MASTER

Nucleation and condensation in mixtures of hydrocarbons

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The natural gases ("dry" and "recombined") investigated in this research have been provided by the Nederlandse Aardolie Maatschappij (NAM).
SUMMARY

Calculations of phase equilibrium of binary gas mixtures have been carried out with the Soave–Redlich–Kwong equation of state.

Dropwise nucleation and condensation is studied for binary mixtures of methane with nonane and nitrogen with nonane, for mixtures containing 85 mole% of methane and 15 mole% of nitrogen where nonane or decane were added, and for "dry" and "recombined" natural gas. The gases are expanded adiabatically by means of an expansion chamber. The initial pressure of the mixtures varies from 1 bar up to 12 bar. In all cases, a similar homogeneous condensation process is observed. Only for "recombined" natural gas, it is found that initially the condensation process has a heterogeneous character.

In the cases of the mixtures with nonane and decane, the partial vapor pressure at the onset of condensation is more than two orders of magnitude larger than the corresponding equilibrium vapor pressure at the same temperature. This is very well predicted by the kinetic theory and the Dillmann and Meier theory. Further, the measured average droplet size is of the same order of magnitude as the one calculated with the model based on classical nucleation theory and Gyarmathy's droplet growth law.
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Nomenclature

\(a, b\): coefficients of the Soave–Redlich–Kwong equation of state
\(b\): evaporation rate
\(c_p\): molar heat capacity at constant pressure
\(c_v\): molar heat capacity at constant volume
\(C\): cluster
\(f\): rate of impigement of single molecules
\(F\): Helmholtz energy
\(g\): number of molecules in a cluster
\(\Delta G\): Gibbs free energy of formation of droplets
\(i\): number of molecules in a cluster
\(i_1, i_2\): intensity functions
\(I\): nucleation rate
\(J\): light intensity
\(j\): number of molecules in a cluster
\(k\): constant of Boltzmann
\(k_{ij}\): binary interaction coefficient
\(m\): molecular mass
\(n\): refractive index
\(n\): number of moles
\(\dot{n}\): concentration
\(N\): relative refractive index
\(N\): normalization constant
\(N\): number of particles
\(p\): pressure
\(P\): power
\(q_0\): model parameter of the Dillmann–Meier model
\(r\): radius
\(R\): universal gas constant
\(s\): distance
\(s\): molar entropy
\(S\): surface area
\(T\): temperature
\(\Delta T\): supercooling
\(u\): molar internal energy
\(v\): molar volume
\(V\): volume
\(x\): mole fraction in the liquid phase
\(y\): mole fraction in the gaseous phase
\(Z\): compressibility factor
\(\alpha\): size parameter
\(\alpha_1, \alpha_2\): model parameters of the Dillmann–Meier model
\(\beta\): impingement rate per unit area
\(\gamma\): disentropic exponent
\(\delta\): angle
\(\kappa\): model parameter of the Dillmann–Meier model
\(\lambda\): wavelength
\(\mu\): chemical potential
\(\rho\): density
\(\sigma\): surface tension
\(\theta\): angle
\(\Xi\): dimensionless surface energy
\(\tau\): model parameter of the Dillmann–Meier model
\(\chi\): saturation ratio
subscripts

\[ \begin{align*}
  c & : \text{critical state} \\
  cl & : \text{classical} \\
  g & : \text{number of molecules} \\
  i & : \text{index} \\
  j & : \text{index} \\
  \text{kin} & : \text{kinetic} \\
  m & : \text{mixture} \\
  r & : \text{relative} \\
  s & : \text{saturation} \\
  \text{tot} & : \text{total} \\
  0 & : \text{initial conditions}
\end{align*} \]

superscripts

\[ \begin{align*}
  e & : \text{equilibrium} \\
  l & : \text{liquid phase} \\
  o & : \text{thermodynamic state} \\
  v & : \text{vapor phase}
\end{align*} \]
CHAPTER 1: INTRODUCTION

Problems involving the kinetics of phase change occur in many branches of science and technology such as chemistry, physics, astrophysics, aerodynamics, meteorology, biology, or engineering. In general, it is possible to distinguish four stages in phase change.

First, the development of the supersaturated state. For a vapor-liquid system, this means that the vapor phase exists at a pressure higher than the saturation pressure at the same temperature. When we deal with a pure component, this state can be described by the saturation ratio defined as

\[ \chi = \frac{p_v}{p_s} \]  

(1.1)

where \( p_v \) represents the actual vapor pressure and \( p_s \) the saturation pressure at the same temperature. This supersaturated state may be a result of a chemical reaction or the consequence of a change in temperature, pressure, tension or other chemical or physical condition.

Second, the generation of the first nuclei of the new phase. Such nuclei may form homogeneously in the interior of the parent phase or may form heterogeneously around ions, dust from any source, on surfaces or any other condensate particles formed by prior condensation of another vapor. The presence of such impurities in sufficient numbers leads to condensation near equilibrium at saturation ratios only slightly larger than unity, while in the absence of all types of foreign nuclei, or in extremely rapid processes where the condensate accumulation on foreign nuclei remains negligibly small, condensation may become much delayed with respect to equilibrium states.

Third, the growth of nuclei to form larger particles or domains of the new phase.

Fourth, relaxation processes such as agglomeration by which the texture of the new phase alters.

In this research, which took place as part of a collaboration program between the Nederlandse Aardolie Maatschappij and the University of Technology of Eindhoven, we shall mainly be concerned by the second stage of the phase change process described previously. Nevertheless, the third step will also appear shortly.

The mean target of this research is the study of the condensation behavior of natural gas. The natural gas which we will consider is principally constituted of methane (CH\(_4\)) and nitrogen (N\(_2\)) in a ratio about equal to 85/15 mole%. Further, a large number of heavier hydrocarbons is present in traces. However, as the carbon number increases, the quantity of the corresponding alcane decreases. For an adiabatic expansion initiated at
temperatures around surrounding temperature (20°C) and a pressure range between 1 and 12 bar, methane as well as nitrogen are in a gaseous state far away from their respective saturation states. Therefore, heavier hydrocarbons such as n-nonane (n-C₉H₂₀) or n-decane (n-C₁₀H₂₂) play a major role in the condensation process.

In order to investigate the condensation process, a series of adiabatic expansions have been performed in a Wilson cloud chamber. During such an expansion the state of the gas changes as described in figure 1.1. Let's suppose that a pure vapor is initially in a state at pressure $p_0$ and temperature $T_0$. During the expansion the state of the gas will cross the saturation line at some point $(p_5, T_5)$. From this point on, the vapor is supersaturated. Along the adiabatic path the state of the gas can be characterized by two parameters, the saturation ratio $\chi$ or the supercooling $\Delta T$ defined as

$$\Delta T = T_s - T$$

(1.2)

where $T = T(p,v)$ is the temperature of the vapor at some point along the adiabatic path and $T_s$ the saturation temperature at the same pressure. At some point $(p^*, T^*)$, the vapor has reached a state of critical supersaturation and the condensation takes place rapidly.

Fig. 1.1: Adiabatic expansion of a pure vapor.
The gas mixtures investigated are the following ones: \( \text{CH}_4/\text{n-C}_9\text{H}_{20}, \text{N}_2/\text{n-C}_9\text{H}_{20}, \) \( \text{CH}_4/\text{N}_2/\text{n-C}_9\text{H}_{20}, \) \( \text{CH}_4/\text{N}_2/\text{n-C}_{10}\text{H}_{22} \) — where in the ternary mixtures 85 mole\% of methane and 15 mole\% of nitrogen are present —, and natural gas. In all these mixtures the number density of nonane or decane (solute) is much smaller than the number density of the remaining(s) component(s) (solvent).

In the case of the binary and ternary mixtures it is assumed that the only component that condenses is the heavy hydrocarbon (nonane or decane), the other gases being inert in the considered pressure and temperature ranges. Then, the nucleation process can be studied with respect to theories for pure vapor. When the condensation process is homogeneous, nuclei are formed by fluctuations in the supersaturated vapor itself. Random collisions lead to the agglomeration of a small number of vapor molecules by successive attachment or loss of single molecules. Occasionally, such a clusters attains the critical size, a size that leads to the formation of stable droplets if one more molecule impinges on the cluster. The theory of homogeneous nucleation aims to predict the rate of formation of these clusters of critical size.

Outline of the report

In chapter 2 calculations of phase equilibrium of binary gas mixtures with the Soave–Redlich–Kwong equation of state will be presented.
In chapter 3 a recent theory of homogeneous nucleation (the so-called kinetic theory) will be derived and compared with the classical theory. Further a review of the Dillmann–Meier theory will be done.
In chapter 4 the experimental set-up and the experimental methods will be described.
In chapter 5 the results of the experiments will be presented. For the test mixtures with nonane and decane, a comparison of the experiments with the theories described in the previous chapter will be made. Further the condensation process of the two binary mixtures will also be presented with respect to the calculations carried out in chapter 2 and eventual real gas effects investigated.
Finally, in chapter 6 the conclusions of this work will be formulated.
CHAPTER 2: PHASE EQUILIBRIUM OF A BINARY MIXTURE

2.1 Theory

2.1.1 Introduction

Consider a heterogeneous closed system containing two components and consisting of a liquid and its vapor (figure 2.1):

![Figure 2.1: Closed system constituted of two phases. The superscripts v and l denote respectively the vapor and liquid phase, x represents the molar fraction in the liquid phase and y the molar fraction in the vapor phase. The subscripts 1 and 2 represent the two components.](image)

We assume that the system has reached a state of internal equilibrium. Given the equilibrium temperature $T$ and the vapor composition $(y_1, y_2)$, we want to know the equilibrium pressure $p$.

This can be achieved with the equilibrium conditions:

\[
\begin{align*}
    p^v &= p^l = p \quad \text{(2.1)} \\
    \mu_i^v &= \mu_i^l \quad \text{for } i=1,2 \quad \text{(2.2)} \\
    (T^v = T^l = T \text{ is given})
\end{align*}
\]

with $\mu$ : chemical potential.

The vapor pressure $p^v$ and liquid pressure $p^l$ are related to the vapor molar volume $v^v$...
and liquid molar volume $v^l$ by an equation of state:

$$p^y = p(v^y, y^1, T) \quad (2.3)$$
$$p^l = p(v^l, x^1, T) \quad (2.4)$$

The chemical potential is a function of three independent variables:

$$\mu^y_1 = \mu(v^y, y^1, T) \quad (2.5)$$
$$\mu^l_1 = \mu(v^l, x^1, T) \quad (2.6)$$

Hence, we have a system of 5 equations:

$$p = p^y \quad (2.7)$$
$$p = p^l \quad (2.8)$$
$$\mu^y_1 = \mu^l_1 \quad (2.9)$$
$$\mu^y_2 = \mu^l_2 \quad (2.10)$$
$$x_1 + x_2 = 1 \quad (2.11)$$

for the 5 unknowns: $p, x_1, x_2, v^y$ and $v^l$.

In order to solve this set of equations, we need to know the explicit dependences of $p^y, p^l, \mu^y_1$ and $\mu^y_2$ on their respective parameters, i.e. we must use an equation of state.

### 2.1.2 Equation of state

The equation of state that we use is the Soave–Redlich–Kwong equation of state, which reads for a pure component [REI 87]:

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b)} \quad (2.12)$$

where $b = \frac{0.08664RT_c}{p_c}$

and $a = \frac{0.42748R^2T_c^2}{p_c} \left[ 1 + f\omega(1 - T_r^{1/2}) \right]^2$

with $f\omega = 0.48 + 1.574\omega - 0.176\omega^2$. 
$T_c, p_c$ and $\omega$ are respectively the critical temperature, critical pressure and acentric factor of the pure component under consideration and $T_r = T/T_c$.

In the case of a binary mixture, $a$ and $b$ are replaced by $a_m$ and $b_m$ as follows:

$$a_m = \sum_{i=1}^{2} \sum_{j=1}^{2} y_i y_j (a_i a_j)^{1/2} (1 - K_{ij})$$

$$b_m = \sum_{i=1}^{2} y_i b_i$$

(or $x_i$ in the place of $y_i$ for the liquid phase)

where $a_i$ and $b_i$ are the parameters for the $i^{th}$ pure component of the mixture, and $K_{ij}$ the binary interaction coefficient between components $i$ and $j$. Values for $K_{ij}$ are given in table 2.1 for several substances.

<table>
<thead>
<tr>
<th>Carbon dioxide</th>
<th>Hydrogen sulfide</th>
<th>Nitrogen</th>
<th>Carbon monoxide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRK</td>
<td>PR</td>
<td>SRK</td>
</tr>
<tr>
<td>Methane</td>
<td>0.093</td>
<td>0.092</td>
<td>0.023</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.053</td>
<td>0.065</td>
<td>0.085</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.136</td>
<td>0.132</td>
<td>0.041</td>
</tr>
<tr>
<td>Propane</td>
<td>0.094</td>
<td>0.089</td>
<td>0.090</td>
</tr>
<tr>
<td>Propane</td>
<td>0.129</td>
<td>0.124</td>
<td>0.088</td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.128</td>
<td>0.139</td>
<td>0.051</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.143</td>
<td>0.132</td>
<td>0.070</td>
</tr>
<tr>
<td>Isopentane</td>
<td>0.133</td>
<td>0.122</td>
<td>0.069</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.130</td>
<td>0.110</td>
<td>0.150</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.110</td>
<td>0.100</td>
<td>0.143</td>
</tr>
<tr>
<td>n-Decane</td>
<td>0.130</td>
<td>0.114</td>
<td>0.099</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.129</td>
<td>0.105</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.077</td>
<td>0.077</td>
<td>0.153</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.113</td>
<td>0.106</td>
<td></td>
</tr>
</tbody>
</table>

**Tab. 2.1:** $K_{ij}$ values for Soave (SKR) and Peng–Robinson (PR) equations [REI 87].

### 2.1.3 Chemical potential

Because we have a pressure – explicit equation of state, it is convenient to calculate thermodynamic properties in terms of the temperature $T$ and total volume $V$. The chemical potential $\mu_i$ of component $i$ is given by:

$$\mu_i = \left[ \frac{\partial F}{\partial n_i} \right]_{T,V,n_j}$$  \hspace{1cm} (2.13)
with \( F \): Helmholtz energy
\( n_{i} \): number of moles of component \( i \)

In appendix A.1 an expression for the chemical potential as a function of the independent variables \( T \) and \( V \) is given:

\[
\mu_{i} = \int_{V}^{\infty} \left[ \frac{\partial F}{\partial n_{i}} \right]_{T,V,n_{j}} \, dV - \frac{RT}{V} \ln \frac{V}{n_{i}RT} + RT + u_{i}^{0} - Ts_{i}^{0} \tag{2.14}
\]

with \( u_{i}^{0} \): molar energy of pure component \( i \) at very low pressure and temperature \( T \)
\( s_{i}^{0} \): molar entropy of pure component \( i \) at very low pressure and temperature \( T \)

### 2.1.4 Solution method

Substitution of (2.12) in (2.7) and (2.8) yields:

\[
\left[ \frac{RT}{v^{v}} - b_{v}^{m} - \frac{a_{v}^{m}}{v^{v}(v^{v} + b_{v}^{m})} \right] - \left[ \frac{RT}{v^{l}} - b_{l}^{m} - \frac{a_{l}^{m}}{v^{l}(v^{l} + b_{l}^{m})} \right] = 0 \tag{2.15}
\]

Combination of (2.7), (2.8), (2.12), (2.9), (2.10) and (2.14) yields after integration of (2.14):

\[
\left[ -RT \ln \frac{v^{v} - b_{v}^{m}}{y_{1}RT} + \frac{b_{v}^{m}RT}{v^{v} - b_{v}^{m}} - \frac{1}{b_{v}^{m}} \left[ 2A_{1}^{v} - \frac{a_{v}^{m}b_{l}^{m}}{b_{v}^{m}} \right] \ln \frac{b_{l}^{m}}{b_{v}^{m}} \right. \\
\left. - RT \ln \frac{v^{l} - b_{l}^{m}}{x_{1}RT} + \frac{b_{l}^{m}RT}{v^{l} - b_{l}^{m}} - \frac{1}{b_{l}^{m}} \left[ 2A_{1}^{l} - \frac{a_{l}^{m}b_{l}^{m}}{b_{l}^{m}} \right] \ln \frac{b_{l}^{m}}{b_{l}^{m}} \right] = 0 \tag{2.16}
\]

\[
\left[ -RT \ln \frac{v^{v} - b_{v}^{m}}{y_{2}RT} + \frac{b_{v}^{m}RT}{v^{v} - b_{v}^{m}} - \frac{1}{b_{v}^{m}} \left[ 2A_{2}^{v} - \frac{a_{v}^{m}b_{l}^{m}}{b_{v}^{m}} \right] \ln \frac{b_{l}^{m}}{b_{v}^{m}} \right. \\
\left. - RT \ln \frac{v^{l} - b_{l}^{m}}{(1-x_{1})RT} + \frac{b_{l}^{m}RT}{v^{l} - b_{l}^{m}} - \frac{1}{b_{l}^{m}} \left[ 2A_{2}^{l} - \frac{a_{l}^{m}b_{l}^{m}}{b_{l}^{m}} \right] \ln \frac{b_{l}^{m}}{b_{l}^{m}} \right] = 0 \tag{2.17}
\]
with \[ A^V_i = y_i a_i + y_j (1 - K)(a_i a_j)^{1/2} \]
\[ A^L_i = x_i a_i + x_j (1 - K)(a_i a_j)^{1/2} \]

\( K = K_{ij} \) is taken as a constant in the whole temperature range (Table 2.1).

