A critical review on anomalous or non-fickian vapor sorption

Wadsö, Lars

1992

A Critical Review on Anomalous or Non-Fickian vapor Sorption

Lars Wadsö
Division of Building Materials
Lund University
Box 118, S-221 00 LUND, Sweden

June 22, 1992

Abstract

In many cases of vapor transport and sorption it has been found that Fick's law can not adequately describe the processes. This paper reviews the experiments made to describe non-Fickian behavior, and the models which help in explaining the phenomena. The non-Fickian (or anomalous) behavior is very complex as non-Fickian sorption in general means everything that is not Fickian. In the present paper is presented a new definition of anomalous behavior which concentrates on the causes of the phenomena, not on its effects.

The articles reviewed provides a massive evidence of non-Fickian behavior in polymers, wood and fibers. The measurements on polymer-penetrant systems being the most valuable as wood and fibers are very complex polymer systems. Certain characteristics of anomalous sorption seems to be found in many systems. This includes absorption at higher vapor concentrations showing more non-Fickian behavior, and that sorption is often found to have two stages, the first of which is Fickian.

Many models of anomalous sorption have been made but none can describe all aspects of non-Fickian behavior seen in experiments. In most models the anomalous behavior is seen as being caused by either a surface concentration which is not in equilibrium with the external vapor pressure, or by interactions between sorption and swelling stresses.

Case II (linear kinetics) is seen by many authors as a second limiting case (Fickian diffusion being the first). This view is not shared by the present author.

Contents

1 Introduction

This is the first version of a critical review on anomalous sorption. I do not consider it a finished product; therefore it is only published as an internal report.

The review is quite compact and can be difficult to read even if I have tried not to use too many terms from polymer chemistry. A list of most of the nomenclature used, and an introduction which explains the basic concepts, is included. The review has <u>not</u> been reviewed with respect to my usage of the english language.

I will continue to penetrate the papers reviewed here so that I can write a second better review which (at least partly) will be used in the articles I write for my thesis.

All comments are encouraged!

The support by the Swedish Council for Building research is gratefully acknowledged.

2 Nomenclature

To shorten the text I have used abbreviations for the most commonly used parameters (which are not the same as in the original articles):

a, b	constants in various equations	
c	concentration of permeant in polymer	kg/m^3
D_c	diffusivity with c as potential	m^2/s
D_p	diffusion coefficient with p as potential	$kg/(m\ s\ Pa)$
E	dimensionless sorption $(\Delta M(t)/\Delta M_f)$	
ℓ	characteristic length (half thickness of rectangular sample)	m
M	weight	kg
ΔM	weight change	kg
p	vapor pressure	Pa
r	radius	m
RH	relative humidity	%
T_g	glass temperature (see page 4)	°C
t	time	s
τ	characteristic time scale	s

The following indices have been used:

d	diffusion
i	initial (at start of sorption)
f	final (at end of sorption, equilibrium value)
r	relaxation
s	saturation (p_s is saturation vapor pressure

3 Introduction

3.1 basic concepts

This review is about transport and sorption of vapors (penetrants) in solid materials (polymers). For each such pair of material and vapor a steady state **sorption isotherm** is defined as the amount of vapor which the material absorbs as a function of the vapor pressure (Fig. 1). In the following such a curve is thought to exist, despite the problems in attaining equilibrium which are described. The sorption curve has the functional form

$$c = c(p) \tag{1}$$

where c is the vapor concentration of the material (in kg/m^3) and p is the vapor pressure (in pressure units of Pa).

The transport by diffusion is usually modelled by **Fick's law**:

$$-g = D_p \cdot \frac{dp}{dx} \tag{2}$$

where g is flow (in units of kg/(m^{2}s)), D_p is the diffusion coefficient (in units of kg/(Pa m s)) and x is distance (in m). Fick's law was originally stated with a potential of concentration:

$$-g = D_c \cdot \frac{dc}{dx} \tag{3}$$

(here the diffusivity D_w has units of m^2/s). These two formulations are as good and D_w can be transformed into D_p, and vice versa, provided the slope of the sorption curve is known ($dw(p)/dp$).

I have used the term **absorption** (which is the opposite of **desorption**), because it is a more general term than adsorption (which usually denotes absorption on a surface).

The terms diffusivity, diffusion coefficient and permeability can have different meanings to researchers working in different fields. In this text I have used **diffusivity** and **diffusion coefficient** interchangably for the diffusional transport coefficient. **Permeability** is the flow of a gas or a liquid under a gradient in total pressure.

One usually differs between two types of measurements: **steady-state measurement** of the moisture flow through a sample placed between two relative humidities, and **non-steady state measurements** of absorption or desorption (called **sorption (rate) measurement** or **transient measurement**).

In steady-state measurements D_p is measured; in non-steady state measurements D_c is the natural result. If the sorption isotherm is linear in the interval considered one of these can be transformed into the other by:

$$dc \cdot D_c = dp \cdot D_p \tag{4}$$

Non-steady state measurements produce sorption rate curves which are initially linear when plotted against the square root of time. The usual practice has therefore been to show sorption results in plots of $\Delta M(\sqrt{t})$ or $E(\sqrt{t})$ (Fig. 1). Fujita (1961) gives 8 features of such Fickian sorption rate curves (see section 1.2).

Integral sorption is a measurement of weight change after the relative humidity has been drastically changed, often from $p = 0$ to near $p = p_s$. **Interval sorption**, which is also called **differential sorption**, is made in many small steps so that the concentration is the sample does not change appreciably during each step.

The **glass temperature** (T_g) of an amorphous polymer is a very important concept. It is a second order transition temperature, i.e. a temperature at which the qualities of a material changes without any heat release. Above T_g the polymer is rubbery and has low relaxation times; below T_g it is glass-like and has long relaxation times. Non-Fickian behavior is usually associated with long relaxation times, and is therefore found below T_g. Crystalline polymers have a melting temperature (T_m) instead of a glass temperature. As many polymers are partly amorphous and partly crystalline they can show both T_g and T_m but both are then rather indistinct.

I have made frequent use of direct quotations (marked with "...", omitted parts shown with [...], [...abc]). In these texts I have not changed anything; therefore these texts do not always conform to the definitions above.
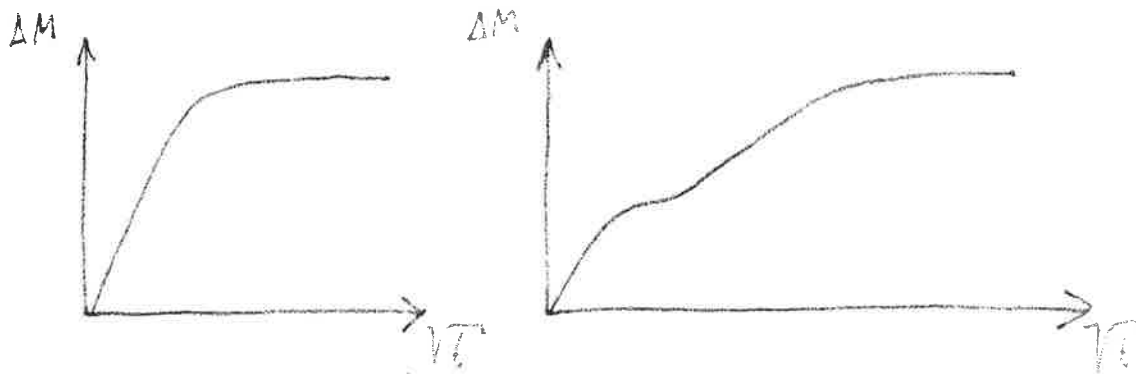
Figure 1: A sorption isotherm (left) and a sorption rate curve (right)

3.2 Fickian behavior

As non-steady state measurements produce sorption rate curves which are initially linear when plotted against the square root of time, the usual practice has been to plot sorption results as $\Delta M(\sqrt{t})$ or $E(\sqrt{t})$ (Fig. 1). Fujita (1961) gives 8 features of <u>Fickian</u> such sorption rate curves which have been used as a test of Fickian behavior:

(a) Both absorption and desorption curves are linear in the region of small values of the abscissa. For absorption the linear region is obtained over 60% or more of [the final weight increase]. When D_w increases markedly with the concentration the absorption is linear almost up to the equilibrium;

(b) Above the linear portions both absorption and desorption curves are always *concave* against the abscissa axis;

(c) The shape of the absorption curve is not very sensitive to the dependance on concentration of D_w. It is often well approximated by the absorption curve for a constant D_w, even when D_w varies appreciably with the concentration. On the other hand, the desorption curve is rather markedly affected by the concentration dependency of D_w;

(d) In both absorption and desorption the concentration distributions in the sample are greatly influenced by the functional form of $D_w(w)$;

(e) When the initial and final concentrations [...] are fixed, the reduced absorption curves for films of different thickness all coincide with each other, yielding a single curve. This applies for the corresponding family of reduced desorption curves;

(f) The single absorption curve so obtained is always above the corresponding single desorption curve when D_w is an increasing function of w. Both coincide over the entire range of the abscissa when and only when D_w is constant. The difference between the two curves becomes more appreciable as D_w increases more sharply with w. If $D(w)$ passes through a maximum the two curves may intersect at some position;

(g) For absorptions from a fixed initial concentration to various final concentrations the initial slopes of the reduced absorption curves are larger as the final concentrations are higher, if D_w increases monotonically with w;

(h) The same relation as (g) applies for reduced desorption curves

Fujita mentions that curves consistent with these criteria, especially with a, b, e and f have been observed for a number of polymer penetrant systems. It is usual practice to regard a given sorption curve as Fickian when it conforms to a and b above.

5

3.3 definitions of anomalous sorption

Generally we have anomalous or non-Fickian sorption when the sorption isotherm together with Fick's law can not alone describe a case of transport or sorption.

Some authors of reviews on anomalous sorption have tried to define anomalous sorption. Fujita (1961) summarizes the features of non-Fickian sorption as follows (compare with the corresponding features for Fickian sorption above) (D is the diffusivity and c_1 is the concentration, t is the time and L for thickness):

(a) In the region of small values of ($\sqrt{t}$) both absorption and desorption curves are not linear;

(b) The absorption curve has an inflection point;

(c) Despite the expectation that D_w should increase with increasing w the paired absorption and desorption plots intersect; the relatively high initial rate of desorption is followed by a very slow rate which leads to intersection of the two curves;

(d) Paired absorption and desorption curves which have the coincident initial slopes do not coincide over the entire region of ($\sqrt{t}$);

(e) The initial slopes of absorption curves from different initial concentrations to a fixed concentration pass through a maximum as the initial concentration increases;

(f) Absorption or desorption curves obtained from varying thickness experiments cannot be reduced to a single curve when plotted against $\sqrt{t}/a$.

All these features do not appear at the same time according to Fujita (1961).

Kishimoto (1972) presents a similar list as Fujita, but also includes that diffusion coefficients determined from steady state measurements are often higher than those from sorption rate measurements.

These lists of non-Fickian features gives rise to a question: Should the results of bad measurements with large errors be called non-Fickian because the sorption rate curves are not linear?

To complement the above definitions I would like to present a definition of non-Fickian behavior which is based on the possible causes of the phenomena, not only on the symptoms:

A transient sorption is non-Fickian if it can not be explained by:

- An equilibrium sorption curve with hysteresis.

- Fick's law with constant or concentration dependant diffusivity.

- External resistances to flow.

- Other sources of error in the measurements (e.g. Temperature changes caused be the sorption).

I have made this definition because I think that we do understand some phenomena (e.g. the surface resistance). We should therefore not say that these cause non-Fickian behaviour. Anomalous sorption behavior should not be caused by experimental errors. This definition should probably be used together with Fujita's, his being the more practical and mine making the researcher think twice before calling a strange sorption phenomena non-Fickian.

As the initial part of a Fickian sorption rate curve is proportional to $t^{0,5}$, non-Fickian sorptions rate curves have similar relationships with an exponent that does not equal 0,5. This has been used by many polymer scientists even if not all rate curves can be fitted to such an expression (see page 16).

This paper is called "A Critical Review on Non-Fickian Sorption". The term "non-Fickian" (explained in the following section) should not be misinterpreted as a criticism of Adolf Fick's original work (a description of which can be found in Tyrell 1964). His law of diffusion, which was derived as an analogy with Fourier's heat conduction law and Ohm's electricity law, is still the base for all calculations of moisture transport. But there are cases where it is not possible to describe transport processes with such a simple equation. This literature review is about such cases.
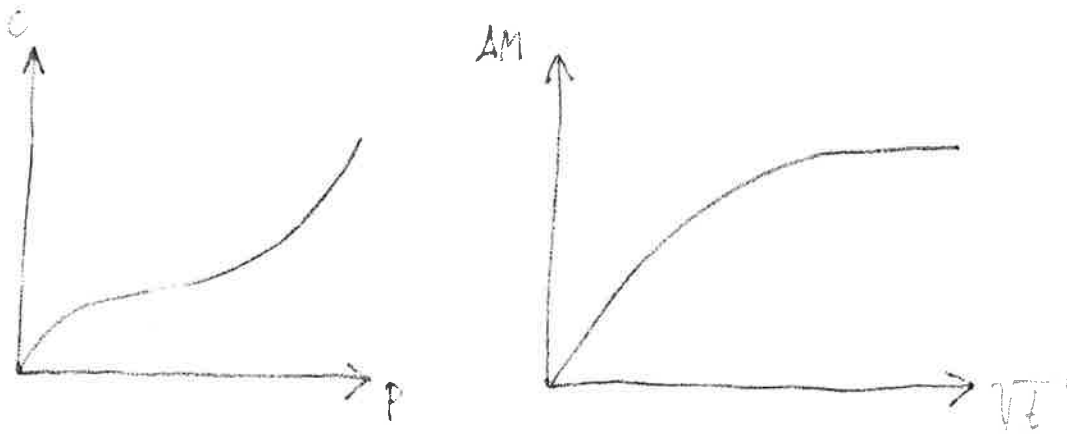
Figure 2: Fickian (left) and non-Fickian (right) sorption rate curves adapted from Kishimoto et al. (1960)

3.4 examples of Fickian and non-Fickian sorption rate measurements

In Fig. 2 are shown two sorption rate curves, one which is Fickian and one which is decidedly non-Fickian (according to the features listed by Fujita 1961).

