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The Browning of Ketchup Due to Oxidation and the Shelf Life of Ketchup Packaged in a Gamma Bottle

presented by

Christine Maria Burgess

has been accepted towards fulfillment of the requirements for

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THE BROWNING OF KETCHUP DUE TO OXIDATION AND ITS SHELF LIFE IN A GAMMA BOTTLE

by

Christine Maria Burgess

A THESIS

Submitted to Michigan State University In partial fulfillment of the requirements for the degree of

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in

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ABSTRACT

THE BROWNING OF KETCHUP DUE TO OXIDATION AND ITS SHELF LIFE IN A GAMMA BOTTLE

by

Christine Maria Burgess

An experiment was performed to measure the oxygen transmission rate through the Gamma squeeze bottle for ketchup and to determine the permeability constant for the Gamma material itself. Another experiment was carried out to study the change in the color of ketchup after long term exposure to an oxygen rich environment and to establish a minimum acceptable redness level for ketchup as measured by a standard chroma meter. The combined results were then used to determine the reaction rate between oxygen and ketchup and to predict the shelf life for color stability of ketchup packaged in the Gamma bottle. The predicted shelf life is 320 days.

Approved:	Robert Y. Ofoli, Major Professor
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To my parents

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NOMENCLATURE

Α	exposed surface area, m ²
Α	desirable reactant characteristic
a	redness color attribute used by Chroma meter, dimensionless
В	primary color blue with wavelength 435.8 nm
В	undesirable product characteristic
b	yellow color attribute used by Chroma meter, dimensionless
С	permeability constant for Gamma material, cc-mil/day-m ² -atm
c	concentration of oxygen, moles/liter
C _i	initial constant oxygen concentration, moles/m ³
C _i	interface oxygen concentration, moles/m ³
C _o	prescribed concentration on the surface of the ketchup, moles/m ³
D	diffusion coefficient for oxygen in ketchup, m ² /s
D	diffusion coefficient for oxygen in the Gamma material, m ² /s
DS	permeability coefficient for the gas in the membrane
E _A	activation energy
f	fraction left to complete steady state
G	primary color green with wavelength 546.1 nm
h	depth of the ketchup, m
k	reaction rate constant, 1/day
L	lightness value used by Chroma meter, dimensionless
L	perimeter, m
Μ	molecular weight, grams/mole
m	mass of oxygen molecule, kg

N	number	of	moles

- n order of reaction, dimensionless
- p partial pressure of gas, atm
- Q critical oxygen consumption, moles/m²
- q dimensionless parameter
- R universal gas constant, 45.61 ml-atm/mole-°R
- R primary color red with wavelength 700 nm
- R_p permeation rate, moles/day
- R_c consumption rate, moles/day
- S solubility, cm³(gas at STP)/cm³(solvent)/atm
- S slant height, m
- T absolute temperature, °R
- t time, days
- \overline{u} average molecular speed, m/s
- V volume of bottle, ml
- x bottle thickness, m
- x_o penetration distance of oxygen into the ketchup, m
- X,Y,Z tristimulus values
- VAR variance
- β collision rate parameter
- Δ symbol for 'change in'
- ϕ flux, moles/s/m²
- symbol for surface integral

1 INTRODUCTION AND LITERATURE REVIEW

Secondary food quality indicators such as flavor, odor, consistency, texture and overall appearance are intentionally regulated by the control of growing and processing conditions. Once packaged in a transparent container or wrap, it is often the color of the food product inside that the consumer notices first, and this visual observation often creates preconceived ideas about the other quality factors. This is particularly true for ketchup packaged in the plastic squeeze bottle [Gould, 1974]. Because color is a key factor used by the consumer in evaluating the acceptability of the product, a major function of the package must be to preserve the desired color of the product inside by controlling a number of deteriorating environmental factors such as light, oxygen, moisture, heat, and contamination. For ketchup in a squeeze bottle, heat, moisture loss, and oxygen consumption lead to the browning over time [Hodge, 1953; Eckerle et al., 1984]. Of the three deteriorating factors, oxidation is considered to be the major cause of browning since moisture loss has not been a problem [Vilece, 1955], and distribution and storage temperatures can be controlled.