Formulae (2.15) to (2.17) are the three equations to be solved for the independent variables \( x_i \), \( v^V \) and \( v^L \).

The method used is the Newton–Raphson method [PRE 89]. An initial guess for the root must be given. When this trial solution lies not too far from the real solution, the equations can be linearised around this root with the Taylor series expansion. Another root, nearer to the real one can be found, and so on until the accuracy corresponding to the chosen convergence limit criterium has been reached.

### 2.2 Results

The program written for the computation of the phase equilibrium of binary mixtures is given in appendix A.2. We have tested our program by comparing the results with two different data sets from the literature.

The first series of calculations has been performed for methane–decane mixtures, for three different molar fractions of n–decane: 50ppm, 100ppm and 200ppm (see figures 2.1, 2.2 and 2.3). Each phase diagram consists of two lines representing our calculations and two series of symbols standing for the respective comparative data. The binary interaction coefficient \( K \) has been taken from the paper of S. P Serbanovic [SER 87]: \( K = 0.02 \).

The phase diagrams have been compared with experimental data presented in the paper: "The indirect measurement of hydrocarbon dewpoints" [RIJ 90]. As the quantity of nonane is increased in the mixture, the SRK equation of state agrees better with the experiments. However for all cases the maximum dewpoint temperature is quite accurate (within 3 K for the worst case).

The second series of calculations has been executed for a carbon dioxide–decane mixture, for two different molar fractions of decane: 20000ppm and 50000ppm (see figures 2.4 and 2.5). The value of the binary interaction parameter \( K \) for these two components is 0.13 (see table 2.1). In this case, our computations have been compared with the computations done by Shell research with their numerical program PVT–pack. Here, the deviations are much smaller since the PVT–pack makes use of the Soave equation of state. The departures may be a consequence of different parameter values. As can be seen from the figures, the upper dewpoint line does not join the lower one. This comes from numerical problems when \( \partial p/\partial T \to 0 \).
Fig. 2.1: (a) $p$–$T$ diagram of the methane–decane system (50ppm $n$–decane). Solid lines: computations. Symbols: [RIJ 87].

(b) Relative deviation from the data sets: $100 \times \frac{p_{\text{cal}} - p_{\text{dat}}}{p_{\text{dat}}}$. 
Fig. 2.2: (a) $p-T$ diagram of the methane–decane system (100ppm $n$–decane).
Solid lines: computations.
Symbols: [RJ 87].
(b) Relative deviation from the data sets:
$100\times \frac{p_{\text{cal}} - p_{\text{dat}}}{p_{\text{dat}}}$.
Fig. 2.3: (a) $p-T$ diagram of the methane–decane system (200ppm n-decane) 
solid lines : computations. 
Symbols : [RIJ 87].
(b) Relative deviation from the data sets: 
$100 \times \frac{(p_{\text{cal}} - p_{\text{dat}})}{p_{\text{dat}}}$.
Fig. 2.4: (a) \( p-T \) diagram of the carbon dioxide-decane system (20000ppm decane). Unbroken lines: computations. Symbols: Shell data.

(b) Relative deviation from the data sets:

\[ 100 \times \frac{P_{\text{cal}} - P_{\text{dat}}}{P_{\text{dat}}} \]
Fig. 2.5: (a) p-T diagram of the carbon dioxide-decane system (50000ppm decane).
unbroken lines : computations.
Symbols : Shell data.
(b) Relative deviation from the data sets:
\[100\times (p_{\text{cal}} - p_{\text{dat}})/p_{\text{dat}}.\]
CHAPTER 3: HOMOGENEOUS NUCLEATION

3.1 Kinetic theory of Katz and Wiedersich versus classical theory

In the following we will derive the expression of the nucleation rate $I$, that is the rate at which stable droplets are formed per unit volume, according to the so-called kinetic theory [KAT 77], and compare it with that of the classical theory. The assumptions that will be made are those retained by the classical theory, with the exception of one: the equilibrium state to which the evaporation rate should be referred. We assume that the internal degrees of freedom of molecules (translational, rotational and vibrational) can be neglected; that the clusters are all spherical and of neutral charge; that the physical properties of a cluster are the same as those of the bulk liquid; and that the growth or decay of clusters occur most entirely by the addition or the loss of single molecules. i.e. cluster growth and decay can be represented by the "reaction":

$$C_i + C_{i-1} \leftrightarrow C_i$$

(3.1)

where $C_i$ represents a cluster containing $i$ molecules (an $i$-mer). The net rate $I_i$ at which clusters containing $i-1$ molecules become clusters containing $i$ molecules is given by the equation:

$$I_i = f_{i-1} n_{i-1} - b_i n_i$$

(3.2)

where $n_i$ is the concentration of $i$-mers, $f_i$ represents the forward rate (i.e. the rate at which a single molecule arrive at the surface of an $i$-mer) and $b_i$ represents the backward rate (i.e. the $i$-mer evaporation rate). Given $f_i$, $b_i$ and the concentrations $n_i$, the nucleation rate could, in principle, be calculated. However, the only term that is known, even approximately, is $f_i$. It is equal to the product $f_3 s_i$ where $\beta$ is the rate at which molecules impinge and condense on the surface per unit area, and $s_i$ is the surface area of an $i$-mer. For an ideal gas:

$$\beta = \frac{\alpha p^v}{\sqrt{2\pi m k T}}$$

(3.3)

where $p^v$ is the vapor pressure, $\alpha$ the condensation coefficient, $m$ the molecular mass of a molecule, $k$ the Boltzmann's constant and $T$ the temperature.

When the system is at equilibrium, the nucleation rate is identically zero for clusters of
all sizes. Since the evaporation rate does not depend on the density of the vapor, equation (3.2) can be used to determine the evaporation rate $b_1$ in terms of equilibrium concentration distribution $n_i^e$ and the forward rate at equilibrium:

$$b_1 = \beta^e s_{i-1}(n_{i+1}^e/n_i^e)$$  \hspace{1cm} (3.4)

where the superscript "e" denotes equilibrium conditions. It is over the choice of equilibrium state for evaluating equation (3.4) that the classical and kinetic theories diverge. In the classical theory, the evaporation rate is obtained by reference to the metastable equilibrium which would exist for a vapor at the same temperature and supersaturation as the vapor in question, constrained to a steady state by so-called Maxwell demons: monomers are continually replenished by the artificial dissociation of clusters which grow beyond a certain size [REI 52, FED 66, McD 63]. In fact, it is not necessary to postulate the existence of a supersaturated vapor to be in thermodynamic equilibrium in order to be able to calculate $b_1$. In the kinetic theory, the saturated state of the vapor at the same temperature as the supersaturated state of interest is chosen as reference state. As a saturated vapor is indeed in equilibrium, the net rate of nucleation $I$ will be equal to zero for all sizes.

Substituting (3.4) into (3.2), rearranging and dividing both sides by $(\beta/\beta^e)^{i-1}$, we have

$$\frac{I_i}{\beta^e s_{i-1}n_{i-1}^e(\beta/\beta^e)^{i-1}} = \frac{n_{i-1}}{n_i^e(\beta/\beta^e)^{i-1}} - \frac{n_i}{n_i^e(\beta/\beta^e)^{i}}.$$  \hspace{1cm} (3.5)

It should be noted that for an ideal gas, $\beta/\beta^e$ reduces to the saturation ratio $\chi$:

$$\frac{\beta}{\beta^e} = \frac{n_i}{n_i^e} = \frac{P}{P_s} = \chi$$  \hspace{1cm} (3.6)

where $P_s$ represents the saturation pressure.

The terms on the righthand side of equation (3.5) differ only in the value of the index $i$. Summing from $i=2$ to an arbitrarily large value $i=g$, successive terms cancel and we obtain

$$\sum_{i=2}^{i=g} \frac{I_i}{\beta^e s_{i-1}n_{i-1}^e(\beta/\beta^e)^{i-1}} = \frac{n_1}{n_1^e(\beta/\beta^e)} - \frac{n_g}{n_g^e(\beta/\beta^e)^g}.$$  \hspace{1cm} (3.7)

Since the rate of change of concentration of i-mers is given by

$$\frac{dn_i}{dt} = I_{i-1} - I_i,$$  \hspace{1cm} (3.8)
at steady state, $I$ becomes a constant for all sizes. Furthermore, when the vapor is
supersaturated and for sufficiently large $g$, the last term in the righthand side of
equation (3.7) becomes negligible compared to the first. This can easily be seen for an
ideal gas, where the righthand side of equation (3.7), after substitution of (3.6),
becomes $1 - n_g/(\chi n^e_g)$. For a sufficiently large value of $g$, both $n_g$ and $n^e_g$ tends to
zero so that for $\chi > 1$, the second term can be neglected in comparison with unity.
Factoring $I$ out of the summation and rearranging gives

$$I = \left[ \frac{n^1}{n^e} \left( \beta / \beta^e \right) \right] \left[ \sum_{i=1}^{n^e} \left[ \beta^i n^e_f (\beta / \beta^e)^i \right] \right]^{-1}. \quad (3.9)$$

Hence, the problem of predicting the rate of nucleation has been reduced to two
simpler problems: a kinetic problem, that of knowing the impingement rate ratio $\beta / \beta^e$, and an equilibrium problem, that of determining the concentration of clusters in
equilibrium with their bulk condensed phase. Given these quantities, the summation in
(3.9) can be evaluated numerically rather easily. However, by making two very accurate
mathematical approximations [COH 70], an analytical solution is possible. The first is
the conversion of the summation to an integral:

$$I = \frac{n^1}{n^e} \left( \beta / \beta^e \right) \left[ \int_1^{n^e} \frac{d j}{\beta^i n^e_f (\beta / \beta^e)^i} \right]^{-1}. \quad (3.10)$$

The second is to write the integrand as an exponential,

$$I = \frac{n^1}{n^e} \left( \beta / \beta^e \right) \left[ \int_1^{n^e} \exp[-H(j)] dj \right]^{-1} \quad (3.11)$$

where

$$H(j) = \ln[\beta^i n^e_f (\beta / \beta^e)^i], \quad (3.12)$$

and making use of the fact that the function $H$ is positive and has a minimum, the
integrand is expanded about its maximum value in a Taylor series, and truncated after
the quadratic term, that is,

$$H(i) \approx H(i^*) + (i - i^*)^2 H''(i^*)/2 \quad (3.13)$$

where $i^*$ is chosen such that the first derivative is zero. A transformation of variables
gives this as a standard integral (i.e. the error function) and (3.11) becomes
To specify $H$ we require an expression for $n_i^*$ in equation (3.12). We assume that the equilibrium cluster population obeys a Boltzmann distribution:

$$n_i^* = N \exp\left[-\frac{\Delta G(i)}{kT}\right]$$  \hspace{1cm} (3.15)

where $N$ is a normalization constant and $\Delta G(i)$ the Gibbs free energy of formation of an $i$–mer in the equilibrium state. In the classical theory, the free energy is derived from thermodynamic arguments pertaining to the constrained equilibrium, giving [ABR 74]

$$\Delta G_{cl}(i) = c_1 i + c_2 i^{2/3}$$  \hspace{1cm} (3.16)

where $c_1$ is the difference in chemical potential between the supersaturated vapor and the saturated vapor: $-kT \ln(\chi)$, and where $c_2 = \sigma s_0$ represents the surface energy. $\sigma$ is the surface tension and the surface area $s_i$ is written as $s_0 i^{2/3}$ where $s_0$ is a constant that depends on the geometry and the volume per molecule $v_m$ (e.g. for spherical molecules $s_0 = 4\pi [3v_m/4\pi]^{2/3}$). In rewriting equation (3.15) to apply to the stable equilibrium of the kinetic theory ($\chi = 1$), it becomes

$$\Delta G_{kin}(i) = c_2 i^{2/3}.$$  \hspace{1cm} (3.17)

In that case, using (3.15), equation (3.12) becomes

$$H(i) = \ln(\beta) + \ln(s_0 i^{2/3}) + \ln(N) - c_2 i^{2/3} + \ln(\beta/v) ,$$  \hspace{1cm} (3.18)

and from its definition ($H'(i^*) = 0$) $i^*$ is then the solution to

$$\Xi^{2/3} - \frac{1}{i} = 3\ln(\chi)/2$$  \hspace{1cm} (3.19)

with $\Xi = \sigma s_0/(kT)$. For most realistic cases $\Xi i^{2/3} >> 1$. With this approximation one obtains
which is identical to the critical size of the classical theory known as the Kelvin–Thomson relation [ABR 74]. Combining then equations (3.12), (3.14), (3.15), (3.17) and (3.20) we finally obtain

\[
I = \frac{n_1}{n_0^2(\beta/\beta^e)} \frac{N\beta s_0}{3} \left(\sqrt{\frac{3}{\pi}}\right)^2 \exp\left(-\frac{4}{27} \frac{\Xi^3}{[\ln(\beta/\beta^e)]^2}\right). 
\]  

(3.21)

Although the rate of nucleation depends slightly on the preexponential density ratio \(n_1/n_0^2\), the real driving force for nucleation arises from the ratio of impingement rates \(\beta/\beta^e\) in the exponential. Given a thermodynamic expression for the density ratio and a kinetic expression for the arrival rate ratio, one can calculate the rate of nucleation. When we deal with an ideal gas, then, substituting (3.6) into (3.21), the expression for the nucleation rate becomes

\[
I = \frac{N\beta s_0}{3} \left(\sqrt{\frac{3}{\pi}}\right)^2 \exp\left(-\frac{4}{27} \frac{\Xi^3}{[\ln(\chi)]^2}\right). 
\]  

(3.22)

As Katz and Donohue [KAT 79] commented, the result of classical theory appears to have been recovered.

However, Girshick and Chiu [GIR 90] have shown that the kinetic theory yields a result which differs from the classical theory. Indeed, the normalization constant \(N\) occurring in the expression for the cluster equilibrium population is not the same in each theory. If in either theory we take \(N = n_0^2\), then

\[
N_{cl} = n_1 
\]  

(3.23)

while

\[
N_{kin} = n_s 
\]  

(3.24)

where \(n_s\) represents the equilibrium monomer concentration for a saturated vapor.

Inserting (3.23) into (3.22) and rearranging in terms of bulk properties, the nucleation rate according to the classical theory for an ideal gas is (with \(\alpha=1\))

\[
I = \left(\frac{\sigma}{kT}\right)^{1/2} \frac{m}{2\pi \rho^{1/2}} \frac{P_{eq}^4}{\sqrt{2\pi m kT}} \frac{\rho^n}{kT} \exp\left[-\frac{4\pi \sigma r^*}{3kT}\right] 
\]  

(3.25)

where \(\rho^1\) represents the density of the bulk liquid. The critical radius \(r^*\) is given by
(3.20) with \( i^* = 4\pi r^*^3/(3\nu m) \), that is,

\[ r^* = \frac{2\sigma m}{kT \ln(x)} \]  

(3.26)

However, it should be noted that the expression for the cluster distribution in the classical theory (equation (3.15)) with \( N \) given by (3.23) is internally inconsistent since it is obviously not satisfied for monomers.

In the kinetic theory, equation (3.15) with \( N \) given by (3.24) is satisfied for monomers if \( \Delta G(1) = 0 \). Indeed, this must hold because \( \Delta G(1) \) represents the difference in chemical potential between a molecule in the vapor and a molecule in the condensed phase for a system at an equilibrium saturation state. But the condition of phase equilibrium is precisely that these chemical potentials are equal, thus \( \Delta G(1) = 0 \). Therefore, \( \Delta G(i) \) can be evaluated simply as the difference in Gibbs free energy between a \( i \)-mer and a monomer, both considered to be in the condensed phase. Taking then the same physical assumptions as in the classical theory, the good expression for the Gibbs energy should be

\[ \Delta G = c_2(i^3 - 1) \]  

(3.27)

Comparing now equation (3.27) with equation (3.17), the difference seems minor. As can easily be verified, the derivatives of \( \Delta G \) with respect to \( i \) are unaffected, hence neither \( i^* \) nor \( H'(i^*) \) are modified. However, in the kinetic theory \( N \) is smaller than in the classical theory by a factor \( n_l/n_s = \chi \), and more important, \( H(i^*) \) in equation (3.14) is now increased by the quantity \( \Xi \), that is, \( I \) is multiplied by \( \exp(\Xi) \).

