SORPTION AND DESORPTION KINETICS

OF CARBON TETRACHLORIDE VAPOR ON WHEAT KERNELS

by

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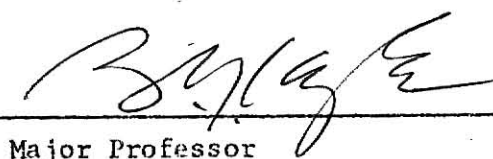
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CHAPTER 1

INTRODUCTION

The increasing world population requires human beings to produce as much food as possible. In terms of total food consumption, cereal grains are the most important food product. Uneven productive ability and occasional catastrophes make it necessary for every country to maintain adequate grain reserves. It is estimated that insects destroy at least 10% of the world production of cereal grains (5). In order to maintain the quality and quantity of the stored grains, fumigation is used to protect against attack by insects and aeration is used to remove fumigant residues before marketing.

Many studies have been done on the fumigation process. Most of them concern the effect of fumigant dosage on insect infestation, toxicant residue and adsorption equilibria. Although useful, many of these studies are qualitative and empirical and can not be used for a systematic analysis of the sorption process. The fundamental phenomena of diffusion behavior of fumigant vapor within grain kernels is very important in selecting more effective fumigants and designing more efficient fumigation and aeration process. Little work of a fundamental nature has been done and a search of literature reveals that Park's study of the sorption kinetics of carbon tetrachloride on wheat (11) was the only one in this area. In his study, experimental data were well represented by an intraparticle diffusion model (or internal diffusion model) and the diffusion coefficient obtained from this model was physically realistic. He investigated only the sorption process, and his experimental method relied on gravimetric measurements and required an extremely long time. Therefore, it is the purpose of the present study to improve the experimental technique and also to study the fundamental phenomena of desorption.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2-1 General Concept:

The process of sorption is generally considered to consist of three consecutive steps (8). This three-step mechanism is described below for the specific case of fumigant sorption in cereal grain kernels:

(1) Diffusion of fumigant molecules from the main body of the gas phase to the external surface of the kernel.

(2) Diffusion into the kernel. The mechanism of this step can be either by a gaseous diffusion through the pore volume, or by surface diffusion along the solid surface of the pores in the kernel, or by solid diffusion through a homogeneous, permeable solid kernel.

(3) Adsorption on the interior surface of the kernel.

A desorption process is usually considered just the reverse of a sorption process and also has a similar three-step mechanism. In general, all of these three steps can contribute to the overall rate of a sorption or desorption process. Models which assume a single rate-controlling step have been developed. There are: the external diffusion model, the intraparticle diffusion model (or internal diffusion model) and the surface adsorption model.

Park and Kyle (12) have shown that the sorption rate of carbon tetrachloride on wheat is controlled by internal diffusion. The first and third step are usually not rate-controlling and will not be included in this study. Details of these two models, the external diffusion model and the surface adsorption model, and several other models based on combined resistances can be found in the literature (8, 11).

2-2 Intraparticle Diffusion Models:

There are several forms of the intraparticle diffusion model as shown in Table 1. The governing equations in all cases originate from Fick's law of diffusion althoguh different diffusion mechanisms are proposed.

$$\frac{\partial c}{\partial t} = D\nabla^2 c \qquad (2.1)$$

Depending on the proposed diffusion mechanism, the concentration units employed in equation 2.1 can be: c, concentration of diffusing component in the fluid contained in the pore space; q, concentration of diffusing component in the permeable solid phase; or N_g, number of diffusing molecules in the gas phase per unit pore length.

McBain (9) and Ward (14) considered that the diffusing substance dissolves in the solid to form a homogeneous solid solution, so the diffusion is through a homogeneous phase and this is similar to the quasi-homogeneous model (4, 10) which assumes the porous adsorbent to be a homogeneous phase. The diffusion coefficient that McBain and Ward described has true physical meaning because they thought the diffusion is through a true homogeneous phase which is like the diffusion of a binary system. For the quasi-homogeneous model, an effective diffusion coefficient is defined in equation 2.1. The equation so defined can not be expected to be meaningful at a point due to the complex structure of the adsorbent, but it is considered to be a valid average.

Damköhler (7) considered that gaseous diffusion in the pores and surface diffusion along the pore surface took place in parallel and was the rate controlling step. he further assumed a linear equilibrium relationship between the concentration of adsorbate in the gas phase and the adsorbed phase and reduced the diffusion equation into the general form shown in Table 1. The diffusion coefficient he described consists of gas diffusivity

Table 1: Intraparticle Diffusion Models

References	McBain (9) Ward (14)	Damköhler (7)	Wicke (15)	Brecher et. al. (4) Miller and Clump (10)
Mechanism	Solid solution process	gaseous diffusion and surface diffusion take place in parallel	gaseous diffusion into macropores	quasi-homogeneous diffusion
Diffusion Equation	$\frac{\partial q}{\partial t} = D_{AB}\nabla^2 q$	$\frac{\partial}{\partial t}(Ng + Na) = D_g\nabla^2 Ng + D_a\nabla^2 Na$	$\frac{\partial q}{\partial t} = D_g\nabla^2 C$	$\frac{\partial q}{\partial t} = De\nabla^2 q$
General Form	$\frac{\partial q}{\partial t} = D_{AB}\nabla^2 q$	$\frac{\partial Ng}{\partial t} = D\nabla^2 Ng$	$\frac{\partial C}{\partial t} = \frac{D_g}{H}\nabla^2 C$	$\frac{\partial q}{\partial t} = De\nabla^2 q$
Diffusion Coefficient D	D_{AB}	$\frac{D_g + AD_a}{1 + A}$	$\frac{D_g}{H}$	D_e

$A = \frac{Ng}{Na}$

$q = HC$

D_g, surface diffusivity D_a and a linear isotherm constant A which is defined by the relation:

$$Na = ANg \qquad (2.2)$$

Another mechansim was proposed by Wicke (15). He assumed that each adsorbent particle has many large macropores which are surrounded by short, numerous micropores. The total surface area of micropores is considerably larger than that of macropores. He further postulated that the micropores filled rapidly due to short length and the controlling step is therefore the gaseous diffusion of adsorbate into the macropores. With these assumptions, he derived a diffusion equation as shown in Table 1. If a linear equilibrium relation q=Hc exists, the diffusion equation can be expressed in terms of c. The diffusion coefficient for this model consists of gas diffusivity in macropores, D_g, and the equilibrium parameter H.

In the present study, equation 2.1 will be used as the basis for analysing the experimental data and estimating the value of the diffusion coefficient. Since this diffusion coefficient is usually sufficient for the design of a sorption or desorption process and due to the complex structure of the wheat kernel, no attempt will be made to explain the physical significance of it.

For a sorption or desorption process at constant temperature and adsorbate partial pressure, applying equation 2.1 to a single adsorbent particle gives:

$$\frac{\partial q}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \qquad (2.3)$$

If equilibrium at the gas-solid interface is assumed, this equation has to be solved with the following boundary condtions:

when   t=0 $q=q_0$ for all r

when   t>0 $q=q_e$ at   r=R

$$\frac{\partial q}{\partial r} = 0 \quad \text{at} \quad r=0$$

where q_e is the concentration which equilibrates with the
adsorbate vapor.

The solution of this equation and boundary conditions can be found in
many places in the literature (6, 11) and is:

$$\frac{q - q_0}{q_e - q_0} = 1 + \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{R} e^{-\delta n^2 t} \tag{2.4}$$

$$\text{where } \delta = \frac{D\pi^2}{R^2} \tag{2.5}$$

Equation 2.4 gives concentration distribution in a adsorbent particle.
Integrating the concentration distribution over the whole particle volume
gives the total amount of adsorbate sorbed, Q_s, or desorbed, Q_d at time t:

$$Q_s = \int_v (q - q_0) \, dv \tag{2.6}$$

$$Q_d = \int_v (q_0 - q) \, dv \tag{2.7}$$

Substituting equation 2.4 into above equations gives:

$$\frac{Q_s}{Q_{es}} = \frac{Q_d}{Q_{ed}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\delta n^2 t} \tag{2.8}$$

$$\text{where } Q_{es} = \frac{4}{3}\pi R^3 (q_e - q_0) \tag{2.9}$$

$$Q_{ed} = \frac{4}{3}\pi R^3 (q_0 - q_e) \tag{2.10}$$

and are the equilibrium amount sorbed or desorbed respectively.

In the present study, q_0 is zero for sorption and q_e is zero for de-
sorption. Rearranging equation 2.8 in terms of the total amount of adsorbate
in the particle at time t, Q_t, gives:

for sorption:
$$\frac{Q_t}{Q_{es}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\delta n^2 t}$$
(2.11)

for desorption:
$$\frac{Q_t}{Q_{ed}} = \frac{Q_t}{Q_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\delta n^2 t}$$
(2.12)

where $Q_0 = \frac{4}{3}\pi R^3 q_0$ and is the initial amount sorbed.

2-3 Structure and Property of Wheat:

Hard red winter wheat was used in this study. An efficient theoretical study of sorption and desorption of fumigants on wheat can not be carried out without a clear understanding of its structrue. Numerous studies in wheat structure have been published. Fig. 2.1 shows the longitudinal section and cross section of a wheat kernel. There are three main parts: endosperm, bran and germ (embryo). Detailed structure of each part and its signifigance to absorption of water and solutes is available in Bradbury et. al. (3).

It has been recognized by many workers that the seed coat (testa) alone may offer more resistance than other parts of a wheat kernel. Due to this non-uniform structure, the sorbed materials usually take some preferred path and diffuse with different velocities (3). Therefore, a realistic modeling is very hard to achieve and this is the reason that general equation with effective diffusion coefficient was used for the present study.

THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH DIAGRAMS
THAT ARE CROOKED
COMPARED TO THE
REST OF THE
INFORMATION ON
THE PAGE.

THIS IS AS
RECEIVED FROM
CUSTOMER.

