the enthalpy of the B-B and A-B interactions (where A represents CH_4 and B the other component) the larger the value of the maxima of the CH_4 mixtures. At the considered temperature, however, the contributions to the entahlpy of the B-B interactions of the mixtures CH_4-A and CH_4-N_2 are negative, whereas those of the B-B interactions of the mixtures CH_4-H_2 and CH_4-He are positive, since, for the latter two mixtures, the repulsive forces become dominant. Therefore the maxima of the former two mixtures are smaller and those of the latter two mixtures larger than the maximum of the CH_4 expansion.

TABLE 2.VI

Data of four methane mixtures

Mixture 1:1	$T_{crit.}$ °K		$\Delta T_{crit.}$ °K	$\tilde{H}^E_{max}$ J/mole
CH_4-A	191	151	40	1000
CH_4-N_2	191	126	65	1250
H_2-CH_4	33.2	191	158	(2000)
He-CH_4	5.2	191	186	(2500)

Table 2.VI shows the difference of the critical temperatures of the components, the measured maximum molar excess enthalpies of the systems CH_4-A and CH_4-N_2 and the estimated values of the same property for the systems H_2-CH_4 and He-CH_4. These estimations were made, since no sufficiently reproducible values were obtained from the experiments. Therefore in figs. 2.6 and 2.7 the 201°K curve ends at 55 and 70 atm., respectively. In the pressure range from 70 to 100 atm. the experimentally determined $\tilde{H}^E$ values, obtained from several runs, varied about 250 J/mole at the same pressure. In these cases the cooling effect results in a temperature drop of 10 to 15°K, so that the temperature of the mixture drops below the critical temperature of methane. Even when the mixing

chamber is heated up before mixing of the gases, it is possible that local condensation of CH_4 takes place, giving rise to instabilities.

In considering the dependence of the heat of mixing on the composition, it is convenient to express the molar excess enthalpy $\tilde{H}^E$ of a binary mixture as a polynomial in the mole fractions:

$$\begin{aligned} \tilde{H}^E &= x_A x_B\{a + (x_A - x_B)b + (x_A - x_B)^2 c\} = \\ &= x_A(1 - x_A)\{a + (2x_A - 1)b + (2x_A - 1)^2 c\} \end{aligned} \qquad (2.4)$$

An analogous relation for the molar excess Gibbs function G^E is mentioned by GUGGENHEIM$^{2)}$. The coefficients a, b and c are by definition independent of x but depend on T and possibly on p. For systems at temperatures, that are high compared with the critical temperature of both components, and at not too high pressures, the coefficients b and c vanish. Then the normal binary collision dependence is present and the relation between $\tilde{H}^E$ and x_A becomes parabolic. At lower temperatures a good approximation is given by eq. (2.4). The curve becomes asymetric and the top

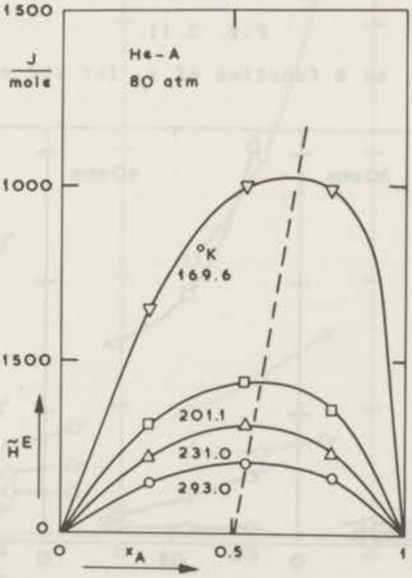

Fig. 2.10.

The molar excess enthalpy, $\tilde{H}^E$, as a function of mole fraction x_A for the system He-A.

shifts in the direction of the less-ideal component. This is illustrated in fig. 2.10, where the molar excess enthalpy $\tilde{H}^E$ is plotted against the mole fraction x_A for the He-A system at 80 atm. and 169.5, 201, 231 and 293°K. If $\tilde{H}^E$ is divided by $4x_A(1-x_A)$ then the dependence on x for a mixture at low density is represented by a straight horizontal line. This is shown in the figs. 2.11, 2.12, 2.13, 2.14 and 2.15 for the systems CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 and He-A, respectively. Here $\tilde{H}^E/4x(1-x)$ is plotted against

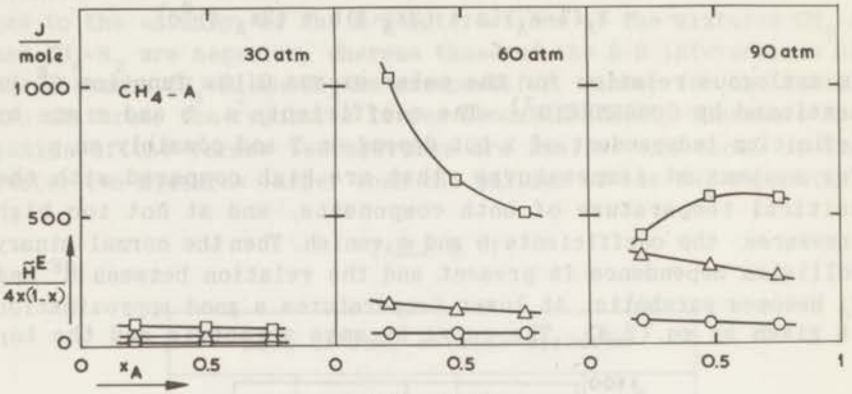

Fig. 2.11.

$\tilde{H}^E/4x(1-x)$, as a function of x_A for the system CH_4-A.

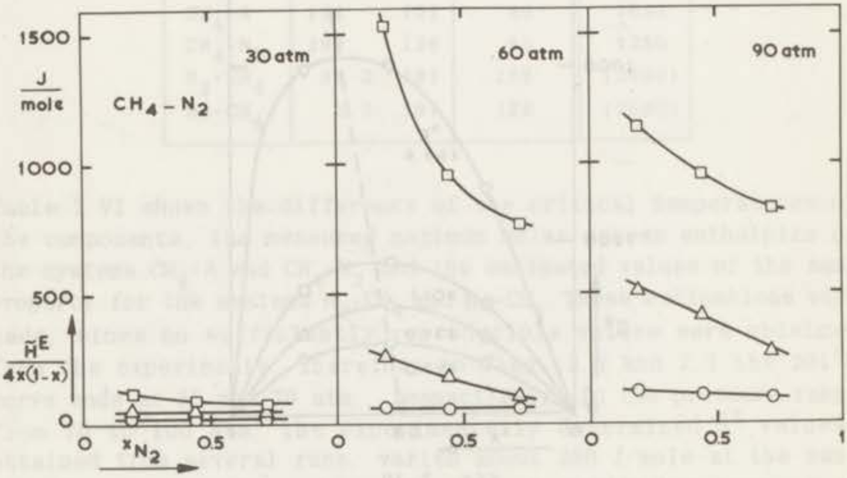

Fig. 2.12.

$\tilde{H}^E/4x(1-x)$, as a function of x_{N_2} for the system CH_4-N_2.

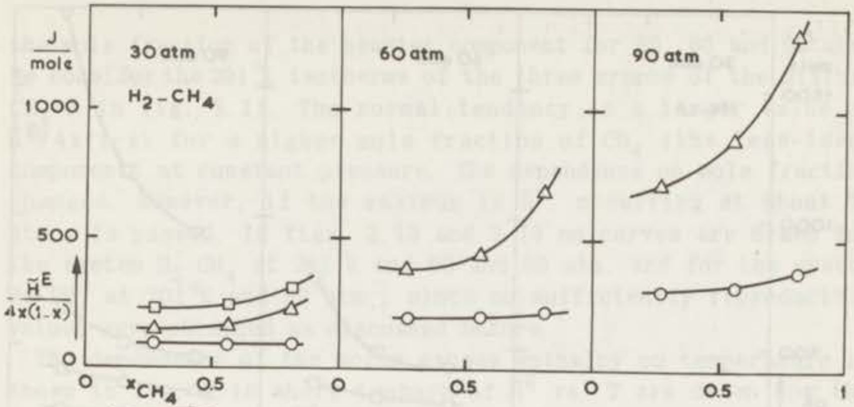

Fig. 2.13.

$\tilde{H}^E/4x(1-x)$, as a function of x_{CH_4} for the system H_2-CH_4.

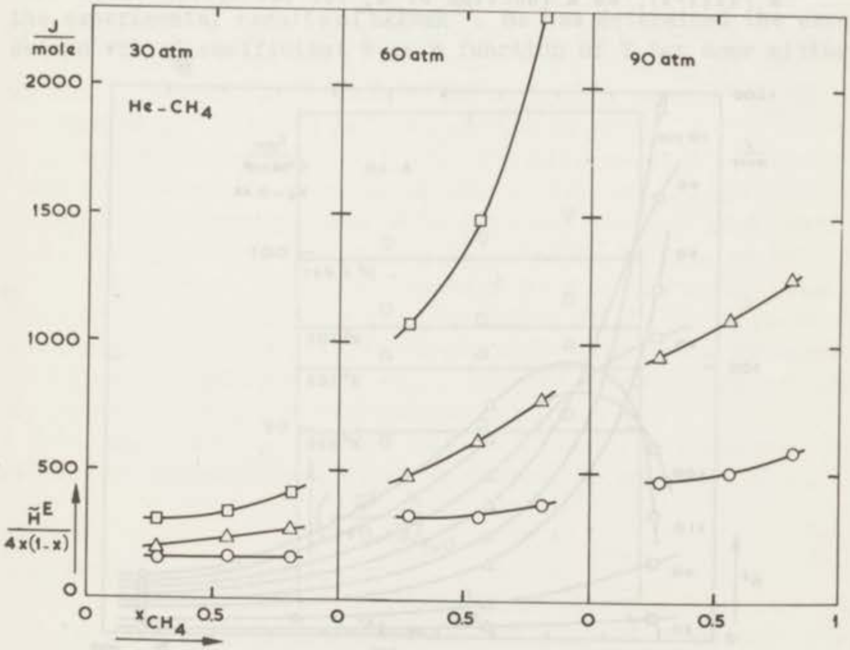

Fig. 2.14.

$\tilde{H}^E/4x(1-x)$, as a function of x_{CH_4} for the system He-CH_4.

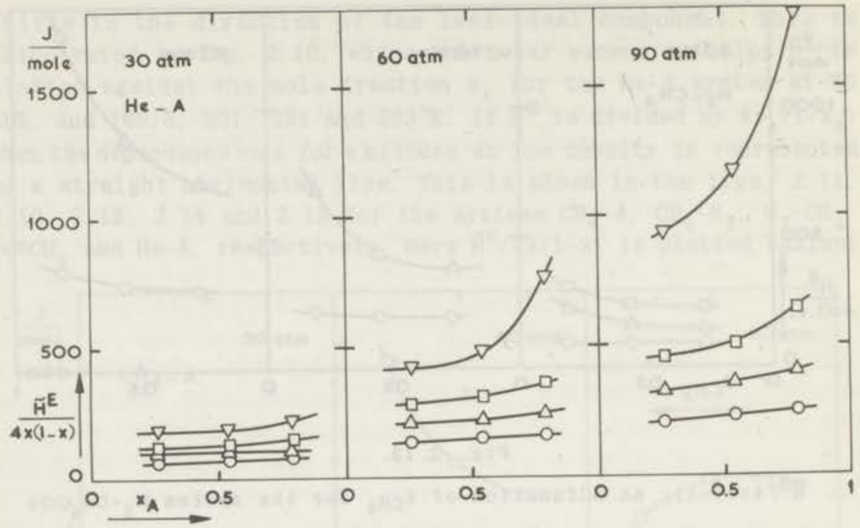

Fig. 2.15.

$\tilde{H}^E/4x(1-x)$, as a function of x_A for the system He-A.

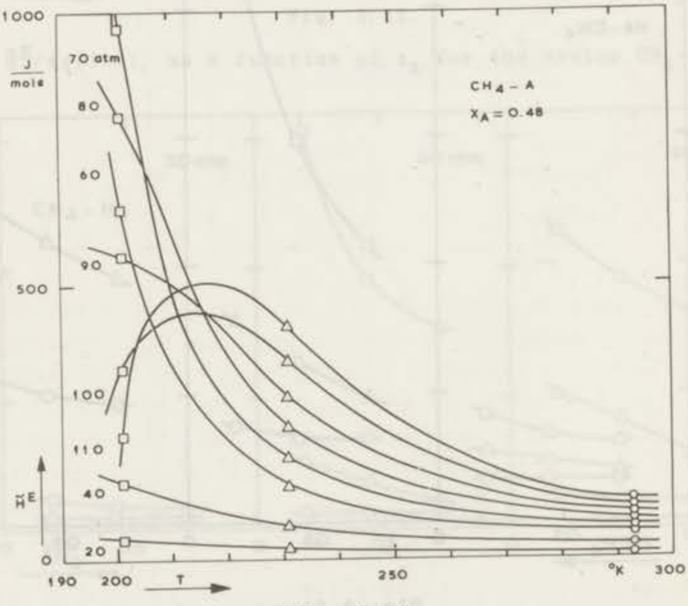

Fig. 2.16.