Combining all these effects, we find finally the following relation between the nucleation rates obtained by the kinetic and classical theories:

\[ I_{\text{kin}} = \frac{\exp(\Xi)}{\chi} I_{\text{cl}} \]  

(3.28)

The factor \( \exp(\Xi) \) represents an often large – and strongly temperature dependent – correction to the classical theory. For example, for \( n \)-nonane \( \Xi(300K) = 11.6 \) while \( \Xi(200K) = 23 \).
3.2 Extension of the classical nucleation theory, the Dillmann and Meier model.

The formulation of nucleation theory described thus far has completely ignored the translational, rotational and vibrational degrees of freedom of embryo and nuclei. An extension of the classical droplet model, where these internal degrees of freedom have been taken into account, has been made by Lothe and Pound [LOT 62]. The Gibbs free energy is written as

\[ \Delta G(i) = \Delta G_{cl}(i) + c_3 \ln(i) + c_4 \]  

(3.29)

where \( c_3 \) and \( c_4 \) are two constants determined within the capillarity approximation on the basis that the vapor is constituted of an ideal mixture of \( i \)-mers. However, the theory was not very successful. For most of the substances, the values of the nucleation rates are a factor \( 10^{12} \) - \( 10^{17} \) higher than the values found with the classical droplet model, far from the experimental values. Only for substances such as ammonia, chloroform or benzene the correct values were predicted [GRU 88].

In 1989, Dillmann and Meier [DIL 89] have somehow modified the model of Lothe and Pound. In the following we shall only give the most important results of the theory, for a more complete treatment the reader is referred to [DIL 90] or [LOO 90]. The equation for the free energy remains the same as in the previous model, but now \( c_2 \) is allowed to be a function of \( i \), corresponding to a size dependence of the surface tension \( \sigma \). For the dependence of \( c_2 \) the following choice was made:

\[ c_2(i) = \kappa(i) \sigma s_0 \]  

(3.30)

with

\[ \kappa(i) = 1 + \alpha_1 i^{-\frac{3}{5}} + \alpha_2 i^{-\frac{3}{5}} \]  

(3.31)

where \( \alpha_1 \) and \( \alpha_2 \) are model parameters. Further, the values of the other coefficients appearing in the expression of the Gibbs energy in the Dillmann–Meier model are

\[ c_3 = \tau kT \]  

(3.32)

and

\[ c_4 = -kT \ln(q_0 V) \]  

(3.33)

while \( c_1 \) is unaffected. \( \tau \) and \( q_0 \) have still to be determined and \( V \) represents the total volume. In this way, the nucleation rate is expressed as

\[ I = \frac{1}{3} \left[ \frac{s_0 \sigma}{kT \pi} (1 + \alpha_1 i^{-\frac{3}{5}} + \frac{9 \tau kT}{2 \sigma s_0 i^{-\frac{3}{5}}} \right)^{\frac{1}{2}} \frac{p}{s_0 \sqrt{2\pi m kT}} \exp \left[ -\frac{\Delta G(i + 1)}{kT} \right] \]  

(3.34)
where the critical cluster size is determined by the real solution of the equation

\[
\frac{\partial \Delta G}{\partial \tau} = \tau x^3 + \frac{1}{3} \alpha_i \frac{\sigma_s}{kT} x^2 + \frac{2\sigma_s}{3kT} x - \ln(x) = 0 \tag{3.35}
\]

where \( x = i^{\frac{1}{3}} \). The model parameters occurring in the Dillmann–Meier model appear in the expression of the particle density as a function of the pressure. In this way they appear in an equation of state and they are determined from the behavior of each substance at the critical point and from the first two virial coefficients.

It should finally be noted that the classical theory is a limiting case of the Dillmann–Meier model when \( \tau = 0 \) (no rotational and vibrational energy), \( \kappa(i) = 1 \) (macroscopic surface tension) and \( q_0 = p^v/kT \).
CHAPTER 4: EXPERIMENTAL SET-UP AND EXPERIMENTAL METHODS

4.1 Introduction

The measurements of the onsets of condensation – or dynamic dewpoints – are performed in the experimental set-up schematically represented in figure 4.1. The vacuum system is mainly constituted of three elements: the cloud chamber, the vacuum chamber and the mixing pump (section 4.2). The experimental procedure can be summarized in the following way: the vapor and the carrier gas successively introduced in the cloud chamber are mixed with the mixing pump in order to obtain a homogeneous mixture. Then, after the opening of the electromagnetic valve connecting the cloud chamber with the vacuum chamber the mixture expands rapidly into the vacuum chamber. During the expansion, the pressure decrease in the cell is registered. Since the expansion is adiabatic, it is possible to compute the temperature decrease from the pressure signal, taking account of real gas effects (section 4.3). During the experiment, a laser beam crosses the expansion vessel. The optical set-up allows the measurement of the scattered light in the forward and backward directions (relative to the direction of propagation of the laser beam) from a small volume – the so-called interaction domain – in the middle of the cell (section 4.4 and 4.5). The extinction of the laser beam along the whole length of the expansion chamber is also measured. The pressure, scattered light and extinction signals are transformed with analog–digital converters and recorded in digital memories which can be read by a computer (section 4.6). When condensation occurs, the scattered light signals, initially insignificant, increase suddenly and the dynamic dewpoint – or Wilson point – can be determined. Furthermore, from the ratio of forward and backward scattered light it is possible to estimate the mean radius of the droplets. Figure 4.2 gives an example of the pressure and scattered light signals for the mixture methane\nitrogen\n–nonane (a) and natural gas (b) for a initial total pressure of 1 bar.

4.2 The vacuum system

The cloud chamber, sketched in figure 4.3, is the vital element of the set–up. It is a cylindrical vessel, with a diameter of 100 mm at the end wall gradually decreasing to 19 mm at the orifice assuring a choking condition at the throat. At two sides of the vessel, facing each other, two windows have been mounted providing optical access for light scattering measurements.
Fig. 4.1: The vacuum system
(a) cloud chamber
(b) vacuum chamber
(c) mixing pump
(d) vapor cell.
Fig. 4.2: Normalized pressure and scattered light signals for the methane-nitrogen-nonane mixture (a), and for natural gas (b). \( I(f) \) represents the forward scattered light and \( I(b) \) the backward scattered light.
A special valve has been implemented at the end wall through which the cell can be filled with the carrier gas. Furthermore, it permits the mixing of the gas–vapor system as described further on.

When this valve is closed, the bottom of the expansion cell is perfectly flat, so that there are no sharp edges inside the vessel. This is necessary in order to avoid vortex shedding during the expansion. The flow in the observation volume can be considered as one-dimensional.
Two pressure transducers are mounted in the end wall of the expansion cell. The one is a piezo resistive sensor (Druck, type PCDR 81) allowing the measurement of the static pressure in the cell up to a pressure of about 13 bar. It gives the initial total pressure of the mixture just before the expansion. The other one is a piezo electric sensor (Kistler, type 603B) permitting the measurement of the dynamic pressure during the expansion. Since velocities in the cell are small, the pressure at the end wall is the same as in the core [LOO 90]. Temperature gradients in the piezo electric transducer are avoided by coating the transducer membrane with a 0.45 mm layer of silicone [LOO 90]. At the top of the cell, a thermometer is mounted in the frame allowing the measurement of the temperature prior to the expansion.

The vacuum chamber is connected with the vessel containing the investigated component – which is in an equilibrium state under saturation pressure – through an electromagnetic valve at one side, and with a mechanical rotary pump (Pfeiffer Balzers, type DUO 016 B) at the other side. The whole system can be brought under a minimum pressure of about 2 Pa. When the system has reached the vacuum state, the electromagnetic valve is opened and the system is filled with the vapor. The vapor pressure is measured with a vacuum pressure sensor (Edwards barocel, range 10 Torr) connected with the vacuum chamber through an electromagnetic valve.

When the system has been filled with the vapor, the cloud chamber and the mixing pump are isolated from the vacuum chamber and filled with the carrier gas until

---

**Fig. 4.4 : The mixing pump.**
the requested total pressure has been reached. The filling of the cell component after component avoids eventual condensation occurring at valves and orifices, and in this way, does not affect the composition of the mixture in the cell. However, this procedure does not provide a homogeneous mixture, unless we wait a very long time. Therefore, a special pump has been designed in which a piston is driven by electromagnetic induction, avoiding problems associated with the sealing of moving parts (see figure 4.4) [MOR 89]. The mixture is then circulated between cloud chamber and mixing pump to form a homogeneous mixture (see figure 4.1).

In the case of natural gas, the gas is directly introduced into the expansion vessel, without mixing. Then, we wait until the pressure is stabilized – which takes from about 5 to 10 minutes – before performing an expansion.

4.3 Cooling during an adiabatic expansion

During the expansion, thermal boundary layers will develop from the walls. However, measurements have shown that within the expansion time, these boundary layers do not reach the interaction domain [DIJ 90], hence, there is no heat exchanged with the surrounding and the process is adiabatic. If the expanding gas can be considered as perfect, then, using the ideal gas law, the pressure $p$, the density $\rho$ and the temperature $T$ can be related by the following relation:

$$\frac{p}{p_0} = \left(\frac{\rho}{\rho_0}\right)^\gamma = \left(\frac{T}{T_0}\right)^\gamma \gamma^{-1},$$

(4.1)

where $p_0$, $\rho_0$ and $T_0$ are respectively the initial pressure, density and temperature of the gas; and $\gamma = c_p/c_v$, where $c_p$ is the molar heat capacity of the gas at constant pressure and $c_v$ the molar heat capacity at constant volume.

When the gas does not behave as a perfect gas, then we must take account of an extra cooling known as the Joule–Kelvin effect. The relation holding for an adiabatic process becomes [LOO 90]:

$$\frac{p}{T} \left[\frac{\partial T}{\partial p}\right]_s = \frac{R}{c_p} Z \left[1 + \frac{T}{Z} \left[\frac{\partial Z}{\partial T}\right]_p\right] =: \beta(p, T),$$

(4.2)

where the derivative expressed in the lefthand side of the formula is carried out at constant entropy $s$, $R$ is the universal gas constant and $Z$ is the compressibility factor defined as:
For a restricted temperature and pressure range, it is possible to write:

\[ \frac{T}{T_0} = \left[ \frac{p}{p_0} \right]^\beta \]  

(4.4)

The thermodynamic variables are computed with the Soave–Redlich–Kwong equation of state.

4.4 Light scattering

A common way to detect condensation in the form of droplets is with light scattering.

Consider a laser beam passing through a gas with refraction index \( m \). When the gas begins to condense in the form of droplets, with refraction index \( n \) with respect to the gas, the path traversed by the light constitutes an inhomogeneous medium and the light is scattered in all directions.

If we make the assumptions that the droplets are all spherical and that the refraction index \( n \) is homogeneous inside the droplet, then, according to the Mie–theory, it is possible to determine exactly the angular energy distribution of the scattered light.

In this paragraph, we shall only give the most important results following from this theory. For a more complete treatment, one can refer to [BOH 83] or [KER 69].

Consider a linear polarized light beam of intensity \( I_0 \) falling on a single droplet of radius \( r \), and being scattered in the direction given by the angles \( \theta \) and \( \delta \) (see figure 4.5). The intensity of the scattered light can be expressed as:

![Fig. 4.5: Schematic representation of the light scattered from a spherical object.](image-url)
where $\lambda$ is the wavelength of the light in the surrounding medium and $R$ the distance between the droplet and the observation point. $i_1$ and $i_2$ are the intensity functions, they are functions of the scattering angle $\theta$, the refraction index $n$ of the droplet and the size parameter $\alpha$ defined as $\alpha=2\pi\lambda/\lambda$. These functions indicate how the scattered intensity is divided between the directions perpendicular and parallel to the scattering plane.

When the scattered light is detected on a circle symmetrical detector, then integration of formula (4.5) from $\delta=0$ to $\delta=2\pi$ yields:

$$I_s = I_0 \left[ \frac{\lambda}{2\pi R} \right]^2 (i_1 + i_2)$$  \hspace{1cm}(4.6)$$

When the scattered light is observed on a circle symmetrical detector within a solid angle between the angles $\theta_1$ and $\theta_2$, the total power absorbed by the detector can be expressed as:

$$P_s = \int_{\theta_1}^{\theta_2} I_s(\alpha, \theta, n) R^2 \sin \theta d\theta$$  \hspace{1cm}(4.7)$$

If only first order scattering occurs (no multiple scattering), then the total intensity scattered by N particles of the same size will simply be:

$$P_{tot} = N P_s$$  \hspace{1cm}(4.8)$$

When the above condition is fulfilled and if all the droplets have the same size, then the measurement of scattered light from the same volume element in two different directions permits the determination of the mean radius of the droplets. The power received in the two directions will be $NP_s(\alpha, n)$ and $NP_s(\alpha, n)$. The ratio of these two powers is only a function of the size parameter $\alpha$ and the refractive index of the droplets.

In the next section, we shall see that the scattering angles from our optical set-up are between $\theta_1=3.8^\circ$ and $\theta_2=4.4^\circ$ for the forward scattered light and between $\theta_1=3.6^\circ$ and $\theta_2=4.2^\circ$ for the backward scattered light. The ratio of the scattering signals for this configuration, a refraction index of 1.403 (n-nonane at 20°C) and a wavelength of 632.8 nm is shown in figure 4.6 for two cases. In the first case (a), all droplets have the same size and the function shows a distinct oscillatory behavior. In the second case (b), it has been assumed that the particle radius follows a gaussian distribution function with a variance of 0.04 $\mu$m. The oscillations have almost disappeared.
Sigma = 0

![Graph](a)

Sigma = 0.04 um

![Graph](b)

Fig. 4.6: Ratio of the forward and backward scattered light. The forward light is scattered between 3.8° and 4.4° and the backward light between 3.6° and 4.2°. n=1.403 and λ=632.8nm.
4.5 The optical set-up

A schematic representation of the optical set-up is given in figure 4.7. A He–Ne laser beam, with a wavelength of 632.8 nm, passes across the cloud chamber through the windows. In order to avoid interferences in the windows, the path of the beam has been slightly tilted with respect to the axis perpendicular to the two windows.

Two similar optical systems allow the measurement of the scattered light in the forward and backward directions. Each system is constituted of a lens and a circle symmetric diaphragm. The light scattered from a volume element – the interaction domain – in the middle of the expansion cell is focused on an optical fiber linked to a photomultiplier (EMI, type 9658B).

The optical systems are adjusted so that both optical fibers receive the light scattered from the same volume element. This is requested in order to calculate the mean radius of the droplets as discussed in the previous paragraph. The adjustments are performed with a self-adhesive paper having good scattering properties. The paper is placed in the middle of the cell and the lens is settled so that the scattered light is focused on the optical fiber. Then the stops are adjusted so that both objects have the

Fig. 4.7: The optical set-up.
same size. The interaction domains for both directions are shown in figure 4.8. From the positions of the different elements of both optical system, it has been calculated that the forward light is scattered within a solid angle between 3.8° and 4.4° and the backward light between 3.6° and 4.2° (see appendix B).

![Normalized interaction domains for the forward and backward scattered light.](image)

**Fig. 4.8**: Normalized interaction domains for the forward and backward scattered light.

4.6 The data acquisition system

The data acquisition system is schematically represented in figure 4.9. The pressure signal and extinction signal are recorded in a 8–bit digital storage oscilloscope (Intron, type DSO–2022) and both scattering signals in a 8–bit transient recorder (Polar, type DS102). The analog voltages are transformed into digits between 0 and 255. The sensitivity and the offset of each signal can be settled in order to obtain an optimal signal in the whole digit range.

The initial values are determined by setting both recorders on a 25% pretriggering, so that the first quart of the experiment gives the offset value of each signal just before the opening of the electromagnetic valve linking the two vessels. Both recorders are externally triggered by a trigger unit having the pressure as input signal.
Fig. 4.9: The data acquisition system.
CHAPTER 5: RESULTS

5.1 Introduction

In this chapter, the experiments performed with the mixtures CH$_4$\text{	extbackslash}n--C$_9$H$_{20}$, N$_2$\text{	extbackslash}n--C$_9$H$_{20}$, CH$_4$\text{	extbackslash}n--C$_9$H$_{20}$ and CH$_4$\text{	extbackslash}n--C$_{10}$H$_{22}$, and with natural gas ("dry" and "recombined") will be presented.