Hairs of Brush

Longitudinal Section of Grain of Wheat
(enlarged approximately 35 times)

Endosperm

Cell filled with Starch Granules in Protein Matrix

Cellulose Walls of Cells

Aleurone Cell Layer (part of endosperm but separated with bran)

Nucellar Tissue

Seed Coat (Testa)

Tube Cells

Cross Cells

Hypodermis

Epidermis

ENDOSPERM

BRAN

Scutellum

Sheath of Shoot

Rudimentary Shoot

Rudimentary Primary Root

Root Sheath

Root Cap

GERM

Crease

ENDO-SPERM

Pigment Strand

BRAN
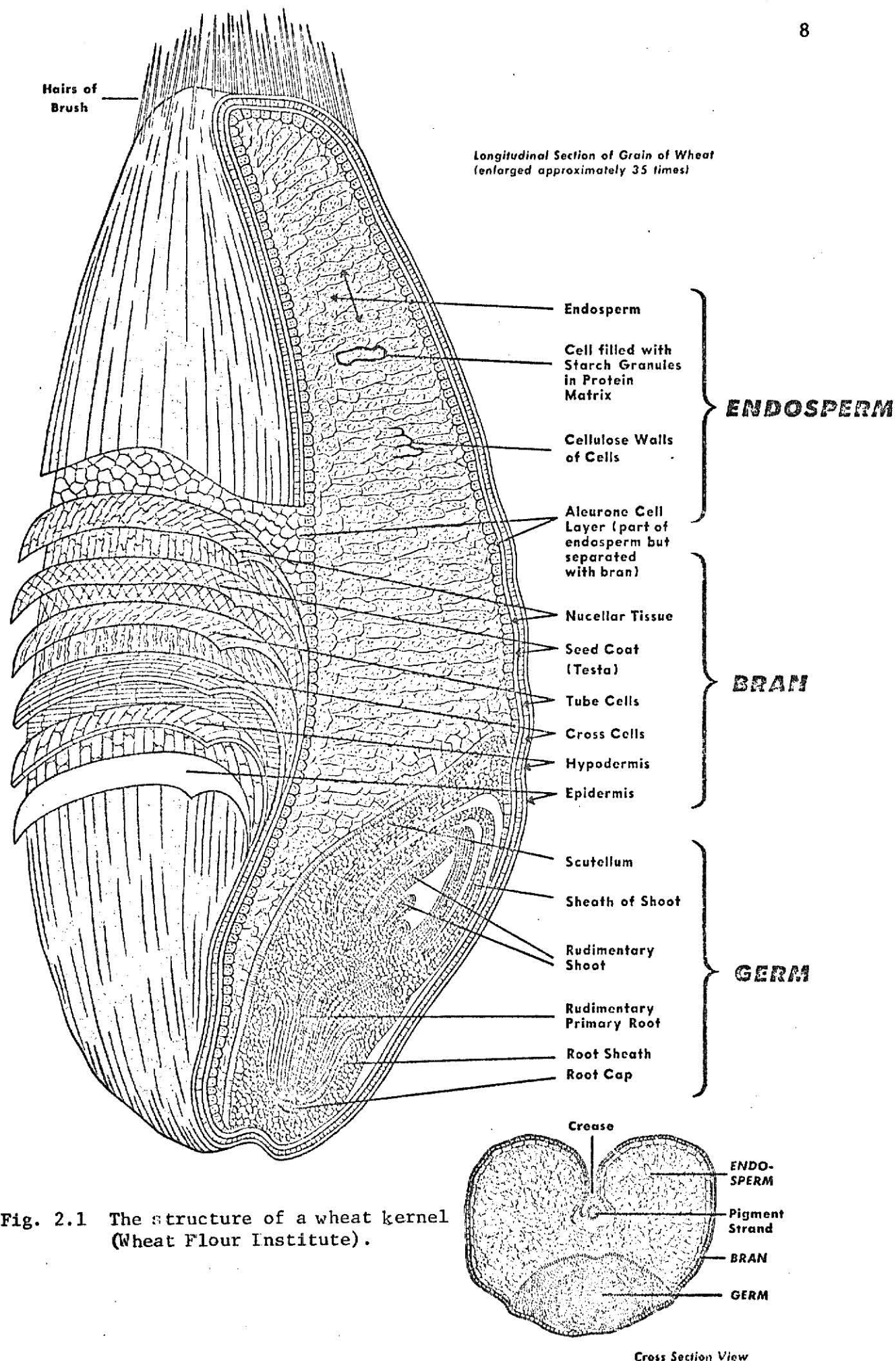
GERM

Cross Section View

Fig. 2.1   The structure of a wheat kernel (Wheat Flour Institute).

CHAPTER 3

EXPERIMENTAL

3-1 Background:

In a previous study, reported by Park and Kyle (12), the sorption

rate of carbon tetrachloride vapor by wheat was determined by measuring

weight changes of a sample of wheat placed in a adsorption chamber where

temperature, relative humidity and partial pressure of carbon tetrachloride

were maintained constant. It was necessary to first let the wheat sample

equilibrate with the water vapor inside the adsorption chamber and then

introduce carbon tetrachloride and record the weight change of the wheat

sample. About 2 to 3 weeks was required for the sample to come to equili-

brium with water vapor and then approximatley 4 to 5 weeks was required

for the sample to reach equilibrium sorption condition with respect to

carbon tetrachloride vapor. Beside this, a blank run under identical

conditions was necessary to correct the amount of carbon tetrachoride sorbed

on the sample pan. Thus, an extremely long time was required for each

run in the previous technique. Additionally, since the moisture content

of wheat is very large (about 12% by weight) compared to the small amount

of carbon tetrachloride sorbed by wheat (about 1% by weight), a slight

change in moisture content would give rise to a weight change of the same

order of magnitude as that due to sorption of carbon tetrachloride. Furth-

ermore, the accuracy of the previous technique relied on a doubtful assumption

that the sorbed carbon tetrachloride does not replace sorbed water mole-

cules and thus the recorded weight change was taken to be the weight of

carbon tetrachloride sorbed.

These disadvantages are the reasons that a new experimental technique which relied on the direct determination of fumigant content of the wheat was developed for the present study. In this method, wheat samples were placed in stoppered glass flasks containing known concentrations of carbon tetrachloride and water vapor. At the desired time, the wheat sample was removed from the flask and analyzed for carbon tetrachloride concentration. Two analytical methods were evalutated to determine the amount of carbon tetrachoride in wheat: a wet aeration and colorimetric determination method (13), and neutron activation analysis. A fair reproducibility of the wet aeration and colorimetric determination method was obtained using an adequate amount of sound wheat kernels (about 2 grams or more), but the neutron activation analysis was not reproducible and was not used in this study.

3-2. Apparatus and Materials:

3-2.1 Apparatus:

The schematic diagram of the experimental apparatus for sorption and desorption experiments is shown in Fig. 3.1. It consists of a salt solution saturator, a water trap and several volumetric flasks placed in a constant temperature chamber. The salt solution saturator is used to maintain a constant relative humidity in the system at a level which will be in equilibrium with the desired moisture content (about 12%) of the wheat. This is done by using a saturated solution of various inorganic salts. The water trap is used to prevent entrained liquid from the saturator from getting into the flasks.

3-2.2 Materials:

Hard red winter wheat harvested in 1975 was used for the present study. Wheat kernels were stored in a desiccator with a saturated aqueous solution of potassium carbonate ($K_2CO_3 \cdot 1\text{-}1/2H_2O$, Mallinckrodt analytical grade) at room
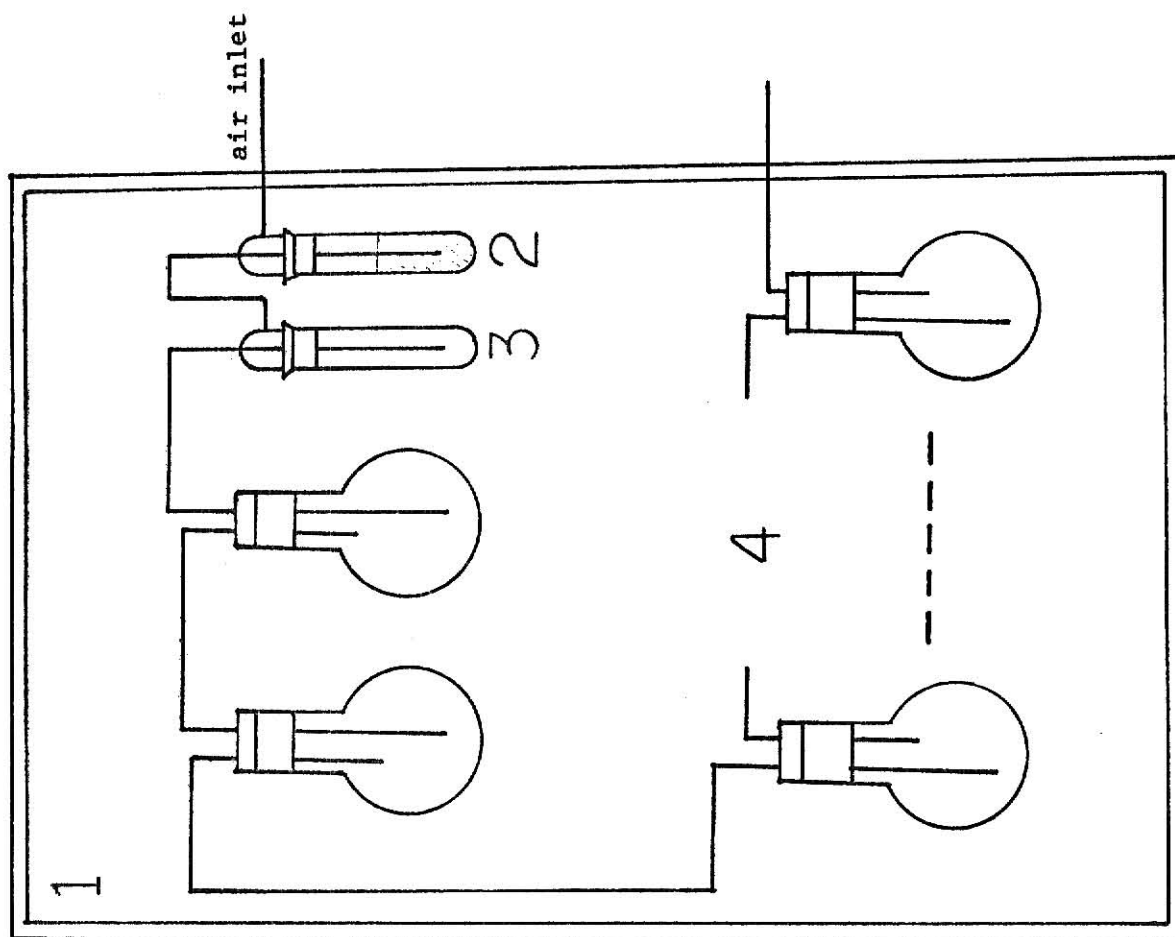
1. Constant temperature chamber

2. Salt solution saturator

3. Water trap

4. Glass flasks

Fig. 3.1 Schematic diagram of the experimental apparatus.

temperature. The relative humidity provided by this salt solution is about 42%. This is the relative humidity in equilibrium with wheat containing approximately 12 wt.% moisture (1) which is in the range used for storage. Approximately one month was allowed for wheat to reach equilibrium with water vapor where the moisture contnet of wheat kernels is 12.27% (dry basis). During a sorption or desorption experiment at 86°F, this moisture content was maintained approximatley by using a satuarated calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$, Mallinckrodt analytical grade) solution in the saturator to provide a relative humidity of 46.8% in the system (11).

