# SORPTION KINETICS AND EQUILIBRIA OF
# CARBON TETRACHLORIDE ON WHEAT[1]

S. W. PARK[2] and B. G. KYLE, Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506

## ABSTRACT

Kinetic and equilibrium data for the sorption of carbon tetrachloride vapor on wheat kernels have been obtained for several levels of carbon tetrachloride partial pressure and over the temperature range 76° to 96° F. For all runs the moisture content of the wheat remained constant at 11.6% (dry basis). The equilibrium isotherm, although incompletely determined, appears to possess the sigmoid shape common to cereal products. Heats of sorption were estimated to range from 8.0 to 8.5 kcal/g mol. The kinetic data were well represented by an internal diffusion model with the diffusivity found to be approximately 1/25th of the published value for the diffusion of water vapor into the wheat kernel. The diffusivity exhibited an exponential temperature dependence with an activation energy comparable to that reported for water vapor.

Much work dealing with the subject of grain fumigation has appeared in the literature although most has been of an empirical and qualitative nature and has provided little understanding of the fundamental phenomena which govern the process. Fumigation should closely resemble chromatographic separation processes and fixed-bed adsorption-desorption operations widely used in the chemical and petroleum industries. Such processes have been successfully analyzed and designed by means of modeling techniques that should also prove useful to the analysis and design of the various fumigation and aeration processes, provided the fundamental phenomena underlying the process are well understood and sufficient data are available to estimate the necessary parameters

---

characterizing the phenomena. It is the purpose of this work to study the sorption of carbon tetrachloride vapor on wheat so that insight into the nature of the sorption process might be obtained. (See glossary of important terms under nomenclature.)

## MATERIALS AND METHODS

The sorption rate of carbon tetrachloride vapor was studied by measuring weight changes of a sample of wheat placed in an adsorption chamber where temperature, humidity, and partial pressure of carbon tetrachloride were maintained constant. A schematic diagram of the experimental apparatus is shown on Fig. 1. Details concerning the apparatus and procedure are given by Park (1).

The air mixture was continuously circulated by a diaphragm pump with the desired partial pressure of carbon tetrachloride being controlled by a saturator maintained at the proper temperature. Another saturator containing a saturated aqueous solution of either potassium carbonate or calcium nitrate was used to maintain the proper humidity so that the moisture content of the wheat would be very close to 11.6% (dry basis) under all experimental conditions. The
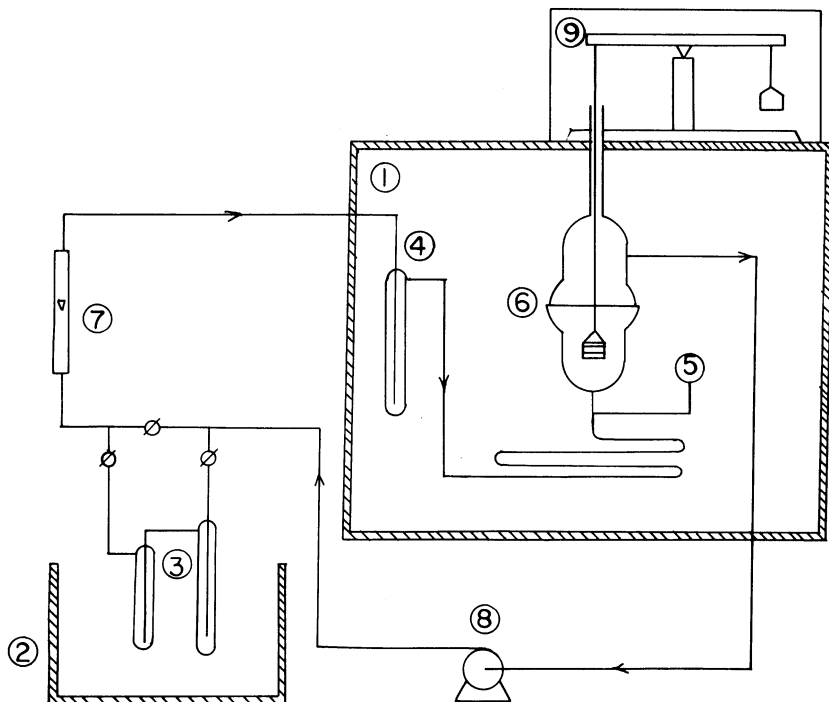


