ELSEVIER

Journal of Food Engineering **28** (1996) 297–306

0260-8774/96/$15.00

0260-8774(95)00044-5

Respiration Rate Model and Modified Atmosphere Packaging of Fresh Cauliflower

C. Ratti,* G. S. V. Raghavan & Y. Gariépy

Agricultural Engineering Department Macdonald Campus, McGill University, Ste-Anne de Bellevue PQ, H9X 3V9, Canada

(Received 19 January 1995)

ABSTRACT

In the first part, the respiration rate of fresh cauliflower was measured in sealed containers at different temperatures. An enzymatic reaction was then used to model the respiration activity as a function of gas concentrations and temperature. An Arrhenius relationship was used in the model to account for the effects of temperature. Predictions derived from the model were in good agreement with the experimental data.

In the second part, the ability of air-diffusion channels to maintain the desired modified atmosphere (MA) compositions (O_2: 2·5–3·5%; CO_2: 0%) in storage chambers was assessed. Fresh cauliflowers were stored at 2·5°C for 21 days in laboratory chambers equipped with channels (D = 2e−3 m) of 0, 0·3, 0·6 and 1 m in length, and for 33 days in chambers equipped with 0, 0·05, 0·15 and 0·25 m diffusion channels. The results have indicated that diffusion channels can be used to maintain MA conditions and that they could accommodate for some fluctuations in the air temperature. Copyright © 1996 Elsevier Science Limited.

NOTATION

A	Surface area [m^2]
Ar	Argon
c	Concentration [mg/l]
CO_2	Carbon dioxide
C_p	Specific heat [J/g °C]
D	Diameter [m]

*Present Address: Planta Piloto de Ingenieriá Química, 12 de octubre 1842, 8000 Bahía Blanca, Argentina.

$D_{O_2-N_2}$	Diffusivity of oxygen in nitrogen [m^2/s]
Gr	Grashof number [−]
h_g	Heat transfer coefficient [W/cm^2 °C]
k	Air thermal conductivity [2/cm°C]
k_i	Kinetic constants ($i = 1, 2, 3$), eqn (5)
$k_{i\infty}$	Regression constants ($i = 1, 2, 3$), eqn (6)
L	Diffusion channel length [m]
m	Mass of the product [kg]
N_2	Nitrogen
Nu	Nusselt number [−]
O_2	Oxygen
$[O_2]$	Concentration of oxygen [mg/l]
Pr	Prandtl number [−]
r	Rate of respiration [mg/kg h]
R	Universal gas constant [J/K mol]
T	Temperature [°C]
t	Time [h]
V_f	Free chamber volume [m^3]
y	Volume gas fraction %
ΔH	Heat of respiration [J/mg CO_2]
ΔH_{ri}	Activation energy of the reaction ($i = 1, 2, 3$), eqn (6) [J/mol]

Subscripts

air	Bulk air
ch	Storage chamber
CO_2	Carbon dioxide
cr	Cold room
g	Gas
o	Initial
O_2	Oxygen

INTRODUCTION

The objective of storage is to extend the shelf life of fresh products by preserving them in their most usable form for consumers and processing industries. Low temperature with high relative humidity and controlled/modified atmosphere (CA/MA) is a common method used to maintain the quality of fresh produce. In this method, the concentration of oxygen (O_2) is generally reduced and the concentration of carbon dioxide (CO_2) increased. CA/MA storage has become a common practice when dealing with fruits but it is not widely utilized for vegetables. One reason for this is the great diversity of plant materials (leaf, stem, sprout, seed, root, etc.) classified as vegetables (Gariépy *et al.*, 1984a). Furthermore, the metabolic activity of these different vegetable organs are more likely to react differently under the same CA/MA condition. The primary benefit that one can expect from the CA/MA storage system is that the produce will maintain its freshness and quality for a longer period than it would if stored under a regular atmosphere (RA).

There are many ways to provide the desired gas composition in the storage environment (Smock, 1979). They can be classified into three major groups (Gariépy *et al.*, 1984b): (1) O_2 control systems; (2) CO_2 control systems and (3) membrane systems in which the gases are allowed to diffuse at different rates according to their chemical and physical properties. One method that can be classified as an O_2 control system is the air-diffusion channel technique. Earlier work by Baugerod *et al.* (1980) has indicated that this system is suitable to maintain O_2 levels over a longer period of time and it is relatively insensitive to changes in barometric pressure and to fluctuations in the storage room temperature. Emond *et al.* (1989) studied the use of perforations (i.e. diffusion channels with length ≈ 0) to maintain the level of oxygen in the storage room and developed a model to predict the gas exchange through these perforations.

