RETENTION OF VOLATILES DURING THE AIR DRYING
OF AQUEOUS CARBOHYDRATE SOLUTIONS

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PROF. DR. IR. H. A. C. THIJSSEN
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Chapter 1

INTRODUCTION

Drying is one of the oldest and most important food preservation methods. The quality of many dried products after rehydration, however, is inferior to that of the fresh products. One of the principal causes of this is the loss of flavour components. This loss is due both to chemical reactions and to the removal of volatile substances together with the water vapour. This escape of volatile substances, which is a purely physical process, is studied more closely in this investigation.

The loss of volatile components during the concentration by evaporation of aqueous solutions with a low dry matter content (e.g. fruit juices, which usually have a dry matter content of 6 to 20 % w/w) is mainly determined by their volatility, \( \alpha_{vw} \), relative to water. This is given by:

\[
\alpha_{vw} = \frac{C_{v,w}}{C_{v,0}} \frac{C_{0,0}}{C_{0,w}}
\]

(1)

in which \( C_v \) is the equilibrium concentration (kg/m\(^3\)) of the component in the vapour phase and \( C_0 \) is the concentration of the component in the liquid. The subscripts \( v \) and \( w \) refer respectively to the aroma component in question and water. If no concentration gradients are present in the liquid, and if the vapour is in equilibrium with this liquid phase and is continuously removed, the following can be derived for the retention of an aroma component:

\[
\frac{M_{0,w}}{M_{0,v}} = \left( \frac{M_{0,v}}{M_{0,v}} \right)^{\alpha_{vw}}
\]

(2)

in which \( M_0 \) and \( M_w \) are respectively the weight of the aroma component and of water present in the solution. The subscripts \( v \) and \( w \) refer respectively to the beginning and the end of evaporation. The value of \( \alpha_{vw} \) for the odour components of fruit juices varies from 0.1 to more than 100, its value for most of the important odour components being between 5 and 50 \(^1\). Even if the boiling point of a flavour component is appreciably higher than 100 °C, \( \alpha_{vw} \) can still have a value of 10-100 if the activity coefficient of the component in question is high at low concentrations. Such high \( \alpha_{vw} \) values should according to equation (2) result in extremely low aroma retention. For aceton in pure water, for example, the value of \( \alpha_{vw} \) for very low concentrations (in the ppm range) is about 70 at 21.5 °C. This means that if only 10 % of the water has evaporated, then almost no aceton (0.06 % of the amount initially present) is left in solution.

With spray drying, which is a technologically very important drying technique, the retention of volatile substances is found to depend strongly on the dry matter content of the juice or extract to be dried \(^2\). The higher the dry matter content, the higher the retention is, up to a certain dry matter content above which the retention does not increase much more. This value is 40-45 % dry matter for coffee extract \(^3\). Thijssen \(^3\) has measured the retention of certain volatiles after the spray drying of coffee extract as a function of the initial dry matter content. The results are plotted in Fig. 1. Likewise with freeze-drying it has been established that the retention of volatile components increases as the

\(^5\) Unless otherwise stated, percentages in this thesis are expressed as percentages by weight.
Figure 1
Retention of volatiles after spray drying of coffee extract as a function of initial dry matter content, measured by Thijssen. 

Figure 2
Acetone retention after freeze-drying, as measured by Rey. (Glucose varied from 50 to 250 g; glycine 100 g; acetone 1.55 g; Earle's balanced salt solution to 1000 mL.)
Dry matter content increases. Rey \(^3\) freeze-dried a salt solution containing 100 g/l glycerine and a little acetone as a model aroma component. The dry matter content was varied by the addition of glucose. The acetone retention measured by Rey is plotted against the initial dry matter content of the solution in Fig. 2. The resemblance between Figs. 1 and 2 is surprising. For both techniques it appears that, after drying a solution with a high initial dry matter content, the loss of odour components is only slight compared with the loss of water. Coffee extract, for instance, can be prepared with a dry matter content of 30%, so that after being dried under optimal conditions it can still contain about 50% of the volatile components \(^8\).

The explanation of this high retention at high initial dry matter contents is the subject of this investigation. According to equation (2), the retention should be lower than 0.01%. From this it can be concluded that, in both processes, the loss of volatile components is not only determined by their volatility relative to water, but that the transport of these components in the liquid also plays a role. Rey \(^3\) considers that the acetone retention after freeze-drying is due to sorption in the already dried outer layer as the mixture of water vapour and acetone passes through it. This explanation could also be applied to spray drying. During drying a concentration gradient is formed in the droplet and the concentration of water at the surface of the droplet can fall to only a few per cent soon after the start of the drying process if the temperature of the drying air is high. The droplet is then surrounded by an almost dry layer \(^7\). As the water and acetone diffuse through this layer, the acetone could be sorbed. Thijssen \(^3\), however, demonstrated that this sorption theory did not hold for coffee extract, since no acetone was sorbed by the dry extract, nor were any of a series of other volatile components. Thijssen showed further that the surprisingly high retention of volatile substances which can occur with spray drying was due to the fact that the diffusion coefficients of aroma components decrease much more sharply than the diffusion coefficient of water with decreasing moisture content of the juice or extract. The diffusion coefficient of acetone, for example, in coffee extract with a moisture content of 5%, was 10\(^3\) times lower than that of water in the same medium. Consequently the dry outer layer, which forms when the droplet is dried very quickly, behaves as a selective membrane, which is permeable to water but practically impermeable to odour components. The acetone retention of a dried droplet of coffee extract could be calculated with the aid of experimentally determined diffusion coefficients. For an extract with an initial dry matter content of 50% and a droplet of 50 microns diameter dried in dry air of 170 °C, the acetone retention turned out to be 98%, assuming no internal circulation.

In this investigation measurements are made with an aqueous solution of partially hydrolysed starch (malto-dextrin) which serves as a model for a juice or extract. A small amount of acetone is added to this malto-dextrin solution as a model odour component. The concentration of the acetone is kept sufficiently low so as not to influence the mass transport in the solution. This condition is in accordance with the practical case of juices and extracts. The investigation is primarily restricted to drying in air. This is mainly because the mass transfer during freeze-drying is much more complicated since it depends not only on the method of drying but also on the method of freezing. To begin with, a number of measurements with the above-mentioned solution are dis-
discussed in Chapter II and III. These include measurement of the acetone retention of droplets and slabs dried in an air stream. From measurements of sorption and other experiments, it appears that the volatile retention cannot be attributed to sorption and that the behaviour must very probably be explained in terms of concentration-dependent diffusion coefficients. In Chapter IV, the influence of the moisture content on the diffusion coefficients of acetone and water is studied in detail with the model system malto-dextrin/water. The acetone content in a drying slab is calculated in Chapter V on the assumption that mass transport takes place exclusively by Fickian diffusion. The calculated values for the acetone retention are in good agreement with experimentally determined values. This corroborates Thiessen's theory about volatile retention. Finally, in Chapter VI, the influence of the most important factors on this retention are discussed and explained more fully.
Chapter II

MEASUREMENT OF ACETONE RETENTION DURING THE DRYING OF AQUEOUS MALTO-DEXTRIN SOLUTION

1. Introduction

The primary aim of the measurements with droplets described in this chapter was to find out whether the retention of volatiles by a malto-dextrin solution during drying proceeds in a manner analogous to that described in the literature for juices and extracts. Furthermore it was the intention to find out more about the influence of the drying conditions on the retention of volatiles. The principal aim of this thesis, however, is to check whether the retention of volatiles can be calculated by solving the differential equations for diffusion. If this proves to be the case, then the volatile retention for different drying processes can be predicted. The above mentioned measurements with droplets are not wholly suitable for testing the mechanism causing retention of volatiles. An accurate calculation of the acetone retention for such droplets is difficult on account of the high loss of acetone which can take place during the formation of a droplet. The loss of a volatile component during this formation period usually amounts to 10-50% [12]. A further complication with droplets lies in the fact that the partial mass transfer coefficient in the gas phase varies over the surface of the droplet [12]. Other difficulties concern the shape of the droplet, which deviated from spherical in these experiments, and the internal circulation which can arise in the droplet during drying. It was therefore decided to carry out some measurements with gelled slabs. These measurements, which were especially designed as a basis of comparison for numerical calculations, are discussed in section 3 of this chapter. Gelation of the malto-dextrin solution was achieved by the addition of a little agar-agar, the object of gelation being both to provide a self-supporting layer and to prevent transport by convection. The slab was made long enough to ensure that the partial mass transfer coefficient across the surface at the last downwind part of the slab was almost constant. Only this part was used for the measurements. The temperature of the slab was kept nearly constant during the drying to avoid complications due to the temperature dependence of diffusion coefficients. The acetone was radioactively labelled, and the acetone content of the dried droplets or slab sections was determined by measuring their radioactivity.

2. Drying of a droplet

2.1 Experimental techniques

A diagram of the drying apparatus used is given in Fig. 3. During drying, not only the acetone content but also the weight and temperature of the droplets were measured. As this could not be done simultaneously on a single droplet, the three sets of measurements were made on different individual droplets dried under identical conditions. Fig. 4 shows the arrangement for measuring the temperature with a chromel-alumel thermocouple (diameter 25 micron). The hot junction was placed in the initial centre of the droplet formed. Droplets of 6 mm³ were dosed with a micrometer syringe and suspended from a nylon thread (diameter 0.3 mm) held in a small frame. The frame was then placed in the drying air. The air temperature was controlled by varying the current in the electric heater. The air temperature was measured
Figure 3
Diagram of the apparatus used for the drying of droplets.

Figure 4
Measurement of the droplet temperature.
continuously with a thermocouple located 6 cm under the droplet. By varying the fraction of the air which passed through a silicagel dryer, its relative humidity was kept constant, except for the higher relative humidities used for the measurements plotted in Fig. 9, which were regulated by injecting some steam into the air stream. To measure the wet bulb temperature, the frame with the droplet was replaced by a frame with a thermocouple wrapped in wetted cotton cloth. In addition, a continuously wetted thermocouple was placed in the air circuit throughout the experiments. This was quite a distance from the droplet and therefore served only as a check on the relative humidity during the drying stage. The air velocity was measured with a rotameter, which had been calibrated against a pitot tube.

The malto-dextrin used for all experiments described in this thesis was of Type T ex Messrs. Scholten, Foxhol, the Netherlands. According to the manufacturer its composition is:

<table>
<thead>
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<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>2.5</td>
</tr>
<tr>
<td>Maltose</td>
<td>27.0</td>
</tr>
<tr>
<td>Oligosaccharides greater than maltose</td>
<td>6.5</td>
</tr>
<tr>
<td>Non-reducing malto-dextrins</td>
<td>59.5</td>
</tr>
<tr>
<td>Minerals</td>
<td>0.5</td>
</tr>
<tr>
<td>Moisture</td>
<td>4.0</td>
</tr>
</tbody>
</table>

To an aqueous solution of this malto-dextrin, 10 ppm 1,3-14C-acetone was added. The acetone had a specific activity of 336 μC/mg (19.5 nC/mM) and was obtained from the Radiochemical Centre, Amersham, England. The acetone content of the droplet was determined by measuring the radioactivity with a liquid scintillation counter (Packard, Tri-Carb). Reproducible measurements with a constant counting efficiency were obtained by always dissolving the droplets in the same way in the counting vials in 1 ml water. Subsequently, 10 ml of a scintillator solution was added, comprising 12 g 2,5-diphenyloxazole, 600 mg 1,4-bis-2-(4-methyl-5-phenyloxazolyl)-benzene and 60 g naphthalene in 1.2 litre dioxanecellosolve (5:1). It was demonstrated that the flocculation of insoluble malto-dextrin did not affect the counting efficiency.

The acetone concentration of the droplet during drying was measured as a function of time. Because a droplet can only be used once for this purpose, each measurement was made on a different droplet. The droplet weight was also measured as a function of time. This was done by weighing the frame together with the droplets under a glass cover. It was necessary to weigh 18 droplets simultaneously in order to achieve the desired accuracy. These 18 droplets were suspended from three nylon threads fixed to a single frame. From the observed changes in acetone concentration and droplet weight, one can derive the relationship between the acetone and moisture contents during the drying of the droplet. Unless otherwise mentioned, the air velocity was 2.8 m/s in an upward direction and the relative humidity was about 10%. The air temperature was 35 °C in most experiments.

2.2 Results

Loss of acetone during drying

The acetone content of a drying droplet of malto-dextrin solution is shown
Figure 5
Acetone content of a drying droplet as a function of its dry matter content.

as a function of the dry matter content in Fig. 5. The curve shows that during the initial drying phase (up to point A) the acetone escapes very rapidly. During this drying phase it was found that the droplet temperature remained virtually constant. We shall call this drying phase Period I. After this period the rate at which the acetone escapes decreases rapidly until, from a certain moment onwards (point B), hardly any further acetone is lost. We shall call the phase from point B onwards Period II. In droplets which are moving relative to the surrounding air, internal currents (toroidal circulation) can be set up\textsuperscript{13, 14}. This internal circulation is due to tangential stresses at the surface caused by the drying air. By putting a little chalk powder in the droplet this movement could be accurately followed with a magnifying glass. The movement first stopped in the forward flow region of the droplet; obviously a thin membrane was beginning to form there. This instant coincides with the moment at which the droplet temperature begins to rise (see the 100 g/l curve in Fig. 6). When Period II begins all internal movement has ceased and the droplet is surrounded by a thin membrane. If a hole is pricked in this membrane, liquid pours out through this hole. The time between Period I and II we shall call the transition period. The precise location of points A and B has been deduced from the temperature measurements and from variations in the movements within the droplet. These points are indicated in Figs. 5 and 6. When droplets of a concentration as high as 400-450 g/l maltose-dextrin were dried, it was found that, at the drying rate used, the "stirring" in the droplet no longer occurred. This indicated that for such droplets there is no Period I and no distinct transition period. Apparently the membrane starts to form immediately all around the droplet. This is in agreement with the set of temperature curves of Fig. 6, from which it can be seen that the curves for 400 and 450 g/l have no horizontal
Figure 6
Temperature-time relationship for drying droplets of malto-dextrin solutions of different initial concentrations. (For clarity, the different curves have been displaced vertically with respect to each other.)

Figure 7
Acetone retention of a dried droplet as a function of the initial malto-dextrin concentration. (Malto-dextrin varied from 100 to 500 g; distilled water to 1000 mL.)
part or kink. Fig. 7 gives the acetone retention after drying as a function of the initial maltodextrin concentration. The higher the maltodextrin concentration, the better the retention. Fig. 8 shows that the acetone retention can also depend on the viscosity of the liquid. The viscosity of a 100 g/l maltodextrin solution is increased 10-fold by the addition of 0.1% carboxymethyl cellulose. For this solution the acetone retention was found to be about three times higher than for the corresponding solution without carboxymethyl cellulose.

![Graph](image)

Figure 8
Acetone content of a drying droplet plotted against time for two solutions with different viscosities.

