MONTE CARLO SIMULATION OF KNUDSEN'S DIFFUSION IN CERAMICS

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The Monte Carlo simulation technique has been described to estimate the Knudsen's coefficient of vapour diffusion through ceramic materials which have nano size pores. The simulation results agree well with the results obtained from theory. A decrease in the length-radius ratios of the capillary pore confirms that shorter length and bigger pore size of capillaries will enable faster molecular transport through the specimen. Subtraction of the estimate of molecular escape probability from total probability helps us obtain a measure of the impedance of vapour molecules within the specimen. Some possible applications of the technique in ceramics along with remarks for extension to complicated diffusion regimes are discussed.

INTRODUCTION

Moisture removal under thermal conditions in the form of vapour from advanced ceramic materials of nano size particles leads to densification of ceramic bodies which contributes to their physical properties. Uneven vapour removal could alter the properties and may even lead to formation of cracks [1] due to uneven capillary contractions in the material when sintered. Hence knowledge of the vapour diffusivity of the sample at different temperatures is important as a means of controlling the time and temperature at which the sample should be heated so that a uniform shrinkage takes place.

In this paper we have described the Monte Carlo technique to model the transport mechanism of water vapour through a nano pore size medium that can be utilized to calculate the diffusion flux of vapour. The previous work [2] on Monte Carlo application in gas diffusion study through porous medium assumes the medium to possess a hexagonal closely packed particular arrangement in three dimensions but the computational scheme varies with each particle sphere size to calculate the porosity that is related to the diffusion coefficient and involves a laborious computation. We have considered a rather simpler one-dimensional medium whose mean pore size is known. By choice of a suitable time parameter the movement of a vapour molecule is monitored within the pore, which enables faster calculation. Finally a way is suggested as to how the time parameter can be bypassed to perform the computations.

THEORETICAL PART

Physical

From the kinetic theory of gases [3], we know that under normal pressure, in bulk diffusion it is the interaction of the molecules which disperse and cause the flux to depend upon the concentration gradient. This is called Fickian diffusion. The mechanism of gas diffusion at low pressure in porous medium, however, changes. In such a situation, the mean free path of molecules within a narrow pore may be larger than the pore diameter and they therefore impinge on the pore walls more frequently than they encounter each other. This is called Knudsen's diffusion [4].

For a cylindrical capillary of length l and radius r ($<< l$) at the ends of which concentrations of gas are c_0 and c_1 the molar flux J is given by

$$J = \pi r^2 \left[\frac{8r}{3} \sqrt{\frac{RT}{2\pi M}} \right] \frac{c_0 - c_1}{l} , \qquad (1)$$

where R is the gas constant, T the absolute temperature and M the molecular weight of gas. The Knudsen's diffusion coefficient is given by the expression within the bracket in equation (1) as

$$D_k = \frac{8r}{3} \sqrt{\frac{RT}{2\pi M}} . \qquad (2)$$

This expression works well if $l > 100r$. In case $l \leq 100r$, Clausing [5] showed that the Knudsen's diffusion

coefficient should be given by the equation

$$D_k = Wl \sqrt{\frac{RT}{2\pi M}} \quad . \tag{3}$$

For different $l / r \leq 100$ there is a weight function W. For $l > 100r$, $W = 8r / 3l$.

From considerations of the kinetics theory, D_k can also be shown [2] to follow the expression

$$D_k = n_T l \sqrt{\frac{RT}{2\pi M}} \quad . \tag{4}$$

From equations (3) and (4) we find that $n_T = W = 8r / 3l$ and hence n_T also becomes a function of l / r. We can provide a statistical estimate of n_T. In a physical sense, n_T in equation (4) means the fraction of gas molecules which can pass through capillary pores of radius r and length l when a definite number of molecules strike the mouth of pores in unit second with a velocity given by the square root term in equation (4).