It will be shown later (page 15) that non-Fickian sorption rate curves can have various forms. Here we restrict ourselves to noting that both Fickian and non-Fickian behavior exists, even for two measurements made in the same way with the same polymer-penetrant system, but under different conditions.

3.5 analogies to non-Fickian behavior

There are basic laws in other scientific fields that corresponds to Fick's law, i.e. they are linear first order equations. Are there also deviations from these simple laws that could be said to be analogies to non-Fickian behavior? There certainly are many such examples where more terms than one are needed to describe experimental observations. Some of these are tabulated below. Note that these examples are not direct analogies, they only serve to illustrate that similar problems have been dealt with by other researchers.

	basic law	deviation
Fick's	mass flow by diffusion $\propto$ mass gradient	non-Fickian behavior
Hook's	strain $\propto$ stress	plasticity, creep
Fourier's	heat flow $\propto$ temperature gradient	convection, radiation
Darcy's	liquid mass flow $\propto$ pressure gradient	deviations at high flow velocities
Ohm's	electrical current $\propto$ voltage difference	time effects with AC

ΔM

abs.

des.

$\sqrt{t}$
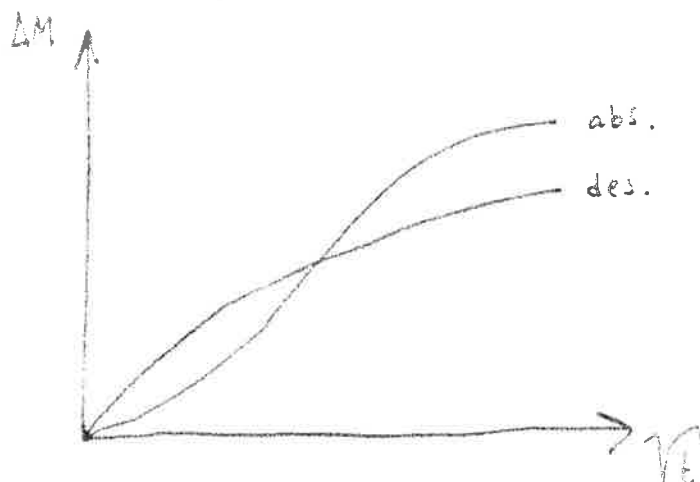
Figure 3: Adapted from Crank & Park 1951

4 Experimental investigations

4.1 polymers

Polymers are natural or synthetic materials composed of very large organic molecules. Except in a few cases I have not stated which polymer-penetrant systems which were used in the different studies as this would have made the review too hard to read (many articles concerns many different systems). The penetrants are usually water vapor for the natural polymers and solvent vapors for the synthetic materials.

The first systematically reported deviations from Fick's law were made in the early fifties (Crank & Park 1951; Long & Richman (1951), Mandelkern & Long 1951) even if there are comments on anomalous behavior in earlier articles (e.g. Hartley 1946).

The anomalous integral sorption rate curves observed did not have any initial linear part, but were concave or convex towards the $\sqrt{t}$-axis (in the latter case they also had an inflection point). The absorption was often initially slower than the desorption, but the two curves crossed each other before reaching equilibrium (see Fig. 3).

Mandelkern & Long (1951) and Park (1953) found inflections in the sorption plots and initially higher sorption in thin films than in thick. They concluded that this could not be caused by behavior in accordance with Fick's law, not even with a concentration dependant diffusivity.

Kokes et al. (1952) and Long & Kokes (1953) made measurements at different temperatures and vapor pressures and found that the behavior was Fickian above T_g, but not below (see page 17). They explained this as being due to the low mobility of the polymer chains below T_g, an explanation than is still used today. The onset of non-Fickian sorption below T_g has been confirmed in other articles (Kishimoto et al. 1961).

Long et al. (1953) and Bagley & Long (1955) made series of interval absorption measurements and found that some sorption rate curves had an initial high slope which later changed to a very slow attainment of equilibrium (Fig. 4). As different film thicknesses were used it was possible to deduce that the initial rapid weight increase was Fickian, whereas the slow second stage was not dependant on thickness. The anomalies in the sorption process was then restricted to the second slower stage.

Bagley & Long (1955) presented more measurements of two-stage curves, some of which had a quasi-equilibrium (the absorption slows down and nearly ceases before starting again). They concluded that "a tentative explanation of these results is that the Fickian, initial sorption stage involves only an elastic expansion of the polymer network without affecting the interchain bonds, and that the rate-determining step for the slow stage is the breaking of these bonds rather than ordinary diffusion".

Measurements were also made of the concentration profiles in polymer samples while they were sorbing a penetrant (Long & Watt 1956, Richman & Long 1960, Long & Richman 1960). It was found that early in the sorption process the surface concentration did only reach a small fraction of its equilibrium value. After that the surface concentration only rose quite slowly. The surface concentration was extrapolated from measurements of the concentration in the sample as it was impossible to measure exactly at the surface of the sample. These authors assumed that it was
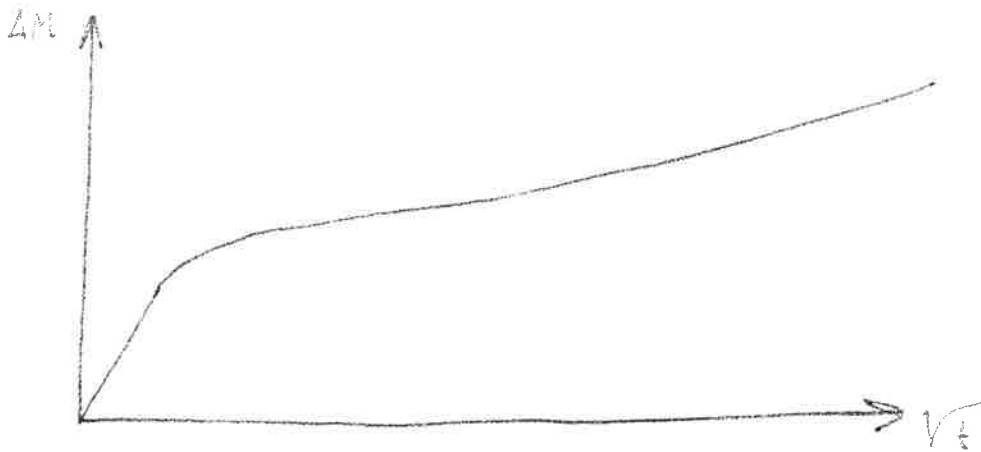
Figure 4: Two-stage absorption curve adapted from Long et al. (1953)

the surface concentration that governed the whole sorption process (see page 23).

Newns (1956, 1959, 1968, 1973, 1974) measured water vapor sorption rates in regenerated cellulose. The resulting curves were linear at low vapor pressure interval sorption, but changed to curves with plateaus and deflections at higher p. Newns also found that if he returned to the p_i before the onset of the second stage of a two stage sorption, no hysteresis was found (the weight of the sample returned to the original weight). If the measurement continued into the second stage a hysteresis effect was found. Two stage behavior was found in both absorption and desorption, but the amount absorbed in the second stage increased as p increased whereas there was little change in the relative amounts desorbed in the two stages. The fraction sorbed in the initial stage at a particular p is smaller if the p had been attained after a succession of small sorptions than if it had been attained after a few larger steps. Ioelovich et al. (1982) have also found anomalous sorption rate curves at higher p for water vapor in cellophane.

A number of articles (Christensen 1959,1965; Sadoh et al. 1958; Sadoh 1960ab; Sadoh & Christensen 1964) have been published about sorption in thin samples of hemicellulose. In these papers diffusion was not considered to be the rate controlling process, but there was some disagreement on how the sorption rate changed with increasing p. In Sadoh & Christensen 1964 this was attributed to the relative thicknesses of the samples measured.

Successive absorptions in very small intervals for several polymer-penetrant systems were studied more closely by Kishimoto et al. (1960) and Odani et al. (1961). They found a pattern in the forms of the successive sorption curves (see page 17) and that the logarithm of the time at which the second stage started was proportional to the initial concentration of the experiment (see page 18).

There is evidence that desorption rate curves are quite normal compared to absorption curves (Kishimoto & Matsumoto 1964), but most articles does only concern absorption measurements.

Alfrey (1965) and Alfrey et al. (1966) studied liquid sorption and found linear kinetics ($E(t)$ is initially a straight line) and called this case II. Similar observations had been made before, but it was Alfrey and co-workers who saw the linear behavior as a limiting type of sorption. They classified diffusion behavior into three categories: case I (Fickian), case II (linear) and anomalous. The latter was thought to be something between the two limiting cases. This view is found in many papers (e.g. Marom 1985), but is not very good according to my opinion (see page 21).

Berens (1977, 1978) and Enscore et al. (1977ab) studied interval sorption into very fine polymer powders. It was found that for nonuniform powders the sorption rate curve could be analysed as a sum of sorption rate curves for different sized particles (this was not and should not be called non-Fickian sorption). At high p anomalous behavior was seen even for uniform powders and this was attributed to the contribution of a relaxation controlled mode of sorption. As integral and interval sorption gave different results "it appears that the presence of a penetrant at the start of a sorption step retards the attainment of equilibrium" (Berens). Enscore et al. found case II behavior in some of their particles.

Mirley et al. (1985) and Schneider et al. (1988) studied sorption on elastomers containing a hard phase. They found a non-Fickian behavior in absorption, which was larger for thinner samples. The anomalous behavior was the result of the hard phase acting like a reinforcement.

9

The swelling of the soft phase (the elastomer) is controlled by the relaxation of the hard phase.

Mee et al. (1985), Sax & Ottino (1985) and Serrano et al. (1987a) also studied the sorption of vapors in polymer blends. Mee et al. found that only a polar solvent at high p/p_s gave anomalous sorption. Sax & Ottino studied the sorption of CO_2, N_2 and O_2 and found anomalous behavior in polymer blends of different volume fractions even if the sorption in the pure components were Fickian. Serrano et al. also found some non-Fickian behavior in the homopolymers.

Some other measurements of anomalous sorption rates should also be mentioned: Park (1961) saw two stage sorption during absorption, but not during desorption. Rogers et al. (1960) found that the sorption became more anomalous when the crystallinity of the polymer increased. Kishimoto & Matsumoto (1964) saw anomalous behavior at temperatures slightly above T_g. Enscore et al. (1977b) found that pre-swelling increased both the rate and the amount of subsequent sorption, and that thermal annealing reduced the same rate and amount. In both cases it was the second relaxation controlled stage that was affected. Barrie et al. (1982) found that larger penetrant molecules produced more non-Fickian behavior in copolymers.

The above mentioned articles are only the most important ones as the literature on non-Fickian behavior in polymers is quite extensive.

A good summary of the situation is given by Enscore et al. (1977a): "The transport of organic molecules in glassy polymers often does not fit the Fickian diffusion model. Fickian diffusion is often encountered in glassy polymers for sorption at low activities and for desorption". Because of the large numbers of polymers and penetrants used in these studies it is hard to make a summary of non-Fickian behavior in polymers. The reader is referred to section 3 for a further discussion of the characteristics of anomalous behavior.

4.2 wood

Wood is a natural polymer with a large porosity. The primary components are cellulose, hemicellulose and lignin, which are ordered in a complicated way in the cell wall. Wood has three principal directions (longitudinal, tangential and radial) which have different moisture transport properties. The results discussed below all refers to works done with water vapor as penetrant.

The first evidence of non-Fickian behavior of wood is an article by Christensen & Kelsey dated 1959. In this they show that the wood cell wall absorbs water vapor slowly at high relative humidity. This is contrary to common belief that the wood cell wall is so thin that there is always local equilibrium between the vapor in the cell cavities and the cell wall. This article is very good; as a matter of fact the rest of the papers reviewed in the section on wood does not contain very much more information on anomalous sorption.

The measurements were done in the absence of air. Therefore there was no influence of external resistances. The measurements were done on samples from 20 μm to 2 mm, with little difference in the results. The authors concluded "that diffusion of water in wood was not the factor controlling the rate of sorption".

Different sized integral and interval sorptions were performed. Judging from the times to half sorption smaller steps in p results in longer sorption times. It was also shown that a sample that was initially dryer will reach a higher moisture content, even if both samples are absorbing moisture at the same p. Similar result was obtained by Hergt and Christensen (1965) and McNamara (1969).

A rise in temperature of the samples was measured but it was in all cases less that 1 K after 12 minutes.

In a later parallell study (Christensen 1960) the wood species used was quite unpermeable so there was a size effect at low p. At high p the result was similar to Christensen & Kelsey (1959). An excellent summary of the above works and measurements on regenerated cellulose can be found in Christensen (1965). The evidence that the rate determining process of thin samples is other than diffusion is summarized in three paragraphs in this article:

"(1) The rate of approach to sorption equilibrium is independent of the thickness of the wood specimen below certain limits [...].