In the above-mentioned experiments the acetone concentration of the solution in the syringe before droplet formation is taken as the initial concentration, i.e. 100%. The highest retention measured was about 80% (see Fig. 7). The acetone loss, however, is not only caused by the drying but a considerable amount of acetone inevitably escapes during the formation of the droplet, during the placing of it in the drying air and during the dissolution of the dried droplet. For this reason we have taken the initial value of the acetone content to be that of a droplet which was not dried, but was otherwise treated in exactly the same way as the dried droplets. As a result of this correction, the acetone retention after drying a droplet of a 340 g/l maltodextrin solution is increased to (97.5 ± 1)%.

The same acetone retention was also found for droplets of a 500 g/l solution. The results given in Table 1 have been obtained in the same way. This table compares the acetone retention of dried droplets of various solutions. In order to test whether other volatile substances would behave similarly, experiments were also carried out with $^{14}$C-benzene, $^{14}$C-ethanol and $^{14}$C-ethyl acetate. Dried droplets of a 500 g/l maltodextrin solution to which 10 ppm of one of these three substances had been added were again
TABLE 1
Acetone retention of some aqueous solutions

<table>
<thead>
<tr>
<th></th>
<th>Initial concentration (%)</th>
<th>Acetone retained in dried droplet (%) (“Corrected values”)</th>
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<tbody>
<tr>
<td></td>
<td>27</td>
<td>83</td>
</tr>
<tr>
<td>Malto-dextrin</td>
<td>27</td>
<td>91</td>
</tr>
<tr>
<td>Dextrin</td>
<td>27</td>
<td>43</td>
</tr>
<tr>
<td>Maltose</td>
<td>27</td>
<td>35</td>
</tr>
<tr>
<td>Saccharose</td>
<td>27</td>
<td>98</td>
</tr>
<tr>
<td>Gum arabic</td>
<td>27</td>
<td>98</td>
</tr>
<tr>
<td>Pectin</td>
<td>5</td>
<td>ca. 28</td>
</tr>
<tr>
<td>Agar-agar</td>
<td>2</td>
<td>ca. 2</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>saturated</td>
<td>ca. 2.5</td>
</tr>
</tbody>
</table>

found, in each case, to have retained (97.5 ± 1)% of the volatile. As benzene, ethanol and ethyl acetate, in contrast to acetone, were found to be strongly absorbed by nylon, a copper wire (diameter 0.5 mm) was used to suspend the droplets. As far as could be detected, the initial acetone concentration had no influence on the percentage acetone retention in the range 10 ppm to 1% acetone.

With regard to the above mentioned correction method, it should be stressed that the initial acetone concentration is not uniform. When drying starts, the outermost layer is already almost acetone-free. In the hypothetic case of a uniform concentration of acetone in the droplet at the onset of drying, the acetone retention can be considerably lower than the “corrected” values reported above, especially in the case of high retention. In the following section, the acetone content of the solution in the syringe is again taken as the initial acetone content.

Influence of the drying conditions
The amount of acetone retained in droplets dried at various humidities of the drying air is plotted in Fig. 9. It is clear that under these experimental conditions acetone is only retained when very dry air is used. Fig. 10 shows the final amount of acetone in a dried droplet as a function of the air velocity during the drying. It was found that at a drying air velocity above about 6.7 m/s, the droplet migrates from its hanging position to the top of the thread. This results in additional stirring in the droplet. Moreover, when the droplet is blown onto the top of the thread, the place where the skin is normally
Figure 9
Acetone retention of droplets dried at various relative humidities.

Figure 10
Acetone retention of droplets dried at different air velocities.
formed last, is no longer protected by the nylon thread. All this explains the sharp decline in retention at air velocities just in excess of 6.7 m/s, as shown in Fig. 10. This air velocity is equal to the rate of free fall of the droplet [5]. The influence of the air temperature on acetone retention is indicated in Fig. 11.

![Figure 11](image)

Acetone retention of droplets dried at different air temperatures.

Up to 100 °C the acetone retention improves as the drying air becomes hotter. Above 100 °C the droplets burst. The retention was then, on average, somewhat lower than at temperatures just below 100 °C, but the retention values at such temperatures were no longer reproducible.

3. Drying of a slab
3.1 Experimental techniques

The slab was made by pouring a warm solution into a Teflon frame held between two glass plates. These plates were removed after the slab had gelled. For initial moisture contents above 55 %, the amount of agar-agar added to the solution was 1 % of the water content. At lower initial moisture contents the amount added was 2.5 % of the maltos-dextrin. Acetone concentration of the solution was 1.00 kg/m³ (0.096 % for a 100 g/l solution), of which 0.15 % was radioactively labelled. The dimensions of the slab were 11.0 × 3.3 × 0.41 cm³. This slab was placed in a horizontal tube and drying air was blown both over and under it with a velocity of (3 ± 0.5) m/s. The air was adjusted to the desired relative humidity by recirculating over dishes containing a drying agent or a saturated salt solution and placed in a climate chamber (see Fig. 12). The variations of the relative humidity near the slab during drying were about ± 4 % absolute, including variations due to possible temperature dependence of the equilibrium relative humidity of the salt solution in the climate chamber. The air temperature was controlled in such a way that the temperature of the slab during drying remained constant at (21.5 ± 1) °C. This was achieved by electric air heaters in the climate chamber, which were connected via a Honeywell Servotronics regulator to a thermocouple in the slab. This thermocouple was positioned in the middle of that part of the slab from which samples were taken. In all cases "slab temperature" means the temperature which was indicated by this thermocouple. The samples were taken at intervals during
Figure 12
Diagram of the apparatus used for the drying of slabs.

Drying from the last (relative to the direction of the air flow) 4 cm of the slab. This was done with a hollow metal cylinder (diameter 2.1 mm) sharpened at one end, which was "screwed" into the slab. The small samples cut out were put into previously weighed vials containing 1 ml water. These vials were then weighed again and, after 10 ml scintillator solution had been added, their radioactivity was measured in order to determine the water and acetone contents of the drying slab as a function of time.

Figure 13
Moisture content, acetone content and the temperature difference between the slab and the drying air (ΔT) as functions of time.
3.2 Results

Fig. 13 is an example of the variation with time of the temperature difference (ΔT) between the slab and the drying air, the moisture content and the acetone content. The end of the "constant-rate period" (see Chapter VI, section 4.1) is seen clearly in the curve for ΔT. From the experiments with droplets it was found that the acetone retention is primarily determined by the initial maltodextrin concentration and the relative humidity (H_r) of the drying air. These two factors were also investigated for the drying of slabs. Fig. 14 shows the

![Figure 14](image1.png)

**Figure 14**
Acetone retention of a dried slab as a function of the initial dry matter content.

![Figure 15](image2.png)

**Figure 15**
Acetone retention of a dried slab as a function of the relative humidity of the drying air.
Figure 16
Acetone content as a function of the moisture content during drying of the slab at two relative humidities ($H_r$) of the drying air.

Figure 17
The approximate coincidence of the end of the constant-rate period and the end of acetone loss (data of Fig. 15).
acetone retention after drying, at an H₂ of (36 ± 4) %, as a function of the initial dry matter content of the slab. Fig. 15 shows the influence of H₂ on the acetone retention after drying a slab with an initial dry matter concentration of 400 g/l. Fig. 16 shows the acetone content as a function of the dry matter content in the drying layer for two relative humidities included in Fig. 15. The end of the constant-rate period could not be determined sufficiently accurately from the drying curves. For the measurements represented in Fig. 15, the end of this period was determined from the corresponding ΔT-time curves (not given in this thesis). The time at which the period ended was found to coincide roughly with the time after which the acetone content became more or less constant, as can be seen from Figs. 13 and 17.
Chapter III
SORPTION OF VOLATILE SUBSTANCES BY MALTO-DEXTRIN

1. Introduction

From the previous chapter it appears that, as far as the retention of volatiles is concerned, the aqueous malto-dextrin solution behaves in a way analogous to a juice or extract. If drying is sufficiently rapid, a layer of malto-dextrin with a low moisture content can form around the droplets or on the slab; this layer is more or less impermeable to volatiles, but permeable to water. A similar selective layer can also be formed from other solutions, which have a high content of hydrophilic carbohydrates and/or proteins. It is demonstrated in this chapter that the acetone retention during drying of a malto-dextrin solution cannot be explained by sorption of the acetone in the almost dry skin. This does not of course alter the fact that, in special cases, sorption can be one of the causes of high retention of certain volatile components after spray drying and freeze drying. Sections 2 and 3 of this chapter deal with the measurement of the equilibrium sorption of a series of volatile substances by malto-dextrin as a function of its moisture content. The malto-dextrin was mixed with chromosorb in order to produce a free-flowing powder even at higher moisture contents. Mixing with chromosorb has the additional advantage of increasing the surface area of malto-dextrin in contact with the vapour, as a result of which the equilibrium concentration is reached quickly. Apart from being a basis for refutation of the sorption theory mentioned, these measurements of the equilibrium concentration were at the same time necessary for the determination of the activity coefficients of the volatiles. These activity coefficients and their dependence on the moisture content are of influence upon the retention of volatiles. This point is examined more closely in Chapters V and VI.

2. Experimental techniques

A 50% aqueous solution of malto-dextrin was mixed with chromosorb (W, non-acid washed, mesh size 60/100, Johns-Manville Products Corp., U.S.A.). The ratio by weight of malto-dextrin to chromosorb was 1:1. The mixture was dried to the desired moisture content in a vacuum evaporator rotating in water at a temperature of 60 to 80 °C. An amount of 3 g of the powder so obtained was placed for 72 hours in a stoppered bottle of about 50 ml, which also contained 10 microlitres of a volatile organic substance on filter paper. Only in the case of acetone sorption it was ascertained that the filter paper did not influence the measurements. The volatiles were radioactively labelled with 14C and the amount of the volatile sorbed was determined by measuring the radioactivity of the powder. For this purpose, 0.5 g of the malto-dextrin sample was dissolved in 1 ml water after the sorption experiment. Subsequently 10 ml of water-miscible scintillator was added and the resulting solution counted with a liquid scintillation counter, as already described in Chapter II. The malto-dextrin and the chromosorb in the scintillator solution caused some quenching in this case. This quenching however did not interfere with the measurements, since care was taken to ensure that the counting vials always contained the same amount of malto-dextrin and chromosorb. The sorption of acetone, ethanol, 1-propanol, 1-butanol, methanol, ethyl acetate and carbon tetrachloride was investigated. Measurements were also made with camphor,
the determination of which was carried out by gas chromatography. The experiments were carried out at room temperature (approx. 20 °C).

3. Results

The amounts of the volatile substances sorbed by the malto-dextrin are shown in Figs. 18 and 19 as functions of the moisture content. It will be seen that methanol and ethanol are still sorbed by the powder down to very low moisture contents. However this does not necessarily mean that methanol and ethanol are able to diffuse into the dry malto-dextrin, but may just as well be

Figure 18
Amount of volatile sorbed by malto-dextrin as a function of its moisture content.

Figure 19
Amount of camphor sorbed by malto-dextrin as a function of its moisture content.
explained by adsorption to or condensation on the surface of the powder (chromosorb and/or malto-dextrin). The sorption of 1-propanol and 1-butanol proved to be analogous to that of ethanol. In Figs. 18 and 19 we see that the moisture content at which the sorption curves start to ascend is dependent on the nature of the volatile substance. This moisture content cannot be determined accurately. Much more accurately determinable is the moisture content at which the sorption curve reaches its half-maximum height (half sum of minimum and maximum). This moisture content is called the "moisture limit" (see Fig. 19). In Fig. 20 this moisture limit is plotted as a function of the diameter of the molecule of the volatile compound. This diameter was measured on molecular models (Courtaulds' Maidenhead Laboratory and Griffin and George Ltd.). The side of the smallest possible square opening through which the molecular model could just pass was taken as the "diameter". From Fig. 20 it will be seen that there is an almost linear relationship between the molecular "diameter" of the volatile substance and the moisture limit, irrespective of other molecule properties such as polarity and molecular weight. When the square root of the ratio of the molecular volume to the maximum linear dimension of the molecule \(^4\) was taken as the "diameter", a fairly close linear relationship was again found.

When malto-dextrin was mixed with sand instead of chromosorb, or when malto-dextrin powder alone was used (in the latter case measurements were only made at moisture content of \(\leq 9\%\)), the same acetone sorption was found as in Fig. 18. This proves that the chromosorb does not influence the observed sorption of acetone. The influence of chromosorb upon the sorption

Figure 20
Moisture limit for sorption in malto-dextrin as a function of the molecular "diameter" of the volatile.
of other volatile substances was not checked. The acetone sorption curve in Fig. 18 remains the same if the sorption time is reduced to 48 hours or increased to 120 hours. From this it can be concluded that the curve presents equilibrium conditions. This cannot be stated with certainty for the low acetone sorption values (below a moisture content of about 10%) on account of the large relative error involved in the measurements within this range.

The sorption curves given in Fig. 18 are inaccurate at high moisture contents (well above the moisture limit). During the determination of the amount of sorbed volatile substance in the malto-dextrin powder, this powder was in the open air for roughly 1 minute, and in this time some of the sorbed substance may have evaporated. This error at moisture contents above the moisture limit cannot be neglected, especially when extremely volatile substances are used, for the diffusion rate in the malto-dextrin increases sharply with increasing moisture content. For this reason another technique was adopted for determining the equilibrium curve of acetone for moisture contents above 14%. A thin layer of malto-dextrin, without chromosorb, was spread on the bottom and wall of a flask. An amount of acetone vapour was introduced into the flask and, after equilibrium had been attained, the concentration of acetone in the gas phase was determined. This was done by taking samples from the flask via a silicon rubber bung and analysing them gas chromatographically. Further details of this method are given in Chapter IV, Section 2.2. The maximum in the acetone curve in Fig. 18, which was determined with the aid of chromosorb, proves to be no longer present when the new determination technique is applied. The activity coefficient of acetone in malto-dextrin, which was calculated from the equilibrium sorption, is plotted against moisture content in Fig. 21. For this calculation the molecular weight of malto-dextrin is taken as 500. The activity coefficient of water in malto-dextrin is also plotted in Fig. 21.

Figure 21
Activity coefficients (γ) of acetone and water in malto-dextrin at varying moisture contents of the latter.
This is calculated from the equilibrium relative humidity curve (Fig. 26), the measurement of which is discussed in Chapter IV.

4. Discussion and additional experiments

The sorption theory of Rey \(^{51}\) presumes that the activity coefficient of volatiles in dry or almost dry malto-dextrin is appreciably lower than that in the malto-dextrin solution to be dried. It can be seen from Figs. 18 and 19, however, that this is not the case for the components studied in this investigation. Fig. 21 shows that the activity coefficient of acetone in malto-dextrin solution in fact increases with decreasing moisture content. Furthermore, this theory is in conflict with the concentration technique developed by Thissen \(^{15,19}\), in which a dry film originating from the juice or extract (e.g. coffee extract) being concentrated, is formed on a very fine metal gauze or in a fibrous material. This principle of this concentration technique is analogous to the drying droplet where the solute itself forms a dry film. The wire gauze or fibrous material serves only as a support to the extremely weak film. Air is blown along one surface of this film while the other side of the film is in contact with a stream of the liquid to be concentrated. On the basis of gas chromatographic analyses it has been claimed that aroma components are retained in the concentrate and that only water passes through the dry film. This has been confirmed on a very small scale with a malto-dextrin solution. A small chamber was constructed, one wall of which consists of filter paper (Schleicher und Schüll 589). This chamber was filled with an aqueous 100 g/l malto-dextrin solution to which 10 ppm acetone had been added (Fig. 22).