Statistical

The Knudsen's diffusion coefficient D_k is the same diffusion coefficient that is presented in Einstein's expression [6] as

$$\overline{Y}^2 = 2Dt \quad . \tag{5}$$

Where $\overline{Y}^2$ is the mean square distance the diffusant molecule travels randomly in time t and the diffusion coefficient $D = D_K$. When $l > 100r$, with the knowledge of D_K from equation (2) we can use equationn (5) to find $\overline{Y}$ which would be the mean distance traveled by molecule in time t. In case $l < 100r$, we can compute $\overline{Y}$ from equation (5) with the knowledge of D_K from equation (3). If ε_i are the random jumps the molecule executes within a narrow pore, that follow a Gaussian distribution with mean zero and standard deviation $\overline{Y} = \sqrt{2Dt}$, then the standard Gaussian deviate of $\varepsilon_i = 1, ..., m$ is written as $(\varepsilon_i\text{-}0) / \overline{Y}$. Here m designates the number of collisions of the molecule with the pore wall. Since a sum of k random numbers ,Υ_i approximates a Gaussian variate, we can generate on the computer pseudo random numbers which lie between 0 and 1 and follow uniform distribution with mean $k/2$ and standard deviation $\sqrt{k/12}$ [7]. So the standard Gaussian variate of ε_i can be equated to the latter as

$$\frac{(\varepsilon_i - 0)}{\overline{Y}} = \frac{\Upsilon_i - k/2}{\sqrt{k/12}} \quad , \tag{6}$$

Knudsen assumed that the angle at which the molecule gets deflected after every collision with the pore wall follows the cosine law. Figure 1 shows that if $2r$ is the

pore diameter, then the molecular jump ε_i after every collision with the pore wall can be represented as

$$\varepsilon_i^2 = x_i^2 + (2r)^2 \quad , \tag{7}$$

$$x_i = \pm\sqrt{\varepsilon_i^2 - 4r^2} \quad , \tag{8}$$

where x_i are increment or decrement in molecule position for $i = 1, 2, ..., m$. Sign of x_i is determined by sign of ε_i. If ε_i is positive, x_i is positive, which means the molecule moves forward towards the pore end at $x = l$ and if ε_i is negative, x_i is negative, which indicates the molecule is deflected back within the capillary towards the pore mouth at $x = 0$.
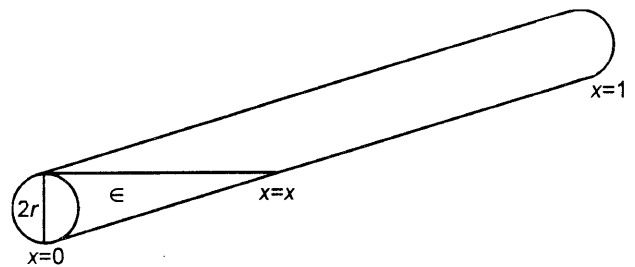

Figure 1. Molecular deflection within cylindrical capillary.

We assume that the molecule starts from the pore mouth and after every collision with the wall the value of x_i obtained on the basis of equation (8) is added to the previous molecular position to determine its latest position within the capillary pore.

In figure 2, $x = 0$ designates the pore mouth in the outer layers of the dried up specimen which are moisture free and compact compared to the interior layers that still contain the bound moisture. When the specimen is heated the vapour molecules fly off from the moisture-air interface in the interior layers and tend to approach the outer surface. The molecules finally strike the pore mouth. Now two events can occur: if the molecule after a multiple number of collisions attains a position $x > l$ then the molecule has passed through the medium. This is recorded as transmission. If, however, the molecule attains a position $x < 0$, then the molecule has been reflected back into the position from where it originated. This is noted as reflection.

Each time we would enter a molecule into the pore and monitor the molecule position x_i calculated on the basis of equations (6) to (8) to know if the molecule has suffered a transmission or a reflection. To know the latest molecule position we would pick up $k = 1$ new random number on the computer every time as every displacement is associated with a collision with the pore wall. If N simulation runs are performed and n is the number of cases of transmission, $n_T = n / N$ is the transmission probability.
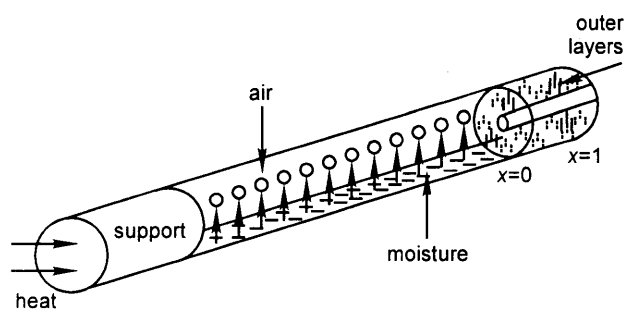
Figure 2. A simplified one-dimensional horizontal view of molecular transport during sintering.