Isobars of $\tilde{H}^E$ vs. T for the system CH_4-A.

the mole fraction of the heavier component for 30, 60 and 90 atm. We consider the 201°K isotherms of the three graphs of the mixture CH_4-A in fig. 2.11. The normal tendency is a larger value of $\tilde{H}^E/4x(1-x)$ for a higher mole fraction of CH_4 (the less-ideal component) at constant pressure. The dependence on mole fraction changes, however, if the maximum in $\tilde{H}^E$, occurring at about 70 atm., is passed. In figs. 2.13 and 2.14 no curves are drawn for the system H_2-CH_4 at 201°K and 60 and 90 atm. and for the system He-CH_4 at 201°K and 90 atm., since no sufficiently reproducible values were obtained as discussed before.

The dependence of the molar excess enthalpy on temperature is shown in fig. 2.16 where isobars of $\tilde{H}^E$ vs. T are drawn for the system CH_4-A for a mole fraction $x_A = 0.48$. Since, for each pressure, only three points are measured, the shapes of the curves are not too well defined.

Since only a few experiments have been done on the excess properties of gaseous mixtures, the possibility of comparing our experiments with that of others is rather limited. We will consider the experimental results of BREWER[3]. He has determined the excess second virial coefficient E as a function of T for some mixtures

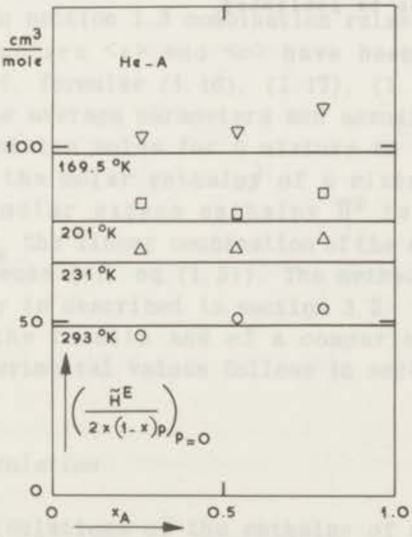

Fig. 2.17.

Comparison of our experimental data with that of Brewer for the system He-A.

including He-A. By using his expression $E = \alpha T^{-1.40}$ one obtains for mixtures at low densities (cf. section 1.2):

$$\frac{\tilde{H}^E}{2x_A x_B p} = \left(E - T\frac{dE}{dT}\right) = 2.40\ E\ .$$

The slope $\tilde{H}^E/p$ at $p = 0$ is determined in our graphs $\tilde{H}^E$ vs. p for the system He-A at 170, 201, 231 and 293°K and at $x_A = 0.26$, 0.54 and 0.79. The results are plotted in fig. 2.17. The horizontal lines represent the values of Brewer. The agreement is satisfactory in view of the accuracy claimed for both experiments and of the accuracy in the determination of the slope $(\tilde{H}^E/p)_{p=0}$ (cf. fig. 2.8).

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2. GUGGENHEIM, E.A., Trans. Faraday Soc. 33 (1937) 151.
3. BREWER, J., to be published.

CHAPTER 3

CALCULATIONS ON THE EXCESS ENTHALPY OF THE MIXTURES CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 AND He-A AT HIGH DENSITIES

3.1 Introduction

In this chapter we will discuss the behaviour of the excess enthalpy for mixtures at higher densities. A qualitative discussion of the shape of the curve of $\tilde{H}^E$ as a function of p has already been given in chapter 2. Here a more quantitative approach will be considered. As mentioned in chapter 1, this approach is based on the "liquid" theories of PRIGOGINE[1)] and SCOTT[2)]. It has been applied to gaseous mixtures of moderately high density by KNOESTER and BEENAKKER[3)]. In section 1.3 combination rules for the average interaction parameters $<\epsilon>$ and $<\sigma>$ have been given for the "liquid" models (cf. formulae (1.16), (1.17), (1.18) and (1.19)). Starting from these average parameters and assuming that the law of corresponding states holds for a mixture as well as for the pure components, the molar enthalpy of a mixture, $\tilde{H}_m$, can be calculated. The molar excess enthalpy $\tilde{H}^E$ is then found by subtracting from $\tilde{H}_m$ the linear combination of the molar enthalpies of the pure components (cf. eq. (1.5)). The method of calculating the excess enthalpy is described in section 3.2.
A discussion of the results and of a comparison between the calculated and experimental values follows in section 3.3.

3.2 Method of calculation

We start the calculations of the enthalpy of a mixture under the assumption that the molar residual enthalpy of a gas (reference gas) $\tilde{H}_R^{res}$ as a function of pressure and temperature is known. We introduce the reduced properties,

$$H^{res*} = \frac{\tilde{H}^{res}}{\tilde{N}\epsilon} \;, \; p^* = \frac{\sigma^3}{\epsilon} p \;, \; T^* = \frac{k}{\epsilon} T \qquad (3.1)$$

where $\tilde{N}$ is Avogadro's number and k is Boltzmann's constant. Assuming that the pure components and the mixture conform to the same reduced equation of state, one has

$$H^{res*} = H^{res*}(p^*, T^*) \; . \qquad (3.2)$$

A relation can be derived between the molar residual enthalpy of a mixture and that of the reference gas. For the "single-liquid" model this results in

$$\tilde{H}_m^{res}(x_A, p, T) = \frac{\langle\epsilon\rangle}{\epsilon_R} \tilde{H}_R^{res}\left(\frac{\langle\sigma\rangle^3 \epsilon_R}{\sigma_R^3 \langle\epsilon\rangle} p, \; \frac{\epsilon_R}{\langle\epsilon\rangle} T\right) \qquad (3.3)$$

In the "two-liquid" model the molar residual enthalpy of the mixture is given by

$$\tilde{H}_m^{res} = x_A \langle\tilde{H}^{res}\rangle_A + x_B \langle\tilde{H}^{res}\rangle_B \qquad (3.4)$$

where $\langle\tilde{H}^{res}\rangle_A$ can be calculated from

$$\langle\tilde{H}^{res}\rangle_A = \frac{\langle\epsilon\rangle_A}{\epsilon_R} \tilde{H}_R^{res}\left(\frac{\langle\sigma\rangle_A^3 \epsilon_R}{\sigma_R^3 \langle\epsilon\rangle_A} p, \; \frac{\epsilon_R}{\langle\epsilon\rangle_A} T\right) \qquad (3.5)$$

and similarly for $\langle\tilde{H}^{res}\rangle_B$.
In the "three-liquid" model the molar residual enthalpy of a mixture is given by

$$\tilde{H}_m^{res} = x_A^2 \tilde{H}_A^{o\;res} + 2 x_A x_B \tilde{H}_{AB}^{res} + x_B^2 \tilde{H}_B^{o\;res} \qquad (3.6)$$

where $\tilde{H}_A^{o\;res}$ and $\tilde{H}_B^{o\;res}$ are the molar residual enthalpies of the pure components and $\tilde{H}_{AB}^{res}$ is obtained from

$$\tilde{H}_{AB}^{res} = \frac{\epsilon_{AB}}{\epsilon_R} \tilde{H}_R^{res}\left(\frac{\sigma_{AB}^3 \epsilon_R}{\sigma_R^3 \epsilon_{AB}} p, \; \frac{\epsilon_R}{\epsilon_{AB}} T\right) \qquad (3.7)$$

Substituting formula (3.6) in formula (1.5) one obtains

$$\tilde{H}^E = 2x_Ax_B\{\tilde{H}_{AB}^{res} - \tfrac{1}{2}(\tilde{H}_A^{o\ res} + \tilde{H}_B^{o\ res})\}$$

This expression shows that the mole fraction dependence of the excess enthalpy calculated with the "three-liquid" model is parabolic.
The interaction parameters $\langle\epsilon\rangle$ and $\langle\sigma\rangle$ belonging to the three models are calculated from the parameters of the pure components, which are taken from HIRSCHFELDER, CURTISS and BIRD[4)]. Table 3.1

Table 3.I

The potential parameters ϵ/k (in $^\circ K$) and σ (in Å) for five systems

Mixture A – B	x_B	$\frac{\langle\epsilon\rangle}{k}$	$\frac{\langle\epsilon\rangle_A}{k}$	$\frac{\langle\epsilon\rangle_B}{k}$	$\frac{\epsilon_{AB}}{k}$	$\frac{\epsilon_{AA}}{k}$	$\frac{\epsilon_{BB}}{k}$	$\langle\sigma\rangle$	$\langle\sigma\rangle_A$	$\langle\sigma\rangle_B$	σ_{AB}	σ_{AA}	σ_{BB}
CH_4-A	0.75	120.4	133.8	120.1				3.56	3.68	3.48			
	0.48	127.4	137.4	123.4	133.2	148.2	119.8	3.67	3.74	3.54	3.61	3.82	3.41
	0.21	138.0	142.8	128.5				3.76	3.78	3.58			
CH_4-N_2	0.72	109.3	127.1	102.4				3.75	3.78	3.73			
	0.44	123.3	135.1	108.8	118.9	148.2	95.9	3.77	3.79	3.74	3.76	3.82	3.72
	0.19	137.0	142.4	114.7				3.80	3.80	3.75			
H_2-CH_4	0.81	114.7	64.5	130.2				3.78	3.36	3.79			
	0.56	77.1	52.5	107.0	74.0	37.00	148.2	3.70	3.32	3.76	3.37	2.93	3.82
	0.27	45.2	39.8	82.4				3.53	3.24	3.67			
He-CH_4	0.81	103.4	32.3	123.8				3.79	3.18	3.80			
	0.56	57.6	23.5	92.7	38.9	10.22	148.2	3.76	3.16	3.78	3.19	2.56	3.82
	0.28	22.3	14.3	57.9				3.65	3.12	3.73			
He-A	0.79	83.0	29.0	99.8				3.39	2.98	3.40			
	0.54	48.2	19.5	76.0	35.0	10.22	119.8	3.35	2.96	3.38	2.99	2.56	3.41
	0.26	20.4	18.0	50.0				3.23	2.91	3.32			

reports the parameters for the pure components and those calculated with the three models for the systems CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 and He-A for three mole fractions. The behaviour of the mole fraction dependence of the parameters $\langle\sigma\rangle$ and $\langle\epsilon\rangle$ has been illustrated in chapter 1 (see figs. 1.4, 1.5 and 1.6, 1.7).

Calculations on the excess enthalpy were performed for three mole fractions of the systems CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 and He-A for the temperatures reported in table 3.II. For each system a suitable reference gas was chosen; the enthalpies of the gases are taken from various tables and graphs, as reported in table 3.II. The choice of a reference gas is highly limited when the interaction parameters of one component are small compared to

TABLE 3.II

Reference gases			
Mixture	Temp. °K	Ref. gas	Table or graph Ref. gas
CH_4-A	201	CH_4	K.O. graph 5)
CH_4-N_2	201	CH_4	K.O. graph 5)
H_2-CH_4	231	N_2	Din 3 6)
He-CH_4	231	H_2	W.S.& B. 7)
He-A	170	H_2	W.S.& B. 7)
id.	id.	A	Din 2 8)

those of the other component of the mixture. As an example we consider the He-CH_4 system with a mole fraction $x_{CH_4} = 0.56$ at $T = 231°K$ using CH_4 as reference gas. The temperature $\langle T \rangle_{He}$ for the He-centered part of the "two-liquid" model is found by multiplying T with $\epsilon_{CH_4}/\langle \epsilon \rangle_{He}$. From the values of ϵ_{CH_4} and $\langle \epsilon \rangle_{He}$, denoted in table 3.I, it follows that $\langle T \rangle_{He} = 1457°K$. For this temperature no data of CH_4 were available. Similar examples can be given for A and N_2. As a consequence we decided to choose H_2 as reference gas for the mixtures He-CH_4 and He-A. However, it should be noted that the use of H_2 or He as reference gases can give deviations as a result of quantum effects. In fact it is possible that the calculated temperature of the reference gas, $\langle T \rangle = (\epsilon_R/\langle \epsilon \rangle)T$, is so low that quantum effects occur in the enthalpy of H_2, whereas these effects may be neglected at the temperature T of the mixture under consideration. We will return to this matter in section 3.3.

3.3 Results and discussion

The curves of the molar excess enthalpies calculated with the three models, have been drawn as plots of $\tilde{H}^E$ against p for the

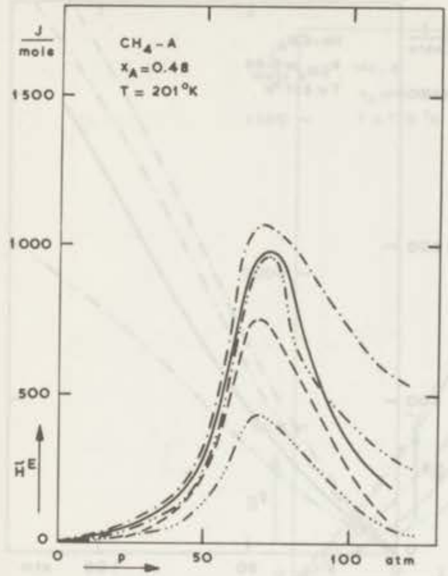

Fig. 3.1.

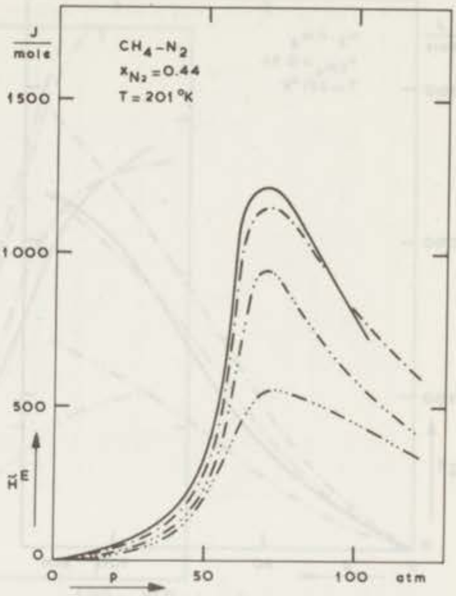

Fig. 3.2.