![Diagram](image)

Figure 22
Apparatus used to form a dry selective layer of malto-dextrin on a filter paper. Area of evaporation surface is 9.8 cm².
After drying for a certain time, the chamber was emptied as far as possible and the acetone and water content of the solution were determined. This procedure was repeated several times, using progressively longer drying times.

![Diagram](image)

Figure 23

Amount of acetone in the liquid in the apparatus shown in Fig. 22 as a function of the amount of evaporated water.

It was also carried out using a chamber filled with distilled water to which 10 ppm acetone had again been added. Fig. 23 shows the amount of acetone in the liquid as a function of the amount of evaporated water. It should be stressed that the amount of acetone present in the membrane itself was only small compared with the amount retained in the concentrate. With the distilled water, the acetone concentration decreased during the evaporation. In later experiments it was found that parchment paper had better properties as a membrane carrier than filter paper.

It could also be demonstrated that explanation of relatively high flavour retention after freeze-drying in terms of the sorption theory is also invalid. After a 1 cm³ block of a frozen 400 g/l malto-dextrin solution containing 0.15 % acetone had been freeze-dried, it was found to contain 40-50 % of the acetone initially present. Subsequently a block of this frozen solution, made up of a nucleus (1 cm³) containing 0.15 % acetone surrounded by a layer ½ cm thick which contained no acetone and which was stained with aniline red, was likewise freeze-dried. The nucleus and outer layer were separated after freeze-drying. The acetone retention of the nucleus was again found to be 40-50 %, whereas no acetone could be detected in the layer.
Chapter IV
MEASUREMENT OF THE DIFFUSION COEFFICIENTS OF WATER AND VOLATILES IN MALTO-DEXTRIN

1. Theory
1.1 Introduction

For the measurements of the diffusion coefficients, the solution is treated as a binary mixture. Thus, for the diffusion of water in the malto-dextrin solution, the malto-dextrin (although a mixture of carbohydrates) is considered as one component, while for the diffusion of acetone in the solution, the water and the carbohydrates are together considered as one component. The diffusion coefficient can then be defined by Fick's first law:

\[ N = -D \frac{\delta C}{\delta x} \]  

(3)

\( N \) is the mass flux of the diffusing component relative to the volume-average velocity (kg/m²s), \( C \) is the concentration (kg/m³) and \( x \) is distance (m). If the small volume change on mixing the components is neglected, the net volume flow with respect to stationary coordinates is zero everywhere within the layer. It can be derived (see Appendix Section 1) that \( D \) is then equal to the mutual diffusion coefficient (mass diffusivity). For a non-stationary unidimensional case and constant \( D \), Eq. (3) leads to the differential equation:

\[ \frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2} \]  

(4)

where \( t \) is time (s). Eqs. (3) and (4), expressed in units relative to a stationary coordinate system, are also valid in a shrinking or swelling layer, provided the net volume flow with respect to stationary coordinates is zero.

The methods for determining \( D \) can be divided firstly into stationary and non-stationary methods. A common example of the former is steady permeation through a membrane. This technique, which is frequently used for determining diffusion coefficients in polymers, is less suitable for malto-dextrin. At moisture contents below 10%, malto-dextrin is very brittle, and it is difficult to make a membrane free from cracks or pinholes. An important non-stationary method is that in which the concentration distribution is observed at a certain time. Another non-stationary method, often used for polymer systems, is the (de)sorption method, in which the amount of diffusant sorbed (or desorbed) is considered. The latter method was adopted for this investigation, in which the sorption of vapour (water or volatile component) in a layer was recorded. Care was taken to ensure that the resistance to mass transfer in the gas phase could be neglected and, as a result, the surface of the layer is in equilibrium with the gas phase. This was achieved by stirring the layer sufficiently rigorously. With the sorption method applied, one possible approach is to keep the concentration of the diffusing component in the gas phase constant and to determine the change in its concentration in the layer. An alternative possibility is to keep the amount of diffusant in the complete system constant and to calculate \( D \) from the change in concentration in the gas phase. Both techniques were in fact applied, and the solutions of Eq. (4) for these two cases are given
respectively in Sections 1.2 and 1.3 of this chapter.

1.2 Constant partial vapour pressure of diffusant

The experiments were performed by bringing one side of the liquid or solid layer into contact with an atmosphere having a constant partial vapour pressure of the diffusing substance. The amount of diffusant, \( q \), taken up by the layer in time \( t \) is given by \(^{21}\)

\[
\frac{q}{q_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \exp \left\{ -\left( \frac{2n+1}{2d^2} \right)^2 \frac{Dt}{d} \right\} \frac{1}{(2n+1)^2} (5)
\]

where \( d \) is the thickness of the layer and \( q_{\infty} \) is the amount sorbed after infinite time, i.e. the equilibrium sorption value. Eq. (5) is also valid for the reverse case of desorption. For short times, sorption is independent of \( d \) and equals the sorption by an infinitely thick layer. The amount sorbed per unit area by a layer with a thickness approaching infinity is given by:

\[
\frac{q}{A} = 2(C_f - C_i) \sqrt{\frac{D}{\pi}}
\]

where \( A \) is the area of sorption and \( C_i \) and \( C_f \) are the initial and final concentration of the layer respectively. The total amount which can be sorbed by the layer is:

\[
q_{\infty} = (C_f - C_i) A d
\]

Combination of Eqs. 6 and 7 gives:

\[
\frac{q}{q_{\infty}} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{D}{d}} \text{; for } \frac{q}{q_{\infty}} \ll 0.5
\]

For very small values of \( q/q_{\infty} \), Eq. (8) is strictly valid. At \( q/q_{\infty} = 0.5 \) the error involved is still less than the experimental error of the measurements. Plotting the experimental value of \( q/q_{\infty} \) against \( \sqrt{t} \) yields a straight line below \( q/q_{\infty} = 0.5 \). The value of \( D \) can be calculated from the slope of this line. For large \( Dv/d^2 \), only the first term of the exponential series in Eq. (5) need be considered. Therefore,

\[
\frac{q}{q_{\infty}} = 1 - \frac{8}{\pi^2} \exp \left( -\frac{\pi^2 Dv}{4d^2} \right) \text{; for } \frac{q}{q_{\infty}} \gg 0.5
\]

The error involved in neglecting the higher order terms is much smaller than the experimental error of the measurements for \( q/q_{\infty} \gg 0.5 \). Since Eqs. (8) and (9) together cover the whole range of \( q/q_{\infty} \), it is unnecessary to use the series of Eq. (5) for the experiments described in this thesis.

1.3 Constant amount of diffusant in the system

With this method an amount of vapour is introduced into a closed space containing a layer and the concentration of the vapour in the gas phase is measured. This concentration is kept uniform by stirring. For this case Crank \(^{22}\)

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has published calculated sorption curves from which the auxiliary graph Fig. 24 has been derived. Here the percentage of vapour finally taken up by the layer is plotted against with \( q/q_{\infty} \) as parameter. When, for one of these values of \( q/q_{\infty} \), the sorption time \( t \) has been determined experimentally, the diffusion coefficient can be deduced from this figure.

Figure 24
Auxiliary graph for the determination of \( D \) from the measurements of sorption by a plane layer when the amount of diffusant in the total system is kept constant (derived from sorption curves published by Crank [22]).
1.4 Concentration-dependent diffusion coefficient and constant partial vapour pressure

The equations in Section 1.2 apply only when $D$ is independent of $C$, $x$ or $t$. When $D$ is a function of $C$ only and the partial vapour pressure of the diffusant is kept constant, $q/t$ (Eq. (8)) is still a linear function of $C^2$ for the first stage of sorption. Eq. (8) can be used to define two unequal diffusion coefficients $D_s$ and $D_u$, which are determined from the initial slopes of the sorption and desorption plots respectively. Provided $D_s$ and $D_u$ relate to the same small concentration range, a mean value for $D$ over this concentration range is given approximately by

$$D = \frac{1}{2} (D_s + D_u)$$  \hspace{1cm} (10)

Therefore, in order to determine the diffusion coefficient of water in malto-dextrin of a particular moisture content, sorption and desorption were measured over a moisture content range around the required value. These ranges varied from about 2% for the lower moisture contents to 7.2% for the highest moisture content used in the experiment. The diffusion coefficient defined by Eq. (8) corresponds to a moisture content somewhere in the chosen range. This was taken to be the average moisture content for the range, i.e. $\frac{1}{2} (C_{1} + C_{2})$.

In addition $d$ was taken to be the average thickness of the layer over the range in question. If the concentration range is small, Eq. (8) is valid for a layer which shrinks during drying (see Appendix Section 3).

2. Experimental techniques

2.1 General

The diffusion coefficients were measured at a temperature of 21.5 °C. In order to prevent spoilage, a small amount of benzoic acid (0.1% or less) was added to the malto-dextrin solution. As malto-dextrin with a moisture content higher than 18% is more or less liquid, some agar-agar (1.0% or less) was added to it in all experiments for which its moisture content was above 18% and also in some cases when its moisture content was below this level. Table 2 gives some experimentally determined values of the diffusion coefficient of acetone in malto-dextrin both with and without 1.62% agar-agar at a moisture content of 17.9%. The effect of the addition of agar-agar is smaller than the experimental error.

### Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>Diffusion coefficient (m²/s x 10¹³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without agar-agar</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>With 1.62% agar-agar</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>1.12</td>
</tr>
</tbody>
</table>
In order to be able to determine the thickness of the malto-dextrin layer from its weight, it is necessary to know the density of malto-dextrin as a function of its moisture content. This was determined by forming a layer (about 4 mm thick) of known weight and moisture content in a weighed and calibrated 100 ml flask. The flask was then half filled with oil (Tellus 11, Shell) of known density. After de-aerating with a water aspirator, the flask was filled up to the calibration line with the oil at a temperature of (21 ± 0.1) °C. Subsequent weighing of the filled flask enabled the density of the layer to be calculated. This was repeated for a number of different moisture contents. Fig. 25 shows the results.

![Graph showing density of malto-dextrin as a function of moisture content.](image)

**Figure 25**
Density of malto-dextrin as a function of its moisture content.

The moisture content of thin layers of malto-dextrin was controlled by equilibrating the layers with saturated salt solutions of known relative humidities, as given by O'Brien. The moisture contents of a 1:1 by weight mixture of malto-dextrin and chromosorb in equilibrium with these solutions at a temperature of 20 °C were measured, which enabled the equilibrium relative humidity curve of malto-dextrin to be plotted. This is shown in Fig. 26. Table 3 lists the salt solutions used.
Equilibrium relative humidity curve of malto-dextrin at a temperature of 20 °C.

**TABLE 3**
Saturated salt solutions used to control the relative humidity and the corresponding moisture contents of the malto-dextrin

<table>
<thead>
<tr>
<th>Solute</th>
<th>$H_r$ (%)</th>
<th>Moisture content of the malto-dextrin (%)</th>
<th>Solute</th>
<th>$H_r$ (%)</th>
<th>Moisture content of the malto-dextrin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>5.5</td>
<td>2.9</td>
<td>NaClO₃</td>
<td>75.0</td>
<td>15.8</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>10.0</td>
<td>2.0</td>
<td>NaCl</td>
<td>76.9</td>
<td>16.4</td>
</tr>
<tr>
<td>LiCl·H₂O</td>
<td>15.0</td>
<td>3.6</td>
<td>NaNO₃</td>
<td>77.7</td>
<td>16.3</td>
</tr>
<tr>
<td>CaCl₂·6H₂O</td>
<td>32.3</td>
<td>6.7</td>
<td>Na₂SO₄·5H₂O</td>
<td>78.0</td>
<td>18.0</td>
</tr>
<tr>
<td>K₂CO₃·2H₂O</td>
<td>44.0</td>
<td>8.0</td>
<td>NH₄Cl</td>
<td>79.6</td>
<td>17.9</td>
</tr>
<tr>
<td>KCNS</td>
<td>47.0</td>
<td>8.6</td>
<td>CO(NH₂)₂</td>
<td>80.7</td>
<td>17.4</td>
</tr>
<tr>
<td>Na₂Cr₂O₇·2H₂O</td>
<td>52.0</td>
<td>9.5</td>
<td>KBr</td>
<td>84.0</td>
<td>20.1</td>
</tr>
<tr>
<td>NaBr·2H₂O</td>
<td>58.0</td>
<td>10.2</td>
<td>KCl</td>
<td>86.4</td>
<td>22.8</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>66.0 **(*)</td>
<td>12.1</td>
<td>K₂Cr₂O₇</td>
<td>88.0</td>
<td>24.1</td>
</tr>
<tr>
<td>NH₄Cl·KNO₃</td>
<td>72.6</td>
<td>14.2</td>
<td>Na₂SO₄·7H₂O</td>
<td>95.0</td>
<td>30.0</td>
</tr>
</tbody>
</table>

*) Taken from a table given by O'Brien. Some of the values are averages. Temperature is 20 °C.  
**) At room temperature, about 20 °C.
2.2 Diffusion coefficient of volatiles

Measurement by gas-liquid chromatography

The diffusion coefficients of acetone and ethyl acetate in malto-dextrin with a water content of 30% and more were measured with the method discussed in Section 1.3 of this chapter (constant amount of volatile in the system). The decrease with time of the concentration of diffusant in the gas phase was measured by gas-liquid chromatography. Fig. 27 shows the experimental set-up. A closed and stirred 200 ml glass vessel contains a small brass dish filled with malto-dextrin containing some agar-agar (1% of the water) and some benzoic acid (0.1% of the malto-dextrin). The change in the moisture content of the malto-dextrin after it had been placed in the vessel could be neglected on account of the relatively small volume of the latter. The vessel is placed in thermostated water with a temperature of (21.5 ± 0.2) °C. The depth of the brass dish, which was roughly equal to the thickness of the malto-dextrin layer, varied from 0.8 to 3 mm. At moisture contents of malto-dextrin above 50% one dish was used with an inside diameter of 14.0 mm, while at moisture contents of 49.5 and 39.5% three of these dishes were used. For the lowest moisture content we used 3 dishes with a diameter of 21.0 mm. The dishes were filled with a warm malto-dextrin solution of the desired moisture content. Before use they were placed for 15 hours or more in a closed vessel, which contained a large amount of malto-dextrin with the same moisture content. Liquid acetone and ethyl acetate, together with benzene as a reference, were mixed in such a proportion that the equilibrium vapour of the solution gave equal peak heights for the three components when analysed on the gas chromatograph. Then, 10 ml of the equilibrium vapour above this mixture was injected.
into the vessel containing the malto-dextrin layer. The initial partial vapour
pressure of acetone was about 12 mm Hg. Gas samples of 25 or 30 microlitres
were taken periodically by inserting the needle of a Hamilton gas-tight syringe
through a silicone rubber slab into the capillary at the top of the vessel. The
samples were analysed on a Carlo Erba gas chromatograph provided with a
flame ionization detector. The 200 x 0.4 cm glass column used was packed with
chromosorb W 140-170 mesh (Johns-Manville Products Corp., U.S.A.) with
10 % Apiezon L (Associated Electrical Industries Ltd., England) as stationary
phase. The column was operated at 90 °C, the injection port at 140 °C. The
carrier gas was nitrogen, which was introduced at a pressure of 0.8 kg/cm².
The peak heights were found to be proportional to the concentration over the
range used, and were therefore taken as a measure for the concentration. The
proportion of benzene sorbed by the malto-dextrin layer was 2-3 % of that
for acetone and 10 %, or less, of that for ethyl acetate. The sorption of benzene
was, therefore, neglected and the peak height of benzene was used as a reference
for the other components. The amount of malto-dextrin present was so chosen
that about 50 % of the acetone vapour initially present was sorbed. This meant
that only 10-12 % of the ethyl acetate vapour was sorbed, resulting in a larger
relative error in the measured sorption of ethyl acetate.