Figure 3. Plot of molecular transmission probability vs. capillary length.

$r = 120.5$ nm

The scheme described above to monitor molecule position within the pore is accomplished by Monte Carlo simulation. From the above considerations it is clear that the method performs a computer experiment on random numbers on the basis of the determinate model represented by equations (1) to (5) above.

Test data

The values of parameters r and l which pertain to capillary pore of the sample need be known in advance to employ the simulation scheme. The other constants R, T, M can be found in tables. In this work, the $M = 18$ g mol^{-1} for water vapour under a pressure of 0.09 bar at 573 °C temperature. The parameter r has a value of 1.5 nm and l has the maximum value of 1500 nm.

RESULTS AND DISCUSSION

Equation (4) reveals that the transmission probability n_T is inversly related to length l. Figure 3 shows that the transmission probability of water vapour molecules decreases as the length increases which indicates that the simulation reproduces the basic relationships between transmission probability and the length. Hence the physical formalism in equation (4) for arbitrary values of length and pore radius is confirmed by the simulation.

The accuracy of the simulation depends on how one chooses the value of t which is the time interval after which the molecule position is monitored. Since the time that elapses between any two molecular collisions with the pore wall is microscopic the molecule cannot be monitored to that resolution and t has to be found in a trial and error manner. In the present study the t value was kept in the range 19.3 to 461.4 nano seconds for which the simulation results matched with the theoretical values. Table 1 shows that for different l / r ratios the theoretical value of n_T and its Monte Carlo estimate (MCE) are in close agreement for the chosen values of
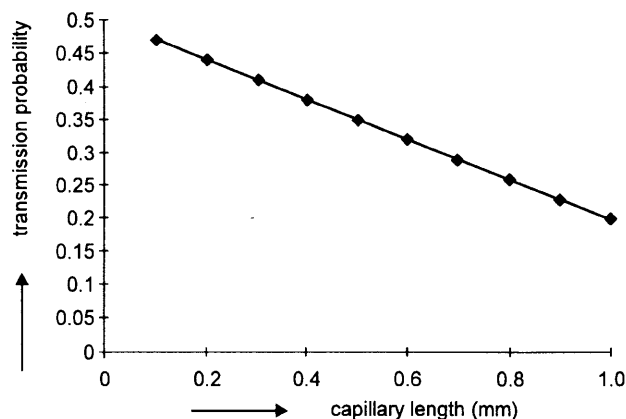
time. The theoretical values of D_k from equation (2) settle to 8.211×10^{-7} m^2 s^{-1}. The estimated values of D_k for different l / r ratios in table 1 fall around this theoretical value. It can be noticed in the table that as the l / r ratio decreases, which implies a decrease in the capillary length and an increase in the radius, the estimated n_T also increases which is physically true as a greater radius and shorter length of capillary will facilitate faster molecular escape.

Since the Knudsen's flow rules out the intermolecular frictions, the simulation assumes that the molecules enter the pore mouth one by one. In case $\varepsilon_i < 2r$ the molecular positions x_i, as obtained from equation (8), become a complex quantity and the run becomes invalid. Hence we introduced the condition that the molecular displacements ε_i given by equation (7) should always be greater in magnitude than the pore diameter. If these conditions are violated the run is treated as invalid and n is not accordingly updated.

There are two salient features of the simulation scheme. It may be noted that while n_T gives the probability of molecular escape, on subtraction of n_T from one, we get the probability of molecular reflection which throws light on the impedance of molecules within the sample per unit time. Table 2 shows that as intervals of monitoring the molecule increase the molecular escape is reduced whereas a molecule monitored at longer intervals has a better escape probability. Choice of t is important insofar as speed and accuracy of n_T are concerned in simulation. A calculation based on the molecular velocity term from equation (4) and the minimum displacement $\varepsilon_i = 2r$ for $x = 0$ from equation (7) suggests that the minimum time that elapses between any two molecular collisions with pore wall comes at around 4 picoseconds. This implies that a large number of collisions would follow in a second's time. Since the

Table 1. An agreement between theoretical values and Monte Carlo estimates of transmission probability for different l / r ratios and the estimated Knudsen's diffusion coefficients.