(2) For successive equal increments of moisture content but over different ranges, e.g., 0 to 3, 3 to 6, 6 to 9, etc., per cent moisture content, the sorption rate decreases markedly as the value of the initial moisture content increases [...].

(3) For moisture content increases having the same final value, the time required to reach equilibrium increases markedly the smaller the moisture content change involved [...]."

If equilibration was by diffusion with an increasing difusivity would lead to the reverse of these observations.

Comstock (1963) measured diffusion by steady state and non steady state methods. When RH<50% the two types of measurements agreed, but at higher vapor pressures the steady state method gave higher diffusivities than the sorption rate measurements. Desorption was found to be faster than absorption. Comstock proposed that this was the effect of the surface not reaching equilibrium concentration immediately and this was discussed in terms of the effect of stress on the attainment of true equilibrium.

A similar study was made by Prichananda (1966) and Skaar et al. (1970). Below is part of Prichananda's own summary of the experimental result

- The tangential diffusion coefficients for desorption were 5 to 10 times larger than the corresponding values for absorption at the higher humidities.

- The tangential diffusion coefficients for absorption and desorption tend to converge at lower humidities.

- The tangential diffusion coefficients for desorption are in the same order of magnitude as the steady-state coefficients.

- The evaluated tangential diffusion coefficients for thin samples are consistently lower than the values for thick samples. This difference is most pronounced for absorption at high humidities.

The above points led Prichananda to the following conclusions:

- Fick's laws are inadequate to completely describe the process of moisture sorption by wood. Moisture diffusion coefficients calculated in the classical manner show anomalous non-Fickian behavior under certain conditions.

- A second process, involving the rate of bond-breaking or of formation of holes or new sorption sites, is superimposed on the classical Fickian behavior under certain conditions.

According to Prichananda the findings were in agreement with the investigations by Christensen & Kelsey (1959) and Christensen (1960).

Liu Tong (1988) also made both steady state and non steady state measurements and found that desorption diffusivities were larger than those measured at absorption.

Choong and Fogg (1968) made permeability and sorption rate measurements on six wood species. The permeabilities varied but the sorption rates were about the same for all samples. The diffusivities measured with desorption were higher than those measured with absorption in all three directions. The initial part of the sorption rate curves was Fickian but the approach to final equilibrium was "very slow and certainly non-Fickian".

Kelly (1968) and Kelly & Hart (1970) made a study of sorption in the absence of air which was similar to Christensen's works, except that they worked with larger samples and made special studies on the heat effects.

Some results from this investigation:

- Fickian diffusion could not generally describe the sorption behavior.

- desorption over the same vapor pressure range was faster than absorption.

- in most cases larger steps in vapor pressure resulted in a higher final concentration.

- heat of sorption appeared to be an important factor controlling the desorption rate.

McNamara (1969) and McNamara & Hart (1971) tried to measure the effect of stress on the diffusion in wood by studying drying rates and moisture content profiles of the drying samples. Interesting results of this study were:

- Reducing the width to thickness ratio so that less gross stress is developed in drying did not substantially affect the calculated values for the diffusion coefficients.

- The calculated integral diffusion coefficient was close to the maximum value reached by the interval diffusion coefficient for the same moisture content step.

- A moisture gradient was found in wood that has apparently reached equilibrium moisture content. This gradient is probably the result of internal stresses that are developed in the drying of wood.

- Equilibrium moisture content is a function of drying rate. This was shown by the fact that the higher air velocity in desorption gave a lower equilibrium moisture content.

A large number of articles in the field of wood science have been concerned with evaluating measurements of the external resistance to moisture flow (Choong & Skaar 1969, 1972; Hart 1977; Rosen 1982; Dekrét & Kurjatko 1986; Avramides & Siau 1987; Wadsö 1989;). It seems that the surface resistances evaluated from sorption rate experiments invariably are very large; much larger than the theoretically calculated resistance of a thin layer of air. In the light of the above mentioned investigations on non-Fickian sorption it seems natural to assume that the effects treated as being caused by external factors in fact are internal sorption anomalies.

In an article by Avramides & Siau (1987) a two stage sorption rate curve is shown (see page 19). This is the only case of clear two stage sorption reported for wood.

Christensen (1967) and Hunt (1989, 1990) have reported that the swelling of a sample is much faster then the sorption of moisture. Christensen gives no information on how is experiments were performed, and gives no explanations to why swelling should be faster than sorption. Hunt's articles are better, giving the half-times of the different processes and discussing a model for the sorption behavior.

Nearly all observations of non-Fickian sorption in wood have been explained by the word 'relaxation'. This seems to be because no one have tried to model such behavior or look for its causes. No usable model of anomalous behavior in wood exists. Christensen (1959) and Sadoh & Christensen (1964) made some attempts to correlate the times to half sorption with p_i and p_f, but did not try to model whole wood. Kelly & Hart (1970) developed a model for sorption which only is a numerical curve fitting. Some of the models developed for polymers could probably be used for the cell wall, the sorption in whole wood being more complicated.

A summary of the experimental evidence for non-Fickian sorption in wood would have to include the following observations:

1. At high vapor pressures absorption becomes slower and attainment of true equilibrium takes very long time.

2. The non-Fickian effects are not as evident in desorption as in absorption.

3. Larger absorption steps come to equilibrium faster than smaller ones.

4. Samples absorb more moisture when the absorption step is larger, even if the final p is the same.

5. Swelling is faster than sorption at higher vapor pressures

These observations are principally the same as for simple polymer-penetrant systems.

4.3 fibers

Fibers are natural or synthetic materials which have a very high length to width ratio. Most of the are polymeric substances used in the textile industry. Because of their very large exposed area the study of fiber sorption is complicated. Most research in this field has been made on wool fibers.

Many studies have been made on the absorption of dyes in fibers, and in many cases have one found anomalous behavior. These anomalies have for some cases been shown to be produced by the dye bath having a finite content of dye or other external factors (Lindberg 1950).

King & Cassie (1940) measured the temperature rise in a bundle of wool which absorbed water vapor from RH=0 to 100%. They found a 40 K increase in a very short time. Therefore they draw

the conclusion that the sorption rate in the absence of heat effects was very high. The sorption was completely controlled by the temperature rise in their measurement .

This effect of temperature has been discussed a lot by researchers on wool and other fiber material (Morton & Hearle 1986). The results of more than one experimental investigation has been proved to be uncertain by later investigations. Armstrong & Stannet (1966) derived more accurate corrections to measurements with heat effects, but I doubt if they are very useful as corrections. Watt & McMahon (1966) studied the influence of temperature changes during sorption and found that both absorption and desorption was delayed when there were such effects. This is natural as an increase in temperature lowers the higher vapor pressure (at the sample in absorption), and the decrease in temperature rises the lowest vapor pressure (at the sample in desorption).

Denton (1956) found a two-stage behavior of sorption into a fiber of regenerated cellulose. The first stage was attributed to the "diffusion of water from the surface to the center of the filament through regions which are immediately accessible". The second stage was controlled by the "transport of water into regions made accessible by an interaction between them and the water already absorbed". Nothing is mentioned of temperature effects but these might have been negligible as the sorption processes continue for a very long time (more than a week).

Haly & Roberts (1956) found that desorption in wool fibers was initially faster than absorption, but that its rate decreased so that the absorption came to equilibrium before the desorption. They measured the weight of samples before and after they had been in an air stream. Each point in their diagram therefore comes from one sample. Mackay et al. (1969) mentions this article as an example of an article "for which there is evidence that the heat-of-sorption effects are small".

Downes & Mackay (1958) found that "the time required to attain final equilibrium [...] depends on the magnitude of the sorption step, and is considerably shorter for large steps as compared with small". This conclusion is probably right even if there are later evidence that heat effects disturbed the measurements. The measurements were made with the vibroscope technique, i.e. one measures the natural frequency of a single fiber, this being a function of the weight of the fiber.

Downes & Mackay (1958) also found two-stage behavior both in absorption and desorption in wool fibers.

Watt (1960ab, Watt & Algie 1961) made measurements which later were "found to have serious limitations for studying rapid-sorption kinetics of water in wool owing to heat-of-sorption effects". Watt (1960b) interrupted the sorption during the first stage and found no hysteresis. An interruption during the second stage did however produce hysteresis. Watt & Kennett (1960) found that the weight of dry wool was dependant on the moisture prehistory.

Mackay et al. (1969) and Mackay & Downes (1969) seems to have made the best measurements of sorption in wool with an improved vibroscope. The first article concerns the instrumentation and an error analysis. The second paper gives the result from the measurement. In the abstract the authors write that "among the more interesting observations, it is shown that:

(i) after a step change in relative humidity, desorption, other than to zero regain, continued for very long times (in excess of eight days) with no sign of termination, whereas absorption reached completion relatively quickly;

(ii) the position of the desorption limb of the regain versus r.h. isotherm is both time- and size-of-step-dependant;

Walker & Harrison (1971, 1972) measured the sorption into small wool samples and large wool bales and found anomalous behavior, but the value of these works are in my opinion uncertain.

It is hard to make any conclusions about sorption in fibers as heat-of-sorption effects have been shown to play a large role in determining the sorption dynamics. The articles of Mackay et al. (1969) and Mackay & Downes (1969) probably describes the best works done. It is probable that the non-Fickian effects seen for other materials also apply to fibers.

4.4 other materials

Very little work on anomalous behavior seems to have been done in other fields of science on anomalous sorption. Bomben (1973) mentions that it could be expected in foodstuffs. He discusses heat and mass transport in structured foods and makes the following remark concerning a discussed theory: "A further limitation [...] is the fact that it assumes that, although the material as a

whole is a non-equilibrium system, there exists a local equilibrium between the phases within each microscopically small cell. In most food materials the solid matrix between the pores is of a colloidal nature which contains water. At low moisture levels this will be where the water is predominantly located. The diffusion coefficient of water inside these matrix/lamellae structures will be very low, and, therefore, the rate-determining factor for the moisture transport is the transport of moisture from the inside of the lamellae to the pores. In such situations there will be no thermodynamic equilibrium between the solid lamellae and the gas phase because of existing water concentration gradients inside the lamellae, and therefore the theory [...] will not apply to the drying of foods in many cases".
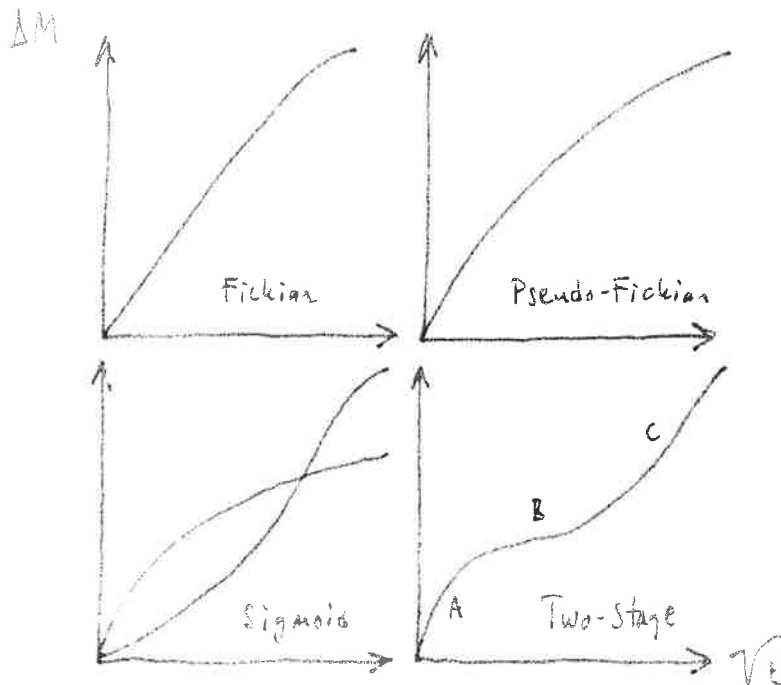
Figure 5: Different forms of sorption rate curves adapted from Roger (1965)

5 Methods of studying anomalous sorption rate curves

The usual practice has been to look for Fickian behavior by plotting the weight change as a function of the square root of time; an initial linear part would imply that the sorption was Fickian. When one looks for anomalous sorption and tries to find its characteristics one have devised new ways of studying the sorption rate curves (which still are the main result from sorption studies).

5.1 different types of sorption rate curves

Kishimoto et al. (1960) characterized sorption rate curves as Fickian, pseudo-Fickian, sigmoid or two-stage (Fig. 5 from Roger 1965):

"**Pseudo-Fickian type a.** The sorption and desorption curves resemble true Fickian curves inasmuch as they do not exhibit any inflection in slope.

    b. The initial portions of the curves are linear, but only over a small part of the total concentration change [...] The approach to final equilibrium is very slow.

Two-stage type Two inflections in slope. The first stage [...] involves

    a. Rapid sorption which apparently obeys Fick's law [...] In some cases, however, the curve may resemble more nearly the pseudo-Fickian type.

    b. Establishment of a quasi-equilibrium [...]

    c. The rate of desorption [from the quasi-equilibrium] obeys Fick's law [...]

The second stage [...] involves:

    d. A slow increase in the overall sorbed concentration without any significant concentration gradient present in the system [...]

    e. Establishment of a true equilibrium [...] after a long period of time.

    f. [...] Desorption from the second stage exhibits a pronounced hysteresis [...].