![Percentage acetone retained in the gas phase](image)

**Figure 26**
Typical sorption curves for acetone by a layer when the amount of diffusant in the
system is kept constant.

Fig. 28 shows a typical curve for the sorption of acetone by a malto-dextrin
layer. The diffusion coefficient can be calculated from this sorption curve with
the help of Fig. 24. In order to check that the measuring vessel was stirred
sufficiently, the sorption of acetone in water (with 1 % agar-agar added) was
measured in the same way. This sorption curve is also given in Fig. 28. The
diffusion coefficient derived from it was found to be $1.19 \times 10^{-9}$ m$^2$/s. The value quoted in the literature is $1.25 \times 10^{-9}$ m$^2$/s at a temperature of 17 °C, which becomes $1.92 \times 10^{-9}$ m$^2$/s at 21.5 °C according to the Stokes-Einstein relation. The agreement between the two values indicates that the stirring was adequate. The standard deviation of the diffusion coefficient of acetone, derived from the spread of the points of the sorption curves, varied from 7% to 22% (at a moisture content of 99%) to 30% to 54% (at a moisture content of 30%). For ethyl acetate this standard deviation varied from 22% to 54%.

Measurement by radioactive labelling

A layer brought into contact with a gas phase reaches equilibrium with that phase within a reasonable time only when the thickness of the layer is adapted to the value of the diffusion coefficients of the diffusants. Consequently a thin layer is needed to measure the diffusion coefficient of acetone or other volatiles in malto-dextrin at moisture contents below 30% where the value of $D$ becomes very small. A thin layer was obtained by coating a small glass bar with malto-dextrin. The bar was then put in a chamber where the vapour pressure of acetone was constant. Measurements were also made with ethyl acetate, benzene and carbon tetrachloride. These volatiles were radioactively labelled and their sorption by the malto-dextrin layer was determined by measuring its radioactivity.

The bars (length 11.8 cm and diameter 4.15 mm) were coated with malto-dextrin over a length of 5.80 cm (see Fig. 29A). This was achieved by withdrawing the bar with a constant velocity of 10 cm per 61 seconds from a 50%

![Figure 29](image)

A) Bar used for the sorption experiments with radioactively labelled volatiles.
B) Tube containing water to dissolve malto-dextrin coating.
aqueous malto-dextrin solution containing 0.1 % benzoic acid. The bar then contained 57.8 mg of solution (standard deviation 3.6 %), from which it follows that the average thickness of the wet layer was 62 microns. The layer was twice as thick at the bottom of the bar as at the top. However, this does not affect the determination of the diffusion coefficient since, for this, only the first linear part of the sorption against log curve and the final equilibrium sorption (qeo) were used. Immediately after withdrawal from the solution, the bars were dried in a hot air current. Temperature of the air was about 80 °C and its velocity about 6 m/s. The drying was stopped when the very first cracks in the layer became visible. The moisture content of the layer then proved to be roughly 9 %. For measurement of the diffusion coefficients at moisture contents above 10 %, the bars were drawn from a solution containing 1.0 % agar-agar (48.9 % malto-dextrin, 0.1 % benzoic acid and 50.0 % water) at a temperature of 50 °C. But the amount of solution on the bars was not sufficiently reproducible in this case. It was therefore necessary to weigh those bars, which were to be used to measure qeo individually. For this 18-30 % range of moisture contents, the layer formed after withdrawing the bars only once from the solution, was rather thin. Therefore after the bars had been dried, the coating procedure was repeated. The coated, dried bars were placed in a chamber containing one of the saturated salt solutions and kept there until the following day. This period was found long enough for the malto-dextrin layer to attain equilibrium with the salt solution. The chamber was stirred (see Fig. 30) and was kept in a box with a constant temperature of (21.5 ± 1) °C, except during the insertion or removal of the measuring bars which was carried out at room temperature (about 20 °C).

Figure 30
Measuring chamber containing five bars of the type shown in Fig. 29A.
In order to measure the sorption curve, the bars were put in another similar chamber containing the same saturated salt solution to which 1% or less radioactively labelled acetone or other volatile had been added. For benzene and carbon tetrachloride, which are only slightly soluble in aqueous solution, the vapour pressure of the volatile in the chamber was equal to the saturated vapour pressure. In order to keep the concentration in the gas phase constant for these two volatiles, the salt solution was saturated with the volatile in question and in addition a capillary filled with liquid benzene or carbon tetrachloride was placed in the measuring chamber. A bar was taken from this chamber at preselected times and put in a tube (see Fig. 29B) containing 1 ml water to dissolve the malto-dextrin layer. (The opening in the cover of the chamber caused by the removal of the tube was closed with a glass stopper.)

The acetone content of this solution was measured by the method described in Chapter II. Fig. 31 shows two curves for the sorption of acetone by malto-dextrin at moisture contents of 20.4% and 10.2%. The diffusion coefficient is calculated from the initial slope of these curves with the aid of Eq. (8). At moisture contents above 12%, the standard deviation of the diffusion coefficient derived from the spread of the points of the sorption curve is 30% or less. The sorption of acetone is very low at low moisture contents of the malto-dextrin layer, which must be very thin in order to reach equilibrium within a reasonable time. This makes the method described unsuitable at moisture contents below 10%. 

Figure 31
Typical curves for the sorption of acetone by a layer of malto-dextrin when the partial vapour pressure of acetone is kept constant.
2.3 Diffusion coefficient of water

The diffusion coefficient of water in malto-dextrin was measured only at moisture contents below 30%, using the method described in Section 1.4 of this chapter. A small brass dish (inner diameter 5.0 cm) was filled with a warm malto-dextrin solution, which contained 1% agar-agar and 0.1% benzoic acid on a dry matter basis. The desired moisture content of the layer was achieved by equilibrating it with a suitable saturated salt solution. The dish was then put on the scale of an analytical balance and its weight recorded. This balance was contained in a box in which both the temperature and the relative humidity were kept constant. To keep the relative humidity constant, trays containing a saturated salt solution were placed in the box. Air was blown at a velocity of between 5.5 and 6.0 m/s along the surface of the malto-dextrin. The experiments were performed at a temperature of (21.5 ± 0.5) °C. After stopping the air flow and releasing the balance (both of which could be done outside the box), the weight of the dish was read off through a glass window in the thermostated box. To investigate whether the air velocity of 6 m/s was sufficient to ensure that the resistance to mass transfer in the gas phase was negligible, desorption of a 5 mm thick layer from 30.0% to 22.8% moisture was measured during the course of 24 hours. Throughout this period, the slope of desorption plotted against $Y_t$ was found to be constant. Moreover we found the same slope for air velocities of both 6 and 12 m/s. This proves that the mass transfer coefficient from the surface of the malto-dextrin layer to the air is sufficiently large. The thickness of the malto-dextrin layer (usually only slightly less than the depth of the dish) was adapted to the expected diffusion coefficient and varied from 0.09 to 0.6 mm. The layer thickness could be determined by weighing, since the density and area of surface of the layer were known. Fig. 22 shows a typical sorption and desorption curve for

![Figure 22](image)

**Figure 22**
Typical curve for the sorption and desorption of water by a layer of malto-dextrin.
water. The very first part of the plot of sorption against \( V \) is not linear. This
non-linearity was observed in many experiments. An explanation might be the
disturbance of the relative humidity in the box when the door is opened to
enable the measuring dish to be placed on the balance. The non-linearity may
also be caused by "non-Fickian" diffusion \(^{26}\).

3. Results

Fig. 33 shows the measured diffusion coefficients of water (\( D_w \)) and acetone
(\( D_k \)) in maltodextrin as a function of its moisture content. The numerical data
are given in Tables 4 and 5. Some measurements of ethyl acetate, benzene and
carbon tetrachloride are included. Table 4 also includes the values derived from
the literature for the diffusion coefficient of acetone \(^{25}\) and benzene \(^{27}\) in water.

![Figure 33](image_url)

The diffusion coefficients of water and some volatiles in maltodextrin at varying
moisture contents of the latter.

These have been corrected to 21.5 °C by means of the Stokes-Einstein relation.
The value of the diffusion coefficients of carbon tetrachloride in water has
been calculated by means of the Wilke-Chang correlation \(^{40}\). It was found that
log \( D \) for water is proportional to the reciprocal of the water concentration
over the range measured. This can be seen for \( D_k \) (i.e. from desorption measure-
ments) in Fig. 34. The equation of the curve is given by

\[
\frac{D_k}{D_{kw}} = 5.0 \exp \left( -\frac{1.6 \rho_w}{C_{kw}} \right)
\]

(11)

where \( \rho_w \) is the density of water. The constant \( D_{kw} \) is the value of \( D_k \) given
by extrapolation of the line in Fig. 34 to a water concentration of 100% (\( D_{kw} = 3.4 \times 10^{-12} \text{ m}^2/\text{s} \)). According to the definition of the diffusion coefficient,
### TABLE 4

Diffusion coefficients of volatiles in malto-dextrin at various moisture contents

| Moisture content of malto-dextrin (%) | D (m²/s) | | | | | |
|--------------------------------------|----------|----------|----------|----------|----------|
|                                      | Acetone  | Ethyl acetate | Benzene | Carbon tetrachloride | |
| a) Measured gas chromatographically, |          |           |          |          |          |
| 100.0                                | 1.4 x 10⁻¹⁹ | 1.3 x 10⁻⁹ | 1.1 x 10⁻⁶⁸ | 9.5 x 10⁻⁸⁹ |           |
| 99.0                                 | 1.2 x 10⁻⁹ | 4.4 x 10⁻⁹ | 1.1 x 10⁻⁶⁸ |           |           |
| 79.2                                 | 6.5 x 10⁻¹⁰| 7.3 x 10⁻¹⁰|           |           |           |
| 69.3                                 | 5.7 x 10⁻¹⁰|           |           |           |           |
| 59.5                                 | 2.9 x 10⁻¹⁰| 3.6 x 10⁻¹⁰| 1.1 x 10⁻⁶⁸ |           |           |
| 49.5                                 | 1.3 x 10⁻¹⁰| 1.7 x 10⁻¹⁰|           |           |           |
| 39.5                                 | 3.1 x 10⁻¹¹|           |           |           |           |
| 30.3                                 | 7.0 x 10⁻¹²|           |           |           |           |
| b) Measured with the tracer method,  |          |           |          |          |          |
| 30.0                                 | 4.4 x 10⁻¹²| 1.1 x 10⁻¹⁴|           | 5.6 x 10⁻¹⁴|           |
| 24.1                                 | 1.8 x 10⁻¹²|           | 5.8 x 10⁻¹⁴| 7.0 x 10⁻¹⁴|           |
| 20.1                                 | 5.0 x 10⁻¹³| 1.6 x 10⁻¹⁴|           |           |           |
| 17.9                                 | 1.1 x 10⁻¹⁳|           |           |           |           |
| 16.3                                 | 4.6 x 10⁻¹⁴|           |           |           |           |
| 14.2                                 | 2.3 x 10⁻¹⁴|           |           |           |           |
| 12.1                                 | 4.0 x 10⁻¹⁵|           |           |           |           |
| 10.2                                 | 1.5 x 10⁻¹⁵|           |           |           |           |

1) After Lemonte 25
2) After Bonoli et al. 27
3) Calculated value

### TABLE 5

Diffusion coefficient of water in malto-dextrin at various moisture contents

| Moisture content of malto-dextrin % | Diffusion coefficient (m²/s) | | | | | |
|-------------------------------------|-----------------------------|-----------|-----------|-----------|-----------|
|                                     | Dₙ | Dₚ | \( \frac{1}{4}(Dₙ + Dₚ) \) | Range of moisture content used (%) | Mean thickness of the layer (mm) | |
| 26.4                                | 1.3 x 10⁻¹¹| 2.5 x 10⁻¹¹| 1.9 x 10⁻¹¹| 22.8-30.0 | 0.601 |
| 21.5                                | 1.2 x 10⁻¹¹| 8.9 x 10⁻¹²| 1.0 x 10⁻¹¹| 20.1-22.9 | 0.426 |
| 20.4                                | 8.5 x 10⁻¹²| 7.2 x 10⁻¹²| 7.9 x 10⁻¹²| 17.9-22.8 | 0.337 |
| 17.2                                | 3.4 x 10⁻¹²| 3.6 x 10⁻¹²| 3.5 x 10⁻¹²| 16.4-17.9 | 0.196 |
| 16.1                                | 3.7 x 10⁻¹²| 2.6 x 10⁻¹²| 3.1 x 10⁻¹²| 14.3-17.9 | 0.497 |
| 15.4                                | 1.8 x 10⁻¹²| 2.3 x 10⁻¹²| 1.9 x 10⁻¹²| 14.3-16.4 | 0.196 |
| 13.2                                | 4.9 x 10⁻¹²| 4.6 x 10⁻¹³| 4.7 x 10⁻¹³| 12.1-14.3 | 0.189 |
| 11.1                                | 7.3 x 10⁻¹⁴| 1.6 x 10⁻¹³| 1.2 x 10⁻¹³| 10.1-12.1 | 0.091 |
$D_w$ in the aqueous malto-dextrin solution is equal to the diffusion coefficient of malto-dextrin in the same solution. At malto-dextrin concentrations approaching zero, the diffusion coefficient of water is consequently equal to the diffusion coefficient of malto-dextrin in pure water. The value of $D_w$ is therefore much lower than that of the self-diffusion coefficient of water, which is $2.2 \times 10^{-9} \text{ m}^2/\text{s}$ [28, 29]. In Fig. 34 $D_j$ was plotted instead of $D_w$, as $D_j$ must be used for the calculation of drying (i.e., desorption) curves in the next chapter. Above a moisture content of 17%, $\log D$ for acetone was also found to be proportional to the reciprocal of the water concentration in the malto-dextrin.