For each experiment, the initial conditions (initial partial pressure $p_1$ of the heavy hydrocarbon, initial total pressure $p_0$ and temperature $T_0$), the pressure $p^*$ when condensation occurs and the corresponding temperature $T^*$ will be given. As explained in the previous chapter, the condensation pressure is determined from the abrupt rise of the scattered light signal. The temperature decrease is then computed from the Soave–Redlich–Kwong equation of state (section 4.3).

In the first four cases – the binary and ternary mixtures – both methane and nitrogen are assumed to be inert with respect to the condensation process, acting merely as a heat reservoir. The partial pressure of the heavy hydrocarbon is then calculated and a comparison is made with the classical nucleation theory (CNT), the kinetic theory (KNT) and the Dillmann and Meier theory (DMT).

For n-nonane, since the experiments with the three different carrier gases (methane, nitrogen and the mixture of both of them) have shown no differences, the average droplet size during the expansion has been evaluated only for the ternary mixture.

5.2 Experiments with CH$_4$\text{	extbackslash}n--C$_9$H$_{20}$ and N$_2$\text{	extbackslash}n--C$_9$H$_{20}$

The experimental data obtained from the expansions of the CH$_4$\text{	extbackslash}n--C$_9$H$_{20}$ and N$_2$\text{	extbackslash}n--C$_9$H$_{20}$ mixtures are respectively given in table 5.1 and 5.2. The initial conditions are measured with an accuracy of about 8 Pa for the partial pressure of the heavy hydrocarbon, 0.5% for the total pressure and 0.1 K for the temperature. The pressure when condensation occurs is determined within about 2% and the corresponding temperature within 1%.

The mole fraction $y_1$ of n-nonane in the mixture, defined as

\[ y_1 = \frac{[n\text{-nonane}]}{[n\text{-nonane} + \text{other gases}]} \]

1Here, the uncertainty due to the use of the SRK equation of state has not been taken into account.
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Tab. 5.1: Experimental data obtained from the measurements with the CH\textsubscript{4}\textbackslash{}C\textsubscript{9}H\textsubscript{20} mixture. The initial conditions, the condensation pressure and temperature, the mole fraction and the partial pressure of nonane at the onset of condensation are tabulated.

\[ y_1 = \frac{n_1}{n_1 + n_2}, \quad (5.1) \]

where \( n_1 \) is the number of moles of nonane and \( n_2 \) the number of moles of the remaining component, has been calculated in the following way: nonane, introduced first into the cloud chamber, in a state far removed from the critical point, is assumed to behave as a perfect gas, hence:

\[ n_1 = \frac{p_1 V}{RT}, \quad (5.2) \]

\( V \) represents the volume of the expansion cell. The number of moles of CH\textsubscript{4} or N\textsubscript{2} introduced next into the cell is calculated according to:
Tab. 5.2: Experimental data obtained from the measurements with the N$_2$\(C_9\)H$_2$O mixture. The initial conditions, the condensation pressure and temperature, the mole fraction and the partial pressure of nonane at the onset of condensation are tabulated.

\begin{equation}
\frac{1}{n_2} = \frac{p_2V}{RTZ_2}
\end{equation}

where \(p_2\) is the pressure of the remaining component approximated by \(p_0 - p_1\) and \(Z_2\) its compressibility factor. \(Z_2\) is computed with the Soave–Redlich–Kwong equation of state. Comparison of this compressibility factor with experimental data [IUP 78 and 79] yielded deviations equal to or smaller than 1%.

Substitution of (5.2) and (5.3) into (5.1), neglecting \(p_1\) against \(p_2/Z_2\), yields:

\begin{equation}
y_1 = \frac{p_1}{p_2} Z_2
\end{equation}

Assuming then that the mixture of nonane with CH$_4$ and N$_2$ behaves as ideal, the partial pressure of nonane when condensation occurs has been determined according to:

\begin{equation}
p_1 = y_1 p^*
\end{equation}

In figures 5.1 and 5.2, the partial pressure when condensation occurs has been plotted against the condensation temperature for each mixture. The measurements form a so-called Wilson line which follows very well the temperature dependence of the
Fig. 5.1: Partial pressure of nonane against temperature at the moment of condensation for the CH₄/C₅H₂O mixture. The triangles represent our measurements, the rhombuses represent the measurements of Adams et al. and the circles represent the measurements of Wagner and Strey. The solid line represents the saturation line of pure nonane according to King–Najar. The dotted line, the broken–dotted line and the broken line are the lines of constant nucleation rate (5 × 10¹² and 10¹⁷ m⁻³s⁻¹) according to respectively the CNT, the KNT and the DMT.

saturation curve of nonane for both cases. Supercooling from about 48 up to 52 K with respect to this line is observed at the onset of condensation. In the same figure, lines of constant nucleation rate (5 × 10¹² and 10¹⁷ m⁻³s⁻¹) are plotted for the CNT, the KNT and the DMT² (the model parameters appearing in the DMT are specified in appendix C.1). These two nucleation rates have been determined as being the limits of observable

²Therefore, the equilibrium saturation pressure curve of nonane given by King–Najar [HUN 88] has been taken.
nucleation rates in our set-up (see Appendix C.2). Furthermore, measurements of Adams et al. [ADA 84] and Wagner and Strey [WAG 84] with argon as carrier gas — where the nucleation rates were respectively measured to be $10^{11}$ and $4 \times 10^{14}$ m$^{-3}$s$^{-1}$ — are also plotted. Adams et al. performed their measurements with a fast expansion chamber where they could visualize and count the drops. In this way they could measure directly nucleation rates. Wagner and Strey carried out their measurements in a two pistons expansion chamber producing supercritical pulses.
They measured the droplet concentration immediately after the end of the supercritical expansion pulse by means of constant angle Mie-scattering. Here too, nucleation rates were directly measured. As can be seen from the figures 5.1 and 5.2, our measurements are in good agreement with those of Adams and Wagner, and it seems that the carrier gas has no influence on the condensation process. A better investigation of an eventual real gas effect is done by plotting the onsets of condensation in a p-T diagram (figures 5.3 and 5.4) for experiments with a constant molar fraction of nonane (280ppm nonane for CH₄ and 285ppm nonane for N₂). The equilibrium saturation curves of the binary mixtures are calculated with the program presented in chapter 2. The supercooling at the onset of condensation is unaffected. However, it seems from these two figures that the onset of condensation is slightly dependent on the initial temperature of the mixture.
A feature which does not appear in the theory.
From all the measurements, it seems that the mixture may indeed be considered as ideal in this pressure range, and that the homogeneous condensation of n-nonane is better described by the DMT and the KNT than by the CNT, the latter overestimating the supersaturation ratio.

Fig. 5.4: Onsets of homogeneous condensation obtained from measurements with N\textsubscript{2}/C\textsubscript{9}H\textsubscript{20} for a constant molar fraction of nonane (285 ppm). The shape of the symbols indicates the initial conditions. The solid line represents the equilibrium saturation curve (see text).
5.3 Experiments with CH₄/N₂/n-C₉H₂₀

The experimental data obtained from the expansions of the CH₄/N₂/n-C₉H₂₀ mixture are given in table 5.3. The carrier gas is composed of 85 mole% of methane and 15 mole% of nitrogen which is approximately the ratio found in natural gas. The partial vapor pressure of nonane has been in all cases 200 Pa. In this case, the parameters used in the SRK equation of state in order to compute the cooling during the expansion have been taken as the weighted average of the two components. In figure 5.5 the partial condensation pressure of nonane is plotted against the condensation temperature. The Wilson points form a cluster in a pressure range of about 5 Pa.

![Figure 5.5: Partial pressure of nonane against temperature at the moment of condensation. The solid line represents the saturation line of pure nonane according to King-Najar. The dotted line, the broken-dotted line and the broken line are the lines of constant nucleation rate (5×10¹² and 10¹⁷ m⁻³s⁻¹) according to respectively the CNT, the KNT and the DMT.](image-url)
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**Tab. 5.3:** Experimental data obtained from the measurements with the $CH_4\backslash N_2\backslash C_9H_{20}$ mixture. The initial conditions, the condensation pressure and temperature, the mole fraction and the partial pressure of nonane at the onset of condensation are tabulated.
Fig. 5.6: Ratio of forward and backward scattered light calculated from the Mie-theory for our experimental configuration, assuming that the radius of the droplets follows a gaussian distribution function with a variance of 0.04μm. Three different values of the refraction index n have been taken.

between 58 and 63 Pa and in a temperature range of 4 K between 216 and 220 K. The supercooling varies from about 47 up to 50 K, as for both binary mixtures discussed in the former section. The condensation process is the same as with the pure components.

The determination of the mean size of the droplets formed during the expansion is a much more difficult task to accomplish. The major reason for this is that we do not know yet the absolute sensitivity of both optical systems. Further, a small change of the refraction index n of the scattering particles has a strong effect on the ratio of forward and backward scattered light as can be seen from figure 5.6. Experimental data on the refraction indices of liquid hydrocarbons at temperatures as low as -50°C - when condensation occurs - are not available, and the solubilities of methane and nitrogen are
unknown. Finally, there are still two other factors affecting the precision of the comparison with the Mie-theory. These are respectively the error in the determination of the effective scattering angles and the uncertainty concerning the actual size distribution of the droplets during the expansion. However, these effects are not as important as the previous ones.

Despite all this, in order to make an estimate of the mean size of the droplets, an artificial scaling of both scattered light signals has been made, based on the measurements performed at 1 bar. Figure 5.7 shows the ratio of forward and backward scattered light of one of them. Under the assumption that the maximum ratio (35) should correspond with the theoretical maximum of figure 4.6b (200), a calibration factor of about 6 is obtained. A similar comparison with the theory for n=1.43 yields a calibration factor of about 4. The value 1.43 is an extrapolation of the refractive index of n-nonane to -50°C [LAN 62]. In this way, an estimate of the mean size of the droplets has been obtained for two different initial pressures, 1 and 9 bar, and a comparison has been made with the results of the simulations [MOR 90]. As can be seen in figure 5.8, the experimental results are of the same order of magnitude as the simulation results, and as expected from Gyarmathy's model, an increase of the total initial pressure of the mixture results in a decrease of the mean size of the droplets [GYA 82]. Finally, an estimate of the error in the determination of the mean droplet radius due to the uncertainty in the actual refraction index of the condensate may be
obtained since an increase of 2% of the refraction index induces a decrease of 15% to 30% of the mean radius of the droplets in the actual range of droplet sizes.
5.4 Experiments with CH$_4$N$_2$n-C$_{10}$H$_{22}$

Table 5.4 gives the experimental data obtained from the experiments with the CH$_4$N$_2$n-C$_{10}$H$_{22}$ mixture. The vapor pressure of n-decane was in all cases 100 Pa. In the same way as with n-nonane, the partial condensation pressure of decane has been plotted against the condensation temperature (figure 5.9). The dynamic dewpoints are found within a

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Tab. 5.4: Experimental data obtained from the measurements with the CH$_4$N$_2$n-C$_{10}$H$_{22}$ mixture. The initial conditions, the condensation pressure and temperature, the mole fraction and the partial pressure of decane at the onsets of condensation are tabulated.
pressure range of 5 Pa (28 – 33 Pa) and within a temperature range of about 10 K (214 – 224 K) along the adiabatic path. Contrarily to n-nonane, experimental data on n-decane are not available. However, here too, the homogeneous condensation of n-decane follows the DMT and the KNT rather than the CNT³.

Figure 5.10 shows the mean radius of the droplets during an expansion starting at 1 bar. Once again two different refraction indices have been taken: 1.41 (20°C) and 1.44 (extrapolation to −50°C) [LAN 62]. The droplet size is, as predicted by the theory, about half the value as for n-nonane.

![Graph showing partial pressure of decane against temperature.](image)

**Fig. 5.9:** Partial pressure of decane against temperature at the moment of condensation. The solid line represents the saturation line of pure decane according to Reid. The dotted line, the broken-dotted line and the broken line are the lines of constant nucleation rate \(10^{12}\) and \(10^{17}\) m\(^{-3}\)s\(^{-1}\) according to respectively the CNT, the KNT and the DMT.

³The calculations have been carried out with the universal equilibrium saturation curve given by Reid et al. [REI 87].
Fig. 5.10: Mean radius of the droplets during an expansion of n-decane starting at 1 bar as a function of time. The solid lines represent the outcome of the simulation, while the crosses and the circles represent the experimental results assuming respectively a refraction index n equal to 1.41 and 1.44.
5.5 Experiments with natural gas

Experiments with "dry" and "recombined" natural gas are respectively given in the tables 5.5 and 5.6. "Dry" gas is a production gas from the "Slochteren" field after separation of the condensate. "Recombined" gas is obtained by mixing "dry" gas and condensate in the same ratio as present in the original production field. A typical composition of both gases is given by Jansen et al. [JAN 90].

In figure 5.11 a typical result is shown for the expansion of "dry" natural gas starting at 1 bar. The ratio of forward and backward scattered light shows a time dependence more or less similar to that of nonane and decane. The same holds for the

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Tab. 5.5: Experimental data obtained from the experiments with "dry" natural gas. The initial conditions, the condensation pressure and the condensation temperature are tabulated.
Tab. 5.6: Experimental data obtained from the experiments with "recombined" natural gas. In this case, two condensation points were observed (see the text). Two bottles were needed in order to execute all the experiments. The last six experiments were performed with the second bottle.
Fig. 5.11: Ratio of forward and backward scattered light obtained from an experiment starting at 1 bar performed with "dry" natural gas. The corresponding individual scattered signals are depicted in figure 4.2b.

Fig. 5.12: Transmission signal from an experiment starting at 1 bar performed with "dry" natural gas. The corresponding pressure and scattered light signals are depicted in figure 4.2b.
transmission signal depicted in figure 5.12. This process is considered to be homogeneous. The onsets of condensation are plotted in a p–T diagram (figure 5.13). The solid line in the same figure represents a numerical computation of the equilibrium saturation curve of "dry" natural gas when alcanes up to $C_{12}$ have been taken into account ($C_{12}$ simulation, [NAM 91]). As can be seen from the figure, the experiments reproduce very well and the temperature dependence of the dewpoint line predicted by the theory is also found in the experiments.

For "recombined" natural gas, with the exception of two experiments, two condensation points were observed. The first one corresponds to heterogeneous
Fig. 5.14: Normalized pressure and scattered signals obtained from an experiment performed with "recombined" natural gas at 1.04 bar. I(f.) represents the forward scattered signal and I(b.) the backward scattered signal.

Fig. 5.15: Transmission signal from the experiment performed with "recombined" natural gas at 1.04 bar (see the previous figure).
condensation around already present nuclei, while the second one corresponds to homogeneous condensation. This can be seen from the scattered and transmitted light signals depicted in figures 5.14 and 5.15. The first onset of condensation is seen from scattered light signals. At this time, no attenuation can be observed on the transmission signal. Only about 20 ms after the rise of the scattered light signals, a first break point is observed on the extinction signal. The transmission decreases then gently until the second discontinuity, where the decrease becomes very strong. This second break point – hardly visible from the scattered signals – has the same typical shape observed when homogeneous condensation occurs as can be seen from the transmission signal of "dry" natural gas in figure 5.12. The oscillations observed in the backward scattered signal and in the ratio of forward and backward signals depicted in figure 5.16 are typical of a (nearly) monodisperse droplet cloud as can be seen from figure 4.6a, while these oscillations shade off when the distribution of the droplet size extends. The oscillations in the first part of the ratio of the two scattered light signals seem thus to indicate a nearly monodisperse cloud as expected from a heterogeneous process where condensation occurs around already present nuclei. The heterogeneous condensation process is also

Fig. 5.16: Ratio of forward and backward scattered light obtained from the experiment performed with "recombined" natural gas at 1.04 bar (see figure 5.14).
slower than the homogeneous one as can be seen from the two different slopes in the transmission signal. Figure 5.17 shows the onsets of heterogeneous condensation for "recombined" natural gas in a p–T diagram. The onsets of condensation of the two experiments showing only one dewpoint are also plotted in the figure (filled symbols). The broken line in the same figure represents a numerical computation of the equilibrium saturation curve of "recombined" natural gas when alcanes up to C_{11} are taken into account (C_{11} simulation, [KSE 90]), while the saturation curve represented by the solid line takes account of alcanes up to C_{18} (C_{18} simulation, [NAM 91]).