Sigmoid type a. The sorption and desorption curves are both nonlinear in the region of small times.

    b. The sorption curve is of sigmoid shape; a single inflection of slope is present, usually at M_t/M_∞ nearly 0.5.

c. The initial rate of desorption is greater than the initial rate of sorption but is followed by a slower rate, so that the curves eventually intersect".

Sorption rate curves which are linear when plotted against time have also been found, especially for liquid sorption (see page 21). All curves except the two-stage curves are conveniently classified with the b—value of the best fitting $a \cdot t^b$ (see below).

5.2   classification according to best fitting exponent

Many researchers (e.g. Jacques et al. 1974, Nicolais et al. 1979, Aminabhavi & Aithal 1990) have classified sorption rate curves according to the best fitting value of b in $E = at^b$ by plotting the curves in a logarithmic diagram. The following values of b can be obtained (see also page 15):

- $b < 0,5$ pseudo-Fickian (or initial two-stage behavior)

- $b = 0,5$ Fickian

- $0,5 < b < 1$ Sigmoid (or later two-stage behavior)

- $b = 1,0$ case II or linear kinetics

- $b > 1,0$ super case II

This way of classifying sorption curves is simple but quite powerful, but it is hard to use it on two-stage curves. In Aminabhavi & Aithal (1990) and other articles from the same laboratory this method have been used to analyse a large number of liquid sorption curves.

5.3   a dimensionless group

Vrentas et al. (1975) and Vrentas & Duda (1986) proposed the use of a dimensionless group which they called "a Deborah number for diffusion". This was defined as:

$$\delta = \frac{\tau_r}{\tau_d} \tag{5}$$

where the dimensionless number δ is the ratio of the characteristic times scales of the relaxation (τ_r) and the diffusion (τ_d). The use of δ is explained as follows:

- if $\delta \gg 1$ the process is relaxation controlled

- if $\delta \approx 1$ the process is controlled by both relaxation and diffusion

- if $\delta \ll 1$ the process is diffusion controlled (Fickian)

The authors gave general expressions for the characteristic times, but that for τ_r is probably very hard to evaluate in most cases. The Deborah number is an interesting concept which increases the understanding of non-Fickian behavior, but in my opinion it is not of much practical use.

Astarita & Nicolais (1983) and Joshi & Astarita (1979) introduced a similar parameter as Vrentas et al., but they did not specify any characteristic time scales.

6   Observed characteristics of anomalous sorption

In this section I discuss the most commonly observed characteristics of anomalous sorption. All topics below are not of equal importance, but I have wanted to make the list as extensive as possible.

6.1   patterns in successive interval sorption curves

Kishimoto et al. (1960) found that successive interval absorptions of vapors in polymers produced a pattern in the forms of successive absorption curves:

For amorphous polymers:

   sigmoid $\rightarrow$ pseudo-Fickian $\rightarrow$ two-stage $\rightarrow$ pseudo-Fickian $\rightarrow$ Fickian

For partly crystalline polymers

   sigmoid $\rightarrow$ psedo-Fickian $\rightarrow$ two-stage $\rightarrow$ sigmoid

or

   pseudo-Fickian $\rightarrow$ two-stage $\rightarrow$ pseudo-Fickian

6.2   absorption vs. desorption

For wood it has been shown by many researchers (Comstock 1963, Skaar et al. 1970, Choong & Fogg 1968, Kelly & Hart 1970, McNamara & Hart 1971 and Liu Tong 1988) that absorption is a slower process than desorption. This has been seen as a consequence of the swelling of the sample or the cell wall in absorption slowing down the rate of absorption.

For polymers it has been reported by many researchers that desorption is initially slower but catches up and eventually comes to equilibrium before absorption. Similar observations have been made for fibers.

Park (1961), Kishimoto & Matsumoto (1964), Enscore et al. (1977b) and Schneider et al. (1988) found that desorption kinetics were more rapid than the corresponding absorption kinetics, and seems to call this a general phenomena.

6.3   influence of T_g and relaxation rate

It was seen quite early (Kokes et al. 1952, Long & Kokes 1953, Kishimoto et al. 1960) that anomalous sorption behavior is for amorphous polymers seen only at temperatures below the glass temperature T_g. At $T < T_g$ the polymer chains can not move freely and the material behaves like a glass. At $T > T_g$ the chains can move more freely and the material becomes easy to deform.

Below T_g, relaxations (i.e. time-dependant mechanical phenomena) take comparatively long time; longer than the characteristic times of the sorption process. As part of the sorption process is dependant on the opening of new sorption sites this will delay the sorption.

Rogers (1985) writes that "non-Fickian behavior usually occurs with glassy polymers, with semicrystalline polymers above T_g, and with polymers with more rigid chain conformations and higher internal viscosity when the penetrant swells the polymer". If the rate of relaxation is slower than the rate of diffusion, the former can control the sorption.

It should be noted that T_g is dependant on permeant concentration as a high concentration acts as a plasticizer. If measurements made at a temperature which is below T_g for the dry polymer are started at $c = 0$, anomalous sorption is often seen. If the concentration is successively increased by interval sorptions T_g may be lowered so much that it becomes lower than the ambient temperature. In such a case the sorption rate curves will become Fickian at higher concentrations. This is the reason for the pattern of successive interval sorption curves for amorphous polymers to end with "Fickian type" (see page 17).
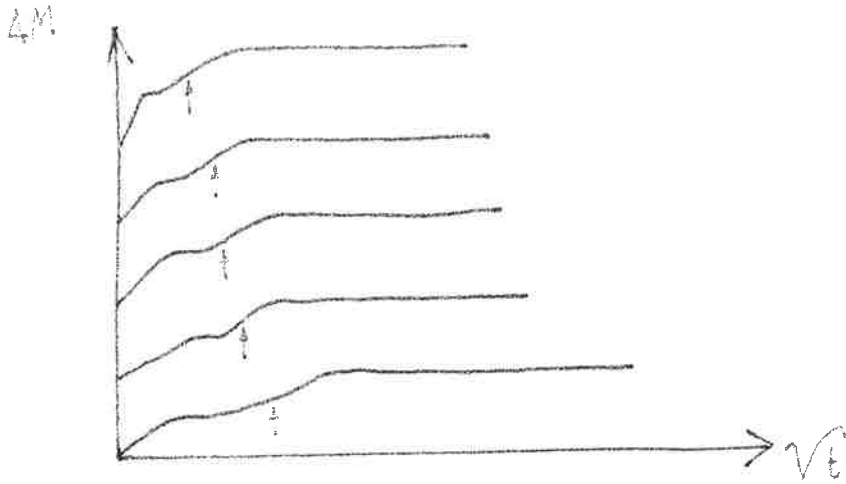
Figure 6: Two-stage curves adapted from Kishimoto et al. (1960)

It should also be noted that measurements of T_g are often made by dynamic methods that give results which depends on the frequency used. One should therefore be careful when matching such data with sorption observations.

6.4 time until inflection during two stage sorption

If the two-stage sorption has a quasi-equilibrium, i.e. the sorption slows down before continuing (see Fig. 6), it will also have an inflection. Kishimoto et al. (1960) found that the logarithm of the time to this inflection was a linear function of the initial concentration in the sample. They called this time t^* and marked it with an arrow in their plots of $c(\sqrt{t})$ (Fig. 6).

A similar characteristic time was used by Sadoh (1960a). He found that $\log(t)$ was a linear function of the moisture concentration in the samples. His t^* was an inflection point in a $E(\log(t))$-diagram. His sorption curves were never plotted as a function of $\sqrt{t}$, but they would probably not have shown any inflections in such a diagram.

6.5 swelling

Rogers (1965) writes that sorption with penetrants that extensively swells the polymer often exhibit anomalous sorption behavior. Bagley & Long (1955), Christensen (1967) and Hunt (1989,1990) have reported that swelling is much faster that the sorption. It could be that it is caused by the sorption of a first stage, the second stage not giving any swelling.

In articles describing anomalous sorption in wood swelling is often described as causing the deviations. It is not clear if it is swelling in the whole sample of wood, or swelling within the cell wall, that is meant.

6.6 heterogeneous and multicomponent systems

These are polymers which contain more than one phase, i.e. composite materials and polyblends, or polymers which are built by more that one type of chain-units (coploymers). Most commercial polymers, including wood and natural fibers, are of this type. Most measurements have been made on simpler polymers than these. Diffusion in composites is complex due to interphase effects (Rogers 1985) and is not completely understood even for systems with Fickian behavior.

It seems that two polymers with Fickian behavior can give non-Fickian behavior in a composite (Sax & Ottino 1985, Shah et al. 1985), but it is more common that non-Fickian components give Fickian behavior when mixed. Marom (1985) writes: "As far as composite materials are concerned the most striking phenomenon with regard to the anomalous behavior is its diminishing or even complete disappearance with the introduction of a reinforcement".

Mirley et al. (1985) and Schneider et al. (1988) found that the addition of a hard phase to an elastomer caused the material to behave anomalous. The absorption on the elastomer was controlled by the relaxation of the hard phase.

Figure 7: An example of sorption with a quasi-equilibrium adapted from Berens (1978)

6.7 characteristics of the stages during two-stage sorption

Long et al. (1953) seems to have been the first to observe and discuss a two-stage sorption rate curve. Since then many researchers have observed this (Bagley & Long 1955; Long & Watt 1956; Newns 1956, 1959; Kishimoto et al. 1960; Long & Richman 1960 etc.) and they all seems to agree on the following points:

- The first stage is Fickian.

- The second stage in non-Fickian and probably relaxation controlled.

Bagley & Long (1955) also found that it was the initial stage that was accompanied by the swelling, the second stage seems to go without any dimensional changes.

Newns (1959) and Watt (1960b) found that no hysteresis could be found if an absorption step was interrupted before the second stage had started. If sorption proceeded into the second stage before the interruption hysteresis was found.

6.8 two-stage sorption rate curves with a quasi-equilibrium

In some cases it have been reported that the sorption seems to come to an end at a 'quasi-equilibrium' before the second stage starts. Fig. 7 from Berens (1978) gives an example of this phenomena. Similar curves have been observed by Long & Watt (1956), Newns 1956, Kishimoto et al. (1960), Odani et al. (1961) and Avramides & Siau (1987) (for wood).

In Fig. 6 is shown one such curve with a quasi-equilibrium at B. It should be noted that the presence of a quasi-equilibrium makes it hard to know when a sorption rate experiment should be finished.

6.9 integral vs. interval sorptions

"It appears that the presence of penetrant at the start of a sorption step retards the attainment of equilibrium" (Berens 1978).

It has been reported that large absorption steps (i.e. integral sorption) are much faster than smaller ones (e.g. Downes & Mackay 1956, Christensen 1959, 1967, Odani et al. 1961, McNamara & Hart 1971, Berens 1978). This could be explained by that the large swelling stresses during the integral sorption makes the sorption proceed faster by increasing the relaxation rate. "It appears that the presence of penetrant at the start of a sorption step retards the attainment of equilibrium" (Berens 1978).

6.10 prehistory of sample

The observations below are not really coupled to anomalous sorption behavior, but are still interesting in the present context.

6.10.1 annealing

Annealing (heat treatment) reduces the free volume in the polymer and makes it harder for the penetrant molecules to diffuse. Inversely a polymer which has been cooled very fast has a large free volume and a high diffusivity. Windle (1984) found a higher front velocity for case II sorption after such fast cooling. This effect is effectively erased by successive cyclic sorptions between high and low c.

6.10.2 pre-swelling

Pre-swelling increases both the rate and the equilibrium absorption (Enscore et al. 1977b), but the effect is completely erased after some cyclic sorptions.

6.10.3 drawing

Windle (1984) reports that a much higher sorption is seen after deformation of a polymer above its elastic limit.

6.11 overshoot

Watt (1960a) saw a maximum in the absorption curve before equilibrium. The measurements were made on wool and it is not clear if there were heat-of-sorption effects.

Berens (1978) reported a sorption rate curve which first rose to a sharp maximum in the first few minutes, then decreased to a minimum before the slow increase toward equilibrium above the level of the first maximum.

Only a few observations have been made of overshoot in sorption curves. In some cases these could be artifacts of the experiment design. Overshoot in liquid sorption curves can be caused by the leaking out of components of the polymer.

6.12 final weight being a function of moisture history

Watt (1960c) reported that there was a maximum amount of retained water in samples being dried in vacuum from RH≈50%. Less water was left if the samples were exposed to lower or higher RH before being dried.

Hergt & Christensen (1965) found similar results for wood dried with different procedures. A maximum amount of retained water when the wood was dried from RH≈50% and a minimum when the samples were dried from the wetted state.

7 Linear Kinetics and Case II

Alfrey (1965) and Alfrey et al. (1966) found that the sorption of liquids in polymers sometimes produced a constant weight increase and called this case II sorption. Earlier observations of such behavior have been made, but Alfrey proposed that this was a second limiting case (the other being Fickian behavior which was called case I). "The essential attributes, namely sharp step-like penetrant profiles moving inwards from the surfaces with constant velocity which give, for sheet specimens, weight gain plots which are also linear with time, have now been frequently observed and widely recorded" (Windle 1984). The practice of plotting sorption data against $\sqrt{t}$ to check for Fickian characteristics sometimes hides the linear kinetics Hopfenberg et al. (1976) have replotted data from Andrews et al. (1973) and found case II behavior. Similarly Kwei (1972) redraw curves from Bagley & Long (1955).