Fig. 3.1. The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system CH_4-A. Calculations are performed with the reference gas CH_4.

———————— experiment
—·—·—·—·— calculated with "single-liquid" model
—··——··——··— calculated with " two-liquid" model
—···——···——···— calculated with "three-liquid" model
— — — — — — calculated with "Kay-rules".

Fig. 3.2. The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system CH_4-N_2. Calculations are performed with the reference gas CH_4. See also the caption of fig. 3.1.

systems CH_4-A (T = 201°K, x_A = 0.48), CH_4-N_2 (T = 201°K, x_{N_2} = 0.44), H_2-CH_4 (T = 231°K, x_{CH_4} = 0.56), He-CH_4 (T = 231°K, x_{CH_4} = 0.56) and He-A (T = 170°K, x_A = 0.79) in figs. 3.1, 3.2, 3.3, 3.4 and 3.5, respectively. For comparison the smoothed experimental curves of $\tilde{H}^E$ of these systems have also been drawn in these figures. The mole fraction dependence of the heat of mixing obtained from calculations and from experiments at 30, 60 and 90 atm. is shown in figs. 3.6, 3.7 and 3.8, where $\tilde{H}^E/4x(1-x)$ is plotted against the mole fraction of the heavier component of the mixtures CH_4-A (201°K), CH_4-N_2 (201°K) and H_2-CH_4 (231°K).
We will start with a few general remarks on the behaviour of the different models and on their relation with experiment, as already given by KNOESTER and BEENAKKER[3)].

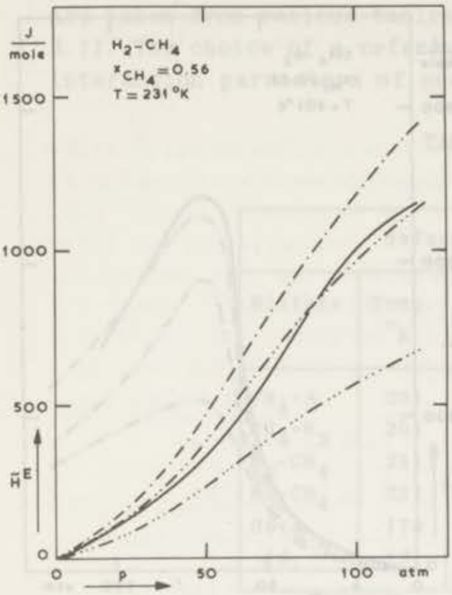

Fig. 3.3.

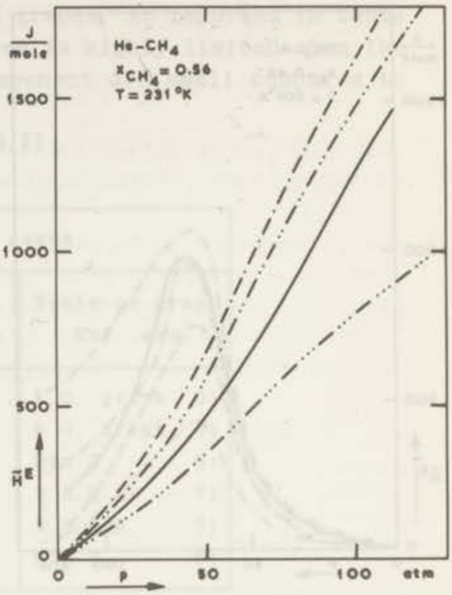

Fig. 3.4.

Fig. 3.3. The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system H_2-CH_4. Calculations are performed with the reference gas N_2. See also the caption of fig. 3.1.

Fig. 3.4. The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system He-CH_4. Calculations are performed with the reference gas H_2. See also the caption of fig. 3.1.

a. The "three-liquid" model neglects other than binary collisions and will give a good approximation of the excess enthalpy at lower densities.
b. The "single-liquid" model is characterized by a total loss of the individuality of the molecules and can be considered as a high density approach. The excess enthalpies calculated with this model are larger than those obtained by experiment.
c. In the "two-liquid" model the molecules have retained a part of their individuality, therefore it might be expected that the excess enthalpy calculated with this model will lie between those obtained with the "three-liquid" and the "single-liquid" model. The results of this model agree satisfactorily with the excess enthalpy obtained from the experiment.

In the following discussion it will become clear that in general

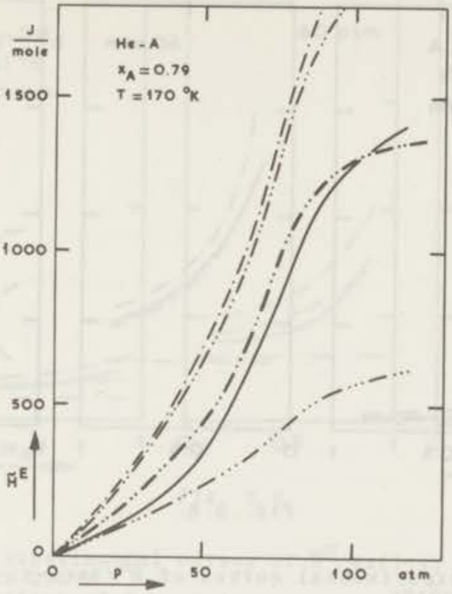

Fig. 3.5.

The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system He-A. Calculations are performed with the reference gases H_2 and A.

$\left.\begin{array}{l}-\cdot-\cdot-\cdot-\\ -\cdot\cdot-\cdot\cdot-\\ -\cdot\cdot\cdot-\cdot\cdot\cdot-\end{array}\right\}$ calculated with reference gas H_2

▬··▬··▬ calculated with reference gas A

See als the caption of fig. 3.1.

the preceding remarks also hold for the mixtures considered by us. At first we remark that all three models are in good qualitative agreement with the experiment. This is shown in figs. 3.1 and 3.2 for the systems CH_4-A and CH_4-N_2, respectively, where the pressure, at which the maximum in $\tilde{H}^E$ occurs, is indicated precisely by these models.

a. The "three-liquid" model. The results obtained with this model agree well with the experimental values for the system He-A at 170 °K up to 30 atm., in spite of the low temperature (about 20 °K above the critical temperature of A). For the four methane mixtures, however, a deviation of the calculated values from the experimental ones occurs at lower pressures. For the systems CH_4-A and CH_4-N_2 (201 °K) this deviation is larger than for the systems H_2-CH_4 and He-CH_4 (231 °K), since the behaviour of the

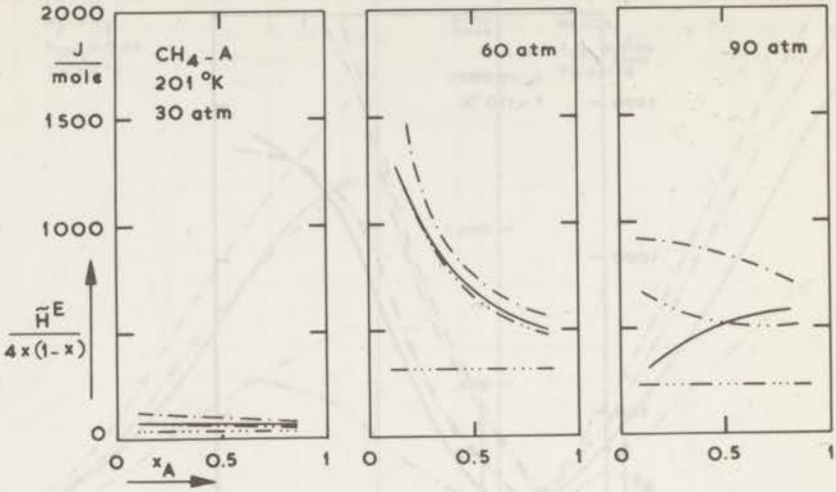

Fig. 3.6.

Calculated and experimental curves of $\tilde{H}^E/4x(1-x)$ vs. x_A for the system CH_4-A at 201°K.
See also the caption of fig. 3.1.

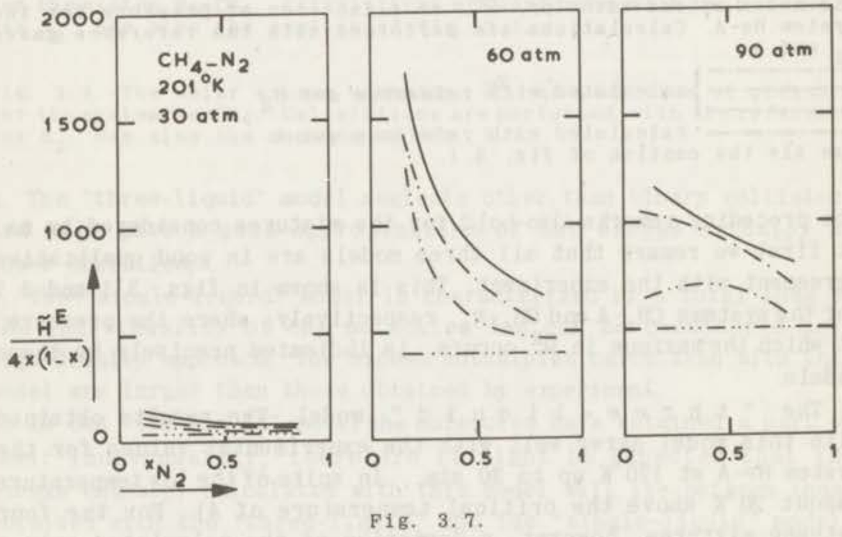

Fig. 3.7.

Calculated and experimental curves of $\tilde{H}^E/4x(1-x)$ vs. x_{N2} for the system CH_4-N_2 at 201°K.
See also the caption of fig. 3.1.

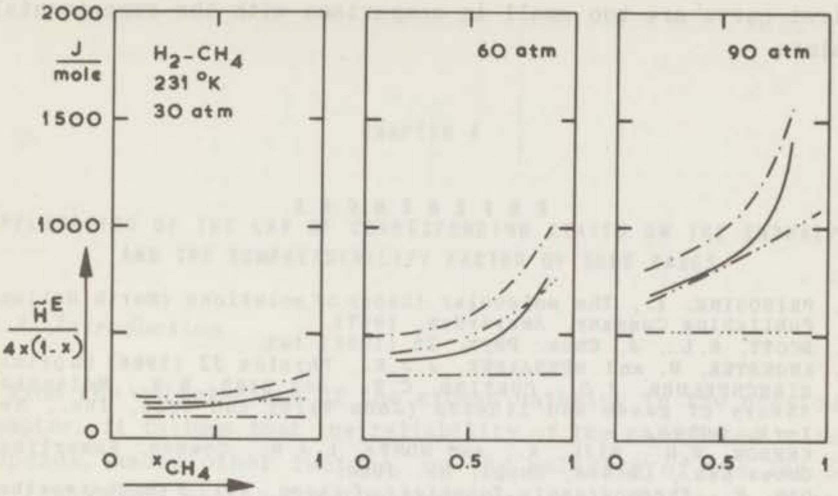

Fig. 3.8.

Calculated and experimental curves of $\tilde{H}^E/4x(1-x)$ vs. x_{CH_4} for the system H_2-CH_4 at 231°K.
See also the caption of fig. 3.1.

first two mixtures is more critical than that of the last two. This is illustrated in fig. 3.1, 3.2 and 3.3, 3.4.

b. The "single-liquid" model. The curves of the excess enthalpy for this model give, for most of the systems, values that are too large, except for the CH_4-N_2 mixture.

c. The "two-liquid" model. The calculated values of $\tilde{H}^E$ for the mixtures CH_4-A and H_2-CH_4 (cf. figs. 3.1 and 3.2) are in good agreement with the experimental ones. However, for the systems He-CH_4 and He-A (cf. figs. 3.4 and 3.5) the results are not very satisfactory. As was already remarked in section 3.2, these discrepancies must be the result of the use of hydrogen as reference gas. For the system He-A at 170°K with mole fraction $x_A = 0.79$ it is also possible to use A as reference gas for calculations with the "two-liquid" model. The results of these calculations are in rather good agreement with the experiment.

d. The "Kay-rules". As mentioned in chapter 1 Kay has given simple combination rules for the critical temperature and pressure. A calculation of $\tilde{H}^E$ with these critical constants is performed for the mixture CH_4-A. The results are plotted in fig. 3.1 as a broken line. The shape of this curve agrees well with that of the experimental curve, however, the values of the first curve are too small in comparison with the experimental values.

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CHAPTER 4

APPLICATION OF THE LAW OF CORRESPONDING STATES ON THE ENTHALPY AND THE COMPRESSIBILITY FACTOR OF SOME GASES

4.1 Introduction

From the calculations of the excess enthalpy in the previous chapter, it follows that the reliability of the calculated values depends, among other factors, on the validity of the law of corresponding states for the thermodynamic properties of the reference gases. Hence, it is interesting to know in how far the law of corresponding states holds for the components of the mixtures under study. Therefore we will compare the reduced enthalpy as a function of the reduced pressure and reduced temperature of the gases argon, nitrogen and methane. Furthermore, we have examined in how far the law of corresponding states holds for the compressibility factor, this is a property experimentally determined. The enthalpy is calculated mostly from p-V-T data.