Proper design of the diffusion channels requires knowledge of the product respiration under the desired MA composition and storage temperature. Respiration data of cauliflower as a function of O_2, CO_2 and temperature could not be found in the literature and should therefore be measured and modelled.

The objectives of this study were: (1) to measure experimentally the changes in respiration activity of fresh cauliflower stored in sealed containers and kept at different temperatures; (2) to model the respiration data using an enzymatic reaction model and an Arrhenius temperature relationship; and (3) to assess the ability of the diffusion channel system to maintain the desired MA composition in chambers filled with fresh cauliflowers.

RESPIRATION RATE MODELLING

Some theoretical considerations on the modelling of the respiration rate are presented in this section. A simple model which takes into account the variations in the temperature of the cauliflower during the process can be obtained from the following energy balance equation:

$$\frac{dT}{dt} = \frac{h_g A}{mC_p}(T_g - T) - \frac{(\Delta H_r)r}{C_p} \tag{1}$$

As there is no noticeable air movement inside the chambers, the heat transfer coefficient h_g can be taken as that for spheres in natural convection. In this case, the Nusselt number (Chapman *et al.*, 1989) is:

$$\mathrm{Nu} = \frac{h_g D}{k} = 2 + 0{\cdot}43(\mathrm{Gr}\,\mathrm{Pr})^{1/4} \tag{2}$$

The value for the heat of respiration (heat involved in the respiration reaction) is about 2·55 cal/mg CO_2 produced and the C_p of fresh cauliflower is 0·93 cal/g °C (Handerburg *et al.*, 1990). Using eqn (2) and the values given above, an estimation of the terms involved in the right-hand side of eqn (1) can be obtained. The second term of eqn (1) can be neglected because for most operating conditions its value is much smaller than the other term. Therefore, the integration of eqn (1) from $t = 0$ to $t = t$ leads to:

$$T = T_g - (T_g - T_o) \exp\left(-\frac{h_g A}{mC_p} t\right) \tag{3}$$

Respiration is basically an enzymatic reaction which can be represented by stoichiometry as:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{Heat} \tag{4}$$

The mechanism of enzymatic reactions has been widely studied (e.g. Laidler *et al.*, 1973). The dependence of the rate of respiration of fresh produce with oxygen can be expressed by a Michael–Menten equation and the functionality with the CO_2 concentration was suggested previously as an uncompetitive inhibition mechanism (Lee *et al.*, 1991). Therefore the equation that represents the rate of respiration can be written as:

$$r = \frac{k_1 c_{O_2}}{[k_2 + (1 + k_3 c_{CO_2}) c_{O_2}]} \tag{5}$$

This type of relationship has been successfully tested with isothermal respiration data of broccoli, apple, banana, tomato, etc. (Lee *et al.*, 1991). The constants k_1, k_2 and k_3 are a function of the temperature of reaction. This functionality can be expressed with an Arrhenius-type relationship:

$$k_i = k_{i\infty} \exp\left(-\frac{\Delta H_{ri}}{RT}\right) \tag{6}$$

where the constants $k_{i\infty}$ and ΔH_{ri} ($i = 1, 2, 3$) are determined through a non-linear regression [Levenberg–Marquardt method, based on Levenberg (1944) and Marquardt (1963)] on experimental data.

MATERIALS AND METHODS

Experimental chambers

The chambers were made from a section of PVC pipe, 0·5 m long and 0·25 m in diameter (Fig. 1). The two extremities of each unit were closed with a square lid of clean acrylic, $6e-3\,m$ thick, and held in place by six threaded rods. Neoprene gaskets were used on both ends to ensure airtightness (Gariépy *et al.*, 1984a). The chambers were sealed and no diffusion channels were installed during the measurement of respiration activity.

Materials

Whole fresh cauliflowers were used for respiration rate and storage experiments. The required amount of this commodity was bought in two different batches from a local wholesale dealer (imported from USA). Each of both experiments (respiration rate or storage) was done with a different batch of cauliflower. Therefore the cultivar (unknown) of the samples and their post-harvest treatment could be assumed to be uniform for each experiment.