Fig. 1. Schematic diagram of experimental system. 1) Environmental chamber; 2) constant temperature bath; 3) CCl₄ saturator; 4) salt solution saturator; 5) temperature and pressure measurement; 6) adsorption chamber; 7) flow meter; 8) pump; and 9) balance.

temperature of the carbon tetrachloride saturator was controlled to within 0.1° F by means of a constant temperature water bath. The adsorption chamber and the saturator containing the saturated aqueous salt solution were located within an environmental chamber where the temperature was controlled to within 0.75° F. Published equilibrium data for water vapor adsorbed on wheat (2) were used to determine the level at which the humidity should be controlled at each temperature so as to achieve the desired 11.6% moisture content.

Precise measurement of weight changes of the wheat sample was accomplished by a modified Christian Becker model AB-4 analytical balance possessing a sensitivity of 0.05 mg. The balance was mounted on a supporting fixture above the environmental chamber. The wheat sample rested on a brass wire sample pan positioned within the adsorption chamber and suspended by a long Nichrome wire attached to the balance beam at the stirrup hook. The adsorption chamber was fabricated from large diameter (80 mm) Pyrex tubing.
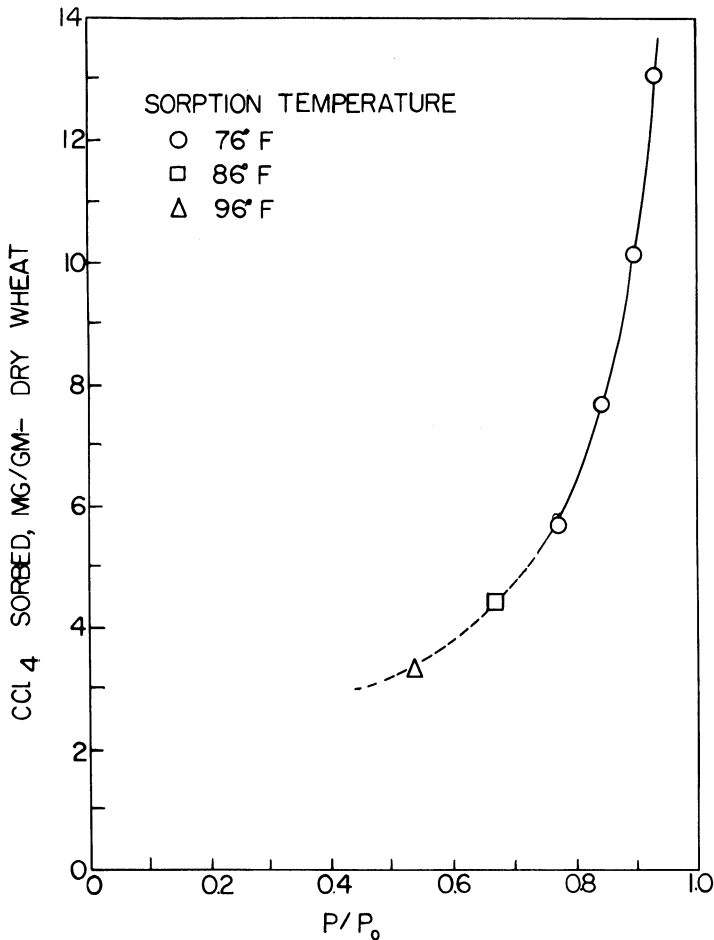


Fig. 2. Equilibrium relation for the sorption of carbon tetrachloride vapor on wheat.

Hard red winter wheat harvested in 1971 was used for this study which was conducted from September 1972 to May 1974. The wheat which had an initial moisture content of 11% (dry basis) was stored at room temperature in a large desiccator containing a saturated aqueous solution of potassium carbonate so that its moisture content would remain in the 11 to 12% range.