Karel (1974) studied the effects of both oxygen and moisture on various packaged products in general and found that protection from environmental gas and vapor exchange through packaging depends as much on the permeability of the packaging material used as it does on the integrity of the seals and closures. Since the squeeze bottle is more than adequate as a barrier against moisture loss, the browning of ketchup in this package is expected to depend almost entirely on the oxygen barrier properties of the bottle material alone since the mouth of the bottle is usually sealed with foil. Whereas an evaluation of the barrier properties of the squeeze bottle is relatively straightforward, a study of the effects of oxygen on the color stability of ketchup is not. The browning of

ketchup by oxidation requires a knowledge of the reaction rate between oxygen and ketchup, a means of measuring color, and a method for relating this to visual evaluation. The latter two requirements are discussed first.

1.1 Color Measurement for Tomatoes

Ordinary light is the collection of electromagnetic waves having wavelengths within a band known as the visible spectrum. The human eye responds to each wave differently by producing the sensation of a particular color associated with the wavelength. In particular, since all objects absorb certain wavelengths from incident light and reflect others, it is only the reflected waves in combination which determine the object's perceived color [Williams et al., 1972]. If an object reflects all of the light rays it receives, it is said to be white. An object is black if it absorbs all the light rays that fall upon it. An object is red if it reflects red light and absorbs all other colors. Strictly speaking however, color is not a property of the object since the illuminating source may be deficient in certain wavelengths. Fluorescent lighting for example is undesirable for color comparisons of tomato products as it makes them appear less red than they would under natural light due to the deficiency of the wavelength perceived as red in fluorescent light [Lamb, 1977]. Incandescent light on the other hand is rich in red and therefore makes tomato products appear redder than they would under normal daylight [Lamb, 1977]. See-through packages may also change the color of tomatoes by attenuating certain incident and reflected waves as they pass through the package. These are only a few reasons why food color quality is difficult to judge [Robinson et al., 1951]. Even without these problems with lighting and packaging, color quality is still difficult to evaluate simply because it is difficult to measure and quantify.

It is the response of the human eye to light containing a collection of wavelengths that makes color measurement complicated. Through different studies conducted by independent researchers [Evans, 1948; Wright, 1969; Clulow, 1972], it was found that color perception may be described in terms of three fundamental variables called hue, saturation, and lightness, using the terminology of the Optical Society of America (OSA). These variables were also called hue, chroma and value, respectively, in earlier literature [Evans, 1948]. The most important of these is hue which is the essential quality of a color which leads the observer to call it primarily red (R), green (G), or blue (B). Physically, hue is quantified by specifying the wavelength of the dominant primary color, R, G, or B, in the mix. Saturation refers to the purity of the dominant primary color or alternatively, the percentage of hue. More common terms associated with saturation are tint and tone which are used to imply a desaturated color often by the addition of white, gray, or black. Lightness refers to the overall brightness or brilliance of the color. Physically, lightness is a measure of the energy or intensity of the collection of wavelengths forming the color. Two colors are perceived as being nearly the same if their hue, saturation, and lightness are the same. Note that this does not require that the complete spectra for the two colors be identical, which indicates that the human eye is selectively stimulated.