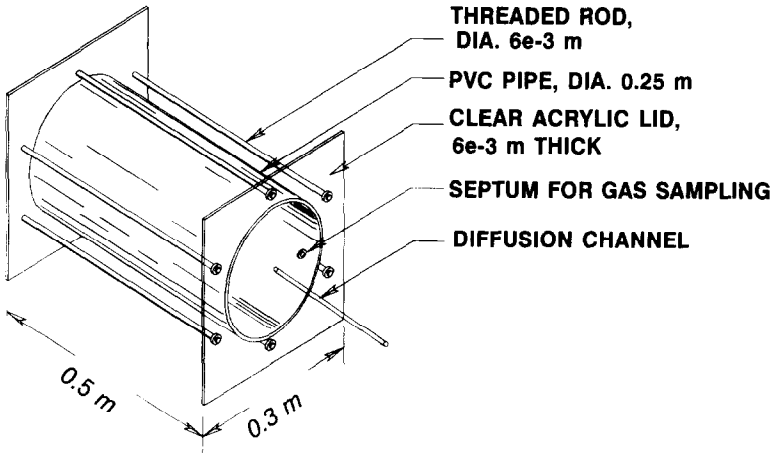

Fig. 1. Schematic of a storage chamber.

Measurement of the respiration rate

The respiration rate of whole cauliflowers was measured as a function of gas composition and at different cold room temperatures. The four temperatures utilized were 1, 6·5, 12 and 23°C. Each temperature was applied to four replicates. Each cauliflower was cleaned, weighed and placed in the experimental chambers. The chambers were then closed and the experiment started.

The temperature of the cauliflowers as well as the ambient temperature of the cold room were recorded with T-type thermocouples. The gas composition was monitored with a Hewlett-Packard 5890A gas chromatograph equipped with a thermal conductivity detector. The set-up used did not allow for the separation of Argon (Ar) from O_2. In this paper, the $Ar+O_2$ gas mixture is referred as O_2 measured levels. The concentration of Ar in the sealed chambers did not change during the experiment and calculation of the respiration rate was based on the changes in O_2 concentration.

Storage under MA

For the storage experiment, diffusion channels made of copper tubing, 2 mm in diameter and of various lengths, were installed on the lid of the chambers in order to control the oxygen exchange rate between the inside and the outside. The experiments of storage were carried out in a cold room set at 2·5°C. The length of the diffusion channels were 0, 0·05, 0·15, 0·25, 0·3, 0·6 and 1 m, (Fig. 1) and completely sealed chambers were used as control. Each treatment was replicated thrice. Bags containing 100 g of hydrated lime were placed in the chambers to prevent any accumulation of CO_2. At the start of the experiment, the chambers were flushed with pure nitrogen (N_2) until the desired initial O_2 compositions of 2·5–3·5% by volume were reached. The measurements of temperature and gas composition were made as described earlier in the respiration rate experiments.

The duration of the experiments was set arbitrarily to 21 days for the chambers equipped with channels of 0, 0·3, 0·6 and 1 m in length and to 33 days in chambers equipped with 0, 0·05, 0·15 and 0·25 m diffusion channels. At the end of each experiment, the quality of the cauliflower was visually assessed and compared. The criteria used to evaluate the end quality of the cauliflower included mass loss, colour and the presence of leaf abscission and mould.

RESULTS AND DISCUSSION

Respiration rate

The progression of the cauliflower respiration rate (in [mg CO_2 produced $kg^{-1}h^{-1}$]) as a function of the available O_2 is presented in Fig. 2. The shape of the curves was characteristic of enzymatic reactions. At high O_2 concentration, the velocity of the reaction was maximum and remained fairly constant over a wide range of concentrations. This rate decreased to zero at low O_2 concentration.

Over the temperature range studied, the influence of temperature on the rate of respiration was as expected. Increases in temperature resulted in increases in the cauliflower respiration rates. The temperature at which the heterogeneous reaction occurs is that of the cauliflower. So the temperature at which the major part of the reaction occurred differed in most cases from that of the cold room. To account for the differences between the initial temperature of the cauliflower and that of the cold room, it was necessary to solve the non-linear regression (eqns (5) and (6)) together with the equation for the variation in cauliflower temperature (eqn (3)).