The sorption rate was determined by placing 20 g of wheat in a single layer on the sample pan, then circulating air of desired humidity until the sample came to equilibrium with respect to water vapor. This usually required about 2 to 3 weeks. When this equilibrium had been established, the air was then circulated through the carbon tetrachloride saturator and the sample weight was recorded at regular intervals. Approximately 4 to 5 weeks were required for the wheat to attain equilibrium with carbon tetrachloride vapor. Before the amount of carbon tetrachloride sorbed by the wheat could be determined, it was necessary to correct the weight measurements for adsorption on the sample pan and for a buoyancy effect due to the high density of carbon tetrachloride vapor. The former correction was determined by making blank runs under identical conditions; the latter was calculated. Runs were made at three temperatures: 76°, 86°, and 96° F and at four levels of carbon tetrachloride partial pressure ranging between 86 and 105 mm Hg.

Because this system is comprised of two sorbable components and because the quantity of carbon tetrachloride sorbed is very much smaller than the quantity of water held by the wheat, there was some concern as to whether the quantity of carbon tetrachloride sorbed could be determined by measurement of a weight change. To resolve this question, a few static equilibrium tests were performed. In these tests, known quantities of wheat and carbon tetrachloride were weighed into a flask of known volume and the gas phase was sampled and analyzed chromatographically after several weeks. The amount of carbon tetrachloride sorbed by the wheat in equilibrium with the final gas composition was calculated via a material balance. These data compared favorably with equilibrium data determined from the weight measurements and confirmed the reliability of the experimental method.

## RESULTS AND DISCUSSION

### Equilibrium Data

The quantity of carbon tetrachloride vapor sorbed by the wheat in equilibrium with the controlled partial pressure of carbon tetrachloride was determined from the last few weight measurements for each kinetic run. These data are shown on Fig. 2. Four data points were determined at 76° F and one each was determined at 86° and 96° F. All of the data were well correlated with Polanyi's potential theory (3) which allows the data at different temperatures to be plotted on a single curve of adsorption potential *vs.* quantity adsorbed. This plot is shown on Fig. 3 and was used to extend the equilibrium curve at 76° F, shown on Fig. 2 as the dashed portion. Although the isotherm is not completely delineated, Fig. 2 indicates that it is essentially sigmoid in shape as was found by Bushuk and Winkler (4) who studied the sorption of organic vapors on wheat flour. Their study included carbon tetrachloride vapor which they show to be sorbed in the range of 0 to about 30 mg per g of flour. This provides an order of magnitude agreement with our range of 0 to 14 mg per g of wheat.

The characteristic curve can be used to calculate isotherms at other temperatures; hence, the heat of sorption can be calculated via the Clausius-Claperon equation (3). This was done and it was found that the heat of sorption ranged from 8.0 to 8.5 kcal/g mol. These numbers appear reasonable; however, they should be regarded only as approximate because of the limited data used to establish the characteristic curve.

### Kinetic Data

It was found that the kinetic data could be well represented by an internal diffusion model for a sphere (5,6).

$$\frac{Q_t}{Q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{\pi^2 n^2 Dt}{r^2}\right)$$