First we will give a short introduction on the law of corresponding states. An extensive discussion of this theory is given by DE BOER$^{1)}$. The law of corresponding states holds if the system of molecules obeys the following assumptions:

1. The internal degrees of freedom are independent of the positions and motions of the centres of mass of the molecules.
2. The classical approximation can be applied to the translational degrees of freedom, i.e. the translational partition function Z^{tr} can be written in the classical form.
3. The total potential energy Φ can be represented by the sum of the interaction potentials $\phi\ (r_{ij})$ of all possible pairs of molecules i and j depending only on their separations r_{ij}.
4. The potential energy of a pair of molecules can be represented by some function f together with two parameters ϵ and σ characteristic for the molecular species,

$$\phi(r) = \epsilon f(\frac{\sigma}{r}) \qquad (4.1)$$

A useful approximation of this function is the Lennard-Jones (6-12) potential:

$$\phi(r) = 4\epsilon\ \{(\tfrac{\sigma}{r})^{12} - (\tfrac{\sigma}{r})^{6}\} \qquad (4.2)$$

Starting with assumption 1, we can write the partition function as $Z^{int}.Z^{tr}$, where Z^{tr} is the translational partition function due to the contribution of the positions and motions of the centres of mass of the molecules and Z^{int} is the internal partition function due to the contribution of all other degrees of freedom (rotation, vibration). For Z^{tr} one has

$$Z^{tr} = \frac{1}{N!\,h^{3N}} \iint \exp\left\{\frac{-H(\vec{r}^{N},\vec{p}^{N})}{kT}\right\} d\vec{r}^{N} d\vec{p}^{N} \qquad (4.3)$$

where the symbols have the usual meaning.

The Hamiltonian is given by

$$H = \sum_{i} \frac{p_i^{2}}{2m} + \Phi(\vec{r}^{N}) \ . \qquad (4.4)$$

The translational partition function can now be written as

$$Z^{tr} = \left(\frac{2\pi mkT}{h^{2}}\right)^{3N/2} Q, \qquad (4.5)$$

where the configurational partition function Q is defined as:

$$Q = \frac{1}{N!} \int \exp\left\{-\frac{\Phi(\vec{r}^{N})}{kT}\right\} d\vec{r}^{N}$$

or, following assumption 3

$$Q = \frac{1}{N!} \int \exp\left\{-\frac{\sum_{i<j} \phi(r_{ij})}{kT}\right\} d\vec{r}^{N} \qquad (4.6)$$

Substituting formula (4.5) in the expression for the free energy $F^{tr} = -kT \ln Z^{tr}$, we obtain

$$F^{tr} = -\frac{3NkT}{2} \ln \left(\frac{2\pi mkT}{h^2}\right) - kT \ln Q \qquad (4.7)$$

Since $p = -(\partial F/\partial V)_{T,N}$, the equation of state will be

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \qquad (4.8)$$

The intermolecular parameters may be used to introduce the reduced properties $r^* = r/\sigma$ and $f(r^*_{ij}) = \phi(r_{ij})/\epsilon$ (cf. assumption 4). The configurational partition function can be written in the form:

$$Q = \frac{\sigma^3}{N!} \int \exp\left\{-\sum_{i<j} \frac{\epsilon f(r^*_{ij})}{kT}\right\} d(\vec{r}^*)^N =$$

$$= \frac{\sigma^{3N}}{N!} Q^*(T^*, V^*) \qquad (4.9)$$

This expression depends only on the reduced temperature $T^* = kT/\epsilon$ and the reduced volume $V^* = \tilde{V}/\tilde{N}\sigma^3$. If now p is expressed in ϵ/σ^3 as a unit, the following equation holds (cf. eq.(4.9)):

$$p^* = \frac{T^*}{\tilde{N}}\left(\frac{\partial \ln Q}{\partial V^*}\right)_{T,\tilde{N}} = \frac{T^*}{\tilde{N}}\left(\frac{\partial \ln Q^*(T^*,V^*)}{\partial V^*}\right)_{T^*} \qquad (4.10)$$

This equation is the reduced equation of state and is a form of the law of corresponding states, i.e. the equation of state reduced with interaction parameters is a universal function for all substances which satisfy the assumptions 1, 2, 3 and 4. For the enthalpy an analogous universal function can be formed, i.e.

the reduced enthalpy as a function of the reduced pressure and reduced temperature:

$$H^* = H^*(p^*,T^*) \ . \qquad (4.11)$$

The reduced enthalpy is given by $H^* = \tilde{H}/\tilde{N}\epsilon$.
Starting from expression (4.11), in section 4.2, we made a comparison between the reduced enthalpies of the gases A, N_2 and CH_4. Furthermore a graphic method is given to examine the validity of the law of corresponding states for the enthalpy. In section 4.3 the same graphic method is performed for the compressibility factor Z of the gases A, N_2, CH_4 and Xe. With help of this method scale factors for T and p are obtained. From these scale factors new values can be found for the intermolecular parameters. The influence of the new parameters on the agreement between the reduced enthalpies of the gases N_2, CH_4 and A and on the agreement between the experimental and calculated values of the excess enthalpy is examined in section 4.4.

4.2 *Comparison of the reduced enthalpies of the gases A, N_2 and CH_4*

In chapter 3 we made use of the existing enthalpy data of the reference gases A, N_2 and CH_4, in order to calculate the excess enthalpy of some mixtures. For the calculations it was assumed that the law of corresponding states holds for the enthalpy in the pressure and temperature ranges under consideration. In this section we will therefore compare the reduced enthalpies of A, N_2 and CH_4 in the same pressure and temperature ranges. To do this a table is composed of reduced enthalpies at regular intervals of reduced temperature and reduced pressure. The residual enthalpy $H^{res}(p,T)$ is obtained from the tabulated total enthalpy by using form. (1.2). Then the residual enthalpy as well as the entries of the table are reduced with the parameters ϵ and σ (see form. (3.1)). Finally, since the values of the reduced enthalpy are desired at values of the reduced pressure and temperature which generally do not correspond with the initial entries of the table, a double three-point Aitken interpolation must be performed. The computations were carried out on an Electrologica X-1 computer of "Het Centraal Reken Instituut, Leiden".

Table 4.I gives the references of the tables or graphs that were used and the interaction parameters for the gases, as obtained from second virial coefficient data; furthermore, the chosen temperature and pressure range of the enthalpies and the estimated errors in the enthalpies given by the authors. The tables 4.II, 4.III, 4.IV and 4.V show the reduced enthalpies as functions of reduced temperature and reduced pressure for the gases CH_4(KOL[2]), N_2(Din[4]), A(Din[6]) and CH_4(Din[4]), respectively.

TABLE 4.I

Some data for the gases CH_4, N_2, A and Xe in order to calculate the reduced enthalpy and the compressibility factor

Gas	Table or Graph	Intermolecular parameters			Enthalpy data			Compressibility factor data		
		ϵ/k °K	σ Å	ref.	Temp. range °K	Press. range atm	Error %	Temp. range °K	Press. range atm	Error %
CH_4	KOL 2)	148.2	3.817	9)	200-475	1-160	1	210-290	30-280	?
	Din 4)				210-470	1-160	2	210-290	35-280	0.5
N_2	Din 4)	95.9 (95.05)	3.718 (3.698)	10) (11))	130-320	1-140	6	140-190	21-210	3
	NBS 5)				-	-	-	130-190	16-200	0.4
A	Din 6)	119.8	3.405	12)	160-400	1-120	0.7	160-230	34-300	2
	vdW 7)				-	-	-	170-230	40-300	0.2
Xe	vdW 8)	225.3	4.070	13)	-	-	-	300-430	30-350	0.2

The degree of agreement between the reduced properties of different gases is influenced by a number of factors. The most important ones are the inaccuracies of the existing tables, the uncertainties in the values of the reduction factors and the deviations from the law of corresponding states.

TABLE 4.II

The reduced residual enthalpy $\frac{\tilde{H}^{res}}{N\epsilon}$ of methane (KOL[2]) $\sigma = 3.817$ Å, $\epsilon/k = 148.2$ °K

p^* \ T^*	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2
.10	- .873	- .738	- .670	- .592	- .535	- .499	- .450	- .393
.12	- 1.091	- .914	- .815	- .720	- .647	- .600	- .535	- .474
.14	- 1.328	- 1.099	- .964	- .856	- .761	- .697	- .615	- .552
.16	- 1.589	- 1.289	- 1.129	- .987	- .883	- .804	- .710	- .635
.18	- 1.878	- 1.493	- 1.277	- 1.117	- 1.001	- .898	- .801	- .720
.20	- 2.175	- 1.704	- 1.434	- 1.249	- 1.116	- .997	- .892	- .799
.22	- 2.476	- 1.922	- 1.605	- 1.384	- 1.229	- 1.105	- .984	- .872
.24	- 2.765	- 2.135	- 1.765	- 1.509	- 1.332	- 1.207	- 1.070	- .951
.26	- 3.015	- 2.338	- 1.932	- 1.634	- 1.510	- 1.298	- 1.152	- 1.028
.28	- 3.226	- 2.528	- 2.101	- 1.760	- 1.733	- 1.382	- 1.231	- 1.102
.30	- 3.397	- 2.700	- 2.252	- 1.887	- 1.834	- 1.479	- 1.313	- 1.176
.32	- 3.516	- 2.856	- 2.385	- 2.019	- 1.790	- 1.592	- 1.397	- 1.252
.34	- 3.630	- 2.994	- 2.517	- 2.138	- 1.860	- 1.686	- 1.478	- 1.324
.36	- 3.710	- 3.110	- 2.648	- 2.253	- 1.969	- 1.770	- 1.560	- 1.393
.38	- 3.784	- 3.215	- 2.762	- 2.360	- 2.061	- 1.853	- 1.639	- 1.461
.40	- 3.845	- 3.306	- 2.863	- 2.459	- 2.150	- 1.934	- 1.714	- 1.526

p^* \ T^*	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0
.10	- .349	- .321	- .316	- .297	- .269	- .261	- .245	- .216
.12	- .424	- .390	- .379	- .355	- .322	- .311	- .290	- .253
.14	- .494	- .456	- .444	- .416	- .379	- .361	- .337	- .300
.16	- .576	- .533	- .509	- .476	- .440	- .418	- .383	- .345
.18	- .660	- .613	- .581	- .537	- .484	- .458	- .427	- .391
.20	- .736	- .684	- .646	- .593	- .531	- .503	- .470	- .432
.22	- .802	- .743	- .701	- .646	- .584	- .550	- .512	- .467
.24	- .869	- .803	- .757	- .698	- .632	- .591	- .550	- .507
.26	- .939	- .866	- .815	- .749	- .677	- .636	- .594	- .548
.28	- 1.010	- .931	- .872	- .800	- .720	- .684	- .640	- .588
.30	- 1.077	- .992	- .926	- .849	- .765	- .725	- .679	- .625
.32	- 1.142	- 1.049	- .978	- .897	- .812	- .759	- .707	- .658
.34	- 1.205	- 1.105	- 1.030	- .944	- .856	- .799	- .745	- .689
.36	- 1.264	- 1.157	- 1.080	- .991	- .897	- .844	- .788	- .722
.38	- 1.323	- 1.211	- 1.131	- 1.037	- .938	- .886	- .827	- .756
.40	- 1.382	- 1.265	- 1.181	- 1.083	- .979	- .927	- .866	- .788