Carbon tetrachloride (CCl_4, Fisher A. C. S. reagent grade, 99% pure) was used as a fumigant in this investigation. Acetone (CH_3COCH_3, Fisher A. C. S. spectranalyzed grade) was used to absorb carbon tetrachloride in the analytical method.

3-3 Analysis:

The amount of carbon tetrachloride in wheat was measured using a wet aeration and colorimetric determination method (13). A schematic diagram of the experimental apparatus for the wet aeration method is shown in Fig. 3.2. It consists of a one liter round-bottom flask (aeration flask), a condenser, two Peligot tubes connected in series, an ice bath, a hot water reservoir maintained at 55-65°C and a heating mantle. The hot condenser is used to condense water vapor and not carbon tetrachloride vapor, and the Peligot tubes are used to absorb the carbon tetrachloride vapor obtained in aeration. For the colorimetric determintation, the apparatus used consists of a Bausch & Lomb Spectronic 600 Spectrophotometer, a constant temperature bath maintained at 70 ± 0.5°C and several glass- stoppered Pyrex 25 ml graduated cylinders.
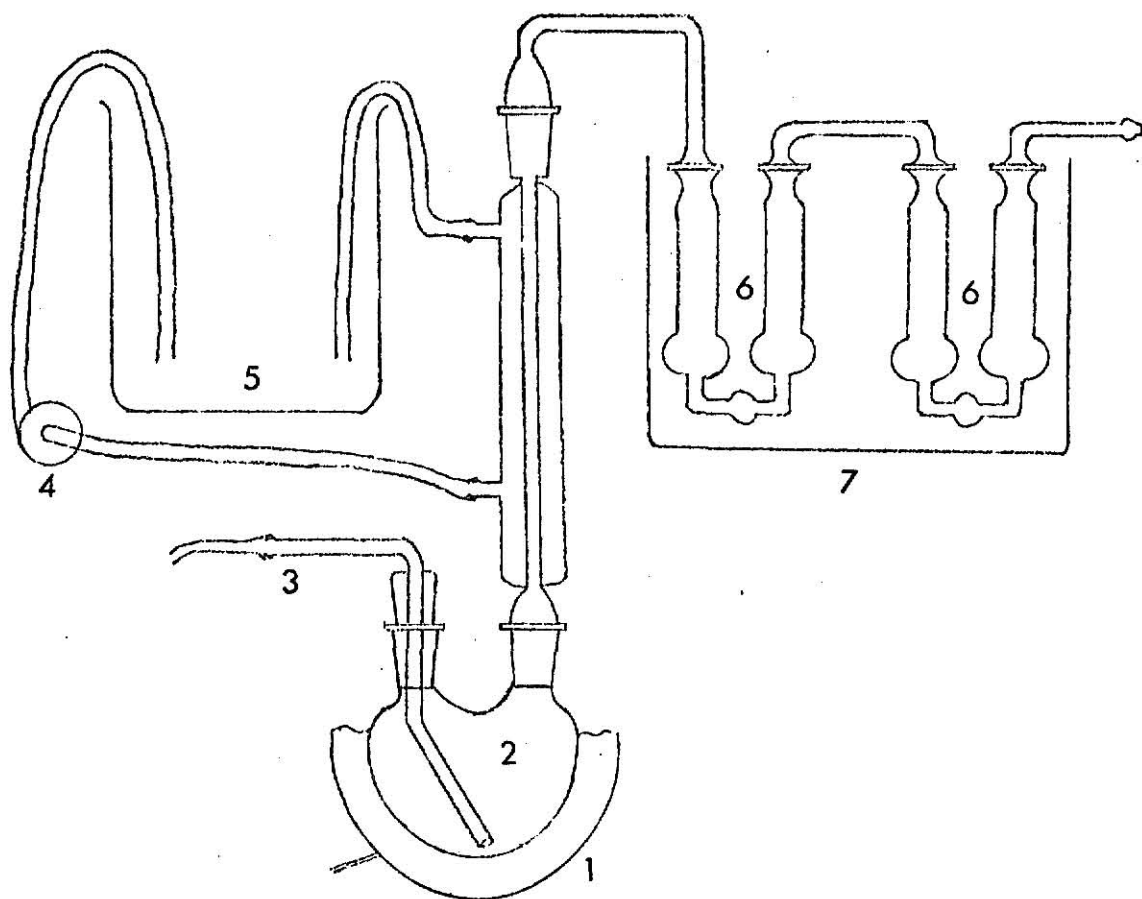
1. Heating mantle   2. Aeration flask

3. Air inlet tube   4. Water pump

5. Hot water reservoir 6. Peligot tubes

7. Ice bath

Fig. 3.2 Schematic diagram of the aeration apparatus.

First, 4 ml acetone was pipeted into each of the Peligot tubes and the apparatus was connected as shown in Fig. 3.2. Then, the weighted wheat sample (about two grams) to be analysed was placed in the aeration flask which contained 530 ml distilled H_2O, 60 ml 1N H_2SO_4, 10 ml of 20% phosphotungstic acid, and a small amount of DC aniform A. The mixture was boiled and refluxed vigorously under the hot condenser (55-65°C) for one hour. The carbon tetrachloride was swept from the boiling suspension by a current of air at a rate of 25-30 ml/min and absorbed in acetone. The carbon tetrachloride-acetone solution was then reacted with Fujiwara reagent at 70°C for exactly 15 minutes to form a color solution. The absorbance of the colored solution at 530 mμ was measured using a Bausch & Lomb Spectronic 600 Spectrophotometer. A standard curve using known concentrations of carbon tetrachloride-acetone solutions was prepared for calibration and the amount of carbon tetrachloride in the wheat was calculated from this curve. Details of this method can be found in the literature (13).

It was difficult to reproduce the analysis using a small quantity of wheat (about one gram). Though better reproducibility was obtained using larger sample size (about two grams or more), a substantial error still existed (about 10% relative error). For this reason the analyses were always conducted in triplicate. In an attempt to determine the cause of the lack of precision, the following analysis of the sampling and analytical procedure was conducted.

The wheat samples to be analyzed were sealed in plastic vials after being taken out of the flasks. The wet aeration process needs about two hours, so there is about four hours difference between the first and the third analysis of the triplicates. If the desorption diffusion coefficient obtained later is used, it is calculated that a maximum of 15% of the carbon

tetrachloride in the wheat would desorb in four hours. Because the wheat samples were sealed in the vials, the desorbed carbon tetrachloride would remain inside the vials and its partial pressure would not be zero all the time, so the amount of carbon tetrachloride desorbed would be much less than 15%. Also, examining the experimental data shows that the order of analysis does not relate to the direction of the error. This indicates that desorption occuring in the samples awaiting analysis is not the main source of the error. To determine the accuracy of the wet aeration and colorimetric determination method, four analyses were run with known quantities of carbon tetrachloride introduced into the aeration flask. It is found that the recovery of the added carbon tetrachloride is almost complete (see Appendix B) indicating that the analytical method is not the source of error either. From this it may be concluded that most of the error comes from sample variability and therefore larger sample size should be used to get better results.

3-4 Procedure:

3-4.1 Sorption Experiment:

First, the apparatus was connected as shown in Fig. 3.1 and the temperature of the system was controlled at the desired value of $86^{o}F$. Then, air was passed thorugh the system to allow the relative humidity in each flask reach a constant value of 46.8% provided by the calcium nitrate saturated solution in the saturator. This is the relative humidity which will be in equilibrium with wheat containing approximately 12% moisture at $86^{o}F$ (1). After that, the system was disconnected and a pre-calculated amount of carbon tetrachloride which gives the desired carbon tetrachloride partial pressure was introduced into each flask using a liquid syringe which can measure a quantity to within $\pm$ .001 ml. The flasks were stoppered and a small amount of high vacuum grease was used to ensure airtight condition during the evaporation of carbon tetrachloride.

Rubber bands or clamps were used to fix the stopper due to the pressure
increase resulting from the evaporation of carbon tetrachloride. After
the evaporation was completed, wheat samples were introduced into each
flask and the flasks were stoppered again. Those wheat samples used had
been equilibrated to the desired moisture content of 12.27% in the
desiccator. At a pre-determined time, the wheat sample was removed from
the flask and the wet aeration and colorimetric determination method
described in section 3-3 was used to determine the amount of carbon
tetrachloride sorbed into the wheat.

A sample calculation of the amount of carbon tetrachloride which will
give the desired partial pressure is given in Appendix A. Since the sorption
process was intended to proceed under constant carbon tetrachloride partial
pressure, the effect of the sorbed carbon tetrachloride on the value of carbon
tetrachloride partial pressure has to be considered. The experiments in this
study were designed so that the partial pressure of carbon tetrachloride
did not decrease by more than five percent.