Implied in the designation of hue, saturation, and lightness as the essential quantities responsible for color perception is that the three primary colors, R, G and B, are the fundamental building blocks for the entire color spectrum. While this is not entirely true, it does provide the basis for the operating principles behind color television and the first analog color measuring device to be discussed, the Munsell disk. The Munsell color comparison system [Hand, 1953] consists of a disk containing adjustable sections of the appropriate primary colors along with black and gray sectors. For some applications, one or more of the primary colors may be replaced by mixtures of primary colors in order to

increase saturation. The Munsell disk used for the color grading of tomatoes for example uses red, black, gray, and yellow (Figure 1). Spinning the disk gives the illusion of a single color made up of a blend of these four. Visual scores for tomatoes are assigned according to USDA standards [Lamb, 1977] by first adjusting the proportions of each color sector mix to visually match the color of the tomato and then specifying the percent of each as with a pie chart. The minimum requirement for USDA grades A and B for ketchup is that the perceived color be equivalent to or better than (contains more red) the color produced by spinning the Munsell disk adjusted to contain 65% red, 21% yellow, and the remainder black or gray. The minimum requirement for grade C is that the color be equal to or better than the color produced using 53% red, 28% yellow and the remainder black or gray. Any sample failing to meet the minimum color requirements for grade C is assigned the substandard grade D, regardless of how the ketchup rates in odor, flavor, and texture [Lamb, 1977]. The major drawback to this method is that color matching is obviously very subjective.

The more elaborate digital color measuring system is completely objective and was developed by the Commission Internationale de I'Eclairage (C.I.E.), also known as the International Commission on Illumination (I.C.I.). The basis for the color measuring devices which rely on this system is again the observation that of all of the colors in the visual spectrum, the three which can be used most successfully in color matching experiments (colorimetry) are red, green, and blue. Consequently, R, G and B have been designated as the primary colors [Williams, 1972]. Unfortunately, pure monochromatic wavelengths for R, G and B or even narrow bands of wavelengths centered around these three simply cannot be mixed in any way to produce certain colors perceived by the eye. For example, the color cyan is a mixture of green and blue with red not added but taken out. The C.I.E. overcame this difficulty with R, G, and B by postulating the existence of



three theoretical but "unreal" primaries which are capable of covering the entire color spectrum by purely additive mixtures. Because these theoretical primaries cannot actually be produced nor appreciated by the eye if they could be produced, they are referred to as "stimuli" rather than primary colors and denoted by tristimulus values X,Y, and Z [Clulow, 1972]. The precise wavelengths of the stimuli in terms of those for R, G and B are [Clulow, 1972]

$$X = 2.3646 R - 0.5151 G + 0.0052 B \tag{1.1}$$

$$Y = 1.4264 G - 0.8965 R - 0.0144 B \tag{1.2}$$

$$Z = 1.0092B + 0.0887G - 0.4681R,$$
(1.3)

Instruments such as the Hunter Color Meter [Gould, 1974] or the Standard Chroma Meter [Minolta, 1988] are designed to capture light reflected off the surface of an object and with the aid of special filters, analyze the spectrum and digitally display the tristimulus values. The only problem with measuring color in this way is that the tristimulus values are either too sensitive or too insensitive to color changes depending on the dominant color (hue) being observed. In an attempt to remedy this situation, these instruments were also designed to display their own individual versions of perception-based stimuli related to the tristimulus values. For the Chroma Meter used in this study, the chromaticity coordinates (a,b) and the lightness factor L are defined in terms of the tristimulus values as

$$a = 500 \left[\left(\frac{X}{X_o} \right)^{\frac{1}{3}} - \left(\frac{Y}{Y_o} \right)^{\frac{1}{3}} \right]$$

$$b = 200 \left[\left(\frac{Y}{Y_o} \right)^{\frac{1}{3}} - \left(\frac{Z}{Z_o} \right)^{\frac{1}{3}} \right]$$
(1.4)
(1.5)

$$L = 116 \left(\frac{Y}{Y_o}\right)^{\frac{1}{3}} - 16$$
 (1.6)

where X_o , Y_o , and Z_o are the tristimulus values of the illuminant used. For example, daylight has the values of $X_o=98.041$, $Y_o=100.00$, and $Z_o=118.103$ [Minolta, 1988]. Physically, the chromaticity coordinates are measures of redness (a) and yellowness (b), respectively. Finally, the OSA key perception variables of hue, saturation and lightness are defined as

$$Hue = \frac{b}{a}$$
(1.7)