TABLE 4.III

The reduced residual enthalpy $\frac{\tilde{H}^{res}}{N\epsilon}$ of nitrogen (Din[4]) σ = 3.718 Å
ϵ/k = 95.9 °K

p* \ T*	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2
.02	- .140	- .127	- .114	- .102	- .093	- .083	- .077	- .071
.04	- .299	- .267	- .237	- .210	- .191	- .172	- .158	- .144
.06	- .465	- .412	- .365	- .323	- .292	- .262	- .239	- .220
.08	- .643	- .563	- .496	- .439	- .395	- .354	- .323	- .296
.10	- .839	- .721	- .631	- .558	- .500	- .448	- .407	- .373
.12	- 1.073	- .892	- .774	- .681	- .608	- .545	- .494	- .450
.14	- 1.346	- 1.074	- .925	- .808	- .719	- .642	- .582	- .529
.16	- 1.641	- 1.277	- 1.085	- .941	- .832	- .741	- .670	- .608
.18	- 1.997	- 1.507	- 1.254	- 1.079	- .948	- .842	- .757	- .688
.20	- 2.407	- 1.762	- 1.434	- 1.221	- 1.067	- .943	- .846	- .767
.22	- 2.789	- 2.020	- 1.623	- 1.367	- 1.187	- 1.044	- .935	- .847
.24	- 3.155	- 2.284	- 1.822	- 1.515	- 1.307	- 1.145	- 1.024	- .928
.26	- 3.588	- 2.542	- 2.031	- 1.669	- 1.430	- 1.248	- 1.114	- 1.008
.28	- 3.908	- 2.805	- 2.230	- 1.818	- 1.551	- 1.349	- 1.202	- 1.088
.30	- 4.121	- 3.100	- 2.428	- 1.966	- 1.671	- 1.450	- 1.290	- 1.167
.32	- 4.274	- 3.326	- 2.602	- 2.105	- 1.787	- 1.549	- 1.377	- 1.245
.34	- 4.340	- 3.485	- 2.756	- 2.236	- 1.901	- 1.648	- 1.464	- 1.323
.36	- 4.399	- 3.612	- 2.886	- 2.356	- 2.010	- 1.745	- 1.549	- 1.398
.38	- 4.440	- 3.704	- 2.993	- 2.465	- 2.113	- 1.839	- 1.634	- 1.472
.40	- 4.468	- 3.767	- 3.080	- 2.563	- 2.209	- 1.929	- 1.715	- 1.544

p* \ T*	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0
.02	- .065	- .059	- .058	- .053	- .048	- .046	- .042	- .040
.04	- .132	- .122	- .115	- .107	- .098	- .093	- .085	- .082
.06	- .202	- .186	- .175	- .162	- .149	- .141	- .131	- .123
.08	- .272	- .250	- .234	- .217	- .201	- .188	- .175	- .165
.10	- .342	- .314	- .294	- .272	- .252	- .236	- .219	- .205
.12	- .413	- .379	- .354	- .327	- .304	- .284	- .263	- .246
.14	- .484	- .445	- .414	- .384	- .355	- .332	- .307	- .287
.16	- .555	- .510	- .474	- .439	- .407	- .378	- .349	- .326
.18	- .627	- .576	- .534	- .494	- .457	- .425	- .392	- .365
.20	- .700	- .641	- .595	- .549	- .507	- .471	- .435	- .404
.22	- .772	- .708	- .655	- .604	- .557	- .517	- .477	- .443
.24	- .846	- .775	- .716	- .659	- .607	- .563	- .519	- .482
.26	- .919	- .841	- .776	- .714	- .657	- .608	- .561	- .520
.28	- .991	- .907	- .836	- .768	- .706	- .653	- .602	- .557
.30	- 1.063	- .972	- .895	- .822	- .756	- .698	- .642	- .594
.32	- 1.134	- 1.037	- .953	- .875	- .804	- .742	- .682	- .631
.34	- 1.204	- 1.100	- 1.011	- .927	- .852	- .786	- .722	- .667
.36	- 1.271	- 1.162	- 1.066	- .978	- .899	- .828	- .761	- .702
.38	- 1.338	- 1.221	- 1.121	- 1.028	- .944	- .869	- .799	- .738
.40	- 1.402	- 1.279	- 1.174	- 1.076	- .987	- .909	- .836	- .772

TABLE 4.IV

The reduced residual enthalpy $\frac{\tilde{H}^{res}}{N\epsilon}$ of argon (Din[6]) σ = 3.405 Å, ϵ/k = 119.8 °K

T^* / p^*	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2
.02	- .148	- .128	- .113	- .100	- .090	- .081	- .073	- .070
.04	- .318	- .272	- .238	- .209	- .185	- .167	- .152	- .142
.06	- .500	- .424	- .366	- .321	- .285	- .257	- .234	- .218
.08	- .694	- .583	- .499	- .436	- .387	- .348	- .317	- .294
.10	- .898	- .748	- .637	- .553	- .488	- .439	- .400	- .370
.12	- 1.109	- .919	- .779	- .672	- .591	- .531	- .482	- .446
.14	- 1.335	- 1.095	- .923	- .793	- .696	- .623	- .565	- .521
.16	- 1.577	- 1.276	- 1.069	- .916	- .801	- .716	- .649	- .597
.18	- 1.836	- 1.465	- 1.219	- 1.040	- .906	- .809	- .733	- .674
.20	- 2.108	- 1.660	- 1.372	- 1.165	- 1.012	- .901	- .818	- .752
.22	- 2.376	- 1.860	- 1.528	- 1.292	- 1.119	- .993	- .900	- .827
.24	- 2.649	- 2.065	- 1.688	- 1.421	- 1.225	- 1.085	- .981	- .902
.26	- 2.859	- 2.258	- 1.844	- 1.547	- 1.330	- 1.175	- 1.062	- .975
.28	- 3.032	- 2.452	- 2.003	- 1.673	- 1.435	- 1.266	- 1.142	- 1.048
.30	- 3.179	- 2.613	- 2.147	- 1.795	- 1.538	- 1.354	- 1.221	- 1.119
.32	- 3.288	- 2.747	- 2.285	- 1.916	- 1.641	- 1.442	- 1.301	- 1.189
.34	- 3.386	- 2.868	- 2.409	- 2.030	- 1.739	- 1.528	- 1.378	- 1.259
.36	- 3.466	- 2.972	- 2.522	- 2.137	- 1.835	- 1.612	- 1.453	- 1.327
.38	- 3.526	- 3.057	- 2.623	- 2.238	- 1.928	- 1.696	- 1.526	- 1.395
.40	- 3.582	- 3.135	- 2.714	- 2.333	- 2.017	- 1.777	- 1.599	- 1.460

T^* / p^*	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0
.02	- .066	- .063	- .060	- .056	- .053	- .048	- .045	- .044
.04	- .134	- .127	- .120	- .113	- .105	- .098	- .092	- .088
.06	- .204	- .192	- .181	- .170	- .158	- .147	- .138	- .131
.08	- .274	- .257	- .241	- .225	- .210	- .195	- .182	- .172
.10	- .344	- .321	- .301	- .281	- .261	- .242	- .226	- .212
.12	- .413	- .385	- .360	- .335	- .311	- .288	- .268	- .251
.14	- .483	- .449	- .419	- .390	- .361	- .334	- .311	- .290
.16	- .553	- .514	- .477	- .443	- .411	- .380	- .353	- .329
.18	- .623	- .578	- .536	- .497	- .461	- .427	- .396	- .369
.20	- .693	- .649	- .595	- .552	- .511	- .473	- .438	- .408
.22	- .763	- .705	- .653	- .605	- .560	- .518	- .480	- .447
.24	- .831	- .768	- .711	- .658	- .608	- .562	- .521	- .485
.26	- .898	- .829	- .767	- .709	- .655	- .606	- .561	- .522
.28	- .964	- .889	- .821	- .759	- .701	- .648	- .600	- .558
.30	- 1.030	- .949	- .875	- .808	- .746	- .689	- .638	- .592
.32	- 1.094	- 1.008	- .928	- .856	- .790	- .729	- .674	- .626
.34	- 1.157	- 1.065	- .980	- .903	- .834	- .768	- .710	- .658
.36	- 1.219	- 1.121	- 1.031	- .949	- .876	- .807	- .745	- .690
.38	- 1.280	- 1.176	- 1.082	- .996	- .917	- .844	- .778	- .720
.40	- 1.339	- 1.230	- 1.130	- 1.040	- .957	- .880	- .810	- .749

TABLE 4.V

The reduced residual enthalpy $\frac{\tilde{H}^{res}}{N\epsilon}$ of methane (Din[4]). $\sigma = 3.817$ Å
$\epsilon/k = 148.2$ °K

T^* / p^*	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2
.02	- .145	- .125	- .119	- .114	- .108	- .098	- .080	- .073
.04	- .293	- .260	- .237	- .220	- .206	- .189	- .162	- .152
.06	- .456	- .398	- .359	- .336	- .309	- .286	- .250	- .228
.08	- .630	- .540	- .483	- .451	- .417	- .381	- .335	- .307
.10	- .831	- .705	- .624	- .570	- .525	- .478	- .423	- .388
.12	- 1.060	- .897	- .786	- .704	- .637	- .574	- .512	- .469
.14	- 1.321	- 1.110	- .954	- .839	- .749	- .674	- .600	- .550
.16	- 1.564	- 1.309	- 1.120	- .982	- .871	- .779	- .693	- .631
.18	- 1.803	- 1.509	- 1.286	- 1.123	- .993	- .882	- .786	- .712
.20	- 2.038	- 1.707	- 1.453	- 1.264	- 1.113	- .984	- .879	- .795
.22	- 2.269	- 1.903	- 1.620	- 1.405	- 1.232	- 1.086	- .969	- .879
.24	- 2.487	- 2.095	- 1.799	- 1.566	- 1.351	- 1.186	- 1.058	- .959
.26	- 2.687	- 2.279	- 1.960	- 1.706	- 1.469	- 1.287	- 1.141	- 1.032
.28	- 2.870	- 2.457	- 2.114	- 1.834	- 1.587	- 1.387	- 1.220	- 1.099
.30	- 3.044	- 2.628	- 2.280	- 1.985	- 1.701	- 1.484	- 1.302	- 1.170
.32	- 3.213	- 2.799	- 2.425	- 2.093	- 1.812	- 1.579	- 1.387	- 1.248
.34	- 3.352	- 2.942	- 2.562	- 2.216	- 1.918	- 1.672	- 1.469	- 1.320
.36	- 3.469	- 3.065	- 2.684	- 2.330	- 2.021	- 1.762	- 1.549	- 1.392
.38	- 3.566	- 3.171	- 2.793	- 2.437	- 2.120	- 1.849	- 1.627	- 1.462
.40	- 3.641	- 3.258	- 2.888	- 2.537	- 2.215	- 1.934	- 1.705	- 1.532

T^* / p^*	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0
.02	- .061	- .055	- .057	- .054	- .052	- .047	- .036	- .033
.04	- .136	- .124	- .118	- .108	- .104	- .095	- .079	- .074
.06	- .207	- .190	- .177	- .163	- .155	- .143	- .123	- .115
.08	- .278	- .255	- .239	- .219	- .207	- .192	- .171	- .159
.10	- .351	- .322	- .299	- .275	- .259	- .240	- .216	- .200
.12	- .422	- .386	- .361	- .331	- .310	- .288	- .260	- .241
.14	- .495	- .452	- .421	- .386	- .365	- .340	- .308	- .282
.16	- .569	- .518	- .482	- .444	- .417	- .388	- .353	- .325
.18	- .642	- .585	- .543	- .500	- .469	- .436	- .397	- .367
.20	- .715	- .652	- .606	- .557	- .521	- .484	- .441	- .406
.22	- .789	- .719	- .670	- .616	- .575	- .531	- .483	- .444
.24	- .860	- .784	- .733	- .672	- .627	- .580	- .525	- .482
.26	- .929	- .849	- .791	- .726	- .678	- .626	- .567	- .520
.28	- .997	- .913	- .847	- .779	- .726	- .671	- .609	- .559
.30	- 1.064	- .975	- .903	- .831	- .775	- .716	- .651	- .597
.32	- 1.131	- 1.035	- .958	- .883	- .822	- .760	- .693	- .636
.34	- 1.196	- 1.094	- 1.012	- .933	- .869	- .805	- .734	- .673
.36	- 1.260	- 1.151	- 1.065	- .981	- .916	- .848	- .774	- .710
.38	- 1.322	- 1.208	- 1.118	- 1.029	- .961	- .892	- .813	- .747
.40	- 1.383	- 1.263	- 1.169	- 1.074	- 1.005	- .934	- .851	- .783

The inaccuracies of the values used for enthalpy, reported in table 4.I, are given for the total enthalpy. Since, especially in the lower pressure range, the residual enthalpy is small compared with the tabulated total enthalpies, these inaccuracies have to be taken larger for the residual enthalpy. To examine the influence of uncertainties in the reduction factors in table 4.VI a comparison is made between H^{res*} of nitrogen calculated with $\epsilon/k = 95.9°K$, $\sigma = 3.718$ Å and with $\epsilon/k = 95.05°K$, $\sigma = 3.698$ Å. The values of both sets of parameters are taken from literature (cf. table 4.I). The deviations of 0.9% in ϵ/k and 0.5% in σ together give a variation in H^{res*} of about 3% in the temperature and pressure range considered.