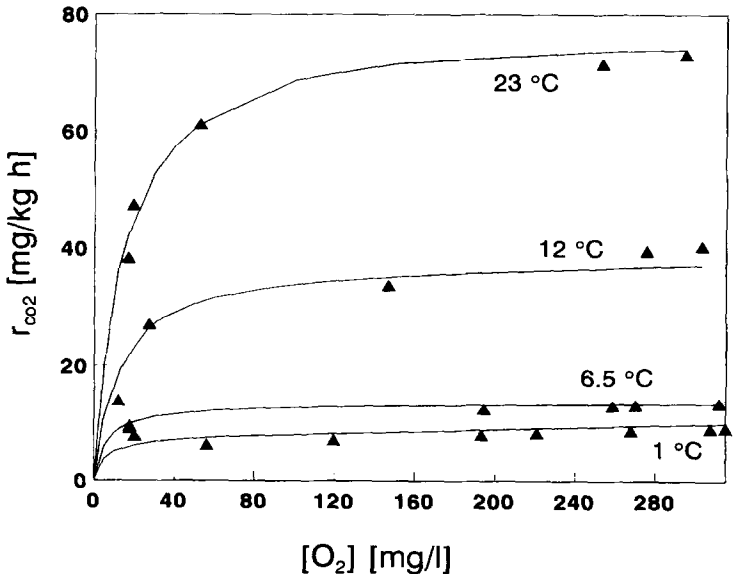

Fig. 2. Observed and predicted respiration rate of fresh cauliflower at different cold room temperatures (1, 6·5, 12 and 23°C), as a function of available O_2.

TABLE 1
Regression Constants of the Respiration Rate Model (eqns (5) and (6))

Parameters	$ln(k_{1\infty})$	$\Delta H_{r1}/R$	$ln(k_{2\infty})$	$\Delta H_{r2}/R$	$ln(k_{3\infty})$	$\Delta H_{r3}/R$
Initial guess	42·86	1·125e4	4·023	4·509e2	1·00	1·00
Final results	45·08	1·189e4	2·578e1	6·703e3	−1·807e2	−2·244e4

Table 1 presents the final values of the non-linear regression constants (eqns (5) and (6)) derived from the experimental data. The initial guess values of the constants are also provided in Table 1 since the stability of the non-linear regression solution is strongly dependent on the initial set of values of the unknown coefficients. The non-linear regression was solved in 11 iterations with a tolerance criterion of 0·0001. The results of the model fitted the experimental data with an average standard error of 6%. A *t*-test was performed to assess the goodness of the non-linear regression fitting. This test indicated that the means of the samples were not significantly different at the 0·05 level.

As shown in Fig. 2, the predictions of the model are in good agreement with the experimental data. The effect of CO_2 on the respiration model was represented by the parameters $\ln(k_{3\infty})$ and $\Delta H_{r3}/R$ (Table 1). Once these values were substituted into eqn (6), they yielded a k_3 value closer to zero. This indicated that the effect of CO_2 on the respiration model was minimal and can therefore be neglected.

Storage under MA

After 3 days of storage, the temperature of the cauliflower reached 2·6°C and this value was maintained for the duration of the experiment. The progression of the cauliflower temperature and the cold room temperature are presented in Fig. 3. Figure 4 shows the experimental results of MA stored cauliflowers in chambers equipped with diffusion channels of 0, 0·3, 0·6 and 1 m length as well as in a closed chamber. The diffusion channels were able to maintain the O_2 concentration at the desired level for a period of about 16 days. There was no marked difference between results among the diffusion channels with length ranging from 0·3 to 1 m.

The effect of smaller lengths (0·05, 0·15 and 0·25 m) was studied in a second part of the storage experiments. Figure 5 shows these results. In this range of tube lengths there were noticeable differences between the final concentrations. This indicated that the length of the diffusion channel controlled the amount of O_2 diffusing into the chambers. Results for 0·25 m length (Fig. 5) were similar to those obtained in the previous experiments (Fig. 4). It can be concluded that tube lengths in excess of 0·25 m (and with the cross-sectional area used in these experiments) yielded no appreciable difference between the final concentrations in the chambers. As can be seen, the concentration of O_2 shows a sudden decrease at near 200 h from the start time of the experiment. This was due to a failure in the refrigeration system for a period of nearly 24 h that caused an increase in the temperature of the cauliflowers. Nevertheless, after the cold room temperature was re-established, the system reached approximately the desired final concentration of O_2. The diffusion channels showed enough stability to control the concentration of O_2 within acceptable levels (see Fig. 5).