Saturation =
$$\sqrt{a^2 + b^2}$$
 (1.8)

$$Lightness = L. (1.9)$$

Yeatman (1960 & 1969) discussed in detail the use of such measurements to quantify color. To completely express the color of a product, a three-dimensional color space covering the key elements of hue, saturation, and lightness must be used. Such a color space based on the chromaticity coordinates and the lightness is shown in Figure 2. A color may be quantified by its position using either rectangular coordinates (a,b,L) or cylindrical coordinates (saturation, arctan (hue), lightness). The latter coordinate system is used most frequently in the literature but with unconventional definitions of hue as a/b and hue angle as arctan(a/b) which amounts to nothing more than a change in reference for the angle from counterclockwise from the x-axis to clockwise from the y-axis.

Little (1975) discusses the origin of the confusion over two definitions of hue and hue angle in the Hunter system and points out that a/b as hue turns out to be more appropriate for tomatoes since this definition is more sensitive to changes in b. Still, there are mathematical problems with either definition of hue. Regardless of which definition is



Figure 2. Chroma Meter Color Space.

used, if the chromaticity coordinate in the denominator is near zero and undergoes a small change from say +0.000001 to -0.000001, the result is an enormous change in both the magnitude and sign of hue. But common sense dictates that a small change in a chromaticity coordinate like this cannot possibly produce such a large perceived difference in color. Hue by either definition then may be unrealistically sensitive to small changes in color and therefore may not be the best measure of color quality.

Ultimately, the perception of color rests with the human eye, which in all probability does not rely on hue alone or saturation alone, but responds to particular combinations of wavelengths in the visible spectrum depending on the illuminating source, the object being viewed, and other factors not accounted for with conventional colorimetry methodology. Perhaps the best way to proceed with evaluating color quality is to admit that since color judgment under identical experimental conditions must still be somewhat subjective, there is a need to statistically correlate objective color measurements with visual scores. Yeatman (1960) found that the empirical formula

$$\frac{2000 a}{L\sqrt{(a^2+b^2)}} = \text{T.C.I.} = \text{Tomato color index}$$
(1.10)

correlated best with the visual scores assigned by trained observers for evaluating the color quality of tomatoes. The higher the visual score, the better the product. The correlation coefficient between the average of the visual scores and the formula was 0.97. Kramer [1959] noted however that color scores based on visual evaluation alone are suspect since observers operating without reference guides tend to drift towards an average evaluation whereby consistently high quality is downgraded and consistently poor quality is upgraded. Even though Yeatman's visual scores are questionable, his raw data for color measurements do reveal a general tendency for the Hunter color values a, b

and L to be related to each other. For example, whenever "a" is high, "b" is generally low and vice versa which means that it may be possible to characterize browning reactions by following the change in only one of these values as the color deteriorates.

One of the few researchers to study color changes resulting from deterioration was Eckerle (1984) who found a correlation between sensory and instrumental testing methods when studying the effects of storage temperature on the deterioration of canned tomato paste. The color of the product was analyzed by two sensory testing methods and three instrumental testing methods. All three instrumental analyses indicated that the product became browner as it deteriorated. Moreover, the Hunter colorimeter values a, b, and L all decreased together as the paste became darker, less red, and less yellow. Sensory tests also concluded that the flavor developed a hay, caramelized, burnt, prune or bitter taste. This was one of the first studies to suggest that periodic color measurements can be used to gauge the overall condition of the product.

1.2 Oxidation Reaction

Vilece (1955) found that oxidation plays an important role in many non-enzymatic food discolorations based on the observation that darkening occurred concurrently with oxygen absorption and carbon dioxide production. She added that acidic foods like ketchup generally absorb oxygen slowly. Hodge (1953) emphasized the complexity of browning reactions due to the many intermediate reactions involved. He discusses several distinct routes leading to the final stage of browning, but adds that it remains to be determined which of these reactions are operative and to what extent one affects another in a given food under a given set of conditions.