TABLE 4.VI

Comparison of the reduced residual enthalpy H^{res*} of N_2 calculated with $\epsilon = 95.9°K$, $\sigma = 3.718$ Å and of N_2' calculated with $\epsilon = 95.05°K$, $\sigma = 3.698$ Å

	T*	1.5		2.0		2.5		3.0	
P*		H^{res*}	Δ	H^{res*}	Δ	H^{res*}	Δ	H^{res*}	Δ
.10	N_2'	-0.868	+0.029	-0.460	+0.012	-0.301	+0.007	-0.210	+0.005
	N_2	-0.839		-0.448		-0.294		-0.205	
.20	N_2'	-2.583	+0.176	-0.971	+0.028	-0.609	+0.014	-0.415	+0.011
	N_2	-2.407		-0.943		-0.595		-0.404	
.30	N_2'	-4.267	+0.146	-1.495	+0.045	-0.918	+0.023	-0.611	+0.017
	N_2	-4.121		-1.450		-0.895		-0.594	
.40	N_2'	-4.554	+0.086	-1.986	+0.057	-1.204	+0.030	-0.794	+0.022
	N_2	-4.468		-1.929		-1.174		-0.772	

The deviations Δ of the H^{res*} values for the gases N_2 (Din[4]), CH_4(KOL[2]) and CH_4(Din[4]) from those of A(Din[6]) are reported in table 4.VII. Argon is chosen as basic gas, because it is a noble gas, for which accurate thermodynamic data are known. The deviations amount to at most about 10% in the range under consideration (except for N_2 at $T^* = 1.5$ and p^* between 0.20 and 0.40, where the deviations are from 20 to 30%). These deviations cannot be ascribed only to the inaccuracies in the enthalpy data

TABLE 4.VII

Comparison of the reduced residual enthalpy H^{res*} for the gases N_2(Din), CH_4(KOL) and CH'_4(Din) with A(Din)

p^* \ T^*		1.5		2.0		2.5		3.0	
		H^{res*}	Δ	H^{res*}	Δ	H^{res*}	Δ	H^{res*}	Δ
.10	A	-0.898		-0.439		-0.301		-0.212	
	N_2	-0.868	+0.030	-0.460	-0.021	-0.301	0	-0.210	+0.002
	CH_4	-0.873	+0.025	-0.499	-0.060	-0.316	-0.015	-0.216	-0.004
	CH'_4	-0.831	+0.067	-0.478	-0.039	-0.299	+0.002	-0.200	+0.012
.20	A	-2.108		-0.901		-0.595		-0.408	
	N_2	-2.583	-0.475	-0.971	-0.070	-0.609	-0.014	-0.415	-0.007
	CH_4	-2.175	-0.067	-0.997	-0.096	-0.646	-0.051	-0.432	-0.024
	CH'_4	-2.038	+0.070	-0.984	-0.083	-0.606	-0.011	-0.406	+0.002
.30	A	-3.179		-1.354		-0.875		-0.592	
	N_2	-4.267	-1.088	-1.495	-0.141	-0.918	-0.043	-0.611	-0.019
	CH_4	-3.397	-0.218	-1.479	-0.125	-0.926	-0.051	-0.625	-0.033
	CH'_4	-3.044	+0.135	-1.484	-0.130	-0.903	-0.028	-0.597	-0.005
.40	A	-3.582		-1.777		-1.130		-0.749	
	N_2	-4.554	-0.972	-1.986	-0.209	-1.204	-0.074	-0.794	-0.045
	CH_4	-3.845	-0.263	-1.934	-0.157	-1.181	-0.051	-0.788	-0.039
	CH'_4	-3.641	-0.059	-1.934	-0.157	-1.169	-0.039	-0.783	-0.034

and the intermolecular parameters, but are also a result of the deviations from the law of corresponding states. To obtain an insight into these deviations over a certain region of p^* and T^*, we have used a graphic method of comparison, analogous to the well-known method for the determination of ϵ and σ from B-coefficients by comparing log $|B^*|$ vs. log T^* plots with log $|B|$ vs. log T plots. We have generalised this method so that it is fit for comparing properties which depend on two variables, in this case the pressure and temperature. For this purpose we have drawn lines of constant value of $\tilde{H}/RT$ (iso-$\tilde{H}/RT$ lines) in the log p, log T plane for A, N_2 and CH_4. The property $\tilde{H}$ is devided by RT since it is necessary that the property plotted is dimensionless. In fig. 4.1 an example is given for A. If the plots are put on transparant paper it is easy to compare the iso-$\tilde{H}/RT$ lines of two plots by placing one on top of the other. If the iso-$\tilde{H}/RT$ line can be brought into coincidence by shifting along the log p and log T axis, it is possible to determine scale factors for the temperature and pressure. However, for the gases A, N_2 and CH_4 it

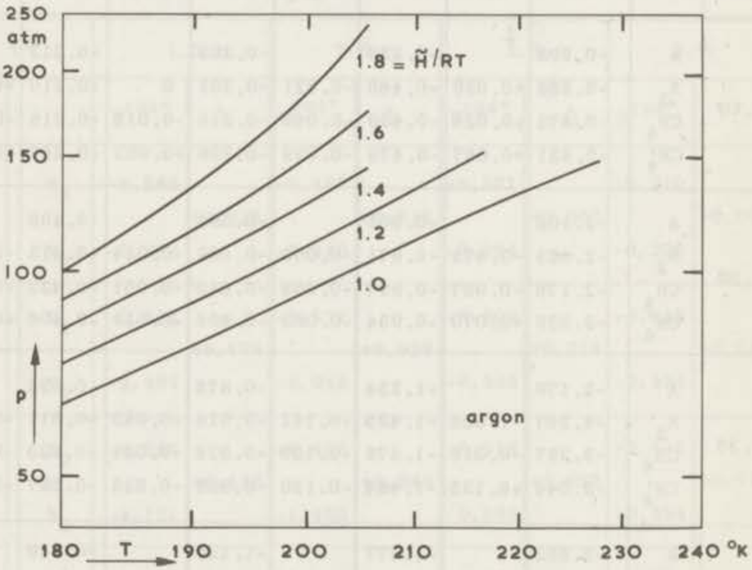

Fig. 4.1.

Pressure p vs. temperature T at constant values of $\tilde{H}/RT$ for the gas A(Din).

proves that no reasonable coincidence can be obtained over the considered region of the p,T plane. This means that no scale factors can be obtained. Hence it is not possible to decrease the deviation in $H^*(p^*,T^*)$ considerably for these three gases by a change in the intermolecular parameters.

4.3 *Comparison of the compressibility factors and the determination of scale factors of the gases A, N_2, CH_4 and Xe*

The composers of the tables used have calculated the enthalpy from the experimental p-V-T data by using a formula, which can always be derived from

$$dH = \left\{V - T\left(\frac{\partial V}{\partial T}\right)_p\right\}dp \qquad \text{or from}$$

$$dH = \left\{T\left(\frac{\partial p}{\partial T}\right)_V - V\left(\frac{\partial p}{\partial V}\right)_T\right\}dV .$$

Since the compressibility factor $Z = p\tilde{V}/RT$ is determined directly from experiments and H is calculated, which may introduce inaccuracies, it is interesting to see if the law of corresponding states gives a better fit for Z. Therefore we have decided to compare the compressibility factors Z of the gases under study. Since Z, like H, also depends on two independent variables, we followed the same procedure as described in section 4.2. In a reduced temperature range from 1.3 up to 2.0 (in the neighbourhood of the critical temperature) and a reduced pressure range from 0.08 up to 0.8 the compressibility factors are obtained from the specific volume or the density as a function of pressure. Table 4.I reports for the gases CH_4, N_2, A and Xe the temperature and pressure range in which the compressibility factors are chosen and the estimated error in Z given by the authors. It should be remarked that in some cases the data on accuracy are incomplete. For comparison, the iso-Z lines are drawn in the log p, log T plane for the gases CH_4(KOL[2]), CH_4(Din[4]), N_2(Din[4]), N_2(NBS[5]), A(Din[6]), A(vdW[7]) and Xe(vdW[8]). Fig. 4.2 represents such a graph for A. The gas xenon is added since very accurate data[8] are available.

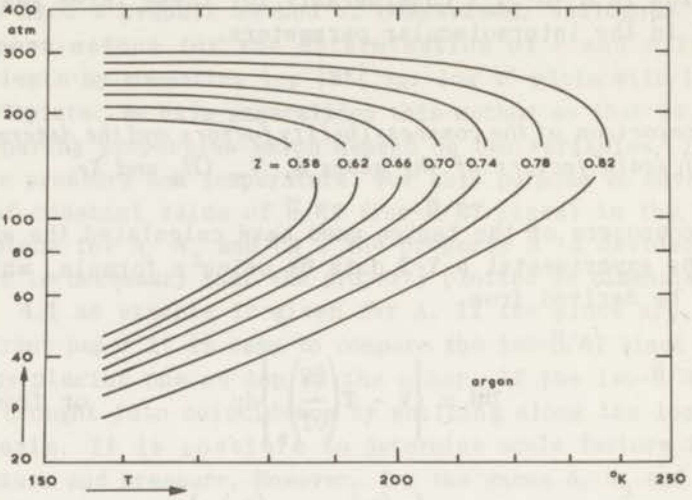

Fig. 4.2.

Pressure p vs. temperature T at constant values of Z for the gas A(Din).

A good coincidence of the iso-Z lines for Z from 5.8 to 8.2 is obtained. In the range T^* from 1.4 to 2.0 the deviation $\Delta Z = (Z_A - Z)/Z_A$ is at most 1.5% for lower pressures and at most 1% for higher pressures. In this case too, an exception has to be made for nitrogen from Din's tables in the lower temperature range; the deviation here is much larger. It is remarkable that this is not the case for NBS data of nitrogen[5]. One has the impression that this deviation points to errors in the work of DIN[4].
If the iso-Z lines are brought into coincidence by shifting along the log p and log T axis, it is possible to determine scale factors for temperature and pressure. From these scale factors the ratio of the parameter of argon ϵ_A and another gas ϵ and the ratio of the parameter of argon σ_A^3 and of another gas σ^3 are obtained. These values and the values of the same ratios from literature[14] are reported in table 4.VIII.

Since the comparison of the iso-Z lines is performed in the neighbourhood of the critical point, we have also determined the scale factors from the critical temperature and the critical pressure of the gases. The values of these critical constants are given in table 4.IX, while the scale factors are given in table 4.VIII. As was to be expected, the values of the latter factors agree well with those of the scale factors obtained from the Z-coincidence.

TABLE 4.VIII

Comparison of scale factors					
Scale factors	Obtained from	CH_4 (KOL)(Din)	N_2 (Din)	N_2 (NBS)	Xe (vdW)
ϵ_A/ϵ	Literature	0.808	1.249	1.249	0.532
	Z-coincidence	0.787	1.200	1.196	0.518
	Crit. constants	0.791	1.194	1.194	0.520
$(\sigma_A/\sigma)^3$	Literature	0.710	0.783	0.783	0.586
	Z-coincidence	0.747	0.863	0.820	0.631
	Crit. constants	0.755	0.833	0.833	0.624

TABLE 4.IX

Critical constants				
	A	N_2	CH_4	Xe
T_c (°K)	150.7	126.2	190.7	289.7
p_c (atm)	48.0	33.5	45.8	57.6

LEVELT[15) has also determined scale factors ϵ_{Xe}/ϵ_A and $(\sigma_{Xe}/\sigma_A)^3$. She compared the minima in the Z vs. density isotherms of A and Xe. BOATO and CASANOVA[16) have obtained new intermolecular parameters holding for Ne, A, Kr and Xe. They studied the quantum deviation from the law of corresponding states of the noble gases, starting from the vapour pressure difference between the isotopes. From this they concluded that the intermolecular parameters of the Lennard-Jones potential, as obtained from the second virial coefficient data, do not describe this effect completely. Slight changes in ϵ and σ appear to be necessary. They give what they call a self consistent set of new parameters valid for the condensed state of these noble gases. The scale factors for Xe obtained by our method agree very well with those of LEVELT and those of BOATO et al., as shown in table 4.X. The difference between the scale factors obtained from the coincidence of Z and those from literature[15) is larger than would be expected from the accuracy of 1% in the intermolecular parameters (cf. table 4.VIII). This might point to the fact that in the region we considered the Lennard-Jones (6-12) potential is not giving a sufficiently good description of the behaviour of the molecules or that the assumption of additivity of pair-interaction potentials (see assumption 3 in section 4.1) is not justified. Unfortunately we cannot separate these two possibilities.

TABLE 4.X

Comparison with other authors					
Scale factors	Levelt	Boato	Z-coinc.	Critical constants	B-Coeff.
ϵ_A/ϵ_{Xe}	0.518	0.520	0.518	0.520	0.532
$(\sigma_A/\sigma_{Xe})^3$	0.633	0.635	0.631	0.624	0.586

4.4 Calculations with ϵ' and σ' obtained from scale factors

With help of the scale factors new intermolecular parameters ϵ' and σ' for N_2, CH_4 and Xe can be found from the given parameters

TABLE 4. XI

Obtained from / Gas	Intermolecular parameters			
	Literature 14)		Scale factors	
	ϵ/k ($^\circ$K)	σ (Å)	ϵ'/k ($^\circ$K)	σ' (Å)
A (Din)	120	3.41	(120)	(3.41)
N_2 (Din)	96	3.72	100	3.58
CH_4 (Din)	148	3.82	152	3.74
Xe (vdW)	225	4.07	232	3.98

TABLE 4. XII

Comparison of the enthalpies reduced with (ϵ',σ') of N_2 (Din) and CH_4(Din) with the reduced enthalpy of A(Din).

T* / p*		1.5		2.0	
		H^{res*}	Δ	H^{res*}	Δ
0.10	A	-0.898		-0.439	
	N_2	-0.889	+0.009	-0.469	-0.030
	CH_4	-0.829	-0.069	-0.474	-0.035
0.20	A	-2.108		-0.901	
	N_2	-2.385	+0.277	-0.977	-0.076
	CH_4	-2.011	+0.097	-0.975	-0.074
0.30	A	-3.179		-1.354	
	N_2	-3.709	-0.530	-1.482	-0.128
	CH_4	-2.985	+0.194	-1.451	-0.097
0.40	A	-3.582		-1.777	
	N_2	-3.970	-0.388	-1.908	-0.131
	CH_4	-3.472	+0.110	-1.880	-0.103

of A (table 4.XI). These new parameters have been used for the calculation of $H^{res^*}(p^*,T^*)$ and for the calculation of $\tilde{H}^E$ as described in chapter 3. The values so obtained can be compared with those that were obtained with the original parameters ϵ and σ.

The residual enthalpies reduced with (ϵ',σ') for CH_4 and N_2 are compared with that for A in table 4.XII. At $T^* = 1.5$ the deviations for N_2 from A have become a factor of 2 smaller than the deviations reported in table 4.VII, where H^{res} was reduced with the original (ϵ,σ). In the other cases, on the contrary, the results do not become significantly better. It turns out that the agreement between the reduced residual enthalpies of the various gases remains considerably worse than that between the compressibility factors of the same gases. This may be the result of inaccuracies in the enthalpy data which are larger than those in the compressibility factors, since in general the enthalpy is a calculated property (cf. section 1.2). An other possibility is that the deviations of the law of corresponding states have larger effect on H than on Z.