The data were fitted to this equation with n = 40 using Bard's (7) nonlinear parameter estimation method. An example of the fit obtained is shown on Fig. 4
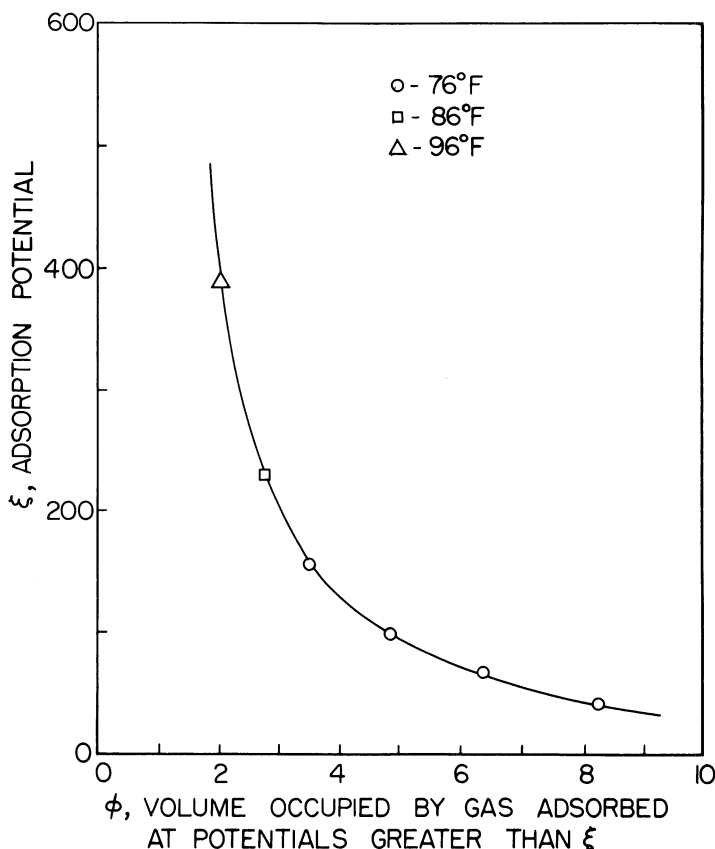


Fig. 3. Characteristic curve of carbon tetrachloride vapor on wheat.

and values for parameter D obtained from the fit are given in Table I. The value of r used to obtain D from the estimated parameter $\pi^2 D/r^2$ was the equivalent spherical radius defined as the radius of a sphere having the same volume as the particle. By means of a pycnometer measurement of the kernel volume, this was found to be 0.165 cm and is very close to the value of 0.170 reported by Becker (8).

It should be noted from Table I that values of D obtained for the four runs at 76° F are very close which would indicate that, at least in this range of carbon tetrachloride sorption, the diffusion coefficient is independent of concentration. This condition is also manifested in the fact that on a plot of $Q_t/Q_e$ vs. time, all four of these runs superimposed to give a single curve.

With an average diffusivity at 76° and those determined at 86° and 96° F, a semilogarithmic plot of diffusivity vs. the reciprocal of the absolute temperature was constructed. As can be seen from Fig. 5, this plot yields a straight line characteristic of exponential relationships. The activation energy for diffusion calculated from the slope of this line was 12.02 kcal/g mol. According to the criteria established by Carmen (9), the magnitude of the diffusivity and the fact that the activation energy for diffusion exceeds the heat of adsorption lead to the conclusion that solid-phase diffusion is the rate-controlling step in the kinetic process.

While no kinetic studies involving the sorption of organic vapors on wheat have been reported, it is instructive to compare the diffusion parameters obtained in this study with values reported from studies involving water. The diffusivities and activation energies for these systems along with those from this study are shown in Table II. While it is observed that the diffusivity for carbon tetrachloride in wheat is much smaller than that of water, the activation energy
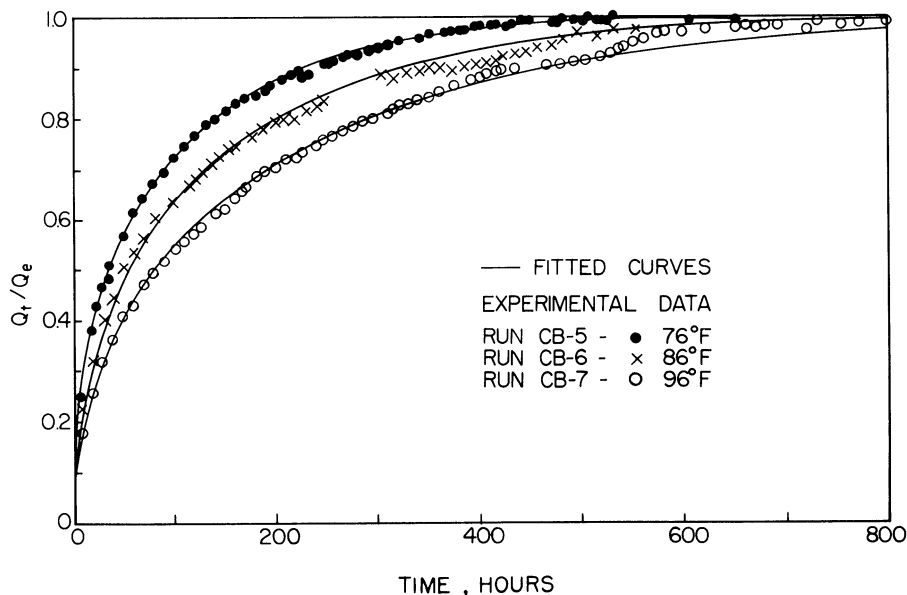