3-4.2 Desorption Experiment:

First, the apparatus was connected as shown in Fig. 3.1 and the temperature
of the system was controlled at the desired value of 86°F. Then, air of
46.8% relative humidity was passed through the system. The 46.8% relative
humidity was provided by a calcium nitrate saturated solution in the satu-
rator. Wheat samples of initial carbon tetrachloride concentration q_0 were
introduced into each flask and air was passed through each flask continuously
during the experiment. At a pre-determined time, the wheat sample was taken
out and the analytic method described in section 3-3 was used to determine
the amount of carbon tetrachloride remaining in the wheat.

Two methods were used to prepare wheat samples of initial carbon tetrachloride concentration q_0. The first was similar to that described for the sorption experiment (section 3-4.1). Equilibrium sorption condition had to be reached in order to get an approximatley uniform carbon tetrachloride concentration within the wheat kernel. In the second method, wheat samples were prepared from a sample of higher carbon tetrachloride concentration, thus the technique was similar to that of a desorption experiment described above. At the desired time, flow of air through the flask containing the wheat samples was stopped and the flask was stoppered for about one month to allow the establishment of a uniform concentration of carbon tetrachloride within each kernel.

CHAPTER 4

RESULTS AND DISCUSSION

4-1 Sound Wheat:

The sorption rate of carbon tetrachloride from the gas phase by wheat
was studied at 86°F, 46.8% relative humidity and 95 mm Hg carbon tetra-
chloride partial pressure. The experimental data obtained are tabulated
in Appendix B and plotted on Fig. 4.1. The figure shows a set of three
data points for each time with considerable scatter among the three points.
The scatter is due to a lack of precision in the analytical method for
determining the amount of carbon tetrachloride in wheat as discussed in
Chapter 3. Rather than plotting the result obtained from the average of
the triplicate analyses, separate results are shown so that a measure of
the uncertainty of the data might be obtained.

The intraparticle diffusion model was used to explain the experimental
data obtained. The rate equation of this model for a sorption process,
previously derived in chapter 2, is:

$$\frac{Q_t}{Q_{es}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\delta n^2 t} \tag{4.1}$$

The two parameters, Q_{es} and δ, in equation 4.1 were evaluated from the
experimental data using Bard's nonlinear parameter estimation method
(2). The summation term in equation 4.1 was calculated up to n=100 or
up to a term for which the contribution to the whole summation is less
than 0.01%. The results of the parameter estimation are summarized in
Table 2 together with the results obtained in a previous study of this
same system by Park (11). A comparison between equation 4.1 with fitted
parameters and experimental data is also shown in Fig. 4.1.

Because of the extremely slow rate of sorption, Park (11) found that
approximately one month was required for wheat to reach equilibrium with
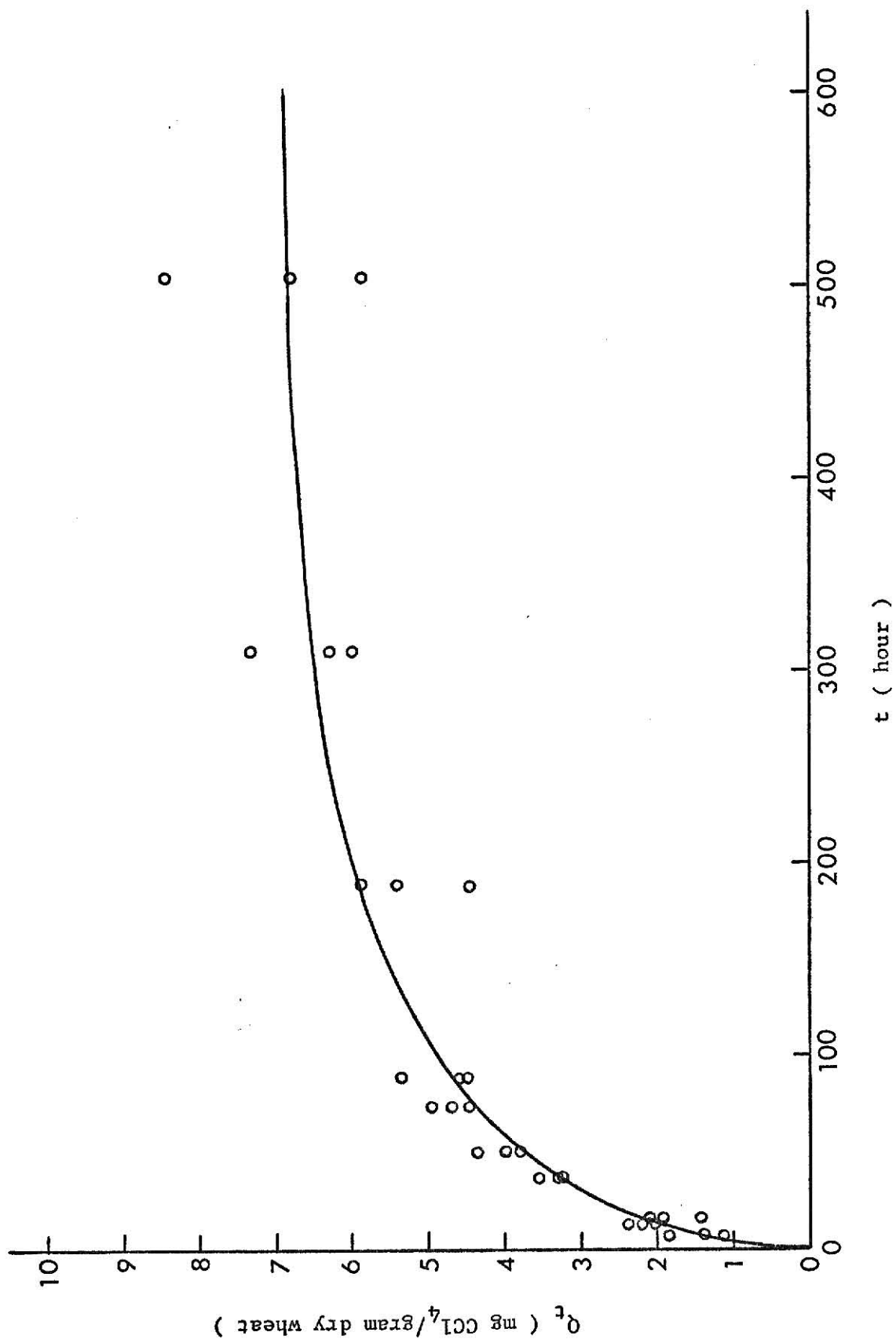the carbon tetrachloride vapor under the experimental conditions employed.

Fig. 4.1 Sorption of carbon tetrachloride by sound wheat.

However, the equilibrium sorption quantity, Q_{es}, can be treated as a unknown parameter and estimated from the experimental data prior to attainment of the equilibrium condition. For the present study, $D = 5.873 \times 10^{-9}$ (cm^2/sec) and $Q_{es} = 7.197$ (mg CCl$_4$/gram dry wheat) were obtained using only the data before 100 hours (where $Q_t/Q_{es} = .68$), while $D = 5.842 \times 10^{-9}$ (cm^2/sec) and $Q_{es} = 6.907$ (mg CCl$_4$/gram dry wheat) were obtained using all of the data (up to 508 hours, where $Q_t/Q_{es} = .98$). Fig. 4.2 shows both the fitted curves using all of the data and the data before 100 hours. The closeness of these two curves and the resulting diffusion coefficients implies that for this system it is safe to perform sorption experiments for times considerably less than required for equilibrium. Thus, considerable time can be saved and good results obtained if Q_{es} is treated as a parameter.

The desorption rate data were taken at 86°F, 46.8% relative humidity and zero carbon tetrachloride partial pressure. Four sets of wheat samples containing different amounts of carbon tetrachloride were used. The experimental data obtained are tabulated in Appendix B and the relative desorption rates are plotted on Fig. 4.3.

Experimental run D-1 is quite different from other runs and will be discussed separately. Again, the intraparticel diffusion model was used to explain the experimental data. The rate equation of this model for a desorption process was also derived in chapter 2 and is:

$$\frac{Q_t}{Q_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\delta n^2 t} \tag{4.2}$$