Fig. 5.17: Onsets of heterogeneous condensation obtained from the measurements with "recombined" natural gas. The shape of the symbols indicates the initial conditions. The two filled symbols represent the two experiments where only one onset point was observed. The two lines are computed equilibrium saturation curves (see text). The experiments executed with the second bottle are indicated by the arrows.
be noted that if the computations up to C_{18} were correct, the assumed composition of the gas cannot be correct since the initial conditions happen to be within the two phases region. This could also provide a possible explanation for the occurrence of heterogeneous condensation. Since the initial pressure in the expansion cell is much lower than the supply pressure, it cannot be excluded that some condensate was formed due to retrograde condensation. Globally, the temperature dependence of the theoretical dewpoint line is also found in the experiments. However, the experimental data show a large scatter. The experimental points can be divided into two classes; points close to the theoretical dewpoint line of the C_{11} simulation, and points that show a supercooling of about 25K with respect to that line. This difference could partly be attributed to the

Fig. 5.18: Onsets of homogeneous condensation obtained from the measurements with "recombined" natural gas. The shape of the symbols indicates the initial conditions. The two filled symbols represent the two experiments where only one onset point was observed. The dotted line gives the approximate temperature dependence of the dewpoint line obtained from "dry" natural gas.
fact that two different bottles were used for the experiments containing possibly two gases with a slightly different composition. As can be seen from the figure, the dewpoints corresponding to the second bottle all belong to the second class.

The onsets of homogeneous condensation are plotted in figure 5.18. They coincide very well with the onsets of condensation of "dry" natural gas. However, the measurements with "dry" gas reproduce much better. Here again, the temperature dependence of the dewpoints predicted by the theory is followed. The agreement of the homogeneous nucleation processes of both gases seems to point out that the same components are involved. These components could be lighter alcanes equally represented in both gases. The cleaning of the gas and the reduction of the dewpoint apparently affects the concentration components responsible for the heterogeneous nucleation processes.
CHAPTER 6: CONCLUSION

The calculations of the equilibrium saturation curves of binary mixtures of alcanes with the Soave–Redlich–Kwong equation of state have shown a good agreement with experimental data.

Expansions of binary mixtures of methane with nonane and nitrogen with nonane, of mixtures containing 85 mole% of methane and 15 mole% of nitrogen with nonane and decane, and with natural gas ("dry" and "recombined") have been described for initial pressures in the range of 1 bar up to 12 bar.

The experiments with nonane and decane have been compared with the predictions of the classical nucleation theory, of the kinetic nucleation theory and of the Dillmann–Meier theory for the condensation of a single vapor. The three theories yield the correct order of magnitude of the supersaturation ratio at the onset of condensation. This means that the partial vapor pressure at the onset of condensation exceeds the corresponding equilibrium vapor pressure by more than two orders of magnitude at the same temperature. However, the results of the KNT and the DMT are significantly better than those of the CNT for both heavy hydrocarbons.

The measured droplet size, although with a relative large error, yields the same order of magnitude as predicted by the CNT incorporated in the numerical model of Morgenstern. The predicted tendency of decreasing droplet size with increasing pressure is experimentally observed.

For natural gas, a similar homogeneous nucleation behavior than the one for nonane and decane has been observed. In the case of "recombined" gas, heterogeneous condensation was observed which is characterized by a relatively slow growth rate of the droplets and a "monodisperse" droplet size distribution. This process was followed by homogeneous condensation with conditions of onset that agree very well with that of "dry" gas.
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APPENDIX
Appendix A

A.1 Thermodynamic properties of gas mixtures

The expression for the chemical potential given in formula 3.14 will be derived with the general limit method. This method assumes that as the pressure on a real gas or gaseous mixture is reduced (resp. the volume is increased) at constant temperature and mole number, the thermodynamic properties of the system approach those of ideal gases.

First, we will derive the thermodynamic properties of the pure gas, and then those of a mixture. Therefore, we will step by step follow the derivation of Beattie [BEA 43].

(A) Pure gas

We assume that for low pressures we may write:

\[ pV = nRT + \frac{n^2 B}{RT} + \mathcal{O}(p^2) \]  \hspace{1cm} (A.1)

or

\[ pV = nRT + \frac{n^2 B}{V} + \mathcal{O}\left( \frac{n^2}{V^2} \right) \]  \hspace{1cm} (A.2)

with 

- \( p \): pressure
- \( V \): volume
- \( T \): temperature
- \( n \): number of moles
- \( B \): parameter dependent on the temperature
- \( R \): universal gas constant
We can now proceed to write down all of the thermodynamic functions of a pure gas in terms of the independent variables \( p \) and \( T \), and \( V \) and \( T \). The reference state of the gas is taken at an arbitrarily chosen pressure \( p_0 \) and temperature \( T_0 \), with a corresponding volume \( V_0 \) for \( n \) moles. Since the thermodynamic functions in which we are interested are all state variables we may proceed from the standard state \((p_0, T_0)\) or \((V_0, T_0)\) to the state \((p, T)\) or \((V, T)\) along any path. We shall use a three-step path involving a state in a region of very low pressure \( p^* \) (or \( V^* \)). Let the mass of gas remain constant and (see also figures A1 and A2):

1. Change the pressure from \( p_0 \) to \( p^* \) (or the volume from the corresponding values \( V_0 \) to \( V^* \)) at the temperature \( T_0 \).
2. Change the temperature from \( T_0 \) to \( T \) with the pressure held constant at \( p^* \) (or the volume at \( V^* \)).
3. Change the pressure from \( p^* \) to \( p \) (or the volume from \( V^* \) to \( V \)) at the temperature \( T \).

Fig. A.1

Fig. A.2
Derivations for the independent variables \( p \) and \( T \): \( H \) and \( S \)

We make use of two relations resulting from the fundamental equations

\[
\left( \frac{\partial H}{\partial p} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_p \quad (A.3)
\]

\[
\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p \quad (A.4)
\]

with \( H \): enthalpy

\( S \): entropy

Further

\[
\left( \frac{\partial H}{\partial T} \right)_p = C_p \quad (A.5)
\]

and

\[
\left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \quad (A.6)
\]

where \( C_p = n \, c_p \) and \( c_p \) is the molar heat capacity at constant pressure. For low pressures \( c_p^* = c_p^* (T) \) .

From (A.3), (A.5) and the integration path (figure A.1):

\[
H(p,T) - H(p_0,T_0) = \int_{p_0}^{p} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp + \int_{T_0}^{T} n \, c_p^* \, dT + \int_{P^*}^{P} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp \quad (A.7)
\]

or

\[
H(p,T) = \int_{P^*}^{P} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dp + n \, h^o \quad (A.8)
\]

where

\[
h^o = h^o_0 + \int_{T_0}^{T} c_p^* \, dT \quad (A.9)
\]
and

\[ n h^0 = H(p_0, T_0) + \int_{p_0}^{p^*} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dp \]

\[ = H(p^*, T_0) \quad \text{(A.10)} \]

From (A.4), (A.6) and the integrating path (figure A.1):

\[ S(p, T) - S(p_0, T_0) = - \int_{p_0}^{p^*} \left( \frac{\partial V}{\partial T} \right)_P dp + \int_{T_0}^{T} \frac{nc^* dT}{T} - \int_{T}^{T_T} \left( \frac{\partial V}{\partial T} \right)_P dp \quad \text{(A.11)} \]

The first and third integrals occurring in the right-hand side of equation (A.11) are improper (they do not converge for \( p \to 0 \)). This difficulty can be fait by the addition and subtraction of a term:

\[ S(p, T) - S(p_0, T_0) = \int_{p_0}^{p^*} \left[ \frac{nR}{P} - \left( \frac{\partial V}{\partial T} \right)_P \right] dp + \int_{T_0}^{T} \frac{nc^* dT}{T} + \int_{T}^{T_T} \left( \frac{\partial V}{\partial T} \right)_P dp - \int_{T_0}^{T} \frac{nR}{P} dp \]

\[ \quad + \int_{p}^{p^*} \left[ \frac{nR}{P} - \left( \frac{\partial V}{\partial T} \right)_P \right] dp - \int_{p_0}^{p^*} \frac{nR}{P} dp - \int_{T_0}^{T} \frac{nR}{P} dT \]

\[ = \int_{p_0}^{p^*} \left[ \frac{nR}{P} - \left( \frac{\partial V}{\partial T} \right)_P \right] dp + \int_{T_0}^{T} \frac{nc^* dT}{T} + \int_{T}^{T_T} \left( \frac{\partial V}{\partial T} \right)_P dp - nR \ln \frac{P}{P_0} \quad \text{(A.12)} \]

or

\[ S(p, T) = \int_{p}^{p^*} \left[ \frac{nR}{P} - \left( \frac{\partial V}{\partial T} \right)_P \right] dp + nS^0 - nR \ln p \quad \text{(A.13)} \]

where

\[ S^0 = S^0 + \int_{T_0}^{T} \frac{c^*_e^*}{T} dT \quad \text{(A.14)} \]

and

\[ nS^0 = S(p_0, T_0) + \int_{p_0}^{p^*} \left[ \frac{nR}{P} - \left( \frac{\partial V}{\partial T} \right)_P \right] dp + nR \ln p_0 \]

\[ = S(p^*, T_0) + nR \ln p^* \]
\[ n s'_a = n s^\circ_a + n R \ln p^* \quad (A.15) \]

**Derivatives for the independent variables \( V \) and \( T \)**

The interesting equations are now:

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \quad (A.16) \]

\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad (A.17) \]

with \( U \): internal energy

and

\[ \left( \frac{\partial U}{\partial T} \right)_V = C_V \quad (A.18) \]

\[ \left( \frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \quad (A.19) \]

where \( C_V = n c_V \) and \( c_V \) is the molar heat capacity at constant volume. For low pressures \( c_V^* = c_V^*(T) \).

From (A.16) and (A.18) and the integration path (figure A.2):

\[ U(V,T) - U(V_0,T_0) = \int_{V_0}^{V*} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV + \int_{T_0}^{T} n c_V^* dT \]

\[ + \int_{T_0}^{V*} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \quad (A.20) \]

or

\[ U(V,T) = \int_{V*}^{V} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV + n u^0 \quad (A.21) \]

with

\[ u^0 = u^0_0 + \int_{T_0}^{T} c_V^* dT \quad (A.22) \]
\[ n u_0 = U(V_0, T_0) + \int_{V_0}^{V_*} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \]
\[ = U(V^*, T_0) \quad (A.23) \]

From (A.17), (A.19) and the integration path (figure A.2):
\[ S(V,T) - S(V_0, T_0) = \int_{V_0}^{V_*} \left( \frac{\partial P}{\partial T} \right)_V \frac{dV}{V} + \int_{V_*}^{T} \frac{n c_i^*}{T} dT + \int_{V_*}^{V} \left( \frac{\partial P}{\partial T} \right)_V \frac{dV}{V} \quad (A.24) \]

and in the same way as for (A.11):
\[ S(V,T) - S(V_0, T_0) = \int_{V_0}^{V_*} \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{n R}{V} \right] dV + \int_{V_*}^{T} \frac{n c_i^*}{T} dT + \int_{V_*}^{V} \frac{n R}{V} dV \]
\[ + \int_{V_*}^{V} \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{n R}{V} \right] dV + n R \ln \frac{V}{V_0} \quad (A.25) \]

or
\[ S(\rho, T) = \int_{V_*}^{V} \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{n R}{V} \right] dV + n R \ln V + n S_0^{0'} \quad (A.26) \]

with
\[ S_0^{0'} = S_0^{0'} + \int_{V_*}^{T} \frac{n c_i^*}{T} dT \quad (A.27) \]

and
\[ n S_0^{0'} = S(V_0, T_0) + \int_{V_0}^{V_*} \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{n R}{V} \right] dV - n R \ln V_0 \]
\[ = S(\rho_0, T_0) + \int_{V_0}^{V_*} \left( \frac{\partial P}{\partial T} \right)_V dV - n R \int_{V_0}^{V_*} \frac{dV}{V} - n R \ln \rho_0 V_0 + n R \ln \rho_0 \]
\[ = \int_{V_0}^{V_*} \left( \frac{\partial S}{\partial T} \right)_V dV - n R \left[ \ln V_* - \ln V_0 \right] - n R \ln \rho_0 V_0 + S(\rho_0, T_0) + n R \ln \rho_0 \]
\[ = \int_{V_0}^{V_*} \left( \frac{\partial P}{\partial T} \right)_V dV - n R \left[ \ln V_* - \ln V_0 \right] - n R \ln \rho_0 V_0 + S(\rho_0, T_0) + n R \ln \rho_0 \]
\[ nS_{0}' = \int_{p_0}^{p^*} \frac{(\partial S)}{(\partial p)} dp + nR\left[ \ln p^* - \ln p_0 \right] - nR\left[ \ln p^*V^* - \ln p_0V_0 \right] \\
\quad - nR \ln p_0V_0 + S(p_0,T_0) + nR \ln p_0 \\
= - \int_{p_0}^{p^*} \frac{(\partial S)}{(\partial p)} dp + \int_{p_0}^{p^*} \frac{nR}{p} dp + S(p_0,T_0) + nR \ln p_0 - nR \ln p^*V^* \\
= \int_{p_0}^{p^*} \left[ \frac{nR}{p} - \frac{(\partial V)}{(\partial T)p} \right] dp + S(p_0,T_0) + nR \ln p_0 - nR \ln p^*V^* \\
= nS_{0}' - nR \ln p^*V^* \\
= nS_{0}' - nR \ln nRT_0 \quad (A.28) \]

Thus, we have

\[ S(V,T) = \int_{V^*}^{V} \left[ \frac{(\partial S)}{(\partial V)} - \frac{nR}{V} \right] dV + \int_{T_0}^{T} \frac{nCV^*}{T} dT \\
+ nR \ln V - nR \ln nRT_0 + nS_{0}' \quad (A.29) \]

with \( nS_{0}' \) given by \((A.14)\).

We can now use the thermodynamic relation

\[ C_p^* - C_V^* = R \quad (A.30) \]

\[ \int_{T_0}^{T} \frac{nCV^*}{T} dT = \int_{T_0}^{T} \frac{nCV^*}{T} dT - \int_{T_0}^{T} \frac{nR}{T} dT \\
= \int_{T_0}^{T} \frac{nCV^*}{T} dT - nR \ln \frac{T}{T_0} \quad (A.31) \]

Substitution in \((A.29)\) yields
\[ S(v,T) = \int_{v_0}^{v} \left[ \frac{\partial P}{\partial v} - \frac{nR}{v} \right] dv + \int_{T_0}^{T} nC_v^\ast dt - nR \ln \frac{T}{T_0} + nR \ln V - nR \ln nRT_0 + nS^0' \]

\[ = \int_{v_0}^{v} \left[ \frac{\partial P}{\partial v} - \frac{nR}{v} \right] dv + nR \ln \frac{V}{nRT} + nS^0' \]  

(A.32)

with \( S^0' \) given by (A.14).

We can now replace \( v^* \) by infinity, so that (A.21) and (A.32) become:

\[ U(v,T) = \int_{v}^{\infty} \left[ P - T \left( \frac{\partial P}{\partial v} \right)_v \right] dv + nu^0 \]  

(A.33)

\[ S(v,T) = \int_{v}^{\infty} \left[ \frac{nR}{v} - \left( \frac{\partial P}{\partial v} \right)_v \right] dv + nR \ln \frac{V}{nRT} + nS^0' \]  

(A.34)

With the definition of the Helmholtz energy:

\[ F = U - TS \]  

(A.35)

it follows

\[ F(v,T) = \int_{v}^{\infty} \left[ P - T \left( \frac{\partial P}{\partial v} \right)_v \right] dv + nu^0 \]

\[- \int_{v}^{\infty} \left[ \frac{nRT}{v} - T \left( \frac{\partial P}{\partial v} \right)_v \right] dv - nRT \ln \frac{V}{nRT} - nTS^0' \]

\[ = \int_{v}^{\infty} \left[ P - \frac{nRT}{v} \right] dv - nRT \ln \frac{V}{nRT} + n(u^0 - TS^0') \]  

(A.36)

and finally

\[ \gamma = \left( \frac{\partial F}{\partial n} \right)_{v,T} \]

\[ = \int_{v}^{\infty} \left[ \left( \frac{\partial P}{\partial n} \right)_v - \frac{RT}{v} \right] dv - RT \ln \frac{V}{nRT} + RT + u^0 - TS^0' \]  

(A.37)
Gas mixture

We begin by defining some notations that we will use:
- The subscript "e" will denote the value of a thermodynamic quantity for a pure gas having the same total volume, temperature, and chemical potential as in a gas mixture. Under these conditions, the pure gas would be in thermodynamic equilibrium with the mixture through a membrane permeable to that gas alone, and since the volume is specified, the values of all extensive as well as intensive properties of the gas would be fixed. Such quantities will be called "equilibrium" quantities.
- When necessary to distinguish between a pure gas and the same gas in a mixture, the subscript "k" will denote the value of a quantity for the pure gas and "i" for the gas in the mixture.