Fig. 4. Comparison of fitted curves with experimental data for the sorption kinetics of carbon tetrachloride vapor on wheat.

for the diffusion process is essentially the same. The smaller diffusivity for carbon tetrachloride is to be expected mainly because of its much larger molecular size; however, the equality of the activation energy is somewhat surprising and requires explanation. The most plausible argument may be advanced in terms of elastic displacement of the adsorbant structure on a molecular scale. Barrer (13) has shown that such elastic displacement can greatly reduce the energy barrier

TABLE I
Diffusion Coefficients Obtained from
Fitting Diffusion Equation to the Experimental Data

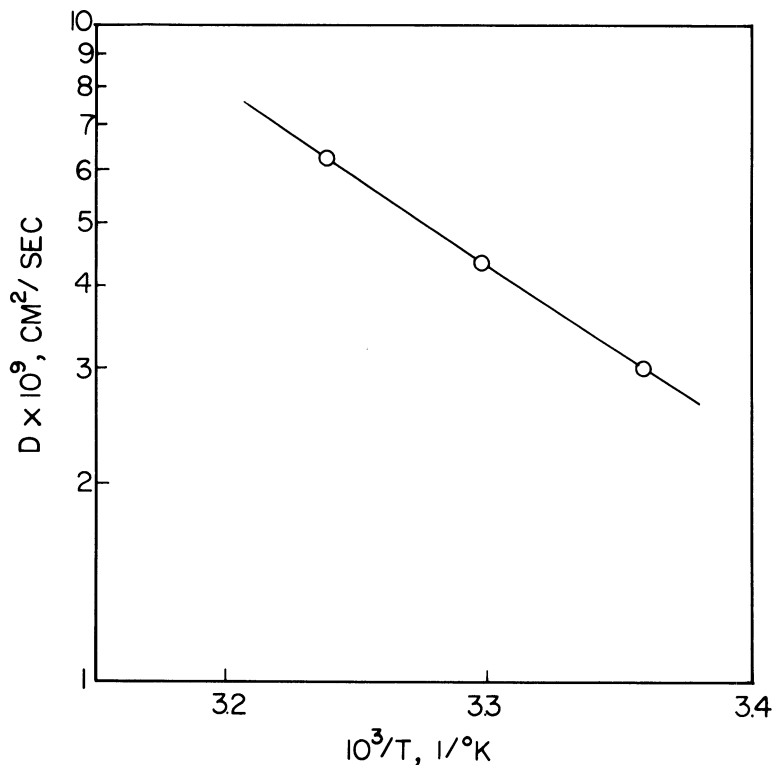| Temperature °F | CCl₄ Partial Pressure mm Hg | D × 10⁸ cm²/sec |
|---|---|---|
| 76 | 86 | 0.29 |
| 76 | 95 | 0.30 |
| 76 | 100 | 0.30 |
| 76 | 105 | 0.26 |
| 86 | 95 | 0.44 |
| 96 | 95 | 0.62 |



Fig. 5. Temperature dependence of the diffusion coefficient.