The parameter δ was evaluated from the experimental data of runs D-2, D-3 and D-4 using Bard's nonlinear parameter estimation method (2). The infinitive series was again calculated up to n = 100 or to a term for which the contribution to the whole summation is less than 0.01%. The resulting parameter is shown in Table 2. Using the parameter obtained, a comparison
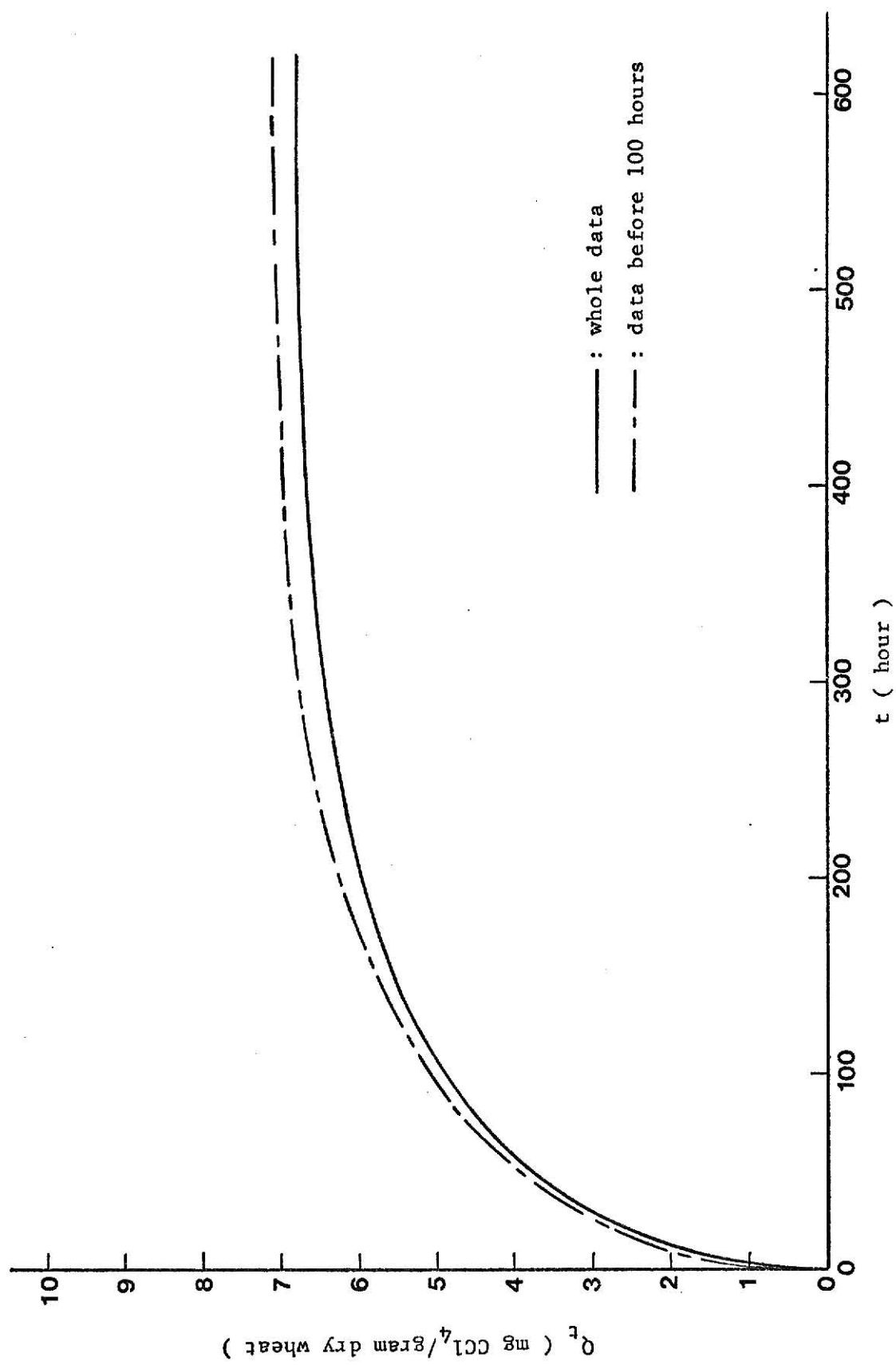
Fig. 4.2 A comparison of fitted curves showing the effect of omitting certain data points.
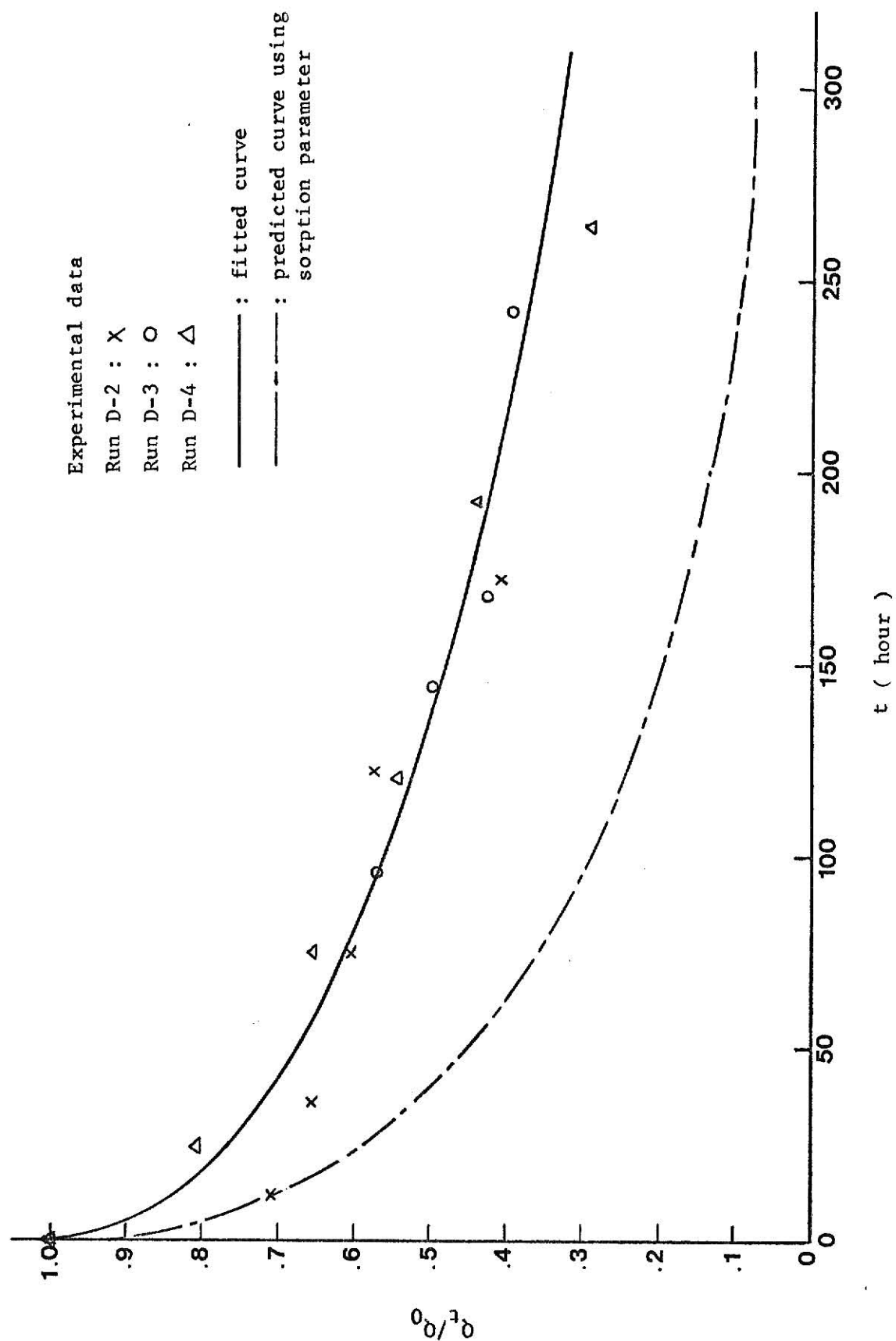
Fig. 4.3 Fitted curve and experimental relative rate of desorption for sound wheat.

between equation 4.2 and the experimental relative rate data is shown in
Fig. 4.3. The data points shown on the figure represent the average deter-
mined from triplicate analyses. A predicted desorption curve using the
diffusion coefficient obtained in the sorption experiment is also shown
in the same figure.

The wheat samples used in experimental run D-1 contained a large
amount of carbon tetrachloride (over 80 mg CCl_4/gram dry wheat). After
the wheat samples were introduced into the flask, liquid was observed on
the flask where the wheat kernels were in contact. Thus, the outer surface
of the wheat kernels used must have been wet with carbon tetrachloride.
During desorption, the carbon tetrachloride at the outer surface of the
kernels would evaporate directly into the gas phase without diffusing
through the interior of the kernels which is a comparatively slow process.
For this reason, these data were not used to find the diffusion coefficient.

Some specific conditions have to be met in order to use the equations
of the intraparticle diffusion model derived in chapter 2. Because the
amount of carbon tetrachloride sorbed by the wheat was small, the temper-
ature of the system was unlikely to change due to a sorption heat effect.
Also, the experiment was designed so that the decrease of carbon tetrachloride
partial pressure was less than 5% (see Appendix A). As for desorption,
the small amount of carbon tetrachloride desorbed was removed by passing
constant humidity air through the system to maintain zero carbon tetra-
chloride partial pressure around the wheat kernels. Thus, both processes
took place at essentially constant temperature and carbon tetrachloride
partial pressure as prescribed by the intraparticle diffusion model.
Salt solutions used in this study were selected to give approximately
the relative humidity which will be in equilibrium with the water inside
the wheat kernels at the operating temperature, so the moisture content
of the wheat would maintain approximately constant.

The experimental data were well correlated by the intraparticle diffusion model as shown in Fig. 4.1 and Fig. 4.3. The diffusion coefficients obtained are of the same order of magnitude as those obtained by Park in a previous study (see Table 2), although both the diffusion coefficient and equilibrium sorption quantity are significantly different from those obtained in Park's study under identical conditions. One possible explanation of these differences is that the wheat samples used were different. Hard red winter wheat harvested in 1971 was used in Park's study, while 1975 hard red winter wheat was used in this study. Another possible explanation is that Park's assumption that the carbon tetrachloride sorbed did not displace any previously sorbed molecules is in error. If this is the case, then the weight changes of the wheat samples recorded in his study were not due to the sorption of carbon tetrachloride only and thus his recorded results would be always lower than the true value. If the equilibrium sorption quantity obtained in present study is the true value, then it is equivalent to every sorbed carbon tetrachloride molecule displacing three water molecules (see Appendix C). This is not unreasonable because the surface area ratio of a carbon tetrachloride molecule to a water molecule is also about three. Though there seems a big difference between the two equilibrium sorption quantities, the two diffusion coefficients are quite close. That is because the diffusion coefficient depends on relative sorption rate (Q_t/Q_{es}) only. If the sorbed carbon tetrachloride molecule does displace water molecules, then both Q_t and Q_{es} recorded in Park's study would be lower than the true values and thus the values of Q_t/Q_{es} would be close to the true relative rates. Actually, if the number of water molecules displaced and desorbed during the whole sorption process remains constant, Q_t/Q_{es} will be equal to the true values and the same diffusion coefficient will be obtained.