We will now show that using the Dalton law, in the regime of very low pressures, we can easily extend the relations found for a pure gas.

\[ P^*_{ek} = (P_{yi})^* \]  \hspace{1cm} (A.38)

From (A.38) it follows directly that

\[ \left( \sum_{k} P_{ek}/P \right)^* = 1 \]  \hspace{1cm} (A.39)

Consider a number of systems, one consisting of a gas mixture and each of the others consisting of one of the pure constituent gases.
Let the equilibrium conditions,

\[ T \text{ (each pure gas)} = T \text{ (mixture)} \]
\[ V \text{ (each pure gas)} = V \text{ (mixture)} \]
\[ \gamma_k = \gamma_i, \quad (k = i = 1, \ldots, n) \]

apply for all variations. For the gas mixture (Gibbs-Duhem):

\[ dp = \left( \frac{S}{V} \right) dT + \sum_i \left( \frac{n_i}{V} \right) d\gamma_i \]

(A.41)

and for each pure gas:

\[ dp_{ek} = \left( \frac{S_{ek}}{V} \right) dT + \left( \frac{ne_{ek}}{V} \right) d\gamma_{ek} \]

(A.42)

From equations (A.41) and (A.42), we have the following relations:

\[ \left( \frac{\partial P}{\partial \gamma_i} \right)_{T, \gamma_j} = \frac{n_i}{V} \]

(A.43a)

\[ \left( \frac{\partial P}{\partial T} \right)_{\gamma} = \frac{S}{V} \]

(A.43b)

and

\[ \left( \frac{\partial p_{ek}}{\partial \gamma_{ek}} \right)_{T} = \frac{ne_{ek}}{V} \]

(A.44a)

\[ \left( \frac{\partial p_{ek}}{\partial T} \right)_{\gamma_{ek}} = \frac{S_{ek}}{V} \]

(A.44b)

Differentiating now equation (A.39) first with respect to one of the \( \gamma \)'s with \( T \) and all of the other \( \gamma \)'s \( (\gamma_j) \) constant, and then with respect to \( T \) with all of the \( \gamma \)'s constant, we find for the region of very low pressure:
\[
\left( \frac{\partial \rho e_k}{\partial y} \right)_k = \left( \frac{\partial \rho}{\partial y} \right)_j y_j
\]
\[\Sigma_k \left( \frac{\partial \rho e_k}{\partial T} \right)_y = \left( \frac{\partial \rho}{\partial T} \right)_y\]

Substitution of (A.43a) and (A.44a) in (A.45) gives:
\[
\frac{n_{ek}^*}{V^*} = \frac{n_i^*}{V^*} \quad \text{or} \quad n_{ek}^* = n_i^*
\]

Substitution of (A.43b) and (A.44b) in (A.46) yields:
\[
\frac{S^*}{V^*} = \left( \frac{\Sigma_k S e_k}{V} \right)^* \quad \text{or} \quad S^* = \Sigma_k S e_k
\]

Finally, with the equations (A.47) and (A.48), and the following thermodynamic relations,

\[
U = TS - pV + \Sigma_i y_i n_i
\]
\[
H = U + pV
\]
\[
F = U - TS
\]
\[
C_v = \frac{\partial U}{\partial T} v, n
\]
\[
C_p = \frac{\partial H}{\partial T} p, n
\]

we can show that the following relations hold:
\[
U^* = \Sigma_k U_k
\]
\[
H^* = \Sigma_k H_k
\]
\[
F^* = \Sigma_k F_k
\]
\[
C_v^* = \Sigma_k C_{v_k}
\]
\[
C_p^* = \Sigma_k C_{p_k}
\]
Corresponding to equation (A.12) for the entropy of a pure gas (in terms of the variables \( p \) and \( T \)), we have for \( \sum_{i=1}^{n} n_i \) moles of a gas mixture of constant composition:

\[
S(p, T) - S(p_0, T_0) = \int_{T_0}^{T} \left[ \frac{\Sigma n_i R}{P} - \left( \frac{\partial V}{\partial T} \right)_{p,n} \right] dT + \int_{p_0}^{p} \left[ \frac{\Sigma n_i R}{P} - \left( \frac{\partial V}{\partial T} \right)_{p,n} \right] dP
\]

\[+ \int_{T_0}^{T} \left[ \frac{\Sigma n_i R}{P} - \left( \frac{\partial V}{\partial T} \right)_{p,n} \right] dT - (\Sigma n_i) R \ln \frac{T}{T_0} \] (A.58)

Now, we shall make use of the following relation:

\[
S(p_0, T_0) + \int_{p_0}^{p} \left[ \frac{\Sigma n_i R}{P} - \left( \frac{\partial V}{\partial T} \right)_{p,n} \right] dP + \Sigma n_i R \ln p_0 =
\]

\[
= S(p_0, T_0) + \int_{p_0}^{p} \left( \frac{\partial S}{\partial P} \right)_T dP + \int_{T_0}^{T} \frac{\Sigma n_i R}{P} dP + \Sigma n_i R \ln p_0 \] (A.59)

\[
= S(p^*, T_0) + \Sigma n_i R \ln p^*
\]

From (A.48), (A.14) and (A.38) we have

\[
S(p^*, T_0) = \Sigma_k S_{ek}(p_0^*, T_0)
\]

\[= \Sigma_k n_{ek} s^{o'}_{0k} - \Sigma_k n_{ek} R \ln p_{ek}^{*}
\]

\[= \Sigma_i n_i s^{o'}_{0i} - \Sigma_i n_i R \ln p^{*}_{y_i} \] (A.60)

With (A.60), (A.58) becomes

\[
S(p^*, T_0) + \Sigma_i R n_i \ln p^* = \Sigma_i n_i s^{o'}_{0i} - \Sigma_i n_i R \ln y_i \] (A.61)

with \( s^{o'}_{0i} \) given by (A.15) for the pure component \( i \).
From (A.57) we have
\[
\int_{T_0}^{T} \frac{C_p^*}{T} \, dT = \int_{T_0}^{T} \frac{\sum_k n_{ek} C_{pk}}{T} \, dT = \int_{T_0}^{T} \frac{\Sigma_i n_i C_{pi}^*}{T} \, dT
\]
(A.62)

Substitution of (A.59), (A.61) and (A.62) in (A.58) gives finally:
\[
S(p,T) = \int_{p*}^{p} \left[ \frac{\Sigma_i n_i R}{T} - \frac{\partial U}{\partial T} \right] \, dp - \Sigma i n_i R ln p_i + \Sigma i n_i c_i^0 \quad \text{(A.63)}
\]

with
\[
S_i^0' = S_i^0 + \int_{T_0}^{T} \frac{C_{pi}^*}{T} \, dT \quad \text{(A.64)}
\]

and \( S_i^0 \) given by (A.15) for the pure component \( i \)

Derivation of the general relations in terms of the variables \( V^* \) and \( T \)

Corresponding to equation (A.20) for the energy of a pure gas, we have for \( \Sigma i n_i \) moles of a gas mixture of constant composition:
\[
U(V,T) - U(V_0,T_0) = \int_{V_0}^{V} \left[ T \frac{\partial p}{\partial T} \right]_{V,n} \, dV + \int_{T_0}^{T} C_{v*} \, dT + \int_{V}^{V} \left[ T \frac{\partial p}{\partial T} \right]_{V,n} \, dV
\]
(A.65)

From (A.53) and (A.22) we have:
\[
U(V^*,T_0) = \sum_k u_{ek} (V^*,T_0) = \sum_k n_{ek} u_{0,k}^o = \sum_i n_i u_{i}^o
\]
(A.66)
and from (A.56):
\[
\int_{v*}^{T} C_v^* dT = \int_{v*}^{T} \sum_{k} \left( n_{ek} C_v^k \right) dT
\]
\[
= \int_{v*}^{T} \sum_{i} n_i C_v^i dT
\]  
(A.67)

Hence, substituting (A.66) and (A.67) in (A.65) we find:
\[
U(v,T) = \int_{T}^{V*} \left[ \frac{\partial P}{\partial T} \right]_{v,n} dV + \sum_{i} n_i U_i^0
\]  
(A.68)

with
\[
U_i^0 = U_i^0 + \int_{v*}^{T} C_v^i dT
\]  
(A.69)

and \( U_i^0 \) given by (A.23) for the pure component \( i \).

Corresponding finally to equation (A.25) for the entropy of a pure gas, we have for \( \Sigma_i n_i \) moles of a gas mixture:
\[
S(v,T) - S(v_o,T_o) = \int_{T_o}^{V*} \left[ \frac{\partial P}{\partial T} \right]_{v,n} dV + \int_{v*}^{T} C_v^* dT
\]
\[
+ \int_{T}^{V*} \left[ \frac{\partial P}{\partial T} \right]_{v,n} \frac{\sum_i n_i R}{V} dV + \sum_i n_i R \ln \frac{V}{V_o}
\]  
(A.70)

Further:
\[
\int_{T_o}^{V*} \left[ \frac{\partial P}{\partial T} \right]_{v,n} \frac{\sum_i n_i R}{V} dV - \sum_i n_i R \ln V_o + S(v_o,T_o) =
\]
\[
= \int_{T_o}^{V*} \left( \frac{\partial P}{\partial T} \right)_{v,n} dV - \int_{T_o}^{V} \sum_i n_i R dV - \sum_i n_i R \ln V_o + S(p_o,T_o)
\]
\[
= \int_{T_o}^{V*} \left( \frac{\partial S}{\partial V} \right)_{T,n} dV - \sum_i n_i R \ln \frac{V^*}{V_o} - \sum_i n_i R \ln V_o + S(p_o,T_o)
\]
\[
\begin{align*}
&= \int_{p_0}^{p^*} \left( \frac{\partial s}{\partial p} \right)_{T,n} \, dp + \Sigma_{i} n_i R \ln \frac{p^*}{p_0} - \Sigma_{i} n_i R \ln \frac{P^*V^*}{P_0V_0} \\
&\quad - \Sigma_{i} n_i R \ln p_0 V_0 + \Sigma_{i} n_i R \ln p_0 + S(p_0,T_0) \\
&= - \int_{p_0}^{p^*} \frac{\partial s}{\partial T} \rho_0 \, dp + \int_{p_0}^{p^*} \frac{\Sigma_{i} n_i R}{\rho_0} \, dp - \Sigma_{i} n_i R \ln p^* V^* \\
&\quad + \Sigma_{i} n_i R \ln p_0 + S(p_0,T_0) \\
&= \int_{p_0}^{p^*} \left[ \frac{\Sigma_{i} n_i R}{\rho_0} - \frac{\partial s}{\partial T} \rho_0 \right] \, dp + S(p_0,T_0) + \Sigma_{i} n_i R \ln p_0 - \Sigma_{i} n_i R \ln p_0 \\
&= \Sigma_{i} n_i S_{oi} - \Sigma_{i} n_i R \ln y_i - \Sigma_{i} n_i R \ln p^* V^* \quad (A.71)
\end{align*}
\]

(From (A.61))

Using then the equation of state at very low pressure:

\[(pV)^* = \Sigma_{i} n_i RT, \quad (A.72)\]

we can rewrite (A.71) as

\[
\begin{align*}
\Sigma_{i} n_i S_{oi} - \Sigma_{i} n_i R \ln y_i &\quad - \Sigma_{i} n_i R \ln p^* V^* = \\
&\quad = \Sigma_{i} n_i S_{oi} - \Sigma_{i} n_i R \ln y_i - \Sigma_{i} n_i R \ln (\Sigma_{i} n_i RT_0) \\
&\quad = \Sigma_{i} n_i S_{oi} - \Sigma_{i} n_i R \ln n_i RT_0. \quad (A.73)
\end{align*}
\]

Further, from equations (A.56) and (A.30) we have

\[
\begin{align*}
V^* \int_{T_0}^{T} \frac{C_v^*}{T} \, dT &\quad = \int_{T_0}^{T} \frac{\Sigma_{i} n_i R \kappa C_v}{T} \, dT \\
&\quad = \int_{T_0}^{T} \frac{\Sigma_{i} n_i C_v}{T} \, dT
\end{align*}
\]
\[
\begin{aligned}
&= \int_{v^*}^{T} \frac{\Sigma_i n_i c_i^*}{T} \, dT - \sum_{v^*}^{T} \frac{\Sigma_i n_i R}{T} \, dT \\
&= \int_{v^*}^{T} \frac{\Sigma_i n_i c_i^*}{T} \, dT - \Sigma_i n_i R \ln \frac{T}{T_0}
\end{aligned}
\]  

(A.74)

Hence, substituting (A.71), (A.73) and (A.74) into (A.70) yields:

\[
S(v,T) = \int_{v^*}^{V} \left[ \left( \frac{\partial P}{\partial T} \right)_{v,n} - \frac{\Sigma_i n_i R}{V} \right] \, dV + \Sigma_i n_i R \ln \frac{V}{n_i RT} + \Sigma_i n_i s_i^{o'}
\]  

(A.75)

with \( s_i^{o'} \) given by (A.64)

Replacing now \( v^* \) by infinity, the expressions for the energy and the entropy of a gas mixture are:

\[
U(v,T) = \int_{v}^{\infty} \left[ p - T \left( \frac{\partial P}{\partial T} \right)_{v,n} \right] \, dV + \Sigma_i n_i u_i^{o}
\]  

(A.76)

\[
S(v,T) = \int_{v}^{\infty} \left[ \frac{\Sigma_i n_i R}{V} - \left( \frac{\partial P}{\partial T} \right)_{v,n} \right] \, dV + \Sigma_i n_i R \ln \frac{V}{n_i RT} + \Sigma_i n_i s_i^{o'}
\]  

(A.77)

From equation (A.35) we can then calculate the Helmholtz energy:

\[
F(v,T) = \int_{v}^{\infty} \left[ p - T \left( \frac{\partial P}{\partial T} \right)_{v,n} \right] \, dV + \Sigma_i n_i u_i^{o}
\]

\[
- \int_{v}^{\infty} \left[ \frac{\Sigma_i n_i R}{V} - T \left( \frac{\partial P}{\partial T} \right)_{v,n} \right] \, dV - \Sigma_i n_i R \ln \frac{V}{n_i RT} - \Sigma_i n_i R T s_i^{o'}
\]

\[
= \int_{v}^{\infty} \left[ p - \frac{\Sigma_i n_i R}{V} \right] \, dV - \Sigma_i n_i R T \ln \frac{V}{n_i RT} + \Sigma_i n_i u_i^{o} - T s_i^{o'}
\]