**TABLE II**
**Parameters for Diffusion into the Wheat Kernel**

| Sorbate | Temperature °F | $D \times 10^8$ cm²/sec | E kcal/g mol | Reference |
|---------|----------------|--------------------------|--------------|-----------|
| Water vapor | 77 | 6.6 | . . . | Babbitt (10) |
| Water vapor | 77 | 8.7 | 12.2 | Becker (11) |
| Liquid water | 77 | 2.4 | 12.3 | Becker (8) |
| Liquid water | 80 | 3.4–4.1 | 11.2–11.9 | Chung et al. (12) |
| Carbon tetrachloride | 76 | 0.30 | 12.2 | Present study |

encountered on diffusion and that the energy of activation for diffusion is insensitive to molecular size and force field. Therefore, if the structure of a wheat kernel is assumed to be elastic, which may be inferred from the swelling known to accompany the sorption of liquid water, the comparable energies of activation for carbon tetrachloride and water may be justified.

Thus, it has been shown that the internal diffusion equation does a good job of representing the kinetic data and that the diffusion parameters obtained from this model are physically realistic. The ability to mathematically represent the single particle sorption behavior augurs well for the successful application of modeling techniques to large masses of grain undergoing fumigation and aeration. Treatment of these processes in a quantitative manner could lead to selection of more effective fumigant compounds, design of more efficient fumigation and aeration systems, and more efficient operation of such existing facilities.

### Nomenclature

| | |
|---|---|
| D | Diffusivity |
| E | Activation energy for diffusion |
| n | Summation index |
| P | Equilibrium partial pressure |
| $P_o$ | Vapor Pressure |
| $Q_e$ | The equilibrium value, or the amount sorbed after infinite time |
| $Q_t$ | Amount sorbed at time t |
| r | Radius of spherical particle |
| R | Gas law constant |
| t | Time |
| T | Absolute Temperature |
| X | Weight of sorbed material |
| $\xi$ | Adsorption potential defined equal to $RT \ln (P_o/P)$ |
| $\phi$ | Volume of sorbed material defined equal to $X/\rho$ |
| $\rho$ | Liquid density of sorbed material |

### Literature Cited

1. PARK, S. W. A theoretical investigation of sorption kinetic models and their application to the sorption kinetics of water vapor and carbon tetrachloride vapor by cereal grains. Ph.D. Dissertation, Kansas State University (1974).
2. ANONYMOUS. Hydroscopicity of seeds, p. 335. Agricultural Engineers Yearbook (1970).

3. BRUNAUER, S. The adsorption of gases and vapors. Princeton University Press: Princeton, N.J. (1943).

4. BUSHUK, W., and WINKLER, C. A. Sorption of organic vapors on wheat flour at 27°C. Cereal Chem. 34: 87 (1957).

5. WARD, A. F. H. The sorption of hydrogen on copper. Part II, The rate of solution. Proc. Roy. Soc. London A133: 522 (1931).

6. WICKE, E. Empirische and Theoretische Untersuchungen der Sorptionsgeschwindigkeit von Gasen an porosen Stoffen I. Kolloid Z. 86: 167 (1939).

7. BARD, Y. Nonlinear parameter estimation and programming. IBM Contributed Program Library, 360D, 13.6003 (1967).

8. BECKER, H. A. On the absorption of liquid water by the wheat kernel. Cereal Chem. 37: 309 (1960).

9. CARMEN, P. C. Flow of gases through porous media. Academic Press: New York (1956).

10. BABBITT, J. D. Observation on the adsorption of water vapor by wheat. Can. J. Res. 27F: 55 (1949).

11. BECKER, H. A. A study of diffusion in solids of arbitrary shape with application to the drying of the wheat kernel. J. Appl. Polymer Sci. 1: 212 (1959).

12. CHUNG, D. S., FAN, L. T., and SHELLENBERGER, J. A. Volume increase of wheat kernels accompanying absorption of liquid water. J. Biochem. Microbiol. Technol. Eng. 3: 377 (1961).

13. BARRER, R. M. Activated diffusion in membranes. Trans. Faraday Soc. 35: 644 (1939).