Table 2 Parameters determined for the intraparticle diffusion model for sorption and desorption of carbon tetrachloride on wheat kernels at 86°F

Process	Reference	Kernel radius (cm)	Kernel Condition	$PCCl_4$ (mm Hg)	Q_{es} or Q_o (mg CCl_4/g dry wheat)	$D \times 10^9$ (cm^2/sec)	Remarks
Sorption	Park (11)	0.165	sound	95	4.253	4.376	
	Present Study	0.165	sound	95	6.907	5.842	
		0.165	sound	95	7.197	5.873	using only data for times less than 100 hours
		0.159	combined	95	6.814	6.008	
Desorption	Present Study	0.165	sound	0	11.10 21.31 4.918	1.687	
		0.153	pearled	0	5.883	4.644	

A puzzling result is why the diffusion coefficients of sorption and desorption in the present study are different. One possible explanation is that the seed coat offers different resistances to diffusing carbon tetrachloride molecules during sorption and desorption. There is no doubt that the resistance to diffusion during desorption is greater than that for sorption. This difference in seed coat resistance might be explained in terms of equilibrium at the solid-gas interface, an assumption commonly used in interphase mass transfer. During sorption the particle surface, or seed coat, would be in equilibrium with air containing considerable carbon tetrachloride vapor and thus some carbon tetrachloride would be dissolved in the surface layer (seed coat). This dissolved carbon tetrachloride might swell or distort the seed coat sufficiently to render it more permeable to diffusing carbon tetrachloride molecules. For the desorption process, there is no carbon tetrachloride vapor in the air and hence none dissolved in the surface layer, thus the seed coat could be tighter and considerably less permeable to diffusing carbon tetrachloride molecules. This may explain why the diffusion coefficient of sorption is almost three to four times as large as the diffusion coefficient of desorption.

4-2 Pearled Wheat:

The second part of this study was conducted using pearled wheat samples to investigate the effect of seed coat on the rates of sorption and desorption. Hard red winter wheat harvested in 1976 was treated in a Barley Pearler for forty seconds, and two screens, No. 6 and No. 7, were used to get wheat samples which had an average spherical radius of 0.153 cm. Both sorption and de-sorption experiments for pearled wheat were conducted under the same operating operating conditions as for sound wheat. All experimental data are tabulated in Appendix B also. Fig. 4.4 shows the sorption experimental data for both sound and pearled wheat. There seems to be little difference between the
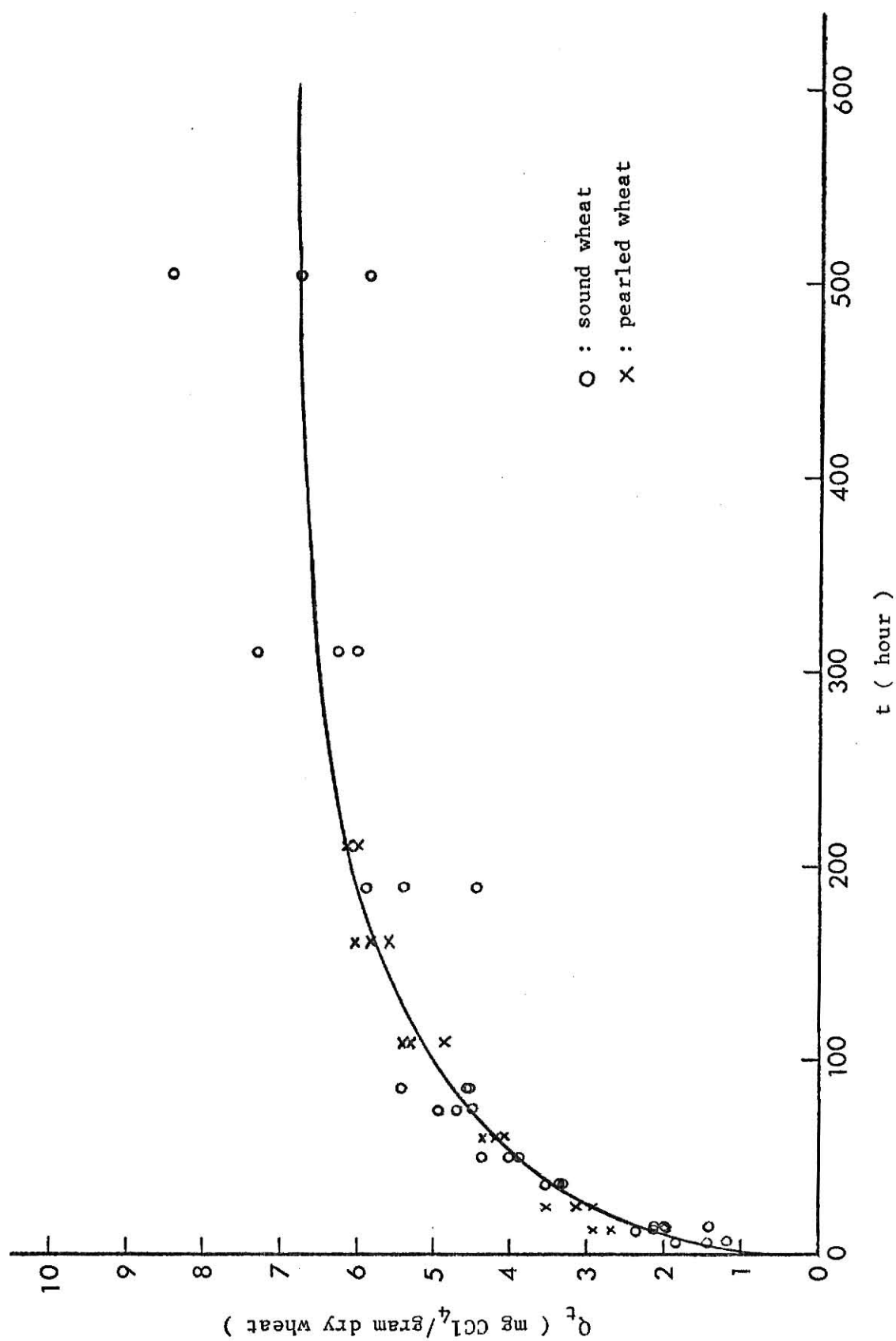
Fig. 4.4 Sorption of carbon tetrachloride by sound and pearled wheat.

sorption behavior of sound and pearled wheat as shown by Fig. 4.4. The rate
equation of the intraparticle diffusion model, Eq. 4.1, was used to correlate
the combined experimental data for sound and pearled wheat. The parameters
were evaluated using Bard's nonlinear parameter estimation method as stated
before and summarized in Table 2. A comparison between equation 4.1 with
fitted parameters and the combined experimental data is also shown in the
same figure.

Desorption rate data are plotted on Fig. 4.5. Equation 4.2 and Bard's
nonlinear parameter estimation method were used to evalute the parameter,
D. This result is also shown in Table 2. · A comparison between equation
4.2 with fitted parameter and the experimental relative rate data of desorp-
tion is also shown in Fig. 4.5. A fitted curve for sound wheat is also
shown in the same figure for comparison.

As shown in Table 2, the diffusion coefficient of desorption for
pearled wheat is much larger than that for sound wheat indicating the
resistance offered by seed coat does exist and is larger than those offered
by other parts of a wheat kernel. Though the diffusion coefficient of
sorption for pearled wheat is also larger than that for sound wheat, there
seems to be little difference. This indicates that the resistance offered
by seed coat is very small during sorption. The combined sorption data
were used to find the diffusion coefficient and a comparison among the
desorption curve predicted with this diffusion coefficient, the experimental
data and its fitted curve for pearled wheat is shown in Fig. 4.6. The
difference between the experimental data and the predicted curve, or the
diffusion coefficients, is small indicating that the seed coat hypothesis
is reasonable. This small difference may be explained by the fact that a
small portion of the seed coat still remained on the pearled wheat kernels.
Because of the nonsperical structure of wheat, it is impossible to remove
all the seed coat (Fig. 2.1).
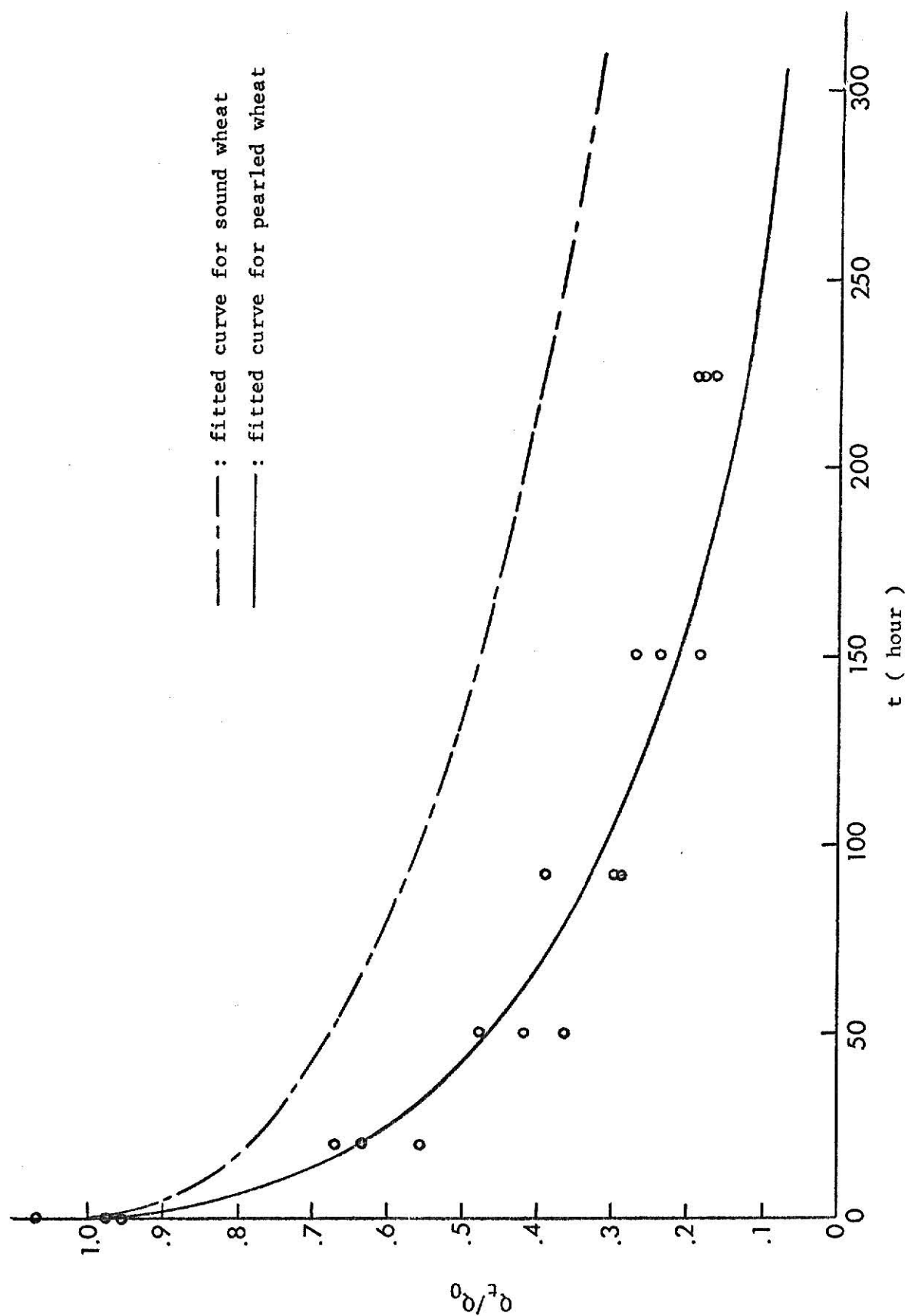
Fig. 4.5 Fitted curve and experimental relative rate of desorption for pearled wheat.