(A.78)
and finally the chemical potential:

\[ \mu_i (\nu, T) = \left( \frac{\partial F}{\partial n_i} \right)_{T, \nu, n_j} \]

\[ = \int_{V} \left[ \left( \frac{\partial E}{\partial n_i} \right)_{\nu, T, n_j} - \frac{RT}{V} \right] dV - RT \ln \frac{V}{n_i RT} \]

\[ + RT + u_i^0 - T s_i^0 \]  \hfill (A.79)
A.2 Listing of the program for the calculation of the phase equilibrium of binary mixtures

program phasetot;
uses mathlib9; {− contains procedure "zroots", see further −}
label 999;
const
  R = 8.3144; {universal gas constant}
  nc = 15; {number of components}
  np = 3;
  mp1 = 4;
type
  real = double;
  Ncomp = array[1..nc] of real;
  RealArrayNP = array[1..np] of real;
  RealArrayNPbyNP = array[1..np,1..np] of real;
  IntegerArrayNP = array[1..np] of integer;
  phase = record
    vap,liq : real;
  end;
var
  j,Nstep,Nstep2 : integer;
  c1,c2 : integer;
  x1,y2,T,KK,Tstep : real;
  dP,dMu1,dMu2 : real;
  dAmdx1,dA1dx1,dA2dx1,dBmdx1 : real;
  a,b,Tc,Pc,omega,Ptrial : Ncomp;
  z : RealArrayNP;
  Am,Bm,A1,A2,P,Mu1,Mu2 : phase;
  num : string[7];
  Ofile1,Ofile2 : string[23];
  outfile1,outfile2 : text;

procedure a_coef(cl,c2 :integer; x1,y2,KK,T : real; Tc,Pc,omega : Ncomp;
  Var a : Ncomp; Var Am,A1,A2 : phase; Var dAmdx1,dA1dx1,dA2dx1: real);
{\(- a : a\_coeff. \text{Soave equation for pure component} \)}
{\(- A m : a\_coeff. \text{Soave equation for mixture} \)}
{\(- A : \text{coeff. appearing in chemical potential} \)}
{\(- \text{dAmdx1, dA1dx1, dA2dx1 : derivatives, necessary for procedure func} \)}

```
var
  H : real;
begin
  a[1] := 0.42748*R*R*Tc[1]*Tc[1]/Pc[1];
  a[1] := a[1]*sqr(1+(1-sqrt(T/Tc[1]))
         *(0.48+1.574*omega[1]-0.176*omega[1]*omega[1]));
         *(0.48+1.574*omega[2]-0.176*omega[2]*omega[2]));
  H := (1-KK)*sqr(a[1]*a[2]);
  Am.vap := (1-y2)*(1-y2)*a[1] + y2*y2*a[2] + 2*(1-y2)*y2*H;
  Am.liq := x1*x1*a[1] + (1-x1)*(1-x1)*a[2] + 2*x1*(1-x1)*H;
  dAmdx1 := 2*(x1*(a[1] + a[2]) - a[2] + (1-2*x1)*H);
  A1.vap := (1-y2)*a[1] + y2*H;
  A1.liq := x1*a[1] + (1-x1)*H;
  dA1dx1 := a[1] - H;
  A2.vap := y2*a[2] + (1-y2)*(1 - KK)*sqr(a[1]*a[2]);
  A2.liq := (1-x1)*a[2] + x1*(1 - KK)*sqr(a[1]*a[2]);
  dA2dx1 := -a[2] + H
end;
```

```
procedure b__coeff(c1,c2 : integer; x1,y2 : real; Tc,Pc : Ncomp;
Var b : Ncomp; Var Bm : phase; Var dBmdx1 : real);
{\(- b : b\_coeff. \text{Soave equation for pure component} \)}
{\(- Bm: b\_coeff. \text{Soave equation for binary mixture} \)}
{\(- dBmdx1 : \text{derivative for func} \)}
begin
  b[1] := 0.08664*R*Tc[1]/Pc[1];
  b[2] := 0.08664*R*Tc[2]/Pc[2];
  Bm.vap := (1-y2)*b[1] + y2*b[2];
  Bm.liq := x1*b[1] + (1-x1)*b[2];
end;
```
procedure init_vap_press_liq(c2 : integer; T : real; Tc,Pc,omega : Ncomp;
    Var P_trial : Ncomp);
    {— Initialization vapor pressure sat.liquid P_trial [Pa]—}
    {— See [Rei 87] page 207 —}
    var
        fO, f1 : real;
        begin
            fO := 5.92714 - 6.09648*Tc[c2]/T - 1.28862*ln(T/Tc[c2]);
            fO := fO + 0.169347*sqr(T/Tc[c2])*sqr(T/Tc[c2])*sqr(T/Tc[c2]);
            f1 := 15.2518 - 15.6875*Tc[c2]/T - 13.4721*ln(T/Tc[c2]);
            f1 := f1 + 0.43577*sqr(T/Tc[c2])*sqr(T/Tc[c2])*sqr(T/Tc[c2]);
            P_trial[c2] := Pc[c2]*exp(f0 + omega[c2]*f1);
        end;

procedure init_root(nc : integer; Var P_trial : Ncomp; Var x : RealArrayNP);
    {— Initialization of the roots x[1] and x[2] : —}
    {— molar volume vapor and molar volume liquid [m3/mol]—}
    {— with the Soave equation, and with P_trial —}
    {— the procedure "zroots" for the resolution of the —}
    {— third degree equation has been taken from [PRE 89] —}
    var
        k : integer;
        a2,a1 : ComplexArrayMP1;
        ep1,ep2,ep,Vr0,Vrd,Pl1 : real;
        zv,zl : ComplexArrayMP1;
        mvol : phase;
        begin
            P_trial[c1] := (1-y2)*P_trial[c2]/y2;
            a2[4].r := P_trial[c2];
            a2[3].r := -R*T;
            a2[1].r := -a[c2]*b[c2];
            a2[4].i := 0.0;
            a2[3].i := 0.0;
            a2[2].i := 0.0;
            a2[1].i := 0.0;
            zroots(a2,3,zl,true);
            for k := 1 to 3 do writeln(zl[k].r,' ',zl[k].i);
            writeln(' Input zliq : ');}
readln(mvol.liq);
a1[4].r := Ptrial[c1];
a1[3].r := -R*T;
a1[2].r := a[c1] - b[c1]*(Ptrial[c1]*b[c1] + R*T);
a1[1].r := -a[c1]*b[c1];
a1[4].i := 0.0;
a1[3].i := 0.0;
a1[2].i := 0.0;
a1[1].i := 0.0;
zroots(a1,3,zv,true);
for k := 1 to 3 do writeln(zv[k].r,' ',zv[k].i);
writeln(' Input zvap : ');
readln(mvol.vap);
x[1] := mvol.vap;
x[2] := mvol.liq;
end;

procedure func(Var x: RealArrayNP; n: integer;
label 999;
var
Var alpha: RealArrayNPbyNP; Var beta: RealArrayNP);
{ - beta : functions to be solved }
{ - x : parameters }
{ - alpha : derivatives dbeta[i]/dx[j] for Newton meth. }

label 999;
var
r1,r2,r3,r4 : REAL;
begin
a_coef(c1,c2,x[3],y2,KK,T,Tc,Pc,omega,a,Am,A1,A2,dAmdx1,dA1dx1,dA2dx1);
b_coef(c1,c2,x[3],y2,Tc,Pc,b,Bm,dBmdx1);
r1 := x[1] - Bm.vap;
r2 := x[2] - Bm.liq;
r3 := x[1] + Bm.vap;
r4 := x[2] + Bm.liq;
beta[1] := -R*T/R1;
beta[2] := R*T*ln(abs(R1))/((1-y2)*R*T));
\[
\beta[2] := \beta[2] + \text{Am.vap} \cdot b[c1]/\text{Bm.vap}/R3;
\]
\[
\]
\[
\beta[2] := \beta[2] - (2 \cdot \text{A1.liq} - \text{Am.liq} \cdot b[c1]/\text{Bm.liq}) \cdot \ln(R4/x[2])/\text{Bm.liq};
\]
\[
\beta[2] := \beta[2] - \text{Am.liq} \cdot b[c1]/\text{Bm.liq}/R4;
\]
\[
\beta[2] := \beta[2] - R^*T \cdot \ln(\text{abs}(R2)/\text{abs}(x[3] \cdot R^*T));
\]
\[
\beta[3] := R^*T \cdot \ln(\text{abs}(R1)/(y2 \cdot R^*T));
\]
\[
\]
\[
\beta[3] := \beta[3] + (2 \cdot \text{A2.vap} - \text{Am.vap} \cdot b[c2]/\text{Bm.vap}) \cdot \ln(R3/x[1]) / \text{Bm.vap};
\]
\[
\beta[3] := \beta[3] + \text{Am.vap} \cdot b[c2]/\text{Bm.vap}/R3;
\]
\[
\beta[3] := \beta[3] - R^*T \cdot \ln(\text{abs}(R2)/\text{abs}(1-x[3]) \cdot R^*T));
\]
\[
\]
\[
\beta[3] := \beta[3] - (2 \cdot \text{A2.liq} - \text{Am.liq} \cdot b[c2]/\text{Bm.liq}) \cdot \ln(R4/x[2])/\text{Bm.liq};
\]
\[
\beta[3] := \beta[3] - \text{Am.liq} \cdot b[c2]/\text{Bm.liq}/R4;
\]
\[
\alpha[1,1] := -R^*T / \text{sqr}(R1);
\]
\[
\alpha[1,1] := \alpha[1,1] + \text{Am.vap} \cdot (2 \cdot x[1] + \text{Bm.vap}) / \text{sqr}(x[1] \cdot R3);
\]
\[
\alpha[1,2] := R^*T / \text{sqr}(R2);
\]
\[
\alpha[1,2] := \alpha[1,2] - \text{Am.liq} \cdot (2 \cdot x[2] + \text{Bm.liq}) / \text{sqr}(x[2] \cdot R4);
\]
\[
\alpha[1,3] := -R^*T \cdot \text{dBmdx1}/(r2^*r2);
\]
\[
\alpha[1,3] := \alpha[1,3] + (\text{dAmdx1} \cdot r4 - \text{Am.liq} \cdot \text{dBmdx1}) / (x[2] \cdot r4^*r4);
\]
\[
\alpha[2,1] := -R^*T / \text{R1};
\]
\[
\alpha[2,1] := \alpha[2,1] - b[c1] \cdot R^*T / \text{sqr}(R1);
\]
\[
\alpha[2,1] := \alpha[2,1] + (2 \cdot \text{A1.vap} - \text{Am.vap} \cdot b[c1]/\text{Bm.vap}) / (x[1] \cdot R3);
\]
\[
\alpha[2,1] := \alpha[2,1] + \text{Am.vap} \cdot b[c1]/\text{Bm.vap} / \text{sqr}(R3);
\]
\[
\alpha[2,2] := R^*T / \text{R2};
\]
\[
\alpha[2,2] := \alpha[2,2] + b[c1] \cdot R^*T / \text{sqr}(R2);
\]
\[
\alpha[2,2] := \alpha[2,2] - (2 \cdot \text{A1.liq} - \text{Am.liq} \cdot b[c1]/\text{Bm.liq}) / (x[2] \cdot R4);
\]
\[
\alpha[2,2] := \alpha[2,2] - \text{Am.liq} \cdot b[c1]/\text{Bm.liq} / \text{sqr}(R4);
\]
\[
\alpha[2,3] := -R^*T / x[3] - R^*T \cdot \text{dBmdx1}/r2;
\]
\[
\alpha[2,3] := \alpha[2,3] - R^*T \cdot b[c1] \cdot \text{dBmdx1}/(r2^*r2);
\]
\[
\alpha[2,3] := \alpha[2,3] - \text{dBmdx1} \cdot (2 \cdot \text{A1.liq} - \\
\text{Am.liq} \cdot b[c1]/\text{Bm.liq} \cdot \ln(r4/x[2]) / (\text{Bm.liq} \cdot \text{Bm.liq})/r4^*r4);
\]
\[
\alpha[2,3] := \alpha[2,3] + dAmdx1 \cdot b[c1]/(r4 \cdot \text{Bm.liq});
\]
\[
\alpha[2,3] := \alpha[2,3] - \text{Am.liq} \cdot b[c1] \cdot \text{dBmdx1}^* (r4 + \text{Bm.liq}) / (\text{Bm.liq} \cdot \text{Bm.liq} \cdot r4^*r4);
\]
\[
\alpha[3,1] := -R^*T / \text{R1};
\]
\[
\alpha[3,1] := \alpha[3,1] - b[c2] \cdot R^*T / \text{sqr}(R1);
\]
\[
\alpha[3,1] := \alpha[3,1] + (2 \cdot \text{A2.vap} - \text{Am.vap} \cdot b[c2]/\text{Bm.vap}) / (x[1] \cdot R3);
\]
\[
\begin{align*}
\alpha_{3,1} & := \alpha_{3,1} + Am\cdot \text{vap} \cdot b[c2]/Bm\cdot \text{vap}/\text{sqr}(R3); \\
\alpha_{3,2} & := R\cdot T/R2; \\
\alpha_{3,2} & := \alpha_{3,2} + b[c2]\cdot R\cdot T/\text{sqr}(R2); \\
\alpha_{3,2} & := \alpha_{3,2} - (2\cdot A2\cdot \text{liq} - Am\cdot \text{liq} \cdot b[c2]/Bm\cdot \text{liq})/(x[2]\cdot R4); \\
\alpha_{3,2} & := \alpha_{3,2} - Am\cdot \text{liq} \cdot b[c2]/Bm\cdot \text{liq}/\text{sqr}(R4); \\
\alpha_{3,3} & := R\cdot T/(1-x[3]) - R\cdot T\cdot dBmdx1/r2; \\
\alpha_{3,3} & := \alpha_{3,3} - R\cdot T\cdot b[c2]\cdot dBmdx1/(r2\cdot r2); \\
\alpha_{3,3} & := \alpha_{3,3} - (2\cdot A2\cdot \text{liq} - Am\cdot \text{liq} \cdot b[c2]/Bm\cdot \text{liq}) \cdot ln(r4\cdot xl)/Bm\cdot \text{liq} ; \\
\alpha_{3,3} & := \alpha_{3,3} - Am\cdot \text{liq} \cdot b[c2]/Bm\cdot \text{liq} \cdot ln(r4\cdot xl)/(Bm\cdot \text{liq} \cdot Bm\cdot \text{liq}); \\
\alpha_{3,3} & := \alpha_{3,3} + (2\cdot dA2\cdot dx1 - (dAmdx1\cdot b[c2]/Bm\cdot \text{liq} - Am\cdot \text{liq} \cdot b[c2]/Bm\cdot \text{liq}) \cdot ln(r4\cdot xl)/Bm\cdot \text{liq} ; \\
\alpha_{3,3} & := \alpha_{3,3} + dBmdx1\cdot (2\cdot A2\cdot \text{liq} - Am\cdot \text{liq} \cdot b[c2]/Bm\cdot \text{liq})/(r4\cdot Bm\cdot \text{liq}); \\
\alpha_{3,3} & := \alpha_{3,3} + dBmdx1\cdot (2\cdot A2\cdot \text{liq} - Am\cdot \text{liq} \cdot b[c2]/Bm\cdot \text{liq})/(r4\cdot Bm\cdot \text{liq}); \\
\end{align*}
\]

\[
\begin{align*}
\alpha_{3,3} & := \alpha_{3,3} - Am\cdot \text{liq} \cdot b[c2]/Bm\cdot \text{liq} \cdot ln(r4\cdot xl)/(Bm\cdot \text{liq} \cdot Bm\cdot \text{liq} \cdot r4\cdot r4); \\
\end{align*}
\]

\[
\begin{align*}
\text{procedure newt_3dim(ntrial : integer; Var x : RealArrayNP; n : integer; tolx, tolf : real);} \\
\{ - Newton–Raphson algorithme in 3 dim. – \}
\end{align*}
\]

\[
\begin{align*}
\text{label 99;}
\end{align*}
\]

\[
\begin{align*}
\text{var}
\end{align*}
\]

\[
\begin{align*}
k, i & : \text{integer}; \\
al1, al2, al3, al4, al5, al6, fac & : \text{real}; \\
errx, errf & : \text{real}; \\
beta, dx & : \text{RealArrayNP}; \\
alpha & : \text{RealArrayNPbyNP};
\end{align*}
\]

\[
\begin{align*}
\text{begin}
\end{align*}
\]

\[
\begin{align*}
\text{for k := 1 to ntrial do}
\end{align*}
\]

\[
\begin{align*}
\text{begin}
\end{align*}
\]

\[
\begin{align*}
\text{func(x,n,alpha,beta);}
\end{align*}
\]

\[
\begin{align*}
\text{al1} & := \alpha_{2,2}\cdot \alpha_{3,3} - \alpha_{2,3}\cdot \alpha_{3,2}; \\
\text{al2} & := \alpha_{3,1}\cdot \alpha_{2,2} - \alpha_{3,2}\cdot \alpha_{2,1}; \\
\text{al3} & := \alpha_{2,1}\cdot \alpha_{3,3} - \alpha_{2,3}\cdot \alpha_{3,1}; \\
\text{al4} & := \alpha_{1,3}\cdot \alpha_{3,2} - \alpha_{1,2}\cdot \alpha_{3,3}; \\
\text{al5} & := \alpha_{1,2}\cdot \alpha_{2,3} - \alpha_{1,3}\cdot \alpha_{2,2}; \\
\text{al6} & := \alpha_{2,3}\cdot \alpha_{3,1} - \alpha_{2,1}\cdot \alpha_{3,3}; \\
\text{fac} & := \text{al1}/(\text{al1}\cdot \alpha_{1,1} - \text{al2}\cdot \alpha_{1,3} - \text{al3}\cdot \alpha_{1,2}); \\
\text{errf} & := 0.0;
\end{align*}
\]
for i := 1 to n do errf := errf + abs(beta[i]);
if errf <= tolf then goto 99;


for i := 1 to n do
begin
  errx := errx + abs(dx[i]);
  x[i] := x[i] + dx[i]
end;

if errx <= tolx then goto 99;

procedure controle(Var x: RealArrayNP; Var P,Mu1,Mu2 : phase;Var dP,dMu1,dMu2 : real);
{
- calculates Pvap, Pliq, Muvap, Muliq from solution-
- and gives the relative differences  
}
var
r1,r2,r3,r4 : real;

begin
  a_coef(c1,c2,z[3],y2,KK,T,Tc,Pc,omega,a,Am,A1,A2,dAmdxl,dAldxl,dA2dxl);
  b_coef(cl,c2,z[3],y2,Tc,Pc,b,Bm,dBmdxl);
  r1 := x[1] - Bm.vap;
  r2 := x[2] - Bm.liq;
  r3 := x[1] + Bm.vap;
  r4 := x[2] + Bm.liq;