sr. No.	l / r	$n_T = (8r / 3l) \times 10^{-3}$ (theoretical)	t (ns)	$n_T \times 10^{-3}$ (MCE)	$D_K \times 10^{-7}$ (m^2 s^{-1})
1	1000	2.667	461.4	2.553	7.861
2	900	2.963	374.5	3.047	8.442
3	800	3.333	296.2	3.300	8.119
4	700	3.810	227.2	3.768	8.120
5	600	4.444	167.4	4.450	8.305
6	500	5.333	116.5	5.045	7.766
7	400	6.667	75.0	6.500	8.010
8	300	8.889	42.5	8.340	7.700
9	200	13.333	19.3	13.714	8.445

Table 2. Monte Carlo estimates of transmission probability for different molecule monitoring time intervals at various l / r ratios.

sl. No.	l / r	t (s)	n_T (MCE)
1	1000	10^{-6}	0.1624
	1000	10^{-4}	0.4665
	1000	10^{-2}	0.4969
2	600	10^{-6}	0.2978
	600	10^{-4}	0.4800
	600	10^{-2}	0.4983
3	200	10^{-6}	0.4333
	200	10^{-4}	0.4936
	200	10^{-2}	0.4996

$$= \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{0} \varepsilon^{-1/2} \left[\left(\frac{\varepsilon}{\sqrt{2Dt}} \right)^2 \right] d\varepsilon \qquad (10)$$

$$q = \int_{0}^{\infty} f(\varepsilon, t) d\varepsilon \qquad (11)$$

$$= 1 - \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{0} \varepsilon^{-1/2} \left[\left(\frac{\varepsilon}{\sqrt{2Dt}} \right)^2 \right] d\varepsilon \qquad (12)$$

From the above arrangement it is clear that p varies from 0 to 0.5 while q varies from 0.5 to 1 so that $p + q = 1$. From the area under the Gaussian curve the value of displacement ε can be directly obtained from Gaussian tables. Computer software with inbuilt Gaussian tables is available. In order to determine the sign of the displacements ε we would generate a random number γ and apply a criterion that if $0.5 < \gamma < 1$, then the displacement ε is positive and the molecule rebounds forward and if $0 < \gamma < 0.5$, then the displacement is negative and the molecules rebounds backward within the pore. In this way equation (6) also can be bypassed.

The above arrangement helps us to compute the molecular displacements without the knowledge of $\overline{Y} = \sqrt{2D_k}\, t$ and thus the time parameter t is bypassed and a knowledge of D_k is not required in advance. In this study we have made use of equations (2) to know $\overline{Y}$ from equation (5) to validate that the simulation technique can reproduce the results produced by theory if the molecule position is monitored within the pore at preset time intervals.

By the above arrangement becomes arbitrary and such a treatment might require a large number of simulation runs in order to arrive at reliable estimates. In this study, the results were obtained within $N = 10^7$ simulation runs which is a fairly large number. However large the number of simulation runs N, the estimates may still be limited. Hence, in practice it may be advisable to employ variance reduction techniques [7] to arrive at reliable estimates.

molecule position if monitored at picosecond intervals would require enormous computer time, the time t can be set in such a way that the simulation scheme speeds up the calculation. Table 1 shows time t chosen in nanoseconds for various l / r ratios to monitor the molecule within the pore that speeds up the simulation process by about 4825 to 115350 times compared to the 4 picoseconds microscopic time and also gives estimates of n_T close to its theoretical values. Table 2 shows that for different l / r ratios, the molecule when frequently monitored has a low transmission probability which however increases as the time to monitor the molecule becomes longer. Table 2 shows that the probability finally settles approximately at a value of 0.49 for $t = 10^{-2}$ s at various l / r ratios.

There is a way to carry out the above simulation scheme without resorting to equation (5). The molecular displacement ε follows a Gaussian distribution with mean 0 and variance $2Dt$ for which the probability p can be written as

$$p = \int_{-\infty}^{0} f(\varepsilon, t) d\varepsilon \qquad (9)$$

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Applications and future potential