——— : fitted curve for sound wheat

——— : fitted curve for pearled wheat

t (hour)

Q_t/Q_0
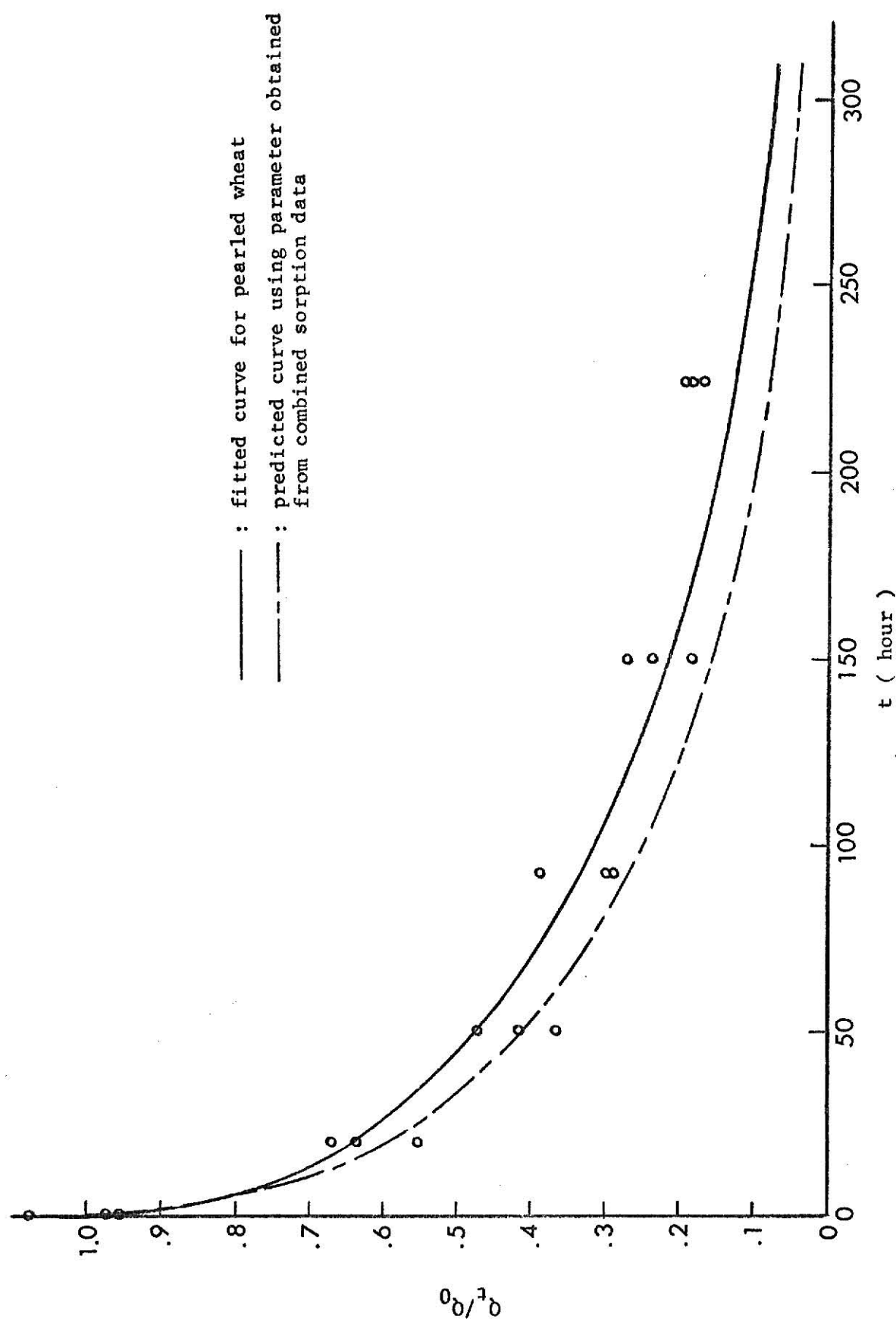
Fig. 4.6 A comparison among experimental data for pearled wheat, its fitted curve and the desorption curve predicted from combined sorption data.

A important fact found in this study is that the effective difussion coefficients of sorption and desorption of carbon tetrachloride on sound wheat are different. This indicates that the study of desorption kinetics is as important as the study of sorption kinetics. It is hoped that the present study may provide a better experimental technique for kinetic studies and some useful information for selecting more effective fumigants and designing better fumigation and aeration processes or improving the existing systems.

CHAPTER 5

CONCLUSIONS

A new experimental technique has been developed and successfully applied to the study of sorption and desorption kinetics of carbon tetrachloride on wheat. This technique is better than the previous one, reported by Park (11), in which the sorption rate of carbon tetrachloride on wheat was determined by measuring the weight changes of a sample of wheat at fixed operating conditions. Park's gravimetric method was subject to the following uncertainties: (1) Because the moisture content of wheat (about 12%, by weight) is much higher than the amount of carbon tetrachloride sorbed on wheat (about 1%, by weight), a slight change in moisture content could produce weight changes on the order of those caused by the sorption of carbon tetrachloride. (2) The accuracy relied on a doubtful assumption that the sorbed carbon tetrachloride molecules do not displace sorbed water molecules. Direct measurement of the carbon tetrachloride content of wheat using a wet aeration and colorimetric determination method in the present technique avoids these disadvantages. Also the average time for each experimental run can be reduced using present technique.

The experimental data were well correlated by the rate equations of the intraparticle diffusion model. The effective diffusion coefficients obtained for all cases are in the order of 10^{-9} cm^2/sec indicating that the controlling mechanisms are solid diffusion (11) for both sorption and desorption processes.

An important fact is the diffusion coefficient of desorption is different from that of sorption. This indicates using only one diffusion coefficient for the study of both fumigation and aeration processes is not adequate.

Thus, the study of desorption kinetics is equally important as the study of sorption kinetics. The difference in diffusion coefficients is explained in terms of different resistances offered by the seed coat during sorption and desorption. Experiments using pearled wheat proved that this seed coat hypothesis is reasonable.

There is still much work in this area to be done in the future. Desorption kinetics should be studied more intensively. The studies of large masses of cereal grains undergoing fumigation and aeration and the studies of multicomponent fumigants which are widely used are very important too. It is hoped that this study may give some information for the design of better fumigation and aeration systems and stimulate others to do further research in this area.

ACKNOWLEDGMENT

NOTATION

A	ratio of number of molecules in the adsorbed phase to those in the gas phase, N_a/N_g
c	adsorbate concentration in free pore space, gas amount/cm^3
D	diffusion coefficient (diffusivity)
D_{AB}	binary diffusion coefficient for system A-B
D_a	surface diffusion coefficient
De	effective diffusion coefficient
D_g	gas phase diffusion coefficient
H	linear isotherm constant from $q = Hc$
N_a	Number of adsorbate molecules per cm pore length in the adsorbed phase
N_g	Number of adsorbate molecules per cm pore length in the gas phase
n	integer
Q_d	amount of adsorbate desorbed at time t
Q_{ed}	equilibrium amount of adsorbate desorbed
Q_{es}	equilibrium amount of adsorbate sorbed
Q_0	initial amount of adsorbate sorbed
Q_s	amount of adsorbate sorbed at time t
Q_t	amount of adsorbate in adsorbent at time t
q	adsorbate concentration in adsorbent
q_e	equilibrium adsorbate concentration in adsorbent
q_0	initial adsorbate concentration in adsorbent
R	average radius of adsorbent particle
r	radial distance
t	time
v	volume of adsorbent particle
δ	parameter as defined in equation (2.5)
π	constant, 3.14159

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APPENDIX   A

CALCULATION OF THE AMOUNT OF CARBON TETRACHLORIDE NEEDED

AND

THE DECREASE OF CARBON TETRACHLORIDE PARTIAL PRESSURE DURING SORPTION

If ideal gas behavior is assumed, the partial pressure of carbon tetrachloride, P'_{CCl_4} , after complete evaporation can be calculated as follow:

$$P'_{CCl_4} = \frac{nRT}{V} = (v\rho/M)\frac{RT}{V} \qquad (A.1)$$

where   v= volume of liquid CCl_4 introduced

ρ= density of liquid CCl_4

M= molecular weight of CCl_4

n= number of moles of CCl_4

R= gas constant

T= temperature

V= volume of the flask

After the evaporation is completed, the stopper has to be removed in order to introduce wheat kernels. If gas mixture is assumed to be homogeneous and pressure equalization occurs, then

$$P_{CCl_4} = \frac{P'_{CCl_4}}{P + P'_{CCl_4}} \times P \qquad (A.2)$$

where P_{CCl_4} = final partial pressure of CCl_4

P   = atmospheric pressure

If we combine equation A.1 with equation A.2 and eliminate P'_{CCl_4} , then the volume of liquid carbon tetrachloride required to obtain a given partial pressure is:

$$v = \frac{P_{CCl_4}}{P - P_{CCl_4}} \frac{PVM}{\rho RT} \qquad (\text{ A.3 })$$