![Graph](image)

Figure 34
Plot of $\log D_j$ against the reciprocal of the water concentration ($C_w$) in the malto-dextrin. ($D_j$ is the diffusion coefficient of water determined from desorption measurements.)

Over the complete range of moisture contents used for the measurements, however, the diffusion coefficient of acetone can be better approximated by the relationship:

$$D = A \exp \left( \frac{B}{VC_w} \right)$$

(12)

This can be seen in Fig. 35, in which the diffusion coefficients of ethyl acetate, benzene and carbon tetrachloride are also included. All the lines in this figure are described by Eq. (12). The respective values of the constants A and B for the volatiles tested are given in Table 6.
Figure 35
Plots of log $D$ against $C_w^{-1/2}$ for a number of volatiles.

### TABLE 6
The values of the constants $A$ and $B$ in Eq. (12) for various volatiles

<table>
<thead>
<tr>
<th>Volatile</th>
<th>$A$ (m$^2$/s)</th>
<th>$B$ (kg/m$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>$2.1 \times 10^{-5}$</td>
<td>309</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>$1.4 \times 10^{-4}$</td>
<td>342</td>
</tr>
<tr>
<td>Benzene</td>
<td>$3.1 \times 10^{-8}$</td>
<td>396</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>$7.6 \times 10^{-3}$</td>
<td>499</td>
</tr>
</tbody>
</table>

4. Discussion

4.1 Diffusion characteristics in malto-dextrin and comparison with other macromolecular systems

The logarithm of the diffusion coefficient of acetone in malto-dextrin is found to be a linear function of moisture content when the latter is less than 25%.

The same holds for $D_w$, below a moisture content of 16%. From the measurements of Fish, it turns out that log $D_w$ in starch and scalded potato is likewise a linear function of the moisture content in the range 0 to 16%.

*) For very low moisture contents this proved to be a better approximation than given by Eq. (12).
moisture. The linear relationship between log D and the concentration of diffusant is found mostly with diffusion in a polymer when the diffusant is readily soluble in the polymer and when its concentration is not too high. At very high concentrations, the concentration dependence becomes less, just as is found for Dm in the malto-dextrin solution (see Fig. 33). The diffusion of water in malto-dextrin is analogous to that usually found for solvents in a polymer.

![Graph](image)

**Figure 36**

Moisture content of the malto-dextrin at which D is equal to $10^{-13}$ m$^2$/s, as a function of the molecular "diameter" of the volatile.

The question arises as to whether a relationship similar to that found between the equilibrium sorption of the volatiles and their molecular "diameter", d, (the linear relation between moisture limit and d in Fig. 20) also exists between D and d. The diffusion coefficients in malto-dextrin are known for only four volatiles. It may be seen from Fig. 36 that these four volatiles do indeed comply with such a relationship. This Figure shows that there is an approximately linear relationship between d and the moisture content of the malto-dextrin at which D is equal $10^{-13}$ m$^2$/s. This moisture content was derived by interpolation according to Eq. (12). Furthermore, Fig. 37 indicates that for these volatiles log D is almost linearly dependent on d. A similar relationship is often met with in the diffusion of gases in polymers. The diffusion coefficients of a large number of gases in an amorphous polymer can in many cases be satisfactorily expressed by a relation of the form:

$$D = G \exp \left(-\Omega d^n\right)$$  \hspace{1cm} (13)

where G, Ω and n are constants characteristic of a particular polymer. The value of n varies from 1 to 2. According to the line drawn in Fig. 37, the values
of these constants for malto-dextrin are:

\[ G = 4.0 \times 10^{-3} \text{ m}^3/\text{s} \]
\[ \Omega = 4.6 \text{ Å}^3 \]
\[ n = 1 \]  \hspace{1cm} (14)

In the following section it will be examined what can be said to explain the diffusion characteristics in malto-dextrin on the basis of what is known about diffusion in polymers in general.

4.2 Qualitative explanation of the diffusion characteristics

The last decades have brought a great variety of experimental and theoretical work on diffusion in polymers. The subject, however, is so complicated that a complete explanation of the diffusion characteristics in malto-dextrin is not yet possible. Only two notable aspects can be made plausible, namely the strong dependence of the diffusion coefficients of water and volatiles on the moisture content and the marked influence of the molecular “diameter” of a volatile component upon its diffusion coefficient. Attempts to describe the diffusion in an amorphous polymer matrix generally make use of the “hole theory”. The “holes” are produced by movements of the polymer chain segments \(^{37}\). The energy necessary for the formation of a hole \((E_h)\) depends on the cohesive energy of the polymer and the chain stiffness. If the energy of a diffusing molecule exceeds a possible energy barrier \((E_m)\), it can jump into a neighbouring hole of sufficient size. If the diffusing molecule is strongly bound to the polymer chain, then \(E_m\) will be large. Thus the diffusion process is characterized by an energy \(E\), which is equal to \(E_h\) plus a possible additional
term $E_m$. One can derive that $E$ is related to the diffusion coefficient as follows \(^29, 30\):

$$D = D_e \exp \left( -\frac{E}{RT} \right)$$

(15)

where the energy of activation for diffusion, $E = E_f + E_m$, is defined per mole. In practice, $D_e$ is usually considered to be independent of temperature. As the moisture content of the malto-dextrin increases, more of the bonds between the hydroxyl groups of neighboring carbohydrate molecules will be disrupted. As a result, these molecules will become more mobile, $E_f$ will be reduced and the diffusion coefficient will therefore increase. If the extent of binding between the flavor molecule and the carbohydrate is low (which is mostly the case in practice), then $E_m$ will be small with respect to the energy necessary to form a sufficiently large hole. Thus the activation energy for diffusion will be primarily determined by $E_m$, which increases markedly with increasing $d$. It may then be expected that $D$ will decrease sharply as $d$ increases. For the very small water molecule, $E_f$ will also be very small. Since, however, the very polar water molecule can be bound to the hydroxyl groups of the malto-dextrin, $E_m$ will no longer be negligible. It is impossible to say just how large $E_m$ is, but it is by no means necessarily equal to the binding energy between a hydroxyl group of the water molecule and a hydroxyl group of the carbohydrate chain. For one can imagine that the water molecule moves along the carbohydrate chain in such a way that binding to one of the hydroxyl groups of the chain begins before the bond with the previous group has been completely disrupted. For the diffusion of water in malto-dextrin with a low moisture content, it appears that $E_f + E_m$ is still smaller than $E$ for the volatiles. The fact that the diffusion coefficient of water in malto-dextrin is higher than that of the volatiles used in these experiments must therefore in the first instance be attributed to the very small size of the water molecule and not to its high polarity. Its polar character is responsible for a strong interaction between it and the malto-dextrin which in fact has the effect of lowering the diffusion coefficient of the water. That this interaction between water and polymer does indeed act so as to lower $D_e$ has been demonstrated by Honeycutt \(^30\) for a system comprising water and partially hydrolyzed derivatives of poly (vinyl acetate).
Chapter V

CALCULATION OF THE WATER AND ACETONE CONTENT IN THE DRYING SLAB

1. Introduction

It follows from Chapter III that the activity coefficient of volatiles in malto-dextrin depends on the water concentration. This dependence becomes especially marked at low moisture contents (near the moisture limit). The activity coefficient of water in malto-dextrin is also a function of the moisture content (see Fig. 21); above a moisture content of 10%, however, it does not vary greatly with the water concentration. In such cases for which the activity coefficients vary with the water concentration, the driving force for mass transfer is not the concentration gradient. For an exact calculation, the gradient of the partial chemical potential of a component should be regarded as the driving force:

\[ N = -BC \frac{\delta \mu}{\delta x} \]  \hspace{1cm} (16)

where \( \mu \) is its chemical potential, \( C \) its concentration, \( N \) its mass flux, and \( B \) its intrinsic mobility. With the three-component system, water / acetone / malto-dextrin, the concentrations of only two components, e.g., water and acetone, are independently variable. For, once \( C_s \) and \( C_w \) have been chosen, the concentration of malto-dextrin is fixed. Since the chemical potential of water \( (\mu_w) \) is independent of \( C_w \), it follows that

\[ \frac{\delta \mu_w}{\delta x} = \frac{\delta \mu_w}{\delta C_w} \cdot \frac{\delta C_w}{\delta x} \]  \hspace{1cm} (17)

Substitution in Eq. (16) and introducing the activity of water \( (a_w) \) gives:

\[ N_w = -BRT \frac{\delta (\ln a_w)}{\delta (\ln C_w)} \cdot \frac{\delta C_w}{\delta x} \quad = -D_n (C_w) \cdot \frac{\delta C_w}{\delta x} \]  \hspace{1cm} (18)

Thus, even if the activity coefficient of water depends on the moisture content, the diffusion can still be described in the normal way by Fick's first law. For the acetone transport, however, this is not valid and instead we find:

\[ \frac{\delta \mu_a}{\delta x} = \frac{\delta \mu_a}{\delta C_a} \cdot \frac{\delta C_a}{\delta x} + \frac{\delta \mu_a}{\delta C_w} \cdot \frac{\delta C_w}{\delta x} \]  \hspace{1cm} (19)

Even if \( \delta C_w/\delta x \) equals zero, there may still be an acetone transport. For the calculations in this chapter, however, the second term on the right-hand side of the equation is neglected. Eq. (19) then assumes the same form as Eq. (17), so that the transport can be described by a Fickian coefficient \( D_n(C_w) \). This is justified if the activity coefficient of acetone is only slightly dependent on \( C_w \).

From Fig. 21 it follows that this is the case above a moisture content of 15%. At moisture contents in the neighbourhood of 11%, however, \( \delta \mu_a/\delta C_w \) is large. As the moisture content at the surface of a drying slab approaches 11%, then the second term, which is of opposite sign to the first term, begins to exert an influence on the flux of acetone \( (N_w) \) leaving the slab. Nevertheless, this second
term has hardly any influence on the final acetone retention after drying. For, as will be seen from the calculations in Section 3 of this chapter, the calculated value of \( N_{\text{w}} \), which is too high on account of the neglection of the second term, is found in any case to approach zero as the moisture content at the surface of the slab becomes low.

2. Differential equations and boundary conditions

In this section only the theoretical case of no shrinkage during drying of the slab is considered. (The next section deals with this shrinkage.) If the second term of Eq. (19) is neglected, then the following is valid for the acetone concentration in the slab:

\[
\frac{\delta C_w}{\delta t} = \frac{\delta}{\delta x} \left( D_w \frac{\delta C_w}{\delta x} \right)
\]  

(20)

\( D_w \) is given by Eq. (12) and Table 6. Since \( D_w \) is a function of \( C_w \), Eq. (20) can only be solved if \( C_w \) is known. The following holds for \( C_w \):

\[
\frac{\delta C_w}{\delta t} = \frac{\delta}{\delta x} \left( D_w \frac{\delta C_w}{\delta x} \right)
\]  

(21)

Since drying of the slab is a desorption process, the diffusion coefficient of water (\( D_w \)) determined from desorption experiments is used in Eq. (21). \( D_w \) is given by Eq. (11). The following initial condition applies to the drying of slabs as described in Chapter II:

\[
\text{at} \quad t = 0, \quad \begin{cases} 
C_w = C_{w0} \\
C_a = C_{ai}
\end{cases} \quad \text{for} \ 0 < x < 2
\]  

(22)

The slab, together with the symbols used, is sketched in Fig. 38. Symbols with the subscript \( e \) relate to the air, while those without this symbol relate to the

Figure 38
Schematic representation of drying slab; the subscript \( e \) refers to the drying air.
slab. The subscript i refers to the interface. For reasons of symmetry, it is sufficient to consider a half slab bounded by the surfaces \( x = 0 \) and \( x = l \). The boundary conditions are:

\[
\begin{align*}
\text{at } x = l, & \quad \frac{\partial C_{\text{gas}}}{\partial x} = \frac{\partial C_{\text{ac}}}{\partial x} = 0 \\
\text{at } x = 0, & \quad \begin{cases} \\
N_{\text{ev}} = -D_{a} \frac{\partial C_{\text{ac}}}{\partial x} = -k_{a}(C_{\text{ac,i}} - C_{\text{ac}}) \\
N_{\text{ev}} = -D_{a} \frac{\partial C_{\text{ac}}}{\partial x} = -k_{a}C_{\text{ac}}
\end{cases}
\end{align*}
\]

(23) \hspace{1cm} (24) \hspace{1cm} (25)

In these equations \( k \) is the partial mass transfer coefficient in the gas phase. The relationship between \( C_{\text{ac,i}} \) and the water concentration at the surface of the slab \( (C_{\text{ac}}) \) in equilibrium with it, is given by the equilibrium relative humidity curve (Fig. 26). This curve could be adequately approximated by the equation:

\[
C_{\text{ac,i}} = F - J \exp (-K C_{\text{ac}})
\]

(26)

where \( F \), \( J \) and \( K \) are constants, given in Table 7. Moreover,

\[
C_{\text{ac}} = H_{c} C_{\text{ac,i}}
\]

(27)

where \( H_{c} \) is the relative humidity of the drying air and \( C_{\text{ac}} \) is the saturated water vapour concentration at the air temperature \( T_{c} \). For the temperature range in question (20 °C-60 °C), the relationship between \( C_{\text{ac}} \) and \( T_{c} \) (expressed in °C) can be approximated by:

\[
C_{\text{ac}} = P \exp ST_{c} - U
\]

(28)

The values of the constants \( P \), \( S \) and \( U \) are given in Table 7. As already mentioned, the slab temperature for the experiments in Chapter II was kept constant at 21.5 °C by regulating \( T_{c} \). The value of \( T_{c} \) can be calculated from the equation representing the heat balance:

\[
\Delta H \cdot n_{\text{wt}} = h (21.5 \text{ °C} - T_{c})
\]

(29)

where \( \Delta H \) is the heat of evaporation of water at 21.5 °C and \( h \) is the partial heat-transfer coefficient in the gas phase. The partial mass transfer coefficient was calculated from the rate of evaporation from a slab consisting of water with 1% agar-agar added. It was found that \( k_{a} = 0.020 \text{ m/s} \). It followed from this measurement and from Eq. (29) that \( h = 28 \text{ J/m}^2\text{ °C} \). With the aid of Equations (26-29), \( C_{\text{ac,i}} \) and \( C_{\text{ac}} \) can be eliminated from the boundary conditions. The values of the constants in these boundary conditions, which are used for the numerical calculations, are compiled in Table 7. The relationship between \( C_{\text{ac,i}} \) and the acetone concentration at the surface of the slab \( (C_{\text{ac}}) \) in equilibrium with it, is given by the curve of Fig. 18 or can be derived from Fig. 21. A more detailed discussion of the boundary conditions of the different-
TABLE 7
The values of the constants used in the boundary conditions Eqs. (22) - (29)

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{w0}$</td>
<td>7.54 kg/m$^3$</td>
</tr>
<tr>
<td>$C_{w1}$</td>
<td>1.023 m$^3$</td>
</tr>
<tr>
<td>$t$</td>
<td>2.05 x 10$^2$ m/</td>
</tr>
<tr>
<td>$k_w$</td>
<td>0.020 m/s</td>
</tr>
<tr>
<td>$k_n$</td>
<td>0.011 m/s</td>
</tr>
<tr>
<td>$h$</td>
<td>28 J/m$^2$ K</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>2.446 x 10$^4$kJ/kg</td>
</tr>
</tbody>
</table>

...tial equation of drying is given by Kauh (11), who also deals with variations in $k_w$ and $h$ as drying proceeds.