The possible application of the above scheme can be found in the preparation of thin films and ceramic membranes by the sol-gel method which is the most favoured way of preparing these ceramics with pores in the nanometer range. When the dried gels are sintered the gel layer on the support shrinks as the vapour and gases within the sample are eliminated. Uneven transport of gases through the layer creates uneven shrinkage and crack - free films may be difficult to obtain. Improvements in sintering process and pore control can be achieved if the transport flux in terms of time and temperature is better understood. A more important application area lies in the nano filtration of gases through ceramic membranes. In both cases the transport of gas or vapour molecules is associated with collisions of the molecules with the pore surface [8] with a mean free path greater than the pore diameter which eliminates the influence of intermolecular collisions within the pore. In Knudsen's diffusion, the gas molecule is assumed to remain desorbed from the pore wall. If the pore diameter is reduced, the potential fields of opposite internal pore surfaces tend to overlap and in such a case transition diffusion regime prevails when both Knudsen's and the micropore diffusions play a significant role. As the pore diameter falls below 2.5 nm, the molecule will always move in the potential field of the pore surface and only micropore diffusion prevails. Micropore systems are a development of recent time in the field of ceramics [8]. Since pore size may vary with position, Monte Carlo may be used to perturb the pore size by a random number within a prescribed pore size range to study the diffusion regimes which display deviations from the Knudsen's model if we know the probability of a molecule being in the potential field of pore surface. To supplement such computer experimentation, some quantitative models which describe potential energy of the nano pore surface as a function of pore radius would be required.

CONCLUSION

The Monte Carlo simulation described in the context of vapour transport through nano-size pores replicates satisfactorily the Knudsen's diffusion model system. The technique shows promise of extension to cover the complicated versions of diffusion when pore size decreases, if supplemented with suitable quantitaive models. Computer experimentation may be an alternative way of studying the separation mechanisms allowing the scope of trial and error experimentation to be significantly reduced.

Acknowledgement

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Submitted in English by the authors.

SIMULACE MONTE CARLO KNUDSENOVY DIFÚZE V KERAMICKÝCH MATERIÁLECH

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Keramické materiály s velikostí částic řádu nanometrů se zhutňují vypuzováním fyzikálně vázané vlhkosti ve formě par v mírném teplotním režimu. Nerovnoměrné vysušování může nejen ovlivnit zhutňování, ale také způsobit vznik trhlin. Znalost difúze par je proto užitečná pro regulaci času a teploty sušení. Molekúly páry procházejí póry velikosti nanometrů Knudsenovou difúzí. Byla provedena simulace typu Monte Carlo za účelem ověření Knudsenova modelu difúze. Schéma simulace dobře odpovídalo uvedenému modelu difúze. Sleduje se dráha molekuly v póru a zaznamenává se buď únik nebo odraz. Bylo zjištěno, že počet úniků molekul pro různé poměry délky póru ku jeho průměru je v rozsahu 15 480 až 135 809. Počet úniků se zvětšuje se zmenšujícím se uvedeným poměrem, což potvrzuje předpoklad, že kratší kapiláry většího průměru urychlují difúzi. Odečtením pravděpodobnosti úniku dle simulace Monte Carlo od celkové pravděpodobnosti umožňuje stanovit veličinu závislou na molekulárním difúzním odporu materiálu.

Prokázalo se, že volba vhodného časového parametru pro sledování polohu molekuly uvnitř póru zvyšuje rychlost výpočtu simulace asi 4 825 až 115 350 krát, ve srovnání se 4 pikosekundami mikroskopického času. Přesnost odhadu pravděpodobnosti úniku rovněž závisí na volbě času jako pravděpodobnosti úniku, která se zvyšuje a posléze stabilizuje s prodlužováním doby sledování molekuly. Pro libovolně zvolenou dobu by bylo proto nutno provést velký počet simulačních výpočtů, aby se zachovala přesnost odhadu počtu úniků, a bylo nutno použít vhodnou statistickou metodu pro stanovení počtu simulačních výpočtů, zvláště v případě, kdy se obejde parametr

času. Možnými obory uplatnění simulace Monte Carlo v keramice jsou vypuzování par z materiálů s póry velikosti nanometrů při výpalu, a filtrace keramickými materiály s póry

této velikosti. Počítačové experimenty tak poskytují logický základ pro studium složitých systémů difúze plynů keramickými materiály.