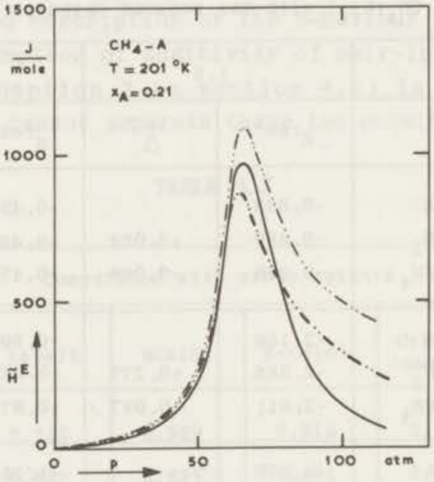

Fig. 4.3.

The molar excess enthalpy, $\tilde{H}^E$, as a function of pressure for the system CH_4-A.

— ·· — ·· — calculated with (ϵ,σ)
———— experiment
— · — ·· — calculated with (ϵ',σ').

In order to examine the influence of the use of the parameters ϵ' and σ' in the calculation of $\tilde{H}^E$ with the "two-liquid" model, we have chosen the mixture CH_4-A with reference gas CH_4. In fig. 4.3 $\tilde{H}^E$ is plotted against p for $T = 201^\circ K$ and $x_A = 0.21$. The experimental values and the values calculated with (ϵ,σ) have been taken from chapter 2 and 3, respectively. The values calculated with (ϵ',σ') are larger than those calculated with (ϵ,σ), but do not give better agreement with the experimental values. The same calculations have been performed on the mixture N_2-CH_4 with reference gas CH_4. The maximal deviations between the values calculated with (ϵ',σ') and with (ϵ,σ) amount to 4%.

Concluding we can state that, for the calculations of the excess enthalpy, it is not useful to apply adjusted values of the intermolecular parameters in order to obtain a better fit with the experiment.

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CHAPTER 5

SURVEY OF THERMODYNAMIC PROPERTIES OF SOME GASES

5.1 Introduction

A survey of the publications, which give tabular or graphical data of thermodynamic properties for a number of gases, has been composed in this chapter. We have chosen the so-called cryogenic fluids: normal-hydrogen, para-hydrogen, helium, neon, nitrogen, carbon monoxyde, oxygen and argon, as well as methane and xenon. We have limited our literature search mainly to four important sources of data, viz. the publications of Din of the British Oxygen Company Ltd. (Din), of the Kamerlingh Onnes Laboratory (KOL), of the National Bureau of Standards (NBS) and of the Van der Waals Laboratory (vdW). For an extensive bibliography of references for thermophysical properties of most of the gases mentioned above the reader is referred to the publication of the NATIONAL BUREAU OF STANDARDS[51].
The survey is limited to the thermodynamic properties, although some publications report at the same time, for instance, the viscosity and the velocity of sound. More limitations will be discussed in the next section.

5.2 The columns of the table

1. Gas. The gases have been arranged according to their molecular weight.
2. Temperature-, pressure- and density range. For a good comparison of the ranges it seems better to write the properties in the same units. When an author did not express the temperature, pressure or density in degrees Kelvin, atmospheres and Amagat units, respectively, we have converted these units. Publications in which only pressures less than 80 atmospheres occur, have not been reported in this survey.

3. Thermodynamic properties. The properties reported in the publications are noted in the columns with the mark 0. If the unit of a property is not the same as noted in the top of the column, this unit has been given. Only the thermodynamic properties of the gasphase have been reported in this survey.

4. Saturation. The mark + means that in the publication considered also properties of saturated vapour are mentioned. Publications reporting only these properties, however, have not been noted in this table.

5. Equation. The small letters refer to the general form of the equation of state which was used by the author. These equations are reported in section 5.4. Some of the equations of state are written in a form, which facilitate calculation of the p-V-T data on a computer (see equation d). The coefficients in the equations of state have been derived from the experimental data and can be found in the references mentioned.

6. References experimental data. The references of experimental p-V-T data have only been inserted if the same author has also derived thermodynamic properties. When several different sources of experimental data have been used it is indicated with *.

7. General indication. The meaning of the abbreviations mentioned in this column is given in the introduction to this chapter.

5.3 Symbols

Z	Compressibility factor
p	Absolute pressure
V	Specific volume
T	Absolute temperature
d	Density
S	Entropy
S_i	Internal entropy
H	Enthalpy
U	Energy
U_i	Internal energy
G	Gibbs free energy
F	Helmholz free energy
C_v	Specific heat at constant volume
C_p	Specific heat at constant pressure

Gas	Temp. range °K	Press. range atm	Density range Am	Thermodynamic properties (units)									
				Z	pV Am	p atm	V $\frac{cm^3}{g}$	d $\frac{g}{cm^3}$	S $\frac{cal}{mole.\,^{\circ}K}$	S_i $\frac{cal}{mole.\,^{\circ}K}$	H $\frac{cal}{mole}$	U $\frac{cal}{mole}$	U_i $\frac{cal}{mole}$
nH_2	98-423		0-840		0	0							
	273-423		9-940		0	0							
	98-423		0-600						0	0	0	0	0
	98-423	1-800			0				0		0	0	
	20-300	1-100					0		$\frac{J}{g.\,^{\circ}K}$		$\frac{J}{g}$		$\frac{J}{g}$
	16-600		1-500	0		0			$\frac{S^{\circ}-S}{R}$		$\frac{H^{\circ}-H}{RT}$		
pH_2	13-100	0,07-340	0.5-960						$\frac{J}{mole.\,^{\circ}K}$		$\frac{J}{mole}$		$\frac{J}{mole}$
	14-100												
	20-300	1-340					0		$\frac{J}{g.\,^{\circ}K}$		$\frac{J}{g}$		$\frac{J}{g}$
	19-340	0.7-340					$\frac{cuft}{lb}$		$\frac{btu}{lb.\,^{\circ}R}$		$\frac{btu}{lb}$		$\frac{btu}{lb}$
He	273-423		9-173		0	0							0
	18-300	0.1-100						0	$\frac{J}{g.\,^{\circ}K}$		$\frac{J}{g}$		
	1-500	0.001-300					0		$\frac{cal}{g.\,^{\circ}K}$		$\frac{cal}{g}$		
	2-20	1-100				0	$\frac{1}{kg}$		$\frac{cal}{g.\,^{\circ}K}$		$\frac{cal}{g}$	$\frac{J}{g}$	
	3-300	0.5-100					0		$\frac{J}{g.\,^{\circ}K}$		$\frac{J}{g}$		$\frac{J}{g}$
	10-310	1-400					$\frac{cuft}{lb}$		$\frac{btu}{lb.\,^{\circ}F}$		$\frac{btu}{lb}$		
CH_4	273-423		19-53		0	0							
	273-423		0-225						0		0	0	
	130-470	1-1000					$\frac{cm^3}{mole}$		0		0		
	110-480	0.1-300					0		$\frac{cal}{g.\,^{\circ}K}$		$\frac{cal}{g}$		

Thermodynamic properties (units)										
G $\frac{\text{cal}}{\text{mole}}$	F $\frac{\text{cal}}{\text{mole}}$	C_v $\frac{\text{cal}}{\text{mole.}^{\circ}\text{K}}$	C_p $\frac{\text{cal}}{\text{mole.}^{\circ}\text{K}}$	Saturation	Graphs included	Eq.	Ref.	Ref. exp. data	Gen. ind.	Remarks
						a	1	1, 2	vdW	
						a	2	2	"	
0	0	0	0				3	1, 2	"	
0	0	0	0				4	1	"	
				+			5	•	NBS	
				+	T-S	e	6	•	"	$S^{\circ}-S$ $H^{\circ}-H$ residual value
		$\frac{\text{J}}{\text{mole.}^{\circ}\text{K}}$	$\frac{\text{J}}{\text{mole.}^{\circ}\text{K}}$	+		a	7	8	"	
				+	T-S H-S	d	9	•	"	
				+	T-S H-S	d	9	•	"	$^{\circ}$R = degrees Rankine
			0			a	10	10	vdW	
					Z-P T-S	c	11	•	-	
				+	log T-S		12	•	KOL	Only a graph (a large size graph separately obtainable)
			$\frac{\text{cal}}{\text{g.}^{\circ}\text{K}}$	+	H-S T-S p-T V-S p-V $p-U_1$ C_p-T Z-p		13	•	NBS	only graphs
				+		d	14	•	"	
					T-S	1	15	12	-	
						a	16	16	vdW	
0	0					a	17	16	"	
		0	0	+	T-S	h	18	•	Din	
					log p-H	g	19	•	KOL	Only a graph (a large size graph separately obtainable)

Gas	Temp. range °K	Press. range atm	Density range Am	Thermodynamic properties (units)									
				Z	pV Am	p atm	V $\frac{cm^3}{g}$	d $\frac{g}{cm^3}$	S $\frac{cal}{mole.\,°K}$	S_i $\frac{cal}{mole.\,°K}$	H $\frac{cal}{mole}$	U $\frac{cal}{mole}$	U_i $\frac{cal}{mole}$
Ne	273-423		0-1080		0	0							
	30-300	0.1-200		0				0					
	25-300	0.1-200						0	$\frac{J}{g.\,°K}$		$\frac{J}{g}$		
	90-673	0-100			0								
	27-320	1-200					$\frac{cuft}{lb}$		$\frac{btu}{cuft\ NTP.\,°K}$		$\frac{btu}{cuft\ NTP}$		
N_2	273-423		187-578		0	0							
	273-423		0-600						0			0	
	148-423		0-760		0				$\frac{J}{mole.\,°K}$	$\frac{J}{mole.\,°K}$	$\frac{J}{mole}$	$\frac{J}{mole}$	$\frac{J}{mole}$
	148-423	0-6000			0				0		0	0	
	64-300	0.1-200					0		$\frac{J}{g.\,°K}$		$\frac{J}{g}$		$\frac{J}{g}$
	78-473	0.9-300					$\frac{l}{mole}$		0		0		
	78-283	1-204									$\frac{btu}{lb}$		
	5000-40000	0.2-100		0				0	0		0		0
	80-700	1-6000					$\frac{cm^3}{mole}$		$\frac{J}{mole.\,°K}$		$\frac{J}{mole}$		
	80-533	0.7-102		0			$\frac{cuft}{lb}$		$\frac{btu}{lb.\,°R}$		$\frac{btu}{lb}$		
CO	273-423		0-600						0		0	0	
	273-423		0-600		0	0							
	70-300	0.1-300						0	$\frac{J}{g.\,°K}$		$\frac{J}{g}$		$\frac{J}{g}$
	273-423	0-300			0				0		0	0	
	68-473	0.15-300					0		$\frac{cal}{g.\,°K}$		$\frac{cal}{g}$		

Thermodynamic properties (units)				Saturation	Graphs included	Eq.	Ref.	Ref. exp. data	Gen. ind.	Remarks
G $\frac{\text{cal}}{\text{mole}}$	F $\frac{\text{cal}}{\text{mole}}$	C_v $\frac{\text{cal}}{\text{mole.}^\circ\text{K}}$	C_p $\frac{\text{cal}}{\text{mole.}^\circ\text{K}}$							
						a	20	20	vdW	
				+	Z-log p		21	20, 23	-	
				+	T-S	d	22	•	-	Only a graph
						a	23	23	-	
						f	24	•	-	NTP means 70°F and 14.696 psia
						a	25		vdW	
	0	0				a	26	25, 27	"	
$\frac{\text{J}}{\text{mole}}$	$\frac{\text{J}}{\text{mole}}$	$\frac{\text{J}}{\text{mole.}^\circ\text{K}}$	$\frac{\text{J}}{\text{mole.}^\circ\text{K}}$			a	28	25, 28, 29	"	
0	0	0	0		T-S H-S H-log p		30	28	"	
				+		d	31	•	NBS	
				+	log p-H	a	32	•	KOL	Only a graph (a large size graph separately obtainable)
				+	p-H		33	33, •	-	
					Z-T d-T U_1-T H-T S-T		34		-	Calculated from partion function Z
		$\frac{\text{J}}{\text{mole.}^\circ\text{K}}$	$\frac{\text{J}}{\text{mole.}^\circ\text{K}}$	+	T-S		18	•	Din	
				+	Z-p H-S	h	35	•	-	
0	0	0	0				36	37	vdW	
						a	37	37	"	
				+	Z-log p T-S	d	38	•	NBS	
0	0	0	0		T-S H-S H-log p		39	37	vdW	
							40	•	KOL	A large size graph separately obtainable

Gas	Temp. range °K	Press. range atm	Density range Am	Thermodynamic properties (units)									
				Z	pV Am	p atm	V $\frac{cm^3}{g}$	d $\frac{g}{cm^3}$	S $\frac{cal}{mole.\,^\circ K}$	S_1 $\frac{cal}{mole.\,^\circ K}$	H $\frac{cal}{mole}$	U $\frac{cal}{mole}$	U_1 $\frac{cal}{mole}$
O_2	273, 293, 323		0-130		0	0							
	273, 293, 323	0-130			0			Am					
	73-473	0.11-300					0		$\frac{cal}{g.\,^\circ K}$		$\frac{cal}{g}$		
	55-300	0.1-300						$\frac{mole}{1}$	$\frac{J}{mole}$		$\frac{J}{mole}$		$\frac{J}{mole}$
A	133-273		0-640		0								
	133-273		0-640										
	133-273	0-1050			0				0	0	0	0	0
	273-423		0-640		0	0							
	273-423		0-640						0		0	0	
	273-423	0-2000			0				0		0	0	
	90-600	1-5000					$\frac{cm^3}{mole}$		$\frac{J}{mole.\,^\circ K}$		$\frac{J}{mole}$		
Xe	273-423		0-520		0	0							
	273-423		0-520						0	0	0	0	0
	273-423	0-2800			0				0		0	0	