3. Correction for shrinkage during drying

The value of the acetone retention calculated from the equations in the previous section is much too high. For a certain case the calculated acetone retention of a dried slab was 52%, whereas in practice this figure was found to be about 10% under the same drying conditions. This is because the appreciable shrinkage of the drying slab has not yet been taken into account. If volume changes due to the mixing of malto-dextrin and water are neglected, then the reduction in volume during drying is equal to the volume of evaporated water. Since the sides of the slab in these experiments are held in position by a frame (see Fig. 12), the slab shrinks only at the expense of its thickness. This shrinkage can now be taken into account by reverting to a new unit of length which shrinks together with the slab thickness, in such a manner that the thickness of the slab expressed in these new units remains equal to its value at the onset of drying. Likewise the concentration is expressed as the number of kilograms in a unit of volume which always contains the same amount of malto-dextrin. The concentration and length expressed in these units, which shrink together with the slab, are denoted by $C$ and $\xi$ respectively. If the volume changes due to the mixing of malto-dextrin and water are neglected and the specific weight of water is $\rho_w$, then the relationship between $x$ and $\xi$ is given by (see Appendix Section 2):

$$dx = \frac{\rho_w - C_{w0} + \Gamma_w}{\rho_w} d \xi$$

(30)

and that between $C$ and $\Gamma$ by

$$C = \frac{\rho_w}{\rho_w - C_{w0} + \Gamma_w} \Gamma$$

(31)

where $C$ and $\Gamma$ (without subscript) denote either the acetone concentrations ($C_w \Gamma_w$) or the water concentrations ($C_w \Gamma_w$). Substitution of these relationships in Eqs. (30) and (21) gives equations in $\Gamma$, $\xi$, and c of similar form but with a
different diffusion coefficient $D'$:

$$\frac{\delta \Gamma}{\delta t} = \frac{\delta}{\delta \xi} \left( D' \frac{\delta \Gamma}{\delta \xi} \right)$$

(32)

in which the new diffusion coefficient is given by:

$$D' = D \left( \frac{\rho_u - C_n}{\rho_w - C_n} \right)^2$$

(33)

although not strictly valid, $\delta \xi$, $\delta \xi$ is introduced for convenience.

Moreover, $C_n$ in the formulae for $D_\infty$ and $D_u$ and the surface concentrations of the slab ($C_{n,1}$ and $C_n$) in the boundary conditions, must also be expressed in the "shrinking" units with the aid of Eq. (31). The equations and boundary conditions thus generated can be numerically solved in the same way as the equations in the previous section. The solutions are expressed relative to the "shrinking" frame of reference. With the aid of Eq. (31), $\Gamma_w$ and $\Gamma_n$ can be reconverted to the more familiar fixed frame of reference ($C_w$ and $C_n$). Conversion of $\xi$ into $x$ can in general only be carried out numerically. The total amount of a component in the slab, however, is equal in both frames of reference. The acetone and water contents measured as described in Chapter II are values of the amount present in the slab and cannot therefore be compared with the corresponding calculated values without any conversion.

4. Solutions of the diffusion equations and discussion

In a number of cases, the differential equations discussed in the previous section were solved numerically with an EL-X computer, by the Mathematisch Centrum in Amsterdam. These solutions agree with the measured values of Chapter II within the limits of experimental error. This agreement can be seen in Figs. 13, 15 and 16. Where, in Figs. 13 and 16, the calculated curves for the acetone and water contents of the drying slab do not coincide with the measured curves, they have been drawn as dashed lines. Fig. 15 gives the acetone retention as a function of the relative humidity of the air. The diffusivity coefficient of water was not measured above a moisture content of 30 %. From the agreement between the measured drying curve and the calculated one in Fig. 13, however, it appears that Eq. (11) is a useful approximation for $D_u$ over the whole moisture content range within which the drying took place (9.6 % - 65.6 % moisture). The calculated moisture and acetone distribution curves corresponding to Fig. 13 are given in Figs. 39 and 40. In these two Figures, the concentrations ($\Gamma$) and the distance in the slab ($\xi$) are expressed in the "shrinking" system of units. After a drying time of 305 minutes the acetone flux for this case had fallen to less than 0.1 % of its initial value, while the water flux amounted to 25 % of its initial value. In order to save computer time, the calculations were always stopped if the acetone flux had diminished to such a negligible level. The average moisture content of the slab corresponding to Figs. 39 and 40 was 35 % after 305 minutes drying. At the same instance the moisture content at the surface of the slab was 9.6 %, which is the moisture content of the slab in equilibrium with the drying air. It can be seen from Fig. 40 that the surface concentration of acetone in the slab falls very rapidly to almost zero. If in these calculations the boundary condition
Figure 39
Calculated moisture distribution curves in a drying slab.

Figure 40
Calculated acetone distribution curves in a drying slab.
for the acetone concentration (25) is replaced by
\[ C_{a1} = 0 \quad \text{for} \quad x = 0 \] (34)

then the same acetone retentions are found. The calculations show in fact that the error introduced in the average acetone concentration in the slab by the approximation (34) becomes negligible after only a few minutes drying. We will return to this point in the next chapter. It was found in Chapter II that almost all the acetone loss during drying of the slabs took place during the constant-rate period (c). This also proved to hold for the calculated curves (see for instance Fig. 15). The latter curves enable the effect to be investigated more accurately. Since the moisture content of the slab during the constant-rate period is still fairly high, \( D_a \) will not at this stage be markedly dependent on \( C_a \). If \( D_a \) is assumed constant for \( t < t_a \), then an estimate of the acetone retention after drying can be made with the aid of Eqs. (8) and (9) by taking \( t \) to be \( t_a \) and \( d \) to be half of the thickness of the slab at the onset of drying.

**TABLE 8**

Acetone retention after drying derived from \( t_a \) and Eqs. (8) and (9), compared with the measured and calculated values shown in Fig. 15

<table>
<thead>
<tr>
<th>( H_a ) (%)</th>
<th>Measured</th>
<th>Calculated</th>
<th>Derived from ( t_a ) and Eqs. (8) and (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>77</td>
<td>—</td>
<td>32</td>
</tr>
<tr>
<td>9</td>
<td>78</td>
<td>70.8</td>
<td>80</td>
</tr>
<tr>
<td>22</td>
<td>49</td>
<td>58.0</td>
<td>61</td>
</tr>
<tr>
<td>31</td>
<td>40</td>
<td>47.5</td>
<td>51</td>
</tr>
<tr>
<td>34</td>
<td>41</td>
<td>—</td>
<td>57</td>
</tr>
<tr>
<td>43</td>
<td>41</td>
<td>—</td>
<td>45</td>
</tr>
<tr>
<td>53</td>
<td>30</td>
<td>18.7</td>
<td>14</td>
</tr>
<tr>
<td>56</td>
<td>6.0</td>
<td>—</td>
<td>13</td>
</tr>
<tr>
<td>69</td>
<td>3.7</td>
<td>4.0</td>
<td>6.7</td>
</tr>
<tr>
<td>78</td>
<td>1.0</td>
<td>—</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 8 compares the acetone retentions determined in this way with the measured and numerically calculated values. The agreement is found to be reasonable. The value of \( D_a \) was taken to be the value for \( t = 0 \) as given by Eq. (12), namely \( 2.8 \times 10^{-16} \text{m}^2/\text{s} \) and \( t_a \) was determined from curves of \( \Delta t \) against time.
Chapter VI

DISCUSSION AND INTERPRETATION OF THE RETENTION OF VOLATILES

1. Introduction
By solving the equations in Chapter V, Section 3, for a series of values of \( H_{a} \), \( k_{w} \), \( l \) and \( C_{w0} \), one can accurately examine the influence of these factors upon the acetone retention after drying. This requires a great deal of computer time and has not been done for this investigation. In this chapter, the influence of the important factors on the retention of volatiles will be examined qualitatively. In addition, the measurements of the acetone retention of droplets (Chapter II) will be discussed in more detail. Finally, the insight gained is utilized to analyze the retention of volatiles during spray drying.

2. Influence of volatility
Provided the surface concentration of a component is very small compared with its initial concentration, a higher volatility will result in a greater loss (and a lower surface concentration) of the component during drying. When, however, volatility reaches such a level that the surface concentration becomes practically zero almost immediately after the onset of drying, then a further increase in volatility can cause no additional loss of the component during drying. One is then able to apply the boundary condition given by Eq. (34), and the volatility plays no further role in the equations to be solved for the calculation of the retention. In this section, we will examine when it is permissible to use Eq. (34) as a boundary condition for calculating the acetone retention of the drying slab. According to Eq. (25), \( C_{w0} \) cannot be equal to zero as long as \( N_{a} \neq 0 \). Neither can \( C_{w} \) be exactly zero in this case, since it is in equilibrium with \( C_{w0} \). The surface concentration \( C_{w} \) can only by approximation be equal to zero, namely when

\[
C_{w} \ll C_{w0}
\]  

(35)

The acetone flux for this case (\( C_{w} \approx 0 \)) is found by differentiation of Eq. (6), which gives:

\[
N_{a} = -C_{w0} \sqrt{\frac{D_{a}}{\pi t}}
\]  

(36)

provided

\[
t \leq t_{a}/2
\]  

(37)

where \( t_{a}/2 \) is the time after which half of the acetone has evaporated from the slab. It follows from Eqs. (25) and (36) that

\[
k_{w} \left( \frac{C_{w0}}{C_{w0}} \right) C_{w} - C_{w0} \sqrt{\frac{D_{a}}{\pi t}}
\]  

(38)

Combination of Eqs. (35) and (38) gives the following condition for a surface concentration of acetone almost equal to zero

\[
k_{w} \left( \frac{C_{w0}}{C_{w0}} \right) > \sqrt{\frac{D_{a}}{\pi t}}
\]  

(39)
or

\[
\tau \gg \frac{D_a C_{ai}^2}{\frac{1}{2} k a^3 C_{sic}^2}
\]

(40)

If an arbitrary numerical factor of 10 is chosen for inequality (40), then this becomes

\[
\tau_{so} = 10 \frac{D_a C_{ai}}{\frac{1}{2} k a^3 C_{sic}^2}
\]

(41)

where \( \tau_{so} \) represents the order of magnitude of the time after which \( C_{ai} \approx 0 \). In order that \( C_{ai} \) may be taken to equal zero from the very onset of drying, the following must hold:

\[
\tau_{so} \ll \tau_{1/2}
\]

(42)

which at the same time satisfies requirement (37). From Eq. (8), it follows that for a slab:

\[
\tau_{1/2} = \frac{\pi}{24} \frac{l^2}{D_a}
\]

(43)

Combination of (41), (42) and (43) gives:

\[
\frac{k_l l}{D_a} \left( \frac{C_{sic}}{C_{ai}} \right) \gg \frac{4 \sqrt{10}}{\pi} \approx 4
\]

(44)

In this inequality

\[
\frac{k_l l}{D_a} = Bi
\]

(45)

where Bi is the Bier number for mass transfer. The values of \( D_a \) in Bi, and of \( C_{sic}/C_{ai} \) must be taken as those at the onset of drying. The quotient \( C_{sic}/C_{ai} \) is a measure of the volatility of the acetone in the solution and is equal to \( C_{sic}/C_{ai} \) in Eq. (1). The reciprocal value of the latter at a temperature of about 20 °C is given by Fig. 18. Inequality (44) can be written as

\[
Bi a \frac{C_{sic}}{C_{ai}} \gg 4
\]

(46)

For a sphere of radius \( r \), Eq. (43) becomes \( \tau_{1/2} = 0.03 r^2/D_a \). The value of \( \tau_{1/2} \) for a sphere is therefore less than that for a slab of similar dimensions (i.e., for \( l = r \)), and the right-hand side of inequalities (44) and (46) become 2.5 times as large, namely 10 instead of 4.

For solutions with a high water content, Bi is of the same order of magnitude for the transport of all volatiles and also of water. If condition (46) is satisfied for a series of components, differences in volatility within the series will have no influence upon the relative losses of the individual components during drying. In fact, the relative losses of the components will depend exclusively on differences in diffusion coefficients.
For the experiments with slabs described in Chapter II, \( B_i \) \( (C_{w,m}/C_{w}) \) is equal to 190, which is appreciably greater than 4, so that condition (46) is fully satisfied. For the experiments with droplets of a dry matter content of 100 g/l and at an air velocity of 2.9 m/s, \( B_i \) \( (C_{w,m}/C_{w}) \) is equal to 67, which is greater than 10. In this latter calculation, the influence of internal circulation in the droplet on the effective value of \( D_a \) has already been taken into account. (As will be seen in the next section, its effective value is increased by a factor of 2.5). For the experiments with droplets, \( C_{w,m} \) is not negligible during the very first stage of drying (the first 0.4 second according to Eq. (41)). For a qualitative discussion, however, like that in Section 4.3 of this chapter, the acetone loss during this time is not important.

3. Condition for almost no loss of volatiles

Applied to water, inequality (46) shows whether the moisture content \( (C_{w,m}) \) at the surface of the malto-dextrin solution attains equilibrium with the drying air directly after the onset of drying. When the solution is dried in nearly dry air, then \( C_{w,m} \) will be almost zero. In this case a dry film forms immediately after the onset of drying and the acetone retention after drying will be close to 100%. Particularly when dry air is used, the surface of the malto-dextrin will not have to attain equilibrium with the drying air immediately after the onset of drying for an acetone retention of nearly 100% to be achieved. The presence of a more or less dry layer at the surface of the malto-dextrin is sufficient to ensure high retention. The minimum value, which \( B_{i,m} \) \( (C_{w,m}/C_{w,i}) \) must have to guarantee almost no loss of volatiles, is denoted by \( G \). The condition for hardly any volatile loss can then be written

\[
B_{i,m} \frac{C_{w,i}}{C_{w}} \geq G
\]

where \( G \) increases with increasing humidity of the air. The value of \( G \) is also determined by the form in which the liquid is dried: its value for a droplet is greater than that for a slab. Moreover \( G \) can depend to some extent on the type of volatile component, on the nature of the solution to be dried and on the liquid temperature. For droplets of a malto-dextrin solution being dried in air of 55 °C and with a relative humidity of about 15%, the value of \( G \) for acetone can be determined from the measurements in Fig. 7. It is found that the loss of acetone is very small from a malto-dextrin concentration of 340 to 450 g/l onwards (after correction for acetone loss during droplet formation, etc.; see Chapter II, Section 2.2). The mean value of \( k_a \) for the complete surface of these droplets was derived from the evaporation rate of water droplets. For the conditions applicable in Fig. 7, \( k_a \) was equal to 0.15 m/s. At a malto-dextrin concentration of 400 g/l, which corresponds to a moisture content of 65.6%, \( C_{w,m}/C_{w,i} = 2.4 \times 10^{-4} \) and, according to Eq. (11), \( D_a = 2.0 \times 10^{-10} \text{ m}^2/\text{s} \). \( B_{i,m} \) \( (C_{w,m}/C_{w,i}) \) is then equal to 21, which represents the value of \( G \) for this case.