<u>Sample calculation for a typical experiment (Run S-1)</u>

$$P_{CCl_4} = 95 \text{ mm Hg}$$

$$P \quad = 736.9 \text{ mm Hg}$$

$$V \quad = 1070 \text{ ml}$$

$$T \quad = 86^\circ F = 303^\circ K$$

$$M \quad = 153.82 \text{ g/g-mole}$$

$$\rho \quad = 1.582 \text{ g/cm}^3$$

$$R \quad = 82.0567 \text{ atm-ml/g-mole } ^\circ K$$

Substituting these values into equation A.3 gives:

$$v = 0.6005 \text{ ml}$$

The maximum decrease of carbon tetrachloride partial pressure during sorption can be estimated approximately as follow:

$$n'' = \frac{Q_{es} W}{M} \qquad (\text{ A.4 })$$

where n''= maximum number of moles of CCl_4 sorbed

Q_{es} = equilibrium sorption quantity

W = amount of wheat used

Then

$$\delta = \frac{n''}{n} = \frac{P''_{CCl_4}}{P_{CCl_4}} = (Q_{es} \; W/M) \frac{RT}{P_{CCl_4} V} \qquad (\text{ A.5 })$$

where P''_{CCl_4} = maximum decrease of CCl_4 partial pressure

δ = fraction decrease of CCl_4 partial pressure

Sample calculation for a typical experiment (Run S-1)

$$P_{CCl_4} = 95 \text{ mm Hg}$$

$$V = 1070 \text{ ml}$$

$$T = 303^{\circ}K$$

$$M = 153.82 \text{ g/g-mole}$$

$$R = 82.0567 \text{ atm-ml/g-mole} \, ^{\circ}K$$

$$Q_{es} = 6.907 \text{ mg } CCl_4 / \text{ gram dry wheat}$$

$$W = 5.741 \text{ g (dry basis)}$$

Substituting these values into equation A.5 gives:

$$\delta = 4.8\%$$

In practice, the amount of carbon tetrachloride sorbed by wheat was less than the above used, so the decrease of carbon tetrachloride partial pressure was always less than 5%. This error could be further reduced using a larger flask or a smaller amount of wheat sample.

APPENDIX B

EXPERIMENTAL DATA

B-1 Sorption Experiment:

Run S-1

Wheat: sound

Temperature: 86 F

Carbon tetrachloride partial pressure: 95 mm Hg

t	Q_t 1	Q_t 2	Q_t 3	$\bar{Q}_t$
6	1.183	1.842	1.405	1.477
12	2.231	2.038	2.363	2.211
14	1.949	2.147	1.415	1.837
36	3.561	3.308	3.274	3.381
50	4.354	3.967	3.811	4.044
74	4.683	4.925	4.497	4.702
88.5	5.368	4.556	4.494	4.806
188	5.890	5.431	4.435	5.252
310	6.002	6.252	7.302	6.519
504	8.401	6.780	5.875	7.019

* Q_t in mg CCl_4 / gram dry wheat

t in hour.

Run S-2

Wheat: pearled

Temperature: 86 F

Carbon tetrachloride partial pressure: 95 mm Hg

t	Q_t			$\bar{Q}_t$
	1	2	3	
12	2.661	2.909	2.254	2.608
24	3.112	3.535	2.912	3.186
40	3.262	3.615	3.315	3.397
60	4.084	4.156	4.354	4.198
109	5.408	4.858	5.365	5.210
160	5.871	6.026	5.632	5.843
210	5.979	6.137		6.058

B-2 Desorption Experiment:

Run D-1

Wheat: sound

Temperature: 86 F

t	Q_t			$\bar{Q}_t$	Q_t/Q_0			$\bar{Q}_t/Q_0$
	1	2	3		1	2	3	
0	86.454	82.503	74.402	81.120	1.066	1.017	0.917	1
12.5	21.288	18.589	14.839	18.239	0.262	0.229	0.183	0.225
36	9.778	10.187	9.387	9.784	0.121	0.126	0.116	0.121
132	6.246	5.710	7.989	6.648	0.0770	0.0704	0.0985	0.0820
265	5.408	5.198	4.977	5.194	0.0667	0.0641	0.0614	0.0640

Run D-2

Wheat: sound

Temperature: 86 F

t	Q_t			$\bar{Q}_t$	Q_t/Q_0			$\bar{Q}_t/Q_0$
	1	2	3		1	2	3	
0	11.865	11.372	10.050	11.096	1.069	1.025	0.906	1
12	7.793	7.263	8.494	7.850	0.702	0.655	0.766	0.707
36	7.352	7.603	6.815	7.257	0.663	0.685	0.614	0.654
75	7.201	6.650	6.330	6.727	0.649	0.599	0.570	0.606
124	6.906	6.197	5.993	6.365	0.622	0.558	0.540	0.574
172	4.401	4.264	4.881	4.515	0.397	0.384	0.440	0.407

Run D-3

Wheat: sound

Temperature: 86 F

t	Q_t			$\bar{Q}_t$	Q_t/Q_0			$\bar{Q}_t/Q_0$
	1	2	3		1	2	3	
0	22.652	21.493	19.774	21.306	1.063	1.009	0.928	1
96	13.145	11.014	12.269	12.143	0.617	0.517	0.576	0.570
144	11.453	9.935	10.381	10.589	0.538	0.466	0.487	0.497
168	9.204	9.139	8.801	9.048	0.432	0.429	0.413	0.425
242	8.572	8.458	8.169	8.400	0.402	0.397	0.383	0.394
408	6.843	7.242	6.773	6.953	0.321	0.340	0.318	0.326

Run D-4

Wheat: sound

Temperature: 86 F

t	Q_t			$\bar{Q}_t$	Q_t/Q_0			$\bar{Q}_t/Q_0$
	1	2	3		1	2	3	
0	5.223	4.817	4.714	4.918	1.062	0.979	0.959	1
24	3.459	4.705	3.738	3.967	0.703	0.957	0.760	0.807
75	3.443	3.240	2.959	3.214	0.700	0.659	0.602	0.654
120	3.026	2.325	2.711	2.687	0.615	0.473	0.551	0.546
192	1.909	2.335	2.202	2.149	0.388	0.475	0.448	0.437
264	1.663	1.445	1.182	1.430	0.338	0.294	0.240	0.291

Run D-5

Wheat: pearled

Temperature: 86 F

t	Q_t			$\bar{Q}_t$	Q_t/Q_0			$\bar{Q}_t/Q_0$
	1	2	3		1	2	3	
0	5.595	6.335	5.720	5.883	0.951	1.077	0.972	1
20	3.244	3.949	3.726	3.640	0.551	0.671	0.633	0.619
50	2.450	2.136	2.780	2.455	0.416	0.363	0.473	0.417
92	1.708	2.288	1.750	1.915	0.290	0.389	0.297	0.326
150	1.598	1.392	1.078	1.356	0.272	0.237	0.183	0.231
224	1.104	1.078	0.994	1.059	0.188	0.183	0.169	0.180

B-3 Test of the Accuracy of the Wet Aeration and Colorimetric Determination
   Method:

Experiment NO.	CCl_4 added	CCl_4 found	Recovery
1	0.8 mg	0.755 mg	94.43%
2	1.0 mg	0.968 mg	96.80%
3	0.2 ml	0.213 ml	106.5 %
4	0.2 ml	0.196 ml	97.92%

APPENDIX C

DISPLACEMENT OF SORBED WATER BY SORBED CARBON TETRACHLORIDE

If every sorbed carbon tetrachloride molecule displaces m water molecules, then:

$$w' = 154\,a - 18\,m\,a \qquad\qquad (\ C.1\ )$$

where w' = weight changes recorded in Park's study (apparent

CCl_4 loading)

a = number of moles of CCl_4 sorbed.

and:

$$\frac{w'}{w} = \frac{154-18m}{154} \qquad\qquad (\ C.2\ )$$

where w = actual loading of CCl_4

m	2	3	4
w'/w	0.766	0.649	0.532

The ratio of equilibrium sorption quantity of Park's study is:

$$4.253/6.907 = 0.616$$

which corresponds to m=3, that is every sorbed carbon tetrachloride molecule displaces three water molecules.

SORPTION AND DESORPTION KINETICS

OF CARBON TETRACHLORIDE VAPOR ON WHEAT KERNELS

by

CHING-CHIAN CHANG

B. S., National Taiwan University, 1972

AN ABSTRACT OF A MASTER'S THESIS

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1977

ABSTRACT

The kinetic behavior of the sorption and desorption of carbon tetrach-
loride on wheat was studied. A new experimental technique, in which a wet
aeration and colorimetric analytical method was used to determine the amount
of carbon tetrachloride in wheat directly, was presented.

Experimental runs were conducted at $86°F$, 46.8% relative humidity and
95 mm Hg carbon tetrachloride partial pressure for sorption, and $86°F$, 46.8%
relative humidity and zero carbon tetrachloride partial pressure for desorp-
tion. It was found that the experimental kinetic data were well represented
by the intraparticle diffusion model. Bard's nonlinear parameter estimation
program was used to evaluate the parameters in the equations. The effective
diffusion coefficient evaluated from the experimental data for all cases were
in the order of 10^{-9} cm^2/sec as reported for previous diffusion studies
involving wheat.

The diffusion coefficient and equilibrium sorption quantity obtained in
present study are different from those obtained in a previous study by Park
under identical conditions. This is believed due to Park's assumption that
the carbon tetrachloride sorbed did not displace any previously sorbed mole-
cules is in error. A calculation shows that every sorbed carbon tetrachloride
molecule should displace three water molecules if the present results are
the true values. This is not unreasonable because the surface area ratio
of a carbon tetrachloride molecule to a water molecule is also about three.

It was found that the diffusion coefficient of sorption is almost four
times as large as the diffusion coefficient of desorption. This was explained
by a hypothesis that the seed coat offers different resistances to diffusing
carbon tetrachloride molecules during sorption and desorption. Experimental

results obtained using pearled wheat shows that the hypothesis is reasonable.

It was concluded that the present experimental technique is better than the previously used one. The controlling mechanism is solid diffusion for both the sorption and desorption processes, but these two processes are characterized by different diffusion coefficients.