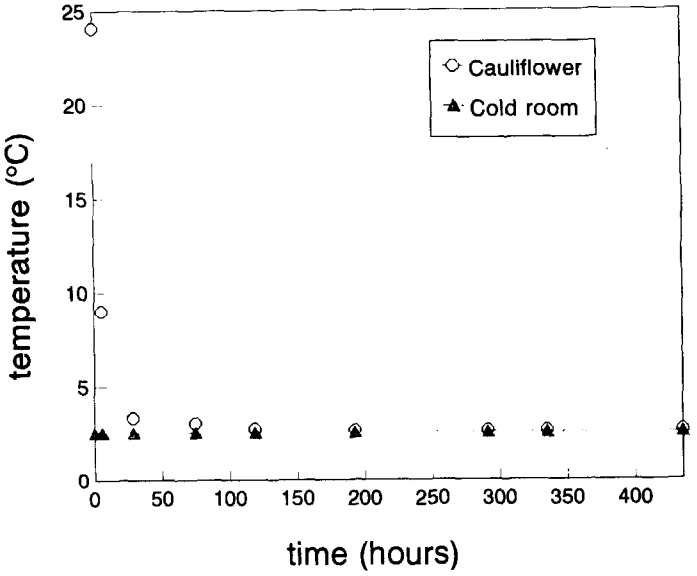

Fig. 3. Variation in the temperature of the cauliflower during the storage.

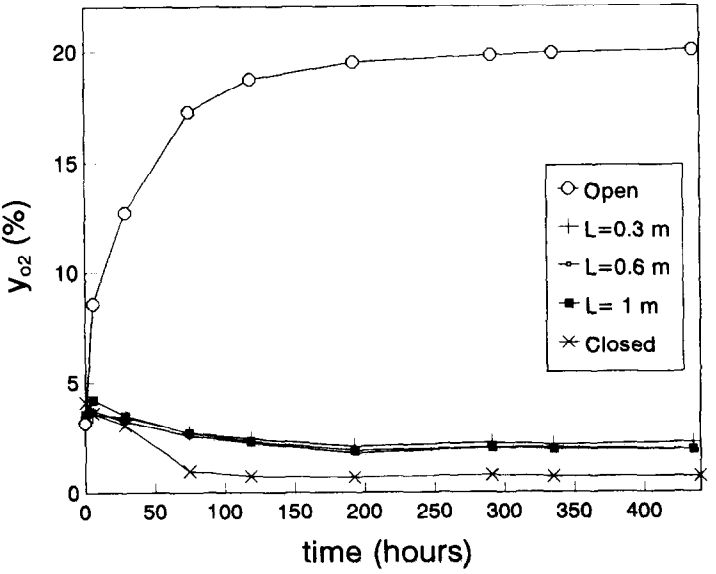

Fig. 4. [O_2] evolution inside the chambers during 21 days of storage.

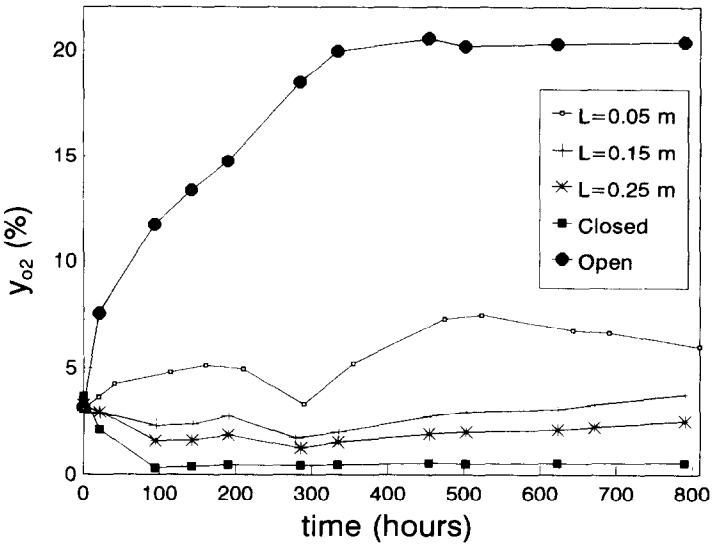

Fig. 5. $[O_2]$ evolution inside the chambers during 33 days of storage.