4. Discussion of the measurements with droplets

4.1 Constant-rate period

In Chapter II (see Fig. 5), the drying of a droplet of malto-dextrin solution is divided into period I, a transition period and period II. Periods I and II
belong respectively to the "constant-rate period" and the "falling-rate period". During the constant-rate period the evaporation rate of water differs only slightly from that from a free water surface, since, on account of the high average molecular weight of the malto-dextrin, its molar concentration in the solution is very low. During the falling-rate period, the evaporation rate is first partially and then exclusively determined by the internal transport of water to the surface. During the transition period (between A and B in Fig. 5), part of the water at the surface of the droplet evaporates at a constant rate and part at a falling rate. This transition period is caused by the fact that the evaporation rate varies from the bottom to the top of the droplet, depending on the variation of the boundary layer of the drying air (see Fig. 41A). Water from

Figure 41
A) Flow pattern around a sphere.
B) Evaporation rates around the surface of a sphere, after Frössling 12). The evaporation rate is proportional to the distance between the curve and point P.

the bottom of the droplet evaporates faster than that from the rest of the surface and will therefore reach the falling-rate period sooner. The rate of evaporation is lowest at that point where the streamlines of air movement diverge from the surface of the droplet. Frössling 12) has measured the evaporation rate around the surface of a naphthalene sphere. This is shown in Fig. 41B in which the distance from a point on the curve to point P is proportional to the rate of evaporation (arbitrary units). There is no transition period with spray drying, since in this case the droplet rotates. The results with droplets in Figs. 5, 6 and 7 and the measurements and calculations with slabs (see Chapter V, Section 4) suggest that, at least for the experiments described in Chapter II, acetone escapes during the constant-rate evaporation only. Use is made of this observation in the ensuing qualitative discussion. Furthermore, for the sake of convenience it is assumed in the discussion that there is no transition period for the measurements with droplets in Chapter II, but only a constant-rate period and a falling-rate period.
4.2 Internal circulation and the influence of viscosity on acetone retention

The equations for fluid motion inside a drop showing internal circulation have been solved by Hadamard. Fig. 42 shows some steady-state path lines for liquid movement in a vertical plane through the centre of a droplet. This figure is taken from a paper by Kronig and Brink. The circulation velocity decreases with decreasing droplet size and with increasing viscosity of the droplet liquid. A literature survey of the behaviour of drops with internal circulation has been compiled by Sideman and Shahai. The circulation pattern in the drops of the 100 g/l maltose-dextrin solution, used in these experiments, resembles that shown in Fig. 42. The circulation time of a chalk powder particle was found to be about 0.9 sec. Since the acetone loss during this time will be small, there is no large gradient of acetone concentration along a streamline, except for those streamlines passing through a thin layer near the surface. The diffusion distance in a droplet showing circulation therefore is shorter than in the case of non-circulation and desorption will occur more quickly. Kronig and Brink have derived that the rate of mass transfer is multiplied by a factor of 2.5 for such a case of internal circulation, provided the surface concentration may be assumed zero. This is confirmed experimentally by Hoertjes et al. and by others. This means that an increase of the viscosity does not necessarily mean an increase of the acetone retention. A higher retention is achieved only if the circulation time is increased to such an extent that desorption during this time becomes considerable. The maximum effect obtainable by increasing the viscosity is achieved when the circulation is totally prevented. When \( C_{\infty} = 0 \), the effective value of \( D_a \) is then decreased by a factor 2.5.

4.3 Influence of the drying conditions on acetone retention

In Section 2 of this chapter it was found that the concentration of acetone at the surface of the droplet can be taken as zero soon after the onset of drying. This means that the loss of acetone from the droplet depends almost exclusively on the effective value of \( D_a \) in the droplet and the duration of the constant-rate period \( (t_c) \). It has not been proved for all cases that acetone escapes only during the time \( t_c \) but, as already mentioned, this is assumed to be valid for
all the experiments of Chapter II. The retention of acetone decreases at increasing relative humidity \( H_r \) of the drying air (see Figs. 9 and 15). This is because the evaporation rate of water \( (N_w) \) then decreases in accordance with Eq. (24), resulting in a longer \( t_s \). In Fig. 9, where the air temperature is kept constant, an increase of \( H_r \) is accompanied by an increase of the liquid temperature. This results in an increase of \( D_w \), in accordance with the Arrhenius equation (Eq. 15) and, thus, in an enhancement of the acetone loss. This is not the case in Fig. 15, since there the slab temperature is kept constant. During the constant-rate period, \( N_w \) is proportional only to the square root of the air velocity, provided \( Re \gg 2 \). The influence of the air velocity (Fig. 10) is therefore not very large. Fig. 11 shows that, below 100 °C, an increase of the air temperature results in a higher acetone retention. This can be explained by the increase in \( N_w \) with increasing air temperature, which results in a reduction in \( t_s \). The influence of the air temperature, however, is less pronounced than that of \( H_r \), since at a higher air temperature (and constant \( H_r \)) the droplet temperature, and thus \( D_w \), increase. This partially offsets the effect of a shorter constant-rate period. Since the moisture content during the constant-rate period is high, the value of \( D_w \) will not differ very much from its value in water. The energy of activation for diffusion in water of a compound with not too high a molecular weight is in the region of 4.6 Kcal/mole. For water \( E = 4.3 \) Kcal/mole \(^{27}\) while for a number of hydrocarbons it is found that \( E = 4.6 \) Kcal/mole \(^{27}\). This means that, in the temperature range used, \( D_w \) increases by a factor of 1.3 when the droplet temperature rises 10 °C.

5. Discussion of the spray drying process

One can assume that the Sherwood number for the small droplets in a spray drying tower is approximately equal to 2 \(^{47,48}\). It therefore follows that

\[
k_w = \frac{D_{aw}}{r} \tag{48}
\]

where \( r \) is the radius of the droplet and \( D_{aw} \) is the diffusion coefficient of water vapour in the gas phase at the so-called film temperature, which can be approximated by the half sum of the temperature of the surface of the droplet and the air temperature. Substitution of Eq. (48) in (47) gives the following condition for only slight loss of volatiles during spray drying:

\[
\frac{D_{aw}}{D_w} \cdot \frac{C_{aw}}{C_{ad}} \gg G \tag{49}
\]

This condition is independent of the droplet size. The left-hand side of the expression increases with increasing dry matter content, owing to the fact that \( D_w \) decreases. The temperature dependence arises above all because \( C_{aw} \) increases markedly with increasing droplet temperature. The influence of temperature may be seen clearly in the light of the following example. When an aqueous 50% solution of malto-dextrin is spray dried at an air inlet temperature of 55 °C and a wet bulb temperature of 20 °C \((H_r = 1/6)\), then:

\[
G = 21 \text{ (see Section 3 of this chapter)}
\]

\[
\frac{C_{aw}}{C_{ad}} = 2.8 \times 10^{-5} \text{ (at 20 °C)}
\]

63
\[ D_w = 1.2 \times 10^{-10} \text{ m}^2/\text{s} \quad \text{(at 20 °C)} \]
\[ D_{we} = 2.7 \times 10^{-5} \text{ m}^2/\text{s} \quad \text{(at 37 °C, half sum of 20 °C and 55 °C)} \]

This gives \( \text{Bi}_w (C^{w*}/C_{we}) = 6 \), which is not sufficient to obtain a high acetone retention after drying. A comparable air temperature is used in the "Biers" spray towers \(^{49, 50, 51}\), so that a high loss of volatiles will occur during this process. Moreover, in a Biers spray tower the air flows in a direction opposite to the droplets, so that the newly formed droplets are surrounded by humid air. In view of the measurements in Fig. 9, no volatile retention of any significance may be expected. When, however, an air inlet temperature of 200 °C is used in a spray tower and the air flows in the same direction as the droplets (as is the usual practice in the food industry), then, if the initial droplet temperature is assumed to be 60 °C, we find:

\[ \frac{C^{w*}}{C_{we}} = 2.1 \times 10^4 \quad \text{(at 60 °C)} \]

\[ D_w = 3.2 \times 10^{-10} \text{ m}^2/\text{s} \quad \text{(at 60 °C; activation energy for diffusion taken as 4.6 Kcal/mole)} \]

\[ D_{we} = 4.0 \times 10^{-5} \text{ m}^2/\text{s} \quad \text{(at 130 °C, \( D_{we} \) taken as being proportional to \( T^{1/2} \))} \]

\( \text{Bi}_w (C^{w*}/C_{we}) \) now becomes equal to 26, which is sufficiently high to satisfy condition (49), provided \( G \) has not increased too much at this higher temperature. Thijsen's measurements with coffee extract (see Fig. 1), which were carried out under comparable conditions, are in agreement with this retention reaching a more or less constant value at an initial concentration of about 50%.

This value, however, is still well below 100%, on account of the loss of volatiles which occurs during forming of the droplets and the additional loss due to the puffing of the droplets. During droplet formation and in the newly formed droplet, which is still vibrating violently, turbulence can develop whereby the effective diffusion coefficients of the volatiles are appreciably increased. Since this turbulence becomes less marked and is more quickly damped as the viscosity of the liquid becomes higher, it may be expected that the retention of volatiles after drying will increase slightly with increasing viscosity. With spray drying, condition (44) is readily satisfied for volatiles with \( \alpha_{we} \gg 1 \). There will therefore be no relationship between the value of \( \alpha_{we} \) for these volatiles and their loss during drying. This is corroborated by the measurements of Thijsen (Fig. 1).
SUMMARY

When juices and extracts with a dry matter content above 40% are spray dried, the retention of aroma components is surprisingly high, even for those components which are much more volatile than water. In this thesis, acetone is taken as a model for a volatile aroma component, and its retention during air drying is investigated in detail and explained. An aqueous solution of partially hydrolyzed starch (malto-dextrin) served as a model juice or extract. The acetone concentration in drying droplets and slabs of this solution was measured and the influence of the most important factors on the acetone retention was examined. More rapid drying generally resulted in a higher acetone retention. The most striking effects on retention were those of the relative humidity of the drying air and the malto-dextrin concentration of the solution. Although, in an aqueous 40% solution of malto-dextrin at 20 °C, acetone is approximately 90 times more volatile than water, an acetone retention of almost 80% was measured after the solution had been rapidly dried. This high retention is found to be caused by an almost dry film which forms at the surface of the liquid. The film is permeable to water but almost impermeable to acetone. Its selectivity is not due to sorption of acetone. This is apparent from, among other things, measurement of the influence of the water concentration on the activity coefficient of acetone in malto-dextrin solution. This activity coefficient increases slightly with decreasing moisture content (from about 8, in nearly pure water, up to 21 at a moisture content of 15%). At a moisture content of about 11%, however, the activity coefficient of acetone becomes very large. This transition point, which was called the "moisture limit", was likewise determined for a series of other volatile substances. A linear relationship was found to exist between the moisture limit for these volatiles and their molecular "diameter".

The selectivity of the almost dry film is found to be due to the fact that the diffusion coefficient of water ($D_w$) in malto-dextrin with a low moisture content is appreciably higher than that of acetone ($D_a$). $D_w$ was determined from measurements of the sorption of acetone by a layer of malto-dextrin at moisture contents above 10%. $D_a$ was derived from sorption and desorption measurements at malto-dextrin moisture contents varying from 10 to 30%. Over the ranges investigated, log $D_a$ was found to be proportional to $C_w^{-1/2}$ and log $D_w$ proportional to $C_w^{-1}$, where $C_w$ is the water concentration (kg/m³) in the malto-dextrin. The diffusion coefficients of benzene, carbon tetrachloride and ethyl acetate were also measured at a few moisture contents. For these three compounds and acetone, log $D$ was approximately proportional to the molecular diameter. The diffusion characteristics of volatiles in malto-dextrin can be qualitatively explained by assuming that diffusion takes place through "holes" which arise between the carbohydrate molecules as a result of thermal agitation. That $D_w$ in malto-dextrin with a low moisture content is in general appreciably greater than the diffusion coefficients of aroma components is, according to this "hole theory", mainly due to the fact that the water molecule is smaller than the molecules of the odour components.

With the help of the expressions derived for $D_w$ and $D_a$, the water content and acetone content of a drying layer of malto-dextrin were calculated by numerically solving the differential equations for diffusion. The boundary conditions of these differential equations are dependent on the activity coeffi-
ciency of water and acetone in malto-dextrin. The calculated water and acetone contents are found to be in good agreement with the experimentally determined values. Both the calculations and, as far as could be established, the measurements indicated that acetone loss upon drying took place almost exclusively during the "constant-rate period". The extent of the acetone loss is primarily determined by the duration of this period. The acetone loss is only very slight if, at the onset of drying, the value of the dimensionless group

\[
\frac{Bi_w C^{eq}_{\text{w}}}{C_w}
\]

is sufficiently large. Here \(Bi_w\) is the Biot number for water transport and \(C^{eq}_{\text{w}}\) is the equilibrium water concentration (kg/m³) in the gas phase corresponding to a water concentration \(C_w\) in the solution to be dried. The minimum value of the group necessary to ensure high acetone retention increases with increasing relative humidity of the drying air. For a droplet it is larger than for a slab. For droplets of malto-dextrin solution being dried in almost dry air of 55 °C, this minimum value is equal to 21.
SAMENVATTING

Bij het sproei-drogen van sappen of extracten met een vaste stof gehalte boven 40% blijkt een verandering hoge retentie op te treden van geurcomponenten, ook al zijn deze zeer veel vliechtiger dan water. In dit proefschrift wordt de retentie van aceton, als model voor een vliechtige geurcomponent, bij het drogen in lucht nader onderzocht en verklaard. Een oplossing in water van gedeeltelijk hydroliseerd zetmeel (malto-dextrine) werd als model voor een sap of extract gebruikt. De acetonconcentratie in drogende druppels en laagjes van deze oplossing werd gemeten en de invloed van de belangrijkste factoren op de acetonretentie werd nagegaan. Sneller drogen bleek in het algemeen te resulteren in een hogere acetonretentie. Het meest opvallend was de invloed op de acetonretentie van de luchtvochtigheid en de malto-dextrineconcentratie van de oplossing. Hoewel aceton in b.v. een 400 g/l malto-dextrine oplossing in water bij 20 °C ca. 90 maal zo vliechtig is als water, werd na snel drogen van deze oplossing een acetonretentie gemeten van bijna 80%. Deze hoge acetonretentie blijkt te worden veroorzaakt doordat zich bij snel drogen een bijna droog laagje op het vloeistofoppervlak vormt. Dit vloeit laat water door, maar bijna geen aceton. De selectiviteit van dit bijna droge laagje wordt niet veroorzaakt doordat het aceton sorsbeert. Dit blijkt onder andere uit meting van de invloed van de waterconcentratie op de activiteitsscificiteit van aceton in de malto-dextrine oplossing. Deze activiteitsscificiteit stijgt weinig bij alsmede vochtgehalte (van ongeveer 8 in bijna zuiver water tot 21 bij een vochtgehalte van 15%). In de buurt van een vochtgehalte van 11% wordt echter de activiteitsscificiteit van aceton zeer groot. Voor een reeks andere vliechtige stoffen werd dit overgangspunt, dat "vochtgrens" genoemd, eveneens bepaald. Er bleek een lineair verband te bestaan tussen de vochtgrens en de molecuul-diameter van deze vliechtige stoffen.