Some information about the sharp moving boundaries comes from visual observations on transparent polymers. Most comes from weight measurements. One system that produces case II behavior and that is also convenient to work with is PMMA and methanol.

It is possible to obtain sharp moving boundaries by having diffusivity with a step-like dependency on the concentration (Crank 1975). These boundaries can, however, not be made to move with a constant velocity as do the case II sorption, so the linear kinetics must have other causes.

In the above mentioned PMMA-methanol system and other systems the following observations have been made (Windle 1984):

- At 30° and below linear kinetics is shown.

- The sharp penetrant front moves at a constant velocity, both if measured by weight change or optically (e.g. by staining the methanol with iodine).

- The time at which the weight gain abruptly stops corresponds to the meeting of the opposing fronts.

- The rate of the front traverse is independent of the concentration of the penetrant.

- Case II sorption in thin specimens gradually becomes Fickian if thicker specimens are used.

- The swollen material behind the front is deformed by stretching in the flow direction.

- As the fronts meet an increase in area and a decrease in thickness can be observed.

- Increasing temperature gives

    - higher rate of sorption.
    - increased equilibrium sorption.
    - a trend away from case II sorption towards Fickian sorption.

Case II behavior is associated with liquid sorption in glassy polymers and it has not been found for elastomers absorbing liquid solvents, although such behavior can be anomalous (Schneider et al. 1986, Aithal & Aminabhavi 1990, Aminabhavi & Aithal 1990, Harogoppad & Aminabhavi 1991ab, Aithal & Aminabhavi 1991).

Many theories have been developed for the case II sorption. Some of the early work on non-Fickian sorption have been used, together with other theories.

The higher rate of sorption at higher temperatures is explained by the diffusivity increasing with temperature. The trend away from case II sorption is explained by that the penetrant supply to the advancing front becomes more difficult as the front velocity increases. The similar explanation can be given to the fact that the thicker specimens show less case II behavior, as the penetrant has to travel a longer distance to get to the front of a thicker specimen.

The dimensional changes which can be seen at the end of case II sorption are attributed to that the restraining effect of the unswollen core disappears as the fronts meet.

Many reported case II sorption plots show an induction period before the linear portion of the curve is established. This has been ascribed to a surface effect, but this is also an intrinsic aspect of some theories for case II sorption

Nearly all experimental evidence of linear kinetics comes from liquid sorption experiments. In the reported cases of vapor sorption producing such behavior (Kwei 1972, Enscore et al. 1977ab) it is not clear whether there is a front with a constant velocity or if the sorption curves just happens to become linear by chance. It is my opinion that case II behavior is caused by liquid sorption or integral sorption under special circumstances. It is not, in my opinion, a second limiting case. This will be discussed below.

Case II is seen by many researchers as a limiting case of pure relaxation controlled sorption; other anomalous behavior should then be a mixture of case I (Fickian) and case II. Petropoulos & Roussis (1967, 1969, 1974) have developed a model for relaxation controlled concentration. This theory predicts linear kinetic when both D and a relaxation parameter are third order functions of the c. This seems to me to be a complicated way of modelling case II behavior, which probably is the result of what happens in the moving boundary (Windle 1984). If it is something that has to happen in the front (e.g. breaking of bonds or crazing) before the front can continue, the velocity will be constant. This is very far from normal vapor sorption, even if it is completely relaxation controlled. It is not necessary to know the exact nature of the processes in the front to realize that such a sorption process can give linear kinetics. Under normal conditions of vapor sorption we can get all kinds of strange sorption curves, but they are probably not caused by a front moving through the material.

Therefore I do not think that general anomalous behavior is a mixture of Fickian and case II behavior. In my opinion case II is a special case found under the extreme conditions of liquid sorption. Normal anomalous behavior is normally caused by slow sorption in the whole sample.

Ottino & Shah (1984) and Enscore et al. (1977a) are examples of papers in which theories are developed for 'the limiting cases', Fickian and case II. These theories are then used to treat normal anomalous sorption behavior. This is not correct in my opinion.

Peterlin's (1965, 1977, 1979) idea that there is a Fickian tail preceding the linearly moving front in case II, is logical.

The super case II reported is recognized as a steepening of a more or less established linear sorption plot. A number of theories have been put forward for this kind of sorption: 'overlapping precursors' in which the two opposing fronts will give rise to an increased sorption when they come near each other, and 'differential swelling stresses' in which an adjustment in the equilibrium sorption of the sample is caused by the release of stresses when the fronts meet.

8 Models of non-Fickian sorption

Numerous attempts have been made to quantify anomalous sorption phenomena. I have tried here to make a complete review of such theories. To give some order to the account I have placed the models under different headings. This has been impossible to do in a completely logical way, but it makes the section easier to read.

The models treated all concern two phase systems in which a penetrant enter into a polymer (or leaves it) with no complications from external factors. More complicated systems are often found in engineering problems. Three models of non-Fickian behavior in three phase systems are given by Chang et al. (1988).

8.1 changing surface concentration

These models are the most successful in that they are the most cited and most used models. In my opinion it is doubtful if the conditions of the surface of the sample could control the sorption in the whole sample. I would think the relaxation in the whole sample should control the sorption.

model 1   Crank & Park (1951) made the first useful model of non-Fickian sorption by introducing a time dependant surface concentration:

$$c_s = c_0(1 - e^{-\beta t}) \tag{6}$$

They reasoned that the surface concentration might not immediately attain its equilibrium value. Instead this could be "established at a finite rate". The calculated sorption curves are sigmoid and show a good likeness with some experimental absorption curves. When absorption curves are sigmoid, the desorption curves are often pseudo-Fickian (see page 5.1). Crank & Park found it "reasonable to assume that, even though the surface concentration rises slowly during [ab]sorption, on desorption it can fall to zero instantaneously when placed in contact with an atmosphere of zero vapor pressure".

This model is probably the most quoted one in the literature on non-Fickian sorption. The first order model of the surface concentration was probably the most natural way to model such a phenomenon, but I am sceptical to the idea that the surface concentration should govern the sorption. If the surface concentration only rises slowly it does so because the whole sample is unable to sorb a large amount of vapor in a short time. The first order model should therefore not be applied on the surface only, but in the whole sample.

This model has recently been used by Narebska et al. (1984a) and Smith & Fisher (1984).

model 2   Long & Richman (1960) found that the surface concentration changed in a more complex way than Crank & Park (1951) had assumed. They found that it initially changed rapidly to a value c_0 (between c_i and c_f), and then slowly increased towards c_f. The first part of this adjustment initially followed $c_s = c_0 + a \cdot t$ (where a is a constant), but this equation can not be used as the c_s can not exceed c_f. They therefore proposed the following equation:

$$c_s = c_0 + (c_f - c_0)(1 - e^{-\beta t}) \tag{7}$$

With this model Long & Richman were able to accurately imitate experimental results with clear two-stage sorption. If the diffusivity is low and β is low there will be a very marked two-stage behavior. In one figure two simulated curves are shown which are very similar except that one shows a two-stage behavior. The only difference between these simulations is that the diffusivity has been changed a factor 100. At least for that case it seems that the diffusivity has a minor influence on the result, which is more a result of β.

The model can imitate two-stage behavior but it is rather doubtful whether one should consider the surface concentration to be the controlling factor. Petropoulos & Roussis (1974) reviewed this theory and found that a more general expression showed that the variation of c_s was only a manifestation of the time dependance of the sorption in the whole sample.

model 3   Joshi & Astarita (1979) develops a model, using theoretical thermodynamic concepts, which in the end turns out to give an identical equation for the weight increase as the model by Long & Richman (1960). The model treats a system with diffusion and relaxation. The coupling between them is expressed with a dimensionless ratio between characteristic relaxation and diffusion times. The model has been used by Wakesman et al (1979).

<u>model 4</u>   Fujita & Kishimoto (see Fujita 1961) found that the above models did not reproduce their measured series of interval sorption. They found it "more reasonable to assume that also the initial increase [of surface concentration was] time dependant" (but they have in fact only added one more first order term to the equation of Long & Richman 1960):

$$c_s = c_0 + (c_1 - c_0)(1 - e^{-\beta_1 t}) + (c_f - c_1)(1 - e^{-\beta_2 t}) \tag{8}$$

With this equations they could reproduce all curve forms found in a series of interval sorptions.

The model of Fujita & Kishimoto contains four parameters (c_0, c_1, β_1 and β_2). It should therefore not surprise that it can accurately reproduce many experimental results; it should probably be considered a numerical model, not a physical one.

8.2   changing diffusivity

I think these models are interesting but I am not convinced that the diffusivity is the rate controlling factor. In my opinion the rate of anomalous sorption is mainly controlled by the rate of sorption, i.e. it is the availability of the sorption sites that governs the sorption process. Nevertheless, these models have been successful in predicting anomalous sorption curves.

<u>model 5</u>   Crank & Park (1951) studied the effect of a surface skin on the sorption rate to try to reproduce absorption and desorption rate curves which crossed each other. They succeeded in this by introducing a very variable diffusivity in the outer layers of the sample (a skin). At the same time "no appreciable linear part will be observed in the sorption curve" and this did not agree with the experimental results they were studying. They concluded that "it seems unlikely that we can reproduce simultaneously the sorption and desorption behaviour to agree with experimental observation by combining the effects of a skin and concentration dependant diffusion".

The experimental sorption rate curves shown in the article have no "appreciable linear part". The absorption curves do however have an initially increasing slope which is not reproduced in the calculated curves which have decreasing slopes.

<u>model 6</u>   Crank & Park (1951) also proposed a diffusivity which was dependant on the history of the diffusion process:

$$\frac{\partial D(t, x)}{\partial t} = \alpha(D_f - D(t, x)) \tag{9}$$

where D_f is the equilibrium diffusivity. They give this equation ("the simplest expression of any physical significance describing the rate of change of the diffusion coefficient") and note that "any sort of rearrangement of polymer molecules, proceeding relatively slowly, will presumably lead to history dependant diffusion". No calculations were made to verify that the model produced relevant sorption rate curves.

I can well imagine a history dependant diffusivity, but think that the effect of such a diffusivity will be rather small compared to other effects (e.g. relaxation producing new sorption sites). Normally the diffusivity does not change very much during interval sorption; Eq. 9 can not produce anything but a diffusivity which slowly changes from its equilibrium value at the initial to its value at the final concentration. During integral sorption the situation might be different as the equilibrium value of the diffusivity can change very much during such a sorption.

<u>model 7</u>   Crank (1953) further develops this theory to account for the observations of one fast and one slow stage in the sorption. He gives the following first order approach:

$$\frac{\partial D(t, x)}{\partial t} = \frac{\partial D_1}{\partial c}\frac{\partial c}{\partial t} + \alpha(D_f - D(t, x)) \tag{10}$$

where D_1 is that part of the diffusivity which can change immediately and D_f is the final diffusivity at equilibrium. This is a further development of Eq. 9 and it is assumed that the concentration at the surface immediately reached c_f. The above equation was evaluated with the following assumptions:

$$D_1 = D_0 e^{ac} \qquad\qquad D_f = D_0 e^{bc} \qquad\qquad \alpha = \alpha_0 e^{\sigma c} \tag{11}$$

where a, b, D_0, α_0 and σ are constants.

According to Crank the above equations with the above assumptions will produce history dependant sorption only if the concentration interval and the thickness of the sample are in certain

where a and b are constants.

The result shown indicates that an increase in stresses set up, a reduction in plasticization, or a decrease in the rate of stress relaxation all reduces the sorption rate. The diagrams are shown with t on the x-axis which makes it hard to compare them with diagrams from other papers.

Linear kinetics can be generated with this model, but it is not associated with sharp penetrant fronts.

8.4   models using irreversible thermodynamics

<u>model 15</u>   Frisch (1964) used irreversible thermodynamics to make a model of anomalous sorption. This includes "a set of unspecified internal parameters which are used to describe the gradual 'freezing' or relaxing of internal degrees of freedom as the system passes through a 'glass-like' transition region" (Crank 1975). The given final equations are very general in nature, but probably not very useful.

Frisch et al. (1969) and Wang et al. (1969) also used irreversible thermodynamics in making a model of strain dependant sorption (se page 26).

8.5   theories based on equilibrium sorption

<u>model 16</u>   I had been proposed by many researchers that sorption was occurring by two distinct modes. Vieth & Sladek (1965) put this on a mathematical form in what has become known as the 'dual sorption model'. The sorption isotherm is made up of two components: one which is linear (Henry's law) and one which is nonlinear (Langmuir sorption). The second component has been termed 'hole-filling'. These molecules are immobilized and do not take part in diffusive transport. The diffusion equation becomes:

$$D \cdot \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}\left[1 + \frac{c_H \cdot b}{a(1 + \frac{b}{a}c)^2}\right] \tag{18}$$

where a is the Henry's law constant, b is a hole affinity constant, and c_H is a hole saturation constant.

Vieth & Amini (1974) discusses both positive and negative deviations from Henry's law. Fenelon (1974) gives "experimental support" to this theory.

Hunt (1990) also used a sorption isotherm model (by Kollmann 1963) to explain why swelling was faster than sorption in thin wood samples at high RH. Kollmann's isotherm model contains three terms: sorption, submicroscopic capillary condensation and microscopic capillary condensation. Hunt assumes that it is the first of these that correlates with swelling, but does not make any model of the kinetics of swelling and sorption.