  P.vap := R*T/(x[1]-Bm.vap) - Am.vap/(x[1]*(x[1]+Bm.vap));
  P.liq := R*T/(x[2]-Bm.liq) - Am.liq/(x[2]*(x[2]+Bm.liq));
  Mul.vap := -R*T*ln(abs(r1))/((1-y2)*R*T); 
  Mul.vap + b(cl]*R*T/r1;
  Mul.vap := Mul.vap - (2*Am.vap - Am.vap*b[c1]/Bm.vap)*ln(r3/x[1])/Bm.vap;
  Mul.vap := Mul.vap - Am.vap*b[c1]/Bm.vap/r3;
  Mul.liq := -R*T*ln(abs(r2)/(x[3]r*T));
  Mul.liq := Mul.liq + b[c1]*R*T/r2;
  Mul.liq := Mul.liq - (2*Am.liq - Am.liq*b[c1]/Bm.liq)*ln(r4/x[2])/Bm.liq;

end;
\[ \text{Mu1.liq} := \text{Mu1.liq} - \text{Am.liq} * b[c1] / Bm.liq / r4; \]
\[ \text{Mu2.vap} := -R^*T^* \ln(\text{abs}(r1) / (y2^*R^*T)); \]
\[ \text{Mu2.vap} := \text{Mu2.vap} + b[c2]^*R^*T / r1; \]
\[ \text{Mu2.vap} := \text{Mu2.vap} - (2^*A2.vap - \text{Am.vap} * b[c2] / Bm.vap) * \ln(r3 / x[1]) / Bm.vap; \]
\[ \text{Mu2.vap} := \text{Mu2.vap} - \text{Am.vap} * b[c2] / Bm.vap / r3; \]
\[ \text{Mu2.liq} := -R^*T^* \ln(\text{abs}(r2) / ((1 - x[3])^*R^*T)); \]
\[ \text{Mu2.liq} := \text{Mu2.liq} + b[c2]^*R^*T / r2; \]
\[ \text{Mu2.liq} := \text{Mu2.liq} - (2^*A2.liq - \text{Am.liq} * b[c2] / Bm.liq) * \ln(r4 / x[2]) / Bm.liq; \]
\[ \text{Mu2.liq} := \text{Mu2.liq} - \text{Am.liq} * b[c2] / Bm.liq / r4; \]
\[ \text{dP} := (\text{P.vap} - \text{P.liq}) / 2 / (\text{P.vap} + \text{P.liq}); \]
\[ \text{dMu1} := (\text{Mu1.vap} - \text{Mu1.liq}) / 2 / (\text{Mu1.vap} + \text{Mu1.liq}); \]
\[ \text{dMu2} := (\text{Mu2.vap} - \text{Mu2.liq}) / 2 / (\text{Mu2.vap} + \text{Mu2.liq}) \]

```plaintext
{ ************ MAIN PROGRAM ************ }
```

```plaintext
begin

{ critical values + acent. factors }
{ see [REI 87] }

{*** methane ***}
Tc[1] := 190.4;  \{ K \}
Pc[1] := 46.0e5;  \{ Pa \}
omega[1] := 0.011;

{*** ethane ***}
Tc[2] := 305.4;
Pc[2] := 48.8e5;
omega[2] := 0.099;

{*** propane ***}
Tc[3] := 369.8;
Pc[3] := 42.5e5;
omega[3] := 0.153;

{*** butane ***}
Tc[4] := 425.2;
Pc[4] := 38.0e5;
```
omega[4] := 0.199;

{*** pentane ***}
Tc[5] := 469.7;
Pc[5] := 33.75e5;
omega[5] := 0.251;

{*** hexane ***}
Tc[6] := 507.5;
Pc[6] := 30.1e5;
omega[6] := 0.299;

{*** heptane ***}
Tc[7] := 540.3;
Pc[7] := 27.4e5;
omega[7] := 0.349;

{*** octane ***}
Tc[8] := 568.8;
Pc[8] := 24.9e5;
omega[8] := 0.398;

{*** nonane ***}
Tc[9] := 594.6;
Pc[9] := 22.9e5;
omega[9] := 0.445;

{*** Decane ***}
Tc[10] := 617.7;
Pc[10] := 21.2e5;
omega[10] := 0.489;

{*** undecane ***}
Tc[11] := 638.8;

{*** dodecane ***}
Tc[12] := 658.2;
\[
\begin{align*}
P_{c[12]} &= 18.2e5; \\
\omega_{c[12]} &= 0.575; \\

\{*** \text{nitrogen} ***\}
T_{c[13]} &= 126.2; \\
P_{c[13]} &= 33.9e5; \\
\omega_{c[13]} &= 0.039; \\

\{*** \text{argon} ***\}
T_{c[14]} &= 150.8; \\
P_{c[14]} &= 48.7e5; \\
\omega_{c[14]} &= 0.001; \\

\{*** \text{carbon dioxide} ***\}
T_{c[15]} &= 304.1; \\
P_{c[15]} &= 73.843e5; \\
\omega_{c[15]} &= 0.239;
\end{align*}
\]

\begin{verbatim}
write(' number output file (7 characters max) :');
readln(num);
Ofile1 := 'c:\result\' + num + '1.prn';
Ofile2 := 'c:\result\' + num + '2.prn';
assign(outfile1,Ofile1);
assign(outfile2,Ofile2);
rewrite(outfile1);
rewrite(outfile2);
close(outfile1);
close(outfile2);
write(' T = '); readln(T);
write(' y2 = '); readln(y2);
write(' <K> = '); readln(KK);
write(' Tstep = '); readln(Tstep);
write(' Nstep = '); readln(Nstep);
write(' Nstep2 = '); readln(Nstep2);
\end{verbatim}
readln(Nstep2);
write(' x1 = ');
readln(x1);
z[3] := x1;

{ Input the 2 components }
write('  input C-number first component (N2=13, Ar=14, CO2=15) :');
readln(cl);
writeln;
write('  input C-number second component
readln( c2);
a_coef(cl,c2,xl,y2,KK,TK,Tc,Pc,omega,a,Am,A1,A2,dAm,dx1,dA1,dx1,dA2,dx1);
b_coef(cl,c2,xl,y2,Tc,Pc,b,Bm,dBm,dx1);
init_vap_press_liq(c2,T,Tc,Pc,omega,Ptrial);
init_root(2,Ptrial,z);
P.vap := 1;
j := 1;
while (j <= Nstep) and (P.vap > 0) do begin
  newt_3dim(100,z,3,1e-11,1e-14);
  controle(z,P,Mu1,Mu2,dP,dMu1,dMu2);
  if j/Nstep2 = round(j/Nstep2) then begin
    writeln('  T = ',T);
    writeln('  Vapour : ',z[1]);
    writeln('  Liquid : ',z[2]);
    writeln('  x1 : ',z[3]);
    writeln('Pvap = ',P.vap:18,'  Pliq = ',P.liq:18);
    writeln('MU1vap= ',Mu1.vap:18,'  MU1liq= ',Mu1.liq:18);
    writeln('Mu2vap= ',Mu2.vap:18,'  Mu2liq= ',Mu2.liq:18);
    writeln('dP= ',dP,'  dMu1= ',dMu1,'  dMu2= ',dMu2);
    append(outfile1);
    append(outfile2);
    writeln(outfile1,T,(P.vap+P.liq)/2e+5);
    writeln(outfile2,T,z[1],z[2],z[3]);
    close(outfile1);
    close(outfile2);
  end;
  T := T + Tstep;
j := j + 1
end;
end.
Appendix B

Determination of the scattering angles

In figure B.1, one of the two identical optical systems is schematically represented. Only the light scattered in a solid angle between the angles $\theta_1$ and $\theta_2$ from the interaction domains is detected. Both angles are determined in the following (rough) way:

\[
d_i = (I + L) \tan(\alpha_i), \quad i=1,2
\]  

(B.1)

further

\[
\tan(\alpha_i) = \frac{s_i}{I},
\]  

(B.2)

so that

\[
d_i = \frac{I + L}{I} s_i.
\]  

(B.3)

Hence

\[
\theta_i = \arctan\left(\frac{d_i}{O_i}\right) = \arctan\left[\frac{(I + L)s_i}{O_i L}\right]
\]  

(B.4)

The object distances $O$ have been determined at half height of the interaction domain (about 1.4 cm, figure 4.8).

**Forward system:**

- $s_1 = 0.975$ cm
- $s_2 = 1.075$ cm
- $O_1 = 26.5$ cm
- $O_2 = 25.1$ cm
- $I = 12.5$ cm
- $L = 9.9$ cm

so that $\theta_1 = 0.0658$ rad $\approx 3.8^\circ$ and $\theta_2 = 0.0766 \approx 4.4^\circ$

![Fig. B.1: optical system](image-url)
Backward system:  
\[ s_1 = 0.975 \text{ cm} \]
\[ s_2 = 1.075 \text{ cm} \]
\[ O_1 = 26.9 \text{ cm} \]
\[ O_2 = 25.5 \text{ cm} \]
\[ I = 12.6 \text{ cm} \]
\[ L = 9.2 \text{ cm} \]

so that \[ \theta_1 = 0.0626 \text{ rad} \approx 3.6^\circ \] and \[ \theta_2 = 0.0728 \approx 4.2^\circ \]
Appendix C

C.1 Model parameters of Dillmann–Meier model

**n-nonane:** \( \tau = 2.190 \)

\[ q_0 = 39.97 \text{ m}^{-3} \]

**n-decane:** \( \tau = 2.184 \)

\[ q_0 = 39.17 \text{ m}^{-3} \]

and \( \kappa(i) \) is determined from (3.31) with

\[ \alpha_1 = \frac{(\kappa_2 - 1) - (\kappa_1 - 1) \cdot 2^{-\frac{2}{3}}}{2^{-\frac{4}{3}} - 2^{-\frac{2}{3}}} \]

and

\[ \alpha_2 = -\frac{(\kappa_2 - 1) - (\kappa_1 - 1) \cdot 2^{-\frac{1}{3}}}{2^{-\frac{4}{3}} - 2^{-\frac{2}{3}}} \]

with

\[ \kappa_1 = -\frac{1}{2^\frac{2}{3}} \ln \left[ \frac{p_s}{q_0 k T} \right] \]

and

\[ \kappa_2 = -\frac{1}{2^\frac{2}{3}} \ln \left[ \left[ \frac{p_s}{q_0 k T} \right] 2^{-1} q_0 B \right] \]

where \( p_s \) represents the saturation pressure, \( B \) the second virial coefficient and \( \Xi = \frac{\sigma_{s,0}}{k T} \).

The physico-chemical properties of the substances are:

**n-nonane:**

\[ \ln(p_s) = -17.56832 \ln(T) + 1.52556 \cdot 10^{-2} T - 9467.4/T + 128.77889 \text{ [Torr]} \] [HUN 90]

\[ \sigma = (24.72 - 0.09347(T - 273.15))/1000 \text{ [N/m]} \] [JAS 72]

\[ B = 0.00216086 \left( 0.1728147 - 0.33/T_r + 0.0086295/T_r^2 - 0.204124/T_r^3 - 0.004163/T_r^4 \right) \text{ [m}^3\text{/mol]} \] [TSO 74]

**n-decane:**

\[ p_s = p_c \exp(f^0 + \omega f^l) \text{ [Pa]} \] [REI 87]

with

\[ f^0 = 5.92714 - 6.09648 T_r - 1.28862 \ln(T_r) + 0.169347 T_r^6 \]

and
\[ f^i = 15.2518 - 15.6875 \, T_r - 13.4721 \ln(T_r) + 0.43577 \, T_r^6 \]

\[ \sigma = \frac{(25.67 - 0.09197 \, (T - 273.15))/1000 \, [\text{N/m}]}{[\text{JAS 72}]} \]

\[ B = 0.00242255 \, (0.175649 - 0.33/T_r + 0.0233359/T_r^2 \]
\[ - 0.218947/T_r^3 - 0.004519/T_r^6 \, [\text{m}^3/\text{mol}] \, [\text{TSO 74}] \]

\[ T_r = T/T_c, \text{ all the critical values have been taken from Reid [REI 87]}. \]

C.2 Determination of the nucleation rates

The minimal observable nucleation rate is roughly determined from the forward scattered light. The principle is the following. First, the minimal power needed to detect a scattered light is determined with the properties of the photomultiplier used. Then, the number of particles necessary to produce this power in the considered solid angle is determined. The nucleation rate is then obtained by dividing this number of particles by the expansion time and by the volume of the interaction domain.

The photomultiplier used for the detection is schematically represented in figure C.1. It is constituted of a cathode, eleven dinodes and an anode. The high voltage \( V \) (about 650 V) permits to the electrons excited by the photons to flow towards the anode. The photomultiplier is then a current source. The current flows through the resistance \( R_b \) where the voltage is measured.

The radiant sensitivity of the cathode is by definition:

\[ E(\lambda) = \frac{I_k}{P} \]

\[ \text{(C.5)} \]

\[ \text{Fig. C.1: Schematic representation of the photomultiplier EMI–9558B.} \]
where $P$ is the radiant power and $I_k$ is cathode current defined as

$$I_k = \frac{P\lambda}{hc} \eta(\lambda) e$$  \hspace{1cm} (C.6)

where $h$ is the constant of Planck, $c$ the velocity of light, $e$ the electron charge and $\eta(\lambda)$ the quantum efficiency of the photocathode at a wavelength of $\lambda$. Substitution of (C.6) in (C.5) yields:

$$E(\lambda) = \frac{\lambda\eta(\lambda)e}{hc} = \frac{\lambda\eta(\lambda)}{1.24} \text{ [mA W}^{-1}]$$  \hspace{1cm} (C.7)

In figure C.2, the quantum efficiency is plotted against the wavelength of the light for different types of photocathodes. For our system (Extended S–20) and $\lambda = 632$ nm, $\eta \approx 7\%$ so that $E(\lambda) \approx 35.7 \text{ mA/W}$.

The electron current is amplified by the dinodes with a factor $G$. For our system (11 dinodes) and $V = 650$ V it is $G \approx 7 \times 10^4$ (see figure C.3). The current through the anode is then:

$$I_a = G*E(\lambda) \approx 2.5 \times 10^3 \text{ A/W}$$  \hspace{1cm} (C.8)

A voltage higher than $V_{\text{min}} = 0.5$ mV is significant, so that the minimal current over the resistance $R_b = 10$ kΩ must be

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig_c_2.png}
\caption{Typical spectral response curves for EMI photocathodes.}
\end{figure}
Fig. C.3: Gain versus overall voltage for multipliers with various numbers of stages.

\[ I_{\text{min}} = V_{\text{min}}/R_b \simeq 5 \times 10^{-8} \text{A} \quad (C.9) \]

which correspond with a power of

\[ P_s^{\text{min}} = I_{\text{min}}/I_a \simeq 2 \times 10^{-11} \text{W} \quad (C.10) \]

The power scattered by a particle in the solid angle between 3.8 and 4.4°, assuming an average droplet radius of 0.1 μm, has been calculated with formula (4.7):

\[ P_s \simeq 1 \times 10^{-15} \text{W} \]

The minimum number of particles present in the interaction domain must then be:

\[ N = \frac{P_s^{\text{min}}}{P_s} \simeq 2000 \quad (C.11) \]

The expansion time is about \( t = 0.04 \text{ s} \). The length of the interaction domain is about 1.5 cm at half height and the laser surface has been measured to 0.45 mm. Therefore the volume of the interaction domain is

\[ V = \pi (0.45 \times 10^{-3})^2 \times 1.5 \times 10^{-2} \simeq 9.54 \times 10^{-9} \text{m}^3 \]

The minimum nucleation rate is then

\[ I_{\text{min}} \simeq \frac{N}{tV} \simeq 5 \times 10^{12} \text{m}^{-2} \text{s}^{-1} \quad (C.12) \]
The maximum possible nucleation rate is estimated by assuming that all the vapor is condensed. Assuming a droplet size of 0.1 \( \mu \text{m} \) and a total number of vapor molecules of 0.5 \( \times 10^{20} \) (2.5 torr), it follows that the maximum nucleation rate is in the order of \( 2 \times 10^{17} \text{ m}^{-3}\text{s}^{-1} \).