The variation of O_2 concentration with time within the storage chamber can be approximated by:

$$\frac{dc_{O_2}}{dt} \cong \frac{cD_{(O_2-N_2)}}{LV_f} \ln\left[\frac{c-(c_{O_2})_{air}}{c-(c_{O_2})_{ch}}\right] - \frac{k_1 c_{O_2}}{k_2+c_{O_2}} \tag{7}$$

The temperature dependence of parameters $D_{(O_2-N_2)}$, k_1 and k_2 will determine the variation of O_2 concentration with time when a temperature step fluctuation is applied to the system. Table 2 shows the temperature variation of k_1, k_2 (calculated from eqn (6) and the constants given in Table 1) and of diffusivity of oxygen in air. As can be seen from the table, if the temperature increases from 2·5 to 23°C, O_2 diffusion through the channel does not increase as fast as product respiration rate. Nevertheless, when the refrigeration is recovered, diffusion through the channel does not decrease as fast as product respiration. Therefore, depending on the product (which determines the funcionality of k_1 and k_2 with temperature) and the duration of the temperature fluctuation, a safe process may be obtained or not.

TABLE 2
Temperature Variation of Parameters k_1, k_2 and $D_{(O_2-N_2)}$

T (°K)	*T (°C)*	k_1	k_2	$D_{(O_2-N_2)}$ *(cm²/s)*
275·66	2·5	6·835	4·262	0·181
296·16	23	139·33	23·265	0·206

The quality evaluation performed indicated that after 33 days of MA storage at 2·5°C, the best results were encountered in chambers with a diffusion channel length of 0·25 m. Cauliflowers stored under this condition had field fresh appearance, good colour, minimal amount of mould and excellent marketability. These conclusions arised after visual assessment of the product. Large differences in the number of leaf abscisions and in the amount of mould were observed in the chambers equipped with other lengths of diffusion channels.

CONCLUSIONS

The rate of respiration of fresh cauliflower was successfully modelled using an enzymatic reaction model which took into account the effect of gas levels and temperature through an Arrhenius functionality. The predictions obtained from this model were in good agreement with the experimental data.

The diffusion channels used in the storage experiments were able to maintain the desired concentration of O_2 during the storage with enough flexibility to account for fluctuations in storage temperature. The analysis of the effect of the length of the diffusion channels upon the final concentration of O_2 in the chamber showed that there are no appreciable differences in O_2 concentrations when the lengths exceeded 0·25 m. After 33 days of storage, the best product quality was observed in the chambers equipped with a 0·25 m diffusion channel length. The O_2 concentration maintained in these chambers was about 2·5%.

REFERENCES

Baugerod, H. (1980). Atmosphere control in controlled atmosphere storage rooms by means of controlled diffusion through air-filled channels. *Acta Horticulturae*, **116**, 179–85.

Chapman, A. J. (1989). *Heat Transfer*, 4th edn. Maxwell Macmillan International Editions, New York.

Emond, J. P., Castaigne, F., Désilets, D. & Toupin, C. (1989). *Mathematical Modeling of Gas Exchange in Modified Atmosphere Package*, Int. Summer Meeting American Society of Agricultural Engineers, Paper No 89-6035, Quebec, Canada.

Gariépy, Y., Raghavan, G. S. V., Plasse, R., Thériault, R. & Phan, C. T. (1984a). Long-term storage of cabbage, celery and leeks under controlled atmosphere. *Acta Horticulturae*, **157**, 193–201.

Gariépy, Y., Raghavan, G. S. V. & Thériault, R. (1984b). Use of the membrane system for long-term CA storage of cabbage. *Can. Agr. Eng.*, **26** (2), 105–9.

Handerburg, R. E., Watada, A. E. & Wang, C. Y. (1990). *The Commercial Storage of Fruit, Vegetables and Florist and Nursery Stocks*. United States Dept of Agriculture, Agricultural Research Service, Agriculture Handbook No. 66.

Laidler, K. J. (1973). *The Chemical Kinetics of Enzyme Reactions*, 2nd edn. Clarendon Press, Oxford.

Lee, D. S., Haggar, P. E., Lee, J. & Yam, K. L. (1991). Model for fresh produce respiration in modified atmospheres based on principles of enzyme kinetics. *J. Food Sci.*, **56** (6), 1580–5.

Levenberg, K. (1944). A method for the solution of certain nonlinear problems in least-squares. *Quart. Appl. Math.*, **2**, 164.

Marquardt, D. W. (1963). An algorithm for least-squares estimation of nonlinear parameters. *J. SIAM*, **11**, 196.

Smock, R. M. (1979). Controlled atmosphere storage of fruits. *Hort. Rev.*, **1**, 301–36.