8.6   theories for multiphase polymers

<u>model 17</u>   Sax & Ottino (1983), Ottino & Shah (1984) and Shah & Ottino (1986) developed a theory for multiphase materials which they called the effective medium theory (EMT). It predicts the overall transport properties for randomly inhomogeneous systems and works best when one of the components has a very much higher diffusivity than the other (for two-phase systems). The actual system is replaced by an effective homogeneous system that exhibits the same properties as the actual material. It has been used by Shah et al. (1985) and Serrano et al. (1987b).

The EMT is a computer-based model which uses the theory of equivalent networks. Earlier models of multiphase systems used series and parallell coupling of the phases. The EMT model is a more general theory in which the coupling of the phases is expressed in more general terms. An important conception is the 'percolation threshold', by which is meant the lowest concentration when one of the components has a continuous phase.

Sax & Ottino (1983) discusses the model without any references to non-Fickian behavior, but Ottino & Shah (1984) uses different transport laws within each phase or domain. They do however restrict themselves to linear kinetics. It is not easy to value a theory which is as complex as this one.

<u>model 18</u>   Wadsö (1992) models anomalous behavior in whole wood specimens as being caused by a finite rate of absorption by the cell wall. The flow into the sample is modeled using Fick's law and data from steady-state measurements. This initial Fickian sorption is absorbed on part of the available sorption sites (fast sorption). A second slower absorption is modeled by a second Fickian process into the cell walls of the sample.

This theory could correctly describe the major part of some anomalous sorption curves, but there were also an extremely slow attainment of equilibrium which the slow Fickian process could not capture. An addition of more time scales would have made the model better, but these time scales would not have such physical relevance as the Fickian subprocesses.

8.7   numerical models

Numerical models are models which are not based on physical models. Putting a model in this group is probably a matter of taste, but it should not be viewed as a depreciation. Berens model below is one of my favorites; it gives the time scales of processes and is very general and easy understandable.

<u>model 19</u>   Sadoh (1960b) proposed the following equation for sorption in thin hemicellulose samples, as the sorption was independent of thickness:

$$E = 1 - e^{-t/\tau} \tag{19}$$

where τ is a viscoelastic "retardation time [...] or network deformation". This first order model imply that the sorption is not at all governed by diffusion.

Even if the model is described in terms of relaxation I have put it in the subsection of numerical models. This might be a mistake, but the article is in japanese which makes it difficult to understand the reasoning behind the model.

<u>model 20</u>   The model by Berens & Hopfenberger (1978, 1979) contains a Fickian term $F(t)$ and a sum of first order relaxation terms. It was used for small spherical particles:

$$\frac{M(t)}{M_f} = a \cdot F(t) + \sum_{n=1}^{m} b_n \cdot e^{-k_n t} \qquad\qquad a + \sum_{n=1}^{m} b_n = 1 \tag{20}$$

The Fickian term contains information about ℓ and D of the specimens.

Enscore et al. 1977a and Berens (1978) uses the model with one or two relaxation terms and gets a good fit to experimental data of various forms. Berens even gets a very good fit to an absorption rate curve which has a minimum by using a negative value of b_2. This shows that the model is a good model, but not much more than a numerical model.

A model such as this is of no general use as it does not include any material dependant parameters in the second part of the equation, but the k_n:s do give the time scales of the sorption process. Therefore a numerical model can be of value even if it does not relate the sorption to any material parameters.

<u>model 21</u>   Kelly & Hart (1970) proposed the following equation for absorption or desorption in wood:

$$c_f - \bar{c} = (at + (c_i - f)^b)^{1/b} \tag{21}$$

where f is a correction factor for the first stage of the sorption. The equation seems to have given a good fit to the experimental curves, but does not seem to have any physical relevance.

<u>model 22</u>   Walker & Harrison (1971) observed that the weight change, when wool was dried, did not obey Fick's law. From their measurements they calculated a mean deviation from Fickian behavior and called this "function S". S was expressed as an eighth degree polynominal in E and used to predict sorption in cylindrical samples:

$$F(E) = S(E)\frac{Dt}{r^2} \tag{22}$$

where $F(E) = Dt/r^2$ for cylindrical samples under Fickian conditions. F seems to depend on the geometry of the sample, but this is not further explained in Walker (1977) where he tests the function S on older measurements made on wooden slabs and cylinders. According to Walker S has no physical base, but seems to give a better fit to experimental data than does Fick's law alone.

I my opinion S is not of much use as it is highly improbable that all anomalous sorption rate curves should show the same deviation from Fickian behavior.

ranges. If they are larger or smaller normal concentration dependant sorption will be the result. This seems to be an effect of the above definition of D_1, D_f and α. In an experiment with interval sorption covering the whole range of p from dry to saturated sample the measured diffusivity will change from D_1 at low p to D_f at high p, and this change may occur in a quite small p-interval if α is large.

Crank also gives some calculated sorption rate curves showing that the following phenomena can be simulated:

- The absorption rate curve can be above (small values of b or large thicknesses) or below (large values of b or small thicknesses). The two curves can also intersect (intermediate values).

- For large values of b the absorption rate curve is sigmoid.

- The sorption proceeds relatively more quickly for thicker samples (when plotted with $\sqrt{Dt/\ell^2}$ on the x-axis).

8.3 strain dependant diffusion

As the models concerned with strain dependant diffusion use quite a lot of equations and definitions I have tried to describe their most important details with words only.

In my opinion these models are good, in that they model a realistic process in the whole sample. The model by Newns is very interesting.

<u>model 8</u>   Crank(1953) proposed a simple model of strain-dependant diffusion. The increasing diffusivity is modelled as a discontinues function of the concentration as this simplifies the mathematics. The resulting concentration profile has a high gradient at a certain position in the sample. The sample is therefore partly swollen and partly dry.

The model used the following relations:

1. The area of the specimen is the same throughout its thickness.

2. The swelling and the strain are uniform in the swollen and the dry parts respectively.

3. The total forces of compression and extension are balanced (the elastic moduli for the dry and swollen polymer are needed).

4. The diffusion coefficients are related to the compression and extension by simple relations. The diffusivity in compression decreases linearly with increasing compression, and the diffusivity in extension increases linearly with increasing extension.

5. The ratio of the diffusivity of the fully compressed polymer to that for the unstressed swollen polymer is the same as the corresponding ratio for the unstressed to the fully extended dry polymer. This simplifies the mathematics.

Crank calculated some sorption rate curves that can be obtained with the model. If the elastic modulus for the dry material is much lower then that of the swollen material (the swollen material is much stiffer) the resulting sorption rate curves looks Fickian. If the elastic modulus of the dry polymer is the larger (the dry material is stiffer) the curves are sigmoid. An interesting effect is that there can be a time when a thin specimen contains more penetrant than a thick specimen.

Crank's model is certainly very interesting and can give good descriptions of some observed anomalies, but it is doubtful whether the diffusivity is strain dependant.

<u>model 9</u>   Newns (1956) correctly predicted several features of two-stage sorption rate curves with a model in which he considered that the first stage sorption swelled the polymer to such an extent that no more sorption could take place before relaxation had decreased the stresses. The hypothetical pressure (Π) at any time during the second stage is

$$\Pi = \frac{RT}{V} \ln \left(\frac{p}{p_f} \right) \tag{12}$$

where V is the partial molar volume of the penetrant. The balancing stress is given by Hook's law:

$$P = \gamma \Delta v \tag{13}$$

25

where Δv is the fractional volume change during the first stage sorption and γ is a constant.

When these two equations are equated expressions for weight increase and fraction sorbed during the initial stage can be developed. The model developed is of a quantitative nature but seems not to have been used very much by Newns or any other researcher. Crank (1975) seems to find the model good as he devotes nearly a page to a description of it. Also Christensen & Kelsy (1959) discusses a similar model.

model 10   According to Rogers (1965) Fujita et al. (1959) have proposed a model which is similar to that of Newns. "The rate of the continuous slow expansion of polymer structure from the state of quasi-equilibrium toward the equilibrium configuration corresponding to the external pressure is assumed to depend primarily on the strength of interchain forces in the presence of penetrant and on the magnitude of the swelling stress caused by a given increment of external pressure. The plasticizing effect of an increasing sorbed concentration will cause a gradual weakening of interactions between chains even when the polymer is in the glassy state" (the quotation is from Rogers (1965) as I do not yet have this reference).

model 11   Christensen (1959) and Sadoh & Christensen (1964) discussed swelling pressure (Eq. 12 above) in the cell walls and thin hemicellulose samples and found that $t_{\frac{1}{2}} \cdot \ln(p_f/p_i)$ were constant ($t_{\frac{1}{2}}$ is the time to half sorption). The same kind of relation was also found when other fractions of sorption were studied. A general formula for these results (which was not given by Christensen or Sadoh & Christensen) would then be:

$$E = f\left(\sqrt{t} \cdot \ln \frac{p_f}{p_i}\right) \tag{14}$$

where f is a single valued function.

It is doubtful whether this equation can be of any general use, but it interesting to note that the logarithmic expressions, which are the result of the expressions for swelling pressure, seems to describe at least some anomalous sorption phenomena.

model 12   Frisch et al. (1969), Wang et al. (1969) and Kwei & Wang (1974) added a second term to the gradient in Fick's law. This should include the effect of the swelling stress of the penetrant:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x} - vc\right) \tag{15}$$

This was called "a generalized diffusion equation". D primarily refers to the swollen region.

By irreversible thermodynamics a solution which can be seen as a sum of a Fickian component and a case II component was developed. The position in a sample with a certain concentration has the following form as a function of time:

$$x = a\sqrt{t} + bt \tag{16}$$

where a and b are constants. If b is small the sorption is Fickian, and if a is small the sorption is case II. This model is very similar to the model by Peterlin (1965, 1977, 1979), but that model is primarily developed for case II sorption.

model 13   Petropoulos & Roussis (1974) extended Crank's (1953) theory by assuming the polymer to have viscoelastic properties. Using computer simulations sigmoid and two-stage sorption rate curves were calculated. It was also possible to generate plots which had long linear portions. The authors discuss extending the model by including more physically relevant relations into the model. "Clearly, the model could become very complicated. It has the advantage, however, that the additional parameters should normally be deducible from the mechanical properties".

The authors forced the model to simulate linear kinetics (case II) by using steeply increasing empirical functions of D and β. The model does however not produce sharp penetrant fronts (even if the weight increase is linear).

model 14   Petropoulos & Roussis (1978) extended their own theory by treating the polymer as a linear viscoelastic medium. The elastic modulus will decay with a first rate function from an initial value to a final value after infinite time. The area of the sample is "constrained to be uniform" which gives a local stress. The diffusivity is modelled as dependant on both c and σ (stress):

$$D(c, \sigma) = D_0 e^{ac+b\sigma} \tag{17}$$

26

8.8 models of case II and super case II

Case II is also termed linear sorption as the weight increase in such a case is proportional to the time. Super case II starts as case II but speeds up after a while (the sorption rate increases even if the sorption is plotted against linear time).

Case II models are models in which a penetrant front traverses the specimen at constant speed (for a rectangular specimen). Such models are developed primarily for liquid sorption or dissolution and can probably not explain anomalous vapor sorption but are included here as they usually are discussed in association with models for vapor sorption.

Anomalous behavior is often seen as a mixture of Fickian and case II behavior. Therefore some of the models described above have been developed for both Fickian and case II behavior. The models in this subsection have, however, been developed specifically to show linear kinetics.

model 23   Peterlin (1965, 1969, 1977, 1979) proposed that case II behavior was the result of Fickian diffusion under special conditions. He assumed that the polymer swelled when a certain c had been reached, and that the diffusivity at the same time increased by some orders of magnitude. For the sake of simplicity he assumed the sample to be half infinite, the swelling to be instantaneous and the diffusivity in the swollen part to be infinitely large. As there also is a diffusivity in the unswollen part a Fickian 'tail' will precede the moving front. Therefore the weight increase will start as a Fickian process. Later the discontinuity "between the region with Fickian diffusion and the swollen network" will move with a constant velocity i.e. show one of the signs of case II sorption.

The diffusion equation was written:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x} - vc\right) \tag{23}$$

The diffusivity is associated with a Fickian tail ahead of the front.