ÖKOTOXIKOLOGIE - UMWELTCHEMIE, TOXIKOLOGIE, ÖKOLOGIE

by Karl Fent

Georg Thieme Verlag, Stuttgart / New York 1998,
288 pages, 178 figures, 63 tables,
flexible softcover, price 78 DM; ISBN 3-13-109991-7

Although environmental problems entered public consciousness since the late 1960s, it was only during the last decade that ecotoxicology has become a firmly established field with well-defined tasks and goals in the interdisciplinary region between environmental chemistry, toxicology and ecology. Karl Fent's texbook, which is based on the author's lectures at the Eidgenössische Technische Hochschule (ETH) and the University Zürich (Switzerland) tries to fill a gap in the German literature on this modern subject. The book is divided into 11 chapters (Introduction, Ecotoxicology and Aspects of Environmental Chemistry, General Principles of Ecotoxicology, Bioavailability and Factors Controlling Ecotoxicity, Methods and Systems of Ecotoxicological Testing, Environmental Chemicals in Living Organisms, Bioaccumulation, Molecular Mechanisms and Effects on Cells, Effects on Individuals and Populations, Effects on Biocommunities and Ecosystems, Practical Aspects of Ecotoxicology: Hazard Assessment).

Ecotoxicology deals with the analysis of effects of chemical substances on the living nature and has to consider all biological levels, from the cell to the ecosystem. This is one of the great complications for practical research. Results of laboratory tests cannot be easily transferred to ecosystems, firstly because (apart from the statistical scatter between individuals) the toxicity of chemicals to living organisms varies enormously between different species and no species is known to be "the most sensitive" for a majority of chemical substances, and secondly because the synergistic behavior of a mixture of several chemical substances in natural environments usually cannot be predicted without great uncertainties. Furthermore one has to differentiate between acute and chronic effects, lethal and sublethal levels etc., so that even on a laboratory scale an objective comparison between the toxicity of different chemicals can be a very complex task. Fent's book tries to provide the necessary prerequisites for an evaluation of toxicity and for an effective hazard assessment.

The introduction, defining the basic concepts and containing a history of ecological disasters, worldwide trends and examples of water, soil and air pollution (with PCB, PCDD, PCDF, organotins, phosphates, nitrates etc.), is followed by a chapter treating ecotoxicology from the viewpoint of environmental chemistry and focussing on the

behavior of chemicals in the enviroment (transport, transfer, transformation) and in sewage purification plants. This second chapter is implemented with important case studies, such as pesticide spills (e.g. the Rhine River pollution during the conflagration of a chemical depot of "Sandoz" at Basle, 1986), oil spills (e.g. the "Exxon Valdez" disaster, 1989) or heavy metal contaminations with direct effects on human beings (e.g. cases of Cd and Hg poisoning in Japan, 1950-70). The third and fifth chapter consider general principles of ecotoxicology and explain in great detail the laboratory testing methods and their significance for real ecosystems. Chapters four, six and seven deal with bioavailability and factors influencing it (pH, ligand complexation, water hardness, temperature, salinity, adaptation and resistency mechanisms), the destiny of environmental chemicals in living organisms (reception, transport, transformation, elimination etc.) and bioaccumulation, while chapters eight, nine and ten give a detailed account of the effects of toxical chemicals on cells (molecular mechanisms, gentoxicity, carcinogens), individuals and populations (with a case study of DDT) as well as biocommunities and ecosystems. The last chapter finally reviews some of the formal aspects of hazard assessment, such as the German law for chemicals (ChemG) and several other relevant laws, as well as their relation to European and worldwide standards.

During recent years it is more and more realized that long-term economic success in any field of chemical technology is not possible without a careful analysis of environmental implications. From the viewpoint of inorganic materials science and engineering mainly gas, dust and heavy metal emissions have to be taken into account. But even such areas as the selection of organic vehicles for ceramic forming processes have to consider ecotoxicological aspects (which delimit e.g. the use of phthalates and some other organics). Fent's book can serve as an easy-to-read introduction to the field of ecotoxicology with up-to-date information for a wide audience (from biology to chemistry) and will certainly be of value for chemical engineers and students of chemical technology, because the introduction of each new technology requires a thorough analysis of possible ecological consequences and must be in accordance with the actual legal prescriptions.

Apart from the contents, which can be attributed merely to the author himself, a quite remarkable feature of this publication is the layout which accentuates the logical hierarchy and considerably enhances the didactic value as a student's textbook. It is clear that a book of these qualities could only be developed by an intimate cooperation between the author and the editorial team of the Georg Thieme Verlag.

W. Pabst