De selectiviteit van het bijna droge filmpje blijkt te worden veroorzaakt doordat de diffusiecoëfficiënt van water (Dw) in malto-dextrine met een laag vochtgehalte aanzienlijk hoger is dan die van aceton (Da). Da werd bepaald uit sorptiemetingen aan een laag malto-dextrine met vochtgehalten boven 10%. Dw werd bepaald uit sorptie en desorptiemetingen bij malto-dextrine vochtgehalten variërend van 10 tot 30%. Het bleek dat log Dw in het gebied waarin gemeten werd, evenredig is met C1,42 en log Da met C4. Da is de waterconcentratie in de malto-dextrine (kg/m3). Bij enkele vochtgehalten werden diffusiecoëfficiënten gemeten van benzene, tetrahydrokoelstof en ethylacetaat. Voor deze 3 stoffen en aceton was log D ongeveer evenredig met de diameter van het betrokken molecuul. Het diffusiegredag van vliechtige stoffen in malto-dextrine kan kwalitatief verklaard worden door aan te nemen dat de diffusie plaats vindt via "gaten", die tussen de koolhydraatomoleculen ontstaan tengevolge van de warmtebeweging. Dat Dw in malto-dextrine met een laag vochtgehalte over het algemeen aanzienlijk groter is dan de diffusiecoëfficiënten van geurcomponenten wordt volgens deze "gaten-theorie" voornamelijk veroorzaakt door het feit dat het watermolecuul kleiner is dan de moleculen van geurcomponenten.

Met behulp van de gemeten relaties voor Da en Dw werd het water en het acetongehalte in een drogende laag malto-dextrine oplossing berekend door de differentiaalvergelijkingen voor diffusie numeriek op te lossen. De randvoorwaarden van deze differentiaalvergelijkingen hangen af van de activiteits-
coëfficiënten van water en aceton in malto-dextrine. De berekende water- en aceton gehaltes blijken goed overeen te stemmen met experimenteel waargenomen waarden. Bij de berekeningen en voor zover kon worden nagegaan ook bij de metingen, bleek dat tijdens droging het acetonverlies vrijwel uitsluitend optrad gedurende de "periode van constante droog snelheid". De duur van deze periode bepaalt in de eerste plaats het acetonverlies. Zeer weinig verlies van vluchtige stoffen treedt op indien bij aanvang van de droging de dimensieloze groep:

\[ \frac{B_{lw} C_{w0}}{C_{e0}} \]

voldoende groot is. Hierin is \( B_{lw} \) het Biot-getal voor watertransport en \( C_{w0} \) de evenwichtswaterconcentratie (kg/m³) in de gasfase, behorend bij een waterconcentratie \( C_w \) in de te drogen oplossing. De waarde die deze groep hiertoe moet hebben, stijgt bij een toename van de vochtigheid van de lucht. Voor een druppel is deze waarde groter dan voor een drogende laag. Voor druppels malto-dextrine oplossing, drogend in bijna droge lucht van 55 °C is deze minimale waarde gelijk aan 21.
APPENDIX

1. Mutual diffusion coefficient

The mutual diffusion coefficient \(D_{ab}\) in a system with components a and b can be defined by:

\[
N_a - \frac{C_a}{C_a + C_b} (N_a + N_b) = -\frac{C_a}{C_a + C_b}D_{ab} \frac{\delta}{\delta x} \left( \frac{C_a}{C_a + C_b} \right)
\]  
(50)

where \(N\) is mass flux relative to stationary coordinates. If no volume change on mixing occurs, the net volume flow is zero, thus:

\[
\frac{N_a}{\rho_a} + \frac{N_b}{\rho_b} = 0
\]  
(51)

where \(\rho\) is density. From Eq. (51), it follows that the net mass flux is given by:

\[
N_a + N_b = \rho N_a
\]  
(52)

where:

\[
\rho = 1 - \frac{\rho_b}{\rho_a}
\]  
(53)

Furthermore, if the partial volumes are constant, it can be derived that

\[
C_a + C_b = \rho C_a + \rho_b
\]  
(54)

which gives:

\[
\frac{\delta}{\delta x} \left( \frac{C_a}{C_a + C_b} \right) = \frac{\rho_b}{(\rho_a + \rho C_a)^2} \frac{\delta C_a}{\delta x}
\]  
(55)

Substitution of Eqs. (52), (54) and (55) in Eq. (50) yields:

\[
N_a = -D_{ab} \frac{\delta C_a}{\delta x}
\]  
(56)

As already pointed out in the literature, this means that \(D_{ab}\) and \(D\) in Eq. (3) are equal, provided no volume change on mixing occurs. (This volume contraction for malto-dextrin/water is, maximally, 6% of the volume of the malto-dextrin.)

2. Deviation of the transformation equations (30) and (31)

The relationship between the malto-dextrin concentrations \(\Gamma_m\) and \(C_m\) is given by:

\[
\Gamma_m = \frac{\nu^*}{V} C_m
\]  
(57)

\(\nu^*\) and \(V^*\) are respectively the unit volumes of the stationary and the shrinking coordinate system, both expressed relative to the former coordinate system.
Since \( \Gamma_m \) is by definition constant and equal to \( C_{\text{mac}} \), it follows from Eq. (57) that:

\[
\frac{V^n}{V} C_m = C_{\text{mac}}
\]  

(58)

If the small volume contraction which occurs upon mixing water and maltodextrin is neglected, the following is valid:

\[
C_m = (1 - \frac{C_{\text{mac}}}{\rho_m}) \rho_m
\]  

(59)

where \( \rho_m \) and \( \rho_m \) are the densities of water and maltodextrin respectively. From Eqs. (58) and (59), it follows that the proportional change in the unit volume is given by:

\[
\frac{V^n - \rho_m - C_{\text{mac}}}{\rho_m - C_{\text{mac}}}
\]  

(60)

and, thus, the concentration in the shrinking units by:

\[
\Gamma = (\frac{\rho_m - C_{\text{mac}}}{\rho_m - C_{\text{mac}}}) C
\]  

(61)

Since the volume change takes place solely at the expense of the slab thickness, the unit of length across the slab is altered by the same factor as the unit volume. Thus,

\[
d\xi = (\frac{\rho_m - C_{\text{mac}}}{\rho_m - C_{\text{mac}}}) dx
\]  

(62)

The shrinkage factor, Eq. (60), can be converted as follows:

\[
(\frac{\rho_m - C_{\text{mac}}}{\rho_m - C_{\text{mac}}}) = \frac{\rho_m (\rho_m - C_{\text{mac}} - C_{\text{mac}} + C_m) - C_{\text{mac}}C_m + C_{\text{mac}}C_m}{\rho_m (\rho_m - C_{\text{mac}})} =
\]

\[
= \frac{\rho_m - C_{\text{mac}} + (\frac{\rho_m - C_{\text{mac}}}{\rho_m - C_{\text{mac}}}) C_m}{\rho_m} = \frac{\rho_m - C_{\text{mac}} + \Gamma}{\rho_m}
\]  

(63)

From Eqs. (61), (62) and (63) follow finally Eqs. (30) and (31) of Chapter V.

3. The initial sorption by a swelling or shrinking layer

In a swelling or shrinking layer the equations quoted in Chapter IV, Section 1.2, can still be used \(^{14}\), provided that the diffusion coefficient and the layer thickness are replaced by \( D' \) and \( \delta' \) respectively, which are the diffusion coefficient and layer thickness expressed in the shrinking system of units.

Eq. (8) then becomes:

\[
\frac{q}{q_{\text{so}0}} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{D' \cdot t}{(\delta')^2}}
\]  

(64)
From Eq. (62) it follows that the relationship between \( d' \) and the slab thickness \( d \), at a certain time at which the average water concentration in the slab equals \( \bar{C}_w \), is given by:

\[
d' = \int_0^d \frac{\rho_w - C_w}{\rho_a - C_{\infty}} \, dx = \left( \frac{\rho_w - \bar{C}_w}{\rho_a - C_{\infty}} \right) d
\]  

(65)

With the aid of Eqs. (33) and (65), we find for Eq. (64):

\[
\frac{q}{q_{\infty}} = \left( \frac{\rho_w - C_w}{\rho_a - C_w} \right) \frac{2}{\sqrt{\pi \cdot D_w t}} \sqrt[3]{\frac{D_w t}{d^3}}
\]  

(66)

\( C_w \) and \( \bar{C}_w \) are functions of \( t \), and \( C_w \) is moreover a function of \( x \). Eq. (66) is by approximation identical with Eq. (8) if:

\[ C_1 \ll \rho_w \quad \text{and} \quad C_2 \ll \rho_w \]  

(67)

or if

\[ C_2 - C_1 \ll \rho_w \]  

(68)

where \( C_1 \) and \( C_2 \) are the initial and final concentrations respectively. In the measurement of \( D_w \), inequality (68) is satisfied, so that Eq. (8) may be applied.
SYMBOLS USED

A  area of (de)sorption surface, or constant in Eq. (12).
a  activity.
B  intrinsic mobility, or constant in Eq. (12).
Bi  Biot number for mass transfer.
C  concentration in liquid or solid phase or, with subscript c, in gas phase (kg/m³).
C∞c  concentration in gas phase in equilibrium with the liquid (kg/m³).
C∞w  saturated water vapour concentration in gas phase (kg/m³).
D  diffusion coefficient in liquid or solid phase or, with index c, in gas phase (m²/s).
D'  diffusion coefficient in a frame of reference based on a fixed amount of malto-dextrin (m²/s).
Dw  diffusion coefficient of water determined from desorption experiments (m²/s).
D∞  constant in Arrhenius relation, Eq. (15), (m²/s).
D∞w  constant in Eq. (11).
Dw  diffusion coefficient of water determined from sorption experiments (m²/s).
d  thickness of a layer (in contact with the gas phase on only one side), or "diameter" of a molecule.
E  energy of activation for diffusion.
E f  energy of "hole" formation.
E m  energy barrier for the "jump" of a diffusant atom into a "hole".
F  constant in Eq. (26).
G  lowest value of Biw (C∞w/Cw) at which hardly any loss of a volatile component takes place during drying; or constant in Eq. (13).
H r  relative humidity of drying air.
h  partial heat transfer coefficient in gas phase.
J  constant in Eq. (26).
K  constant in Eq. (26).
k  partial mass transfer coefficient in gas phase.
l  half thickness of a slab (in contact with the gas phase on both sides).
log  logarithm to the base 10.
M  weight of a component present in a solution (kg).
M∞c  weight of a component present in a solution at the end of evaporation (kg).
N  mass flux per unit area (kg/m²/s).
P  constant in Eq. (28).
p  \( 1 - \theta_w/\Theta_w \).
q  total amount (de)sorbed after time t (kg).
q∞  total amount (de)sorbed after infinite time, i.e. equilibrium (de)sorption (kg).
\( R \)  gas constant.
\( Re \)  Reynolds number.
\( r \)  droplet radius (shape of droplet considered as a sphere).
\( S \)  constant in Eq. (28).
\( Sh \)  Sherwood number.
\( T \)  absolute temperature (°K).
\( T_a \)  air temperature (°C).
\( t \)  time.
\( t_{50} \)  time after which \( C_{eq} \approx 0 \).
\( t_s \)  duration of constant-rate period.
\( t_{1/2} \)  time at which \( q/q_{50} = \frac{1}{2} \).
\( U \)  constant in Eq. (28).
\( x \)  length coordinate.
\( \alpha_{ac} \)  volatility of acetone or aroma component relative to water.
\( \Gamma \)  concentration in a frame of reference based on a fixed amount of malto-dextrin (kg/m³).
\( \gamma \)  activity coefficient.
\( \Delta H \)  latent heat of evaporation of water.
\( \Delta T \)  temperature difference between drying air and slab.
\( \mu \)  chemical potential.
\( \rho \)  density (kg/m³).
\( \xi \)  length coordinate in a frame of reference based on a fixed amount of malto-dextrin (m).
\( \Omega \)  constant in Eq. (13).
\( % \)  percentage by weight (unless otherwise stated).

**SUBSCRIPTS** (where not already mentioned)

\( a \)  acetone or aroma component.
\( c \)  gas phase or drying air.
\( i \)  interface (liquid or solid phase).
\( ic \)  interface (gas phase).
\( l \)  liquid.
\( o \)  \( t = 0 \).
\( w \)  water.
REFERENCES

32. S. Prager and F. A. Long, J. Am. Chem. Soc. 73 (1951) 4072.
47. W. F. Manning and W. H. Gauvin, A. I. Ch. E. J. 6 (1960) 84.
STELINGEN

1. De veronderstelling van Gur-Arie, Nelson en Steinberg, dat de door hen gemeten volumecontractie bij sorptie van water door meel uitsluitend wordt veroorzaakt door waterbinding is onjuist. 

2. Merson en Morgan suggereren dat de door hen gemeten invloed van de concentratie van de vloeistof op de permeatiesnelheidscoefficiënt (K) bij omgekeerde osmose wordt veroorzaakt door de afhankelijkheid van K van de druk. Deze suggestie is in strijd met in dezelfde publicatie genoemde metingen.
R. L. Merson en A. I. Morgan Jr., Food Technol. 22 (1968) 631.

3. Geheel ten onrechte houden Hall en Lawrence bij hun meting van de diffusiecoëfficiënt van water (D) in macaroni geen rekening met de afhankelijkheid van D van de waterconcentratie.

4. De veronderstelling van Reid en zijn medewerkers, dat bij omgekeerde osmose de grote diffusiesnelheid van water door de cellulaire-aanstaal membranden ontstaat doordat het water waterstofbruggen kan vormen met de polymeermatrix, is niet in overeenstemming met experimenten van Honeycutt.

5. Saravacos en Moyer interpreteren hun metingen over de invloed van de druk op de aромarentie bij vacuum drogen onjuist.

6. De bewering van Michaels, dat met een membraan, in contact met een vloeistof waarin het onbepaald oplosbaar is, geen permeatieproces uitgevoerd kan worden, is niet juist.

7. Extrapolering vanuit de huidige stand van de techniek heeft omgekeerde osmose geen toekomst bij het concentreren van voedingsmiddelen.

18 februari 1969

L. C. Menting
Retention of volatiles during the air drying of aqueous carbohydrate solutions

Errata

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<td>After Eq. 33</td>
<td></td>
<td>Although not strictly valid, Eq. 32 is also used for acetone.</td>
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