5.4 Equations of state

a. $pV = A + Bd + Cd^2 + Zd^3 + Dd^4 + Yd^5 + Ed^6 + Fd^7 + Gd^8$

b. $pV = A + Bp + Cp^2 + Dp^4 + Ep^6$

c. $V = \dfrac{RT}{p} + \dfrac{E}{(p+1)^{1/2}} + F - \exp[-(A+Bp)T - (Cp+D)]$

d. $$p = RTd + \left(Rn_1T+n_2+\frac{n_3}{T}+\frac{n_4}{T^2}+\frac{n_5}{T^4}\right)d^2 + (Rn_6T+n_7)d^3 + n_8d^4 +$$

$$+ \left(\frac{n_9}{T^2}+\frac{n_{10}}{T^3}+\frac{n_{11}}{T^4}\right)d^3 \exp\left(\frac{-n_{12}d^2}{T}\right) + \left(\frac{n_{13}}{T^2}+\frac{n_{14}}{T^3}+\frac{n_{15}}{T^4}\right)d^5 \exp\left(\frac{-n_{12}d^2}{T}\right) +$$

$$+ n_{16}d^5 + n_{17}d^6$$

e. $\dfrac{pV}{RT} = 1 + Bd + (\tfrac{1}{2}B^2+C)d^2 + \left(\dfrac{1}{6}B^3+BC\right)d^3 + \left(\dfrac{1}{24}B^4+\tfrac{1}{2}C^2+\tfrac{1}{2}B^2C\right)d^4 + \ldots$

Thermodynamic properties (units)				Saturation	Graphs included	Eq.	Ref.	Ref. exp. data	Gen. ind.	Remarks
G $\frac{\text{cal}}{\text{mole}}$	F $\frac{\text{cal}}{\text{mole}}$	C_v $\frac{\text{cal}}{\text{mole. }^\circ\text{K}}$	C_p $\frac{\text{cal}}{\text{mole. }^\circ\text{K}}$							
						a	41	41	vdW	
					log p-H		40	*	KOL	A large size graph separately obtainable
				+			42	*	NBS	
						a	43	43	vdW	
0	0	0	0				44	43	"	
						a	45	45	"	
0	0	0	0				46	45	"	
0	0		0		T-S H-S H-log p		47	45	"	
		$\frac{\text{J}}{\text{mole. }^\circ\text{K}}$	$\frac{\text{J}}{\text{mole. }^\circ\text{K}}$	+	T-S		48	*	Din	
						a	49	49	vdW	
0 0	0 0	0 0	0 0				50	49	"	

f. $\frac{p}{dRT} - 1 = \sum_{qr} \left[a_{qr} \frac{d^r}{T^q} \right]$ where: q, r = 0, 1; 1, 1; 3, 1; 0, 2; 1, 2; 3, 2; 3, 3; 3, 4; 1, 5; 3, 6; 3, 8; 3, 10.

g. $pV = A + Bd + Cd^2(1-bd) + Dd^3\log(1-bd)$

h. $p = RTd + \left(B_oRT - A_o - \frac{C_o}{T^q}\right)d^2 + (bRT-a)d^3 + a\alpha d^6 + \frac{cd^3}{T^2}(1+\gamma d^2)\exp(-\gamma d^2)$

i. $p = \frac{RT(1-C/VT^3)}{V^2}\left[V + B\left(1-\frac{b}{V}\right)\right] - \frac{A}{V^2}\left(1-\frac{a}{V}\right)$

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SAMENVATTING

De thermodynamische grootheden van gasmengsels worden nog vrij algemeen bepaald op basis van p-V-T metingen. Met behulp van de p-V-T gegevens wordt een toestandsvergelijking opgesteld en daaruit worden de thermodynamische grootheden afgeleid. Deze methode wordt bv. gevolgd voor het bepalen van de enthalpie van een mengsel (H_m). Een nadeel van deze methode is echter, dat door de berekening de nauwkeurigheid van H_m nadelig beinvloed wordt. Bovendien is men meer geinteresseerd in het verschil tussen de enthalpie van het mengsel en de lineaire combinatie van de enthalpieën van de zuivere componenten, de zgn. excess enthalpie (H^E). Daar H^E meestal een kleinere waarde heeft dan H_m dient men, teneinde een redelijke nauwkeurigheid in H^E te bereiken, deze direct te bepalen. Voor vloeistofmengsels zijn reeds soortgelijke experimenten uitgevoerd. Voor gasmengsels zijn ons alleen bekend de bepalingen van de molaire exces enthalpie ($\tilde{H}^E$) door KNOESTER, TACONIS en BEENAKKER en van het molaire volume exces ($\tilde{V}^E$) door ZANDBERGEN en BEENAKKER voor de mengsels H_2-N_2, H_2-A en N_2-A. De eerste grootheid wordt wel mengwarmte genoemd, daar deze de hoeveelheid warmte voorstelt nodig om de gassen onder gelijk blijvende druk en temperatuur te doen mengen. Het in dit proefschrift beschreven onderzoek is een voortzetting van de reeds genoemde mengwarmte bepalingen. Hierbij werden de gasmengsels CH_4-A, CH_4-N_2, H_2-CH_4, He-CH_4 en He-A onderzocht.

In hoofdstuk 1 wordt een beschrijving gegeven van het gedrag van de mengwarmte. Uit het feit dat voor mengsels bij lage dichtheden slechts binaire botsingen tussen de moleculen beschouwd behoeven te worden, kan worden afgeleid dat $\tilde{H}^E$ lineair in de druk en parabolisch in de concentratie is. Voor mengsels met hoge dichtheden wordt gebruik gemaakt van de vloeistof theorieën van SCOTT en PRIGOGINE. Zij passen de wet van overeenstemmende toestanden toe op het mengsel en op de zuivere componenten. Deze wet zegt dat thermodynamische grootheden dimensieloos gemaakt (gereduceerd), met bijvoorbeeld de parameters ϵ en σ van de Lennard-Jones potentiaal, onder gelijkwaardige condities (gelijke gereduceerde druk en temperatuur) aan elkaar gelijk zijn. Hoofdstuk 1 wordt besloten met een bespreking van de keuze der gasmengsels.

In hoofdstuk 2 worden de mengwarmte experimenten besproken. Voor de metingen is gebruik gemaakt van een stromingscalorimeter waarin continu gassen onder gelijke druk en temperatuur gemengd worden. Daar bij de onderzochte mengsels steeds een afkoeling bij menging optreedt, kan deze door het toevoeren van warmte gecompenseerd worden. De mengwarmte wordt nu berekend uit de hoeveelheid toegevoerde warmte en de doorgestroomde hoeveelheid gasmengsel. De resultaten zijn verwerkt in tabellen en grafieken. Bij 293°K bestaat een bijna lineair verband tussen $\tilde{H}^E$ en p zoals reeds afgeleid was in hoofdstuk 1. Bij lagere temperaturen treedt een maximum in $\tilde{H}^E$ vs. p op. De waarde van dit maximum hangt af van de mate van idealiteit van de andere component van het CH_4 mengsel. Zo varieert dit maximum van 1000 J/mole voor CH_4-A tot ca 2500 J/mole voor He-CH_4 bij 201°K. Hoofdstuk 2 eindigt met een vergelijking van de resultaten voor He-A in het lage druk gebied, met de experimenten over de B-coefficient van Brewer.

De in hoofdstuk 1 genoemde vloeistof theorieën worden in hoofdstuk 3 toegepast op de onderzochte gasmengsels. Bij de berekening van $\tilde{H}^E$ wordt het mengsel beschouwd als een zuiver gas dat voldoet aan de wet van overeenstemmende toestanden. Met behulp van bekende gegevens van een referentiegas kan de enthalpie van het mengsel ($\tilde{H}_m$) worden berekend. $\tilde{H}^E$ volgt dan uit $\tilde{H}_m$ en de enthalpieën van de zuivere componenten. De overeenstemming van de berekende met de experimentele waarden voor $\tilde{H}^E$ bij de laagste temperaturen is bevredigend voor zo ver geen gebruik gemaakt behoeft te worden van He of H_2 als referentiegassen. Bij deze gassen kunnen namelijk quantum effecten een rol gaan spelen.

Daar bij de berekening van $\tilde{H}^E$ uitgegaan is van de geldigheid van de wet van overeenstemmende toestanden, is het interessant om na te gaan of deze aanname gerechtvaardigd is. In hoofdstuk 4 blijkt dat de gereduceerde enthalpieën van N_2, A en CH_4 (de gebruikte referentiegassen) afwijkingen vertonen van maximaal ca 10%. In dit hoofdstuk is tevens een methode ontwikkeld die het mogelijk maakt om grootheden afhankelijk van twee variabelen grafisch te vergelijken. Op deze wijze kan men over een bepaald druk- en temperatuurgebied een duidelijk inzicht krijgen in hoeverre de wet van overeenstemmende toestanden voldoet voor bv. de enthalpie of de toestandsgrootheid $Z = pV/RT$. Bovendien schept deze methode de mogelijkheid de waarden van de parameters ϵ en σ aan te passen voor een bepaald druk- en temperatuurgebied. Voor de gassen N_2, CH_4 en Xe werden in het gebied rond het kritische punt afwijkende waarden voor ϵ en σ gevonden.

Daar bij de berekeningen gebleken is, dat een handzaam overzicht van tabellen met thermodynamische gegevens van veel gebruikte gassen ontbreekt, is in hoofdstuk 5 een dergelijk overzicht opgenomen voor een negental gassen.

STELLINGEN

I. De wijze waarop Senftleben de invloed van een electrisch veld op transport grootheden van het gas $CHCl_3$ verklaart is onjuist.

Senftleben, H., Ann. Phys. 7 (1965) 274.

II. Bij de berekening van de botsingsdoorsnede van een intermoleculaire wisselwerking in het geval van een centraal symmetrische potentiaal geven de methode van Landau en Lifshitz en die van Schiff dezelfde resultaten. Deze equivalentie wordt ook gevonden wanneer men uitgaat van een hoekafhankelijke potentiaal.

Bernstein, R.B., Molecular Beams, J. Ross ed., (Interscience Publishers, New York, 1966)
Reuss, J., Physica 31 (1965) 597.

III. De wijze waarop Druyvesteyn aantoont dat de structuur van de gemengde supergeleidende toestand voorgesteld door het Abrikosov-model stabieler zou zijn dan die voorgesteld door het lagen-model is aan bedenkingen onderhevig.

Druyvesteyn, W.F., Proefschrift Eindhoven (1965).

IV. De bewering van Ewing en Trajmar, dat tengevolge van de ongeveer gelijke grootte van de moleculaire parameters ϵ en σ voor de H_2-Ne en Ne-Ne wisselwerking de H_2 moleculen in Ne vloeistofcellen passen zonder grote afwijkingen te veroorzaken, is aanvechtbaar.

Ewing, G.E. en Trajmar, S., J. Chem. Phys. 42 (1965) 4038.

V. Door de lijnen van gelijke Z $\left(= \frac{pV}{RT}\right)$-waarden van verschillende gassen te vergelijken kan informatie verkregen worden betreffende de betrouwbaarheid van de thermodynamische gegevens van deze gassen.

Dit proefschrift, hoofdstuk 4.

VI. De door Ganguly beschreven brugschakeling is niet essentieel verschillend van de reeds bekende overbrugde T-schakelingen, terwijl de voordelen die zijn schakeling eventueel zou kunnen bieden niet voldoende door hem worden onderkend.

Ganguly, U.S., Proc. IEEE 54 (1966) 419.

VII. Uit de publicatie van Claiborne en Morse is niet met zekerheid vast te stellen of zij aan een volledig supergeleidend preparaat gemeten hebben, daar een essentieel gegeven omtrent de door hen gebruikte opstelling voor adiabatische demagnetisatie ontbreekt.

Claiborne, L.T. en Morse, R.W., Phys. Rev. 136 (1964) A893.

VIII. De aanduiding "gel-filtratie" voor een scheidingsmethode naar molecuulgrootte, geeft aanleiding tot misverstanden met betrekking tot de werking van het bij deze methode gebruikte apparaat.

IX. De door Roder en Goodwin aangegeven waarden voor de coefficienten van de viriaalreeks voor de soortelijke warmte bij constante druk van para-waterstof geven slechts in een deel van het door hen gegeven temperatuurgebied de gewenste beschrijving.

Roder, H.M. en Goodwin, D., NBS. Techn. Note Nr. 130 (1961) 3.

X. Het verdient aanbeveling om het natuurkunde-practicum voor studenten in de medicijnen zo in te richten, dat het verband tussen de uit te voeren proeven en de bestaande medische apparatuur duidelijk naar voren wordt gebracht.

XI. De musische vorming in het Nederlandse lager- en middelbaar onderwijs is onvoldoende.

Stellingen behorende bij het
proefschrift van B. van Eijnsbergen