Peterlin uses irreversible thermodynamics in his reasoning. Frisch (1980) notes that Peterlin's theory "contrasts with the views of almost all other investigators who seems to believe that there are some mechanistic differences between Case I and Case II". I also agree with Frisch (1980) when he says that the "model in no way relates the constant case II velocity v to the diffusion problem". Peterlin (1977) writes that one "has the rather unexpected result that the same mathematical formalism [...] yields both types of diffusion: Type I for constant or approximately constant and Type II for extremely pressure or concentration dependant D, S [= c/p] and P [permeability...] Type I diffusion is a very special case confined to ideally linear systems with constant D and S". The last statement is not true and the whole theory seems strange.

model 24   Jaques et al. (1974) modelled super case II sorption as arising from the interaction of two Fickian tails ahead of the linearly traversing fronts.

model 25   Sarti's (1976) theory for case II sorption is based on the crazing which is seen accompanying the sorption front in polystyrene systems. Reported kinetics of crazing in dry polymer under mechanical load is used in the model.

model 26   Tu (1976) and Tu & Ouano (1977) describes a model of the dissolution of a glassy polymer in a solvent. The system is modeled as having three parts: the glassy polymer, a rubbery gel layer, and the liquid solution. As the dissolved polymer are carried away, and the glassy polymer contains very little penetrant, the system will look the same at all times there are polymer left to swell and dissolve. Therefore the front will travel into the material at constant speed.

model 27   Asterita & Sarti (1978) have modelled case II behavior by solving the diffusion equation behind the moving front. The solvent flow is proportional to the advancement of the front times the concentration jump across the front. This produces linear weight increase and a front moving with constant velocity.

model 28   Sarti (1979) presented a model in which the swelling at the moving front was the rate determining process. The stress was evaluated in terms of penetrant concentration and the velocity of the front was expressed in terms of swelling stress. This theory is similar to the one described in Sarti (1976).

model 29   Thomas & Windle (1980, 1982) have developed a theory which produces sharp diffusion fronts propagating at constant velocity, and a linear weight gain. This theory models the viscous response to the osmotic pressure of the penetrant at the front. Two basic parameters are used: D and the viscous flow rate of the glassy polymer.

model 30   Enscore et al. (1977a) made a very straight forward model of case II sorption by introducing a case II relaxation constant k (in units of kg/(m²s)) by supposing that the case II front also travels with a constant velocity in a sphere. The expression for the absorption in a single sphere becomes

$$\frac{\mathrm{d}M}{\mathrm{d}t} = k \cdot 4\pi r^2 \tag{24}$$

where r is the position of the advancing front (the corresponding equation for the rectangular case would simply be $\mathrm{d}M/\mathrm{d}t=k$). After some simple calculations one gets the following equation for the dimensionless sorption:

$$E = 1 - (1 - \frac{kt}{R\,c_f})^3 \tag{25}$$

for a sphere of radius R (in the corresponding equations for cylinders and slabs the exponent is changed to 2 and 1 respectively).

9 If you want to read ten articles on non-Fickian behavior...

This review contains a long list of references, but these are not all the ones I have had to read... . I would like to suggest ten papers and articles which I think are good. I have chosen them as they are easy to read, contains interesting information about the subject, and/or have been cited a lot. Here they are:

1. Crank & Park (1951) contains both experimental data and two kinds of models for anomalous sorption. Probably the most cited article in this branch of science.

2. Crank (1953) further develops a model.

3. Long & Richman (1960) is one of the articles by Long and co-workers. Concentration profiles are measured which show two-stage behavior. A model is also proposed. Richman & Long (1960) describes the apparatus used.

4. Christensen & Kelsey (1959) is a extensive original article on measurements of sorption on thin samples of wood. Christensen (1965) is a nice english summary of the work.

5. Skaar et al. (1970) is a summary of Prichananda's work on anomalous sorption in larger specimens of wood.

6. Mackay et al. (1969) and Mackay & Downes (1969) contains the best work on wool with the vibroscope technique. Impressive error analysis.

7. Petropoulos & Roussis (1974) is a description of three kinds of models for non-Fickian sorption. Nice to read.

8. Berens (1978) is a nice article on sorption in small spheres of PVC.

9. Thomas and Windle (1980) is a very nice article on case II behavior.

10. Jacques et al. (1974) is a well written account of super case II.

10 References

Aithal U.S. & Aminabhavi T.M. (1990) "Sorption and Diffusion of Organic Solvents in Polyurethane Elastomers" Polymer 31 1757-1762

Aithal U.S. & Aminabhavi T.M. (1991) "Molecular Transport of Some Industrial Solvents Through a Polyurethane Membrane" J. App. Polymer Sci. 42 2837-2844

Alfrey T. (1965) Chem. Eng. News 43 64

Alfrey T., Gurenee E.F. & Lloyd W.G. (1966) J. Polymer Sci. C12 249

Aminabhavi T.M. & Aithal U.S. (1990) "Interaction of Some Highly Aggressive Solvents and Effect of Temperature on the Transport Characteristics of Polyurethane" J. Appl. Polymer Sci. 41 2113-2131

Andrews E.H., Levy G.M. & Willis J. (1973) "Environmental Crazing in a Glassy Polymer: the Role of Solvent Absorption" J. Mat. Sci. 8 1000-1008

Armstrong A.A. & Stannett V. (1966) "Temperature Effects During the Sorption and Desorption of Water Vapor in High Polymers. I. Fibers with Particular Reference to Wool" Die Makromoekulare Chemie 90 145-160

Astarita G. & Nicolais L. (1983) "Physics and Mathematics of Heat and Mass Transfer in Polymers" Pure & Appl. Chem. 55:5 727-736

Astarita G. & Sarti G. (1978) "A Class of Mathematical Models for Sorption of Swelling Solvents in Glassy Polymers" Polymer Eng. Sci. 18:5 388-395

Avramides S. & Siau J.F. (1987) "An Investigation of the External and Internal Resistance to Moisture Diffusion in Wood" Wood Sci. Technol. 21 249-256

Bagley E. & Long F.A. (1955) "Two-stage Sorption and Desorption of Organic Vapors in Cellulose Acetate" J.Am.Chem.Soc. 77 2172-2178

Barrie J.A., Munday K., Kuo D., Jamail.I., Williams M. & Spencer H.G. (1982) "Gas Transport in Graft and Block Copolymers" 28th Mocromol. Symp. IUPAC p.747

Berens A.R. (1977) "Diffusion and Relaxation in Glassy Polymer Powders: 1. Fickian Diffusion of Vinyl Chloride in Poly(vinyl chloride) Polymer 18 July 697-704

Berens A.R. (1978) "Analysis of Transport Behavior in Polymer Powders" J. Membrane Sci. 3 247-264

Berens A.R. & Hopfenberg H.B. (1978) "Diffusion and Relaxation in Glassy Polymer Powders: 2. Separation of Diffusion and Relaxation Parameters" Polymer 19 489-496

Berens A.R. & Hopfenberg H.B. (1979) "Induction and Measurement of Glassy-State Relaxations by Vapor Sorption Techniques" J. Polymer Sci.:Phys. Ed. 17 1757-1770

Bomben J.L. (1973) "Aroma Recovery and Retention" in "Advances in Food Research" ed. Chichester C.O. et al. Academic Press

Chang S-S, Guttman C.M., Sanchez I.C. & Smith L.E. (1988) in "Food and Packaging Interactions" ed. Hotchkiss J.H., ACS symp. ser. 365 106-117

Christensen G.N. (1959) "The Rate of Sorption of Water Vapour by Wood and Pulp" Appita J. 13 112-123

Christensen G.N. (1960) "Kinetics of Sorption of Water Vapour by Wood" Aust.J.Appl.Sci. 11:2 295-304

Christensen G.N. (1965) "The Rate of Sorption of Water Vapor by Thin Materials" in "Humidity and Moisture" ed. Wexler A., New York Reinhold Publ 279-293

Christensen G.N. (1967) "Sorption and Swelling within Wood Cell Walls" Nature (Lond.), February 25 782-784

Christensen G.N. & Kelsey K.E. (1959) "Die Geschwindigkeit der Wasserdampfsorption durch Holz" Holz als Roh- und Werkstoff 17:5 178-188

Choong E.T. & Fogg P.J. (1968) "Moisture Movement in Six Wood Species" For. Prod. J. May 1968 66-70

Choong E.T. & Skaar C. (1969) "Separating Internal and External Resistance to Moisture Removal in Wood Drying" Wood Sci. 1 200-202

Choong E.T. & Skaar C. (1972) "Diffusivity and Surface Emissivity in Wood Drying" Wood Fiber 4 80-86

Comstock G.L. (1963) "Moisture Diffusion Coefficients in Wood as Calculated from Adsorption, Desorption, and Steady State Data" For. Prod. J., March 96-103

Crank J. (1953) "A Theoretical Investigation of the Influence of Molecular Relaxation and Internal Stress on the Diffusion in Polymers" J.Polym.Sci. XI:2 151-168

Crank J. (1975) "The Mathematics of Diffusion" Oxford Univ. Press 254-265

Crank J. & Park S.G. (1951) "Diffusion in High Polymers; Some Anomalies and Their Significance" Trans. Faraday Soc. 47 1072-1084

Dékret A. & Kurjatko S. (1986) "Surface Conditions During the Diffusion of Water Vapors in Wood" (in Slovakian with an English summary) Drevársky Výskum 109

Denton P. (1956) "The Water Absorption Characteristics of Monofilament Cellulose" Shirley Institute Memoirs 29 119-134

Downes J.G. & Mackay B.H. (1958) "Sorption Kinetics of Water Vapour in Wool Fibers" J.Polym.Sci. XXVIII 45-67

Enscore D.J., Hopfenberg H.B. & Stannett V.T. (1977a) "Effect of Particle Size on the Mechanism Controlling n-Hexane Sorption in Glassy Polystyrene Microspheres" Polymer 18 August 793-800

Enscore D.J., Hopfenberg H.B., Stannett V.T. & Berens A.R. (1977b) "Effect of Prior Sample History on n-Hexane Sorption in Glassy Polystyrene Microspheres" Polymer 18 November 1105-1110

Fenelon B.F. (1974) "Experimental Support of 'Dual Sorption' in Glassy Polymers" in "Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids" Ed. Hopfenberg H.B. Plenum Press

Frisch H.L. (1964) "Isothermal Diffusion in Systems with Glasslike Transitions" J. Chem. Phys. 41:12 3679-3683

Frisch H.L. (1980) "Sorption and Transport in Glassy Polymers - A Review" Polymer Eng. Sci. 20:1 2-13

Frisch H.L., Wang T.T. & Kwei T.K. (1969) "Diffusion in Glassy Polymers. II" J. Polymer Sci. A-2 7 879-887

Fujita H, (1961) "Diffusion in Polymer-Diluent Systems" Fortsch. Hochpolym.-Forsch. 3 1-47

Fujita H., Kishimoto a: & Odani H. (1959) Progr. Theoret. Phys. (Kyoto) Suppl. 10 210

Haly A.R. & Roberts N.F. (1956) "The Interaction of Wool and Water. I. The Diffusion of Water in Wool Fibres" Proc. Int. Wool Textile Res. Conf. Australia 1955 D-182-194

Harogoppad S.B. & Aminabhavi T.M. (1991a) "Interactions of Substituted Benzenes With Elastomers" Polymer 32:5 870-876

Harogoppad S.B. & Aminabhavi T.M. (1991b) "Diffusion and Sorption of Organic Liquids through Po,ymer Membranes. 5. Neoprene, Styrene-Butadiene-Rubber, Ethylene-Propylene-Diene Terpolymer, and Natural Rubber versus Hydrocarbons (C_8-$C_1$6)" Macromolecules 24 2598-2605

Hart C.A. (1977) "Effective Surface Moisture Content of Wood During Sorption" Wood Sci. 9:4 194-201

Hartley G.S. (1946) "Diffusion and Swelling of High Polymers. Part 1.- The Swelling and Solution of a High Polymer Solid Considered as a Diffusion Process" Trans. Faraday Soc. 42B 6-11

Hergt H.F.A. & Christensen G.N. (1965) "Variable Retention of Water by Dry Wood" J. Appl. Polym. Sci. 9:2345-2361

Hopfenberg H.B., Nicolais L. & Drioli E. (1976) "Relaxation Controlled (Case II) Transport of Lower Alcohols in Poly(methyl methacrylate)" Polymer 17 March 195-198

Hunt D.G. (1989) "Two classical theories combined to explain anomalies in wood behavior" J.Material Sci.Letters 8 1474-1476

Hunt D.G. (1990) "Longitudinal Shrinkage-Moisture Relations in Softwood" J. Materials Sci. 25 3671-3676

Ioelovich M., Kreitus A., Kaimins I. & Strazds E. (1982) "Study of the Diffusion of Water Vapour into Cellulose" (in russian) Khimiya Drevesiny 1 31-37

Jacques C.H.M., Hopfenberg H.B. & Stannett V. (1974) "Super Case II Transport of Organic Vapors in Glassy Polymers" Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids" Ed. Hopfenberg H.B. Plenum Press

Joshi S. & Astarita G. (1979) "Diffusion-Relaxation Coupling in Polymers which Show Two-Stage Sorption Phenomena" Polymer 20 April 455-458

Kellt M.W. (1968) "Moisture Movement in Small Specimens of Yellow Poplar (Liridendron tulipifera L.) and White Oak (Quercus Alba L.) in the Absence of Air" Ph.D. thesis, North Carolina State University at Raleigh

Kelly M.W. & Hart A.C. (1970) "Water Vapor Sorption Rates by Wood Cell Walls" Wood and Fiber 1:4 270-282

King G. & Cassie A.B.D. (1940) "Propagation of Temperature Changes Through Textiles in Humid Atmospheres. Part I.-Rate of Absorption of Water Vapour by Wool Fibres" Trans. Faraday Soc. 36 445-465

Kishimoto A. & Matsumoto K. (1964) "Effect of Film Thickness upon the Sorption of Organic Vapors in Polymers Slightly above Their Glass Transition Temperatures" J. Polymer Sci. A 2 579-687

Kishimoto A., Fujita H., Odani H., Kurata M. & Tamura M. (1960) "Successive Differential Absorptions of Vapors by Glassy Polymers" J. Phys. Chem. 64 594-598

Kokes R.J., Long F.A. & Hoard J.L. (1952) "Diffusion of Acetone Into Polyvinyl Acetate Above and Below the Second-Order Transition" J. Chem. Phys. 20:11 1711-1716

Kollmann F. (1963) "Zur Theorie der Sorption" Forch. Gebiete Ingenieurwesens 29:2 33-41

Kwei T.K. (1972) "Diffusion in Glassy Polymer. IV. Comments on Anomalous Behavior" J. Polymer Sci. A-2 Notes 10:9 1849-1851

Kwei T.K. & Wang T.T. (1974) "Diffusion in Glassy Polymers" in "Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids" Ed. Hopfenberg H.B. Plenum Press

Lindberg J. (1950) "Rate of Acid Sorption by Wool Fibers" Textile Res. J. June 381-384

Liu Tong (1988) "Moisture Transport in Wood and Wood-Based Panels - Comparison of the Cup and Sorption Methods" Träteknikcentrum, Stockholm, Sweden I 8802014

Long F.A., Bagley E. & Wilkens J. (1953) "Anomalous Diffusion of Acetone into Cellulose Acetate" J. Chem. Phys. 21 1412-1413

Long F.A. & Kokes R.J. (1953) "Diffusion of Benzene and Methylene Chloride Vapors Into Polystyrene" J. AM. Chem. Soc. 75 2232-2237

Long F.A. & Richman D. (1951) "Concentration Gradients for Diffusion of Vapors in Glassy Polymers and their Relation to Time Dependant Diffusion Phenomena" J.Am.Chem.Soc. 82 513-519

Long F.A. & Richman D. (1960) "Concentration Gradients for Diffusion of Vapors in Glassy Polymers and their Relation to Time Dependent Diffusion Phenomena" J. Am. Chem. Soc. 82:3 513-519

Long F.A. & Watt I. (1956) "Concentration Gradients During Sorption of Vapor Into Polymers in the Glassy State" J. Polymer Sci. XXI:99 554-557

Mackay B.H., Stearn A.E. & Downes J.G. (1969) "The Kinetics of Water-Vapour Sorption in Wool. Part I: An Improved Sorption Vibroscope" J. Textile Inst. 359-377

Mackay B.H. & Downes J.G. (1969) "The Kinetics of Water-Vapour Sorption in Wool. Part II: Results Obtained with an Improved Sorption Vibroscope" J. Textile Inst. 378-394

Mandelkern L. & Long F.A. (1951) J. Polymer Sci. 6 457

Marom G. (1985) "The Role of Water Transport in Composite Materials" 341-374 in. "Polymer Permeability" Ed. Comyn J., Elsevier Appl. Sci. Publ.

McNamara W.S. (1969) "Effects of Stress on the Diffusion of Moisture in Wood" Ph.D. thesis, North Carolina State University at Raleigh

McNamara W.S. & Hart C.A. (1971) "An Analysis of Interval and Average Diffusion Coefficients for Unsteady-State Movement of Moisture in Wood" Wood Sci. 4:1 37-45

Mee C.F., Goydan R. & Schneider N.S. (1985) "Vapor Interactions With a Phase Segregated Polyurethane" 32nd Sagamore Army Materials Res. Conf. Proc. 405-413

Mirley C.L., Sung N.H. & Schneider N.S. (1985) "Sorption and Diffusion Behavior of Styrene-Butadiene Block Copolymers" Polymeric Mat. Sci. Eng. 53 325-329

Morton W.E & Hearle J.W.S. (1986) "Physical Properties of Textile Fibres" The Textile Institute ISBN 0900 739 878

Newns A.C. (1956) "The Sorption and Desorption Kinetics of Water in a Regenerated Cellulose" Trans. Faraday Soc. 52 1533-1545

Newns A.C. (1959) "The Sorption and Desorption Kinetics of Water in a Regenerated Cellulose" J. Polymer Sci. XLI 425-434

Newns A.C. (1968) "Sorption and Desorption Kinetics of the Cellulose + Water System. Part 1. Successive Sorptions from Dryness" Trans. Faraday Soc. 52 1533-1545

Newns A.C. (1973) "Sorption and Desorption Kinetics of the Cellulose and Water System. Part 2. Low Concentrations on the Lowest Sorption Limb of the Hysteresis Loop" J. Chem. Soc. Faraday I 69 444-448

Newns A.C. (1974) "Sorption and Desorption Kinetics of the Cellulose and Water System. Part 3. The Rates of Sorption on the Lowest Sorption Limb of a Hysteresis Loop" J. Chem. Soc. Faraday I 278-284

Nicolais L., Drioli E., Hopfenberg H.B. & Apicella A. (1979) "Effects of Orientation on the Penetration, Crazing, and Dissolution of Polystyrene by n-Hexane" Polymer 20 459-464

Odani H., Hayashi J. & Tamura M. (1961) "Diffusion in Glassy Polymers. II. Effects of Polymer-penetrant Interaction; Diffusion of Ethyl Methyl Ketone in Atactic Polystyrene" Bull. Chem. Soc. Japan 34 817-821

Ottino J.M. & Shah N. (1984) "Analysis of Transient Sorption and Permeation of Small Molecules in Multiphase Polymer Systems" Polymer Eng. Sci. 24:2 153-162

Park G.S. (1953) "An Experimental Study of the Influence of Various Factors on the Time Dependant Nature of Diffusion in Polymers" J. Polymer Sci. XI:2 97-115

Peterlin A. (1965) "Diffusion in a Network with Discontinuous Swelling" Polymer Lett. 3 1083-1087

Peterlin A. (1969) "Diffusion in Glassy Polymer with Discontinuous Swelling II. Concentration Distribution of Diffusant as Function of Time" Die Makromolekulare Chemie 124 136-142

Peterlin A. (1977) "Diffusion with Discontinuous Swelling III. Type II Diffusion as a Particular Solution of the Conventional Diffusion Equation" J. Res. Nat. Bureau of Standards Phys. and Chem. (USA) 81A:2-3 243-250

Peterlin A. (1979) J. Polymer Sci. Phys. Ed. 17 1741

Petropoulos J.H. & Roussis P.P. (1967) J. Chem. Phys 47 1491

Petropoulos J.H. & Roussis P.P. (1969) J. Polymer Sci. C22 917

Petropoulos J.H. & Roussis P.P. (1974) "A Discussion of Theoretical Models of Anomalous Diffusion of Vapors in Polymers" in "Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids" Ed. Hopfenberg H.B. Plenum Press

Petropoulos J.H. & Roussis P.P. (1978) "The Influence of Transverse Differential Swelling Stresses on the Kinetics of Sorption of Penetrants by Polymer Membranes" J. Membrane Sci. 3 343-356

Prichananda C. (1966) "A Study of Some Aspects of Moisture Sorption Dynamics in Wood" Ph.D. thesis State University College of Forestry at Syracuse

Richman D. & Long F.A. (1960) "Measurements of Concentration Gradients for Diffusion of Vapors in Polymers" J. Am. Chem. Soc. 82:3 509-512

Rogers C.E. (1965) "Solubility and Diffusivity" in "Physics and Chemistry of the Organic Solid State" ed. Fox D. et al. Interscience Publ. New York

Rogers C.E. (1985) "Permeation of Gases and Vapours in Polymers" 11-73 in. "Polymer Permeability" Ed. Comyn J., Elsevier Appl. Sci. Publ.

Rogers C.E., Stannett V. & Szwarc M. (1960) "The Sorption, Diffusion, and Permeation of Organic Vapors in Polyethylene" J. Polymer Sci. XLV 61-82

Rosen H.N. (1982) "Predicting Wood Surface Moisture Content During Water Vapor Sorption" Wood Sci. 14:3 134-137

Sadoh T. (1960) "The Effects of Moisture Content and Temperature upon the Rate of Moisture Adsorption by Hemicellulose" Japan Wood Res. Soc. J. 6:2 45-48

Sadoh T. (1960) "Factors Limiting the Rate of Moisture Adsorption by Hemicellulose" Japan Wood Res. Soc. J. 6:2 219-222

Sadoh T. & Christensen G.N. (1964) "The Rate of Sorption of Water Vapour by Hemicellulose" Aust.J.Appl.Sci. 15 297-308

Sadoh T., Yamanaka H. & Kadita S. (1958) "On the Diffusion of Water in a Hardwood Hemicellulose" J. Japan Wood Res. Soc. 4 146-150

Sarti G. (1976) Polymer 20 827

Sarti G. (1979) "Solvent Osmotic Stresses and the Prediction of Case II Transport Kinetics" Polymer 20 827-832

Sax J.E. & Ottino J.M. (1983) "Modeling the Transport of Small Molecules in Polymer Blends: Application of Effective Medium Theory" Polymer Eng. Sci. 23:3 165-176

Sax J.E. & Ottino J.M. (1985) "Influence of Morphology on the Transport Properties of Polystyrene/polybutadiene blends. 1. Experimental Studies" Polymer 26 1073-1080

Schneider N.S., Illinger J.L. & Cleaves M.A. (1986) "Liquid Sorption in a Segmented Polyurethane Elastomer" Polymer Eng. Sci. 26:22 1547-1551

Schneider N.S., Macknight W.J. & Sung N.H. (1988) "Relaxation-Coupled Diffusion in Several Elastomeric Materials" Polymer Mat. Sci. Eng. 58 957-961

Serrano M., MacKnight W.J., Thomas E.L. & Ottino J.M. (1987a) "Transport-Morphology Relationships in Segmented Polybutadiene Polyurethanes: 1. Experimental Results" Polymer 28

1667-1673

Serrano M., MacKnight W.J., Thomas E.L. & Ottino J.M. (1987b) "Transport-Morphology Relationships in Segmented Polybutadiene Polyurethanes: 2. Analysis" Polymer 28 1674-1679

Shah N. & Ottino J.M. (1986) "Effective Transport Properties of Disordered Multi-Phase Composites: Application of Real-Space Renormalization Group Theory" Chem. Eng. Sci. 41 283-296

Shah N., Sax J.E. & Ottino J.M. (1985) "Influence of Morphology on the Transport Properties of Polystyrene/Polybutadiene Blends: 2. Modelling Results" Polymer 26 1239-1246

Skaar C., Prichananda C. & Davidson R.W. (1970) "Some Aspects of Moisture Sorption Dynamics in Wood" Wood Sci. 2:3 179-185

Thomas N.L. & Windle A.H. (1980) "A Deformation Model for Case II Diffusion" Polymer 21 613-619

Thomas N.L. & Windle A.H. (1982) "A Theory of Case II Sorption" Polymer 23 529-542

Tu Y.O. (1977) "A Multi-Phase Stefan Problem Describing the Swelling and the Dissolution of Glassy Polymer" Quart. Appl. Math. July 269-285

Tu Y.O. & Ouano A.C. (1977) "Model for the Kinematics of Polymer Dissolution" IBM J. Res. Develop. March 131-142

Tyrell H.J.V. (1964) "The Origin and Present Status of Fick's Diffusion Law", J. Chem. Education 41:7 397-400

Vieth W.R. & Amini M.A. (1974) "Generalized Dual Sorption Theory" in "Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids" Ed. Hopfenberg H.B. Plenum Press

Vieth W.R. & Sladek K.J. (1965) "A Model for Diffusion in a Glassy Polymer" J. Colloid Sci. 20 1014-1033

Vrentas J.S. & Duda J.L. (1986) 36-68 in Vol. 5 of "Encyclopedia of Polymer Science and Engineering" J.Wiley N.Y.

Vrentas J.S., Jarzebski C.M. & Duda J.L. (1975) "A Deborah Number for Diffusion in Polymer-Solvent Systems" AIChE J. 21:5 894-901

Wadsö L. (1989) "The Sorption Method - Old and New Ideas" LUTVDG/(TVBM-3040) ISSN 0348-7911 Div. of Building Materials, Lund University, Sweden

Wadsö L. (1992) "A Model for Non-Fickian Sorption of Water Vapour in Wood" Submitted to Int. Drying Symp. August 1992 in Montreal, Canada

Wakesman L.S., Schneider N.S. & Sung N.H. (1989) "Toluene Diffusion in Natural Rubbers" Polymer Prep. (Am. Chem. Soc.) 30:1 34-35

Walker I.K. (1977) "Changes of Bound Water in Wood: I. Non-Fickian changes of weight at 25°C" New Zealand J. Sci. 20:3-10

Walker I.K. & Harrison W.J. (1971) "Diffusion of Regain in Bulk Wool. Part 6 - Non-Fickian Changes of Weight at Normal Atmospheric Temperature" New Zealand J. Sci. 13:240-255

Walker I.K. & Harrison W.J. (1972) "Diffusion of Regain in Bulk Wool. Part 7 - Weight Changes in Commercial Bales of Wool" New Zealand J. Sci. 15:240-254

Wang T.T., Kwei T.K. & Frisch H.L. (1969) J. Polymer Sci. 2 7 2019

Watt I.C. (1960a) "Kinetic Studies of the Wool-Water System. Part I: The Influence of Water Concentration" Textile Res. J. June 443-450

Watt I.C. (1960b) "Kinetic Studies of the Wool-Water System. Part II: The Mechanisms of Two-Stage Absorption" Textile Res. J. September 644-651

Watt I.C. & Algie J.E. (1961) "Kinetic Studies of the Wool-Water System. Part III: The Mechanisms of Sorption at High Water Concentration" Textile Res. J. September 793-799

Watt I.C. & Kennett R.H. (1960) "Variations in the Equilibrium Weight of Wool at Zero Humidity" Textile Res. J. July 489-494

Watt I.C. & McMahon G.B. (1966) "The Effects of Heat of Sorption in the Wool-Water Sorption System" Textile Res. J. August 738-745

Windle A.H. (1984) "Case II Sorption" 75-118 in. "Polymer Permeability" Ed. Comyn J., Elsevier Appl. Sci. Publ.æ