Labuza (1982) proposed that for foods in general, the loss in nutrient value and other less tangible quality attributes such as color could be described by the chemical reaction

$$A \rightarrow B$$
 (1.11)

where A is a desirable characteristic and B is an undesirable one. Applied to an oxidation reaction with fresh ketchup, A could then be either a physical quantity or a color attribute associated with fresh red ketchup and B the same but associated with brown ketchup. Labuza further noted that the decrease in A per unit time could be described by an expression of order n

$$-\frac{dA}{dt} = k A^n \tag{1.12}$$

where k is the reaction rate constant, n is the order of the reaction, and t is time. For most reactions, k is strongly temperature dependent [Latham, 1964] and n is 0 or 1, although fractional orders have been found to occur [Labuza, 1982]. Fractional orders generally indicate a complex multistage reaction. Once k and n are measured, the extent of reaction for any length of time t can be determined, and the shelf life of the product with respect to color degradation can be established when the barrier properties of the package are also known. These ideas were applied to the oxidation of ketchup in a Gamma bottle.

2 OBJECTIVES

The objectives of the study are:

1. To measure the amount of oxygen consumed by a fixed quantity of ketchup in a closed oxygen rich environment over time and relate this to appropriate color measurements.

2. To measure the oxygen diffusion rate through a Gamma bottle without ketchup. Since the Gamma bottle is a composite of polypropylene (PP) (for structure) and ethylene vinyl alcohol (EVAL) (for barrier properties), a secondary objective of this part is to evaluate the mix .

3. To predict the shelf life of ketchup in a Gamma bottle using the results of the two separate experiments described above.

3 EXPERIMENTAL METHODS AND RESULTS 3.1 Ketchup Browning Experiment

In order to verify that browning does not take place unless ketchup is exposed to air, several glass jars were filled to capacity with fresh ketchup and surface color readings were taken using a Chroma Meter (Minolta, 1988). The average of the chroma values were found to be a=19.6, b=9.3, and L=28.2. Metal lids were then screwed onto the jars and sealed around the rims with wax so that no air could get into the jars between the threads. With the ketchup totally deprived of air in this way, the jars were then placed in a cabinet held at 21.1° C. After 1 month, the lids were removed and the ketchup chroma values were again measured. The average values were found to be a=19.5, b=9.1, and L=28.0. This slight change in color, most likely due to aging, was insignificant when compared to the larger changes in color that occur when ketchup is exposed to air. Although this identifies exposure to air as a requirement for browning, it does not prove that oxygen is responsible nor does it show that oxygen is consumed during browning.

In order to verify that it is oxygen that causes browning and that oxygen is actually consumed by the ketchup in the process, eleven 400 ml beakers fitted with lids containing gas sample extraction ports were filled with 50 ml of fresh ketchup and sealed as shown in Figure 3. The headspace contained an oxygen concentration of 21.4% when the beakers were sealed and stored under standard conditions of 21.1°C and 50% RH. After 3 days, a gas sample was extracted from one of the beakers and analyzed on the gas chromatograph (GC) for oxygen concentration. The result was 21.102% as shown in Table 1. The sealed lid was then taken off the beaker and a surface color measurement was taken using the same Chroma Meter. Similar measurements were taken from the



Figure 3. Setup for the Oxygen Consumption Experiment.

Beaker #	Days	Headspace O ₂	8	b	L	
	tested	concentration,	(red)	(yellow)	(lightness)	
		%				
1	0	21.40	19.67	9.33	28.66	
2	3	21.10	19.36	8.07	27.75	
3	6	20.97	18.61	7.47	83.72	
4	10	20.89	18.52	7.87	27.75	
5	17	20.70	18.05	7.67	27.77	
6	27	19.98	17.27	7.71	27.72	
7	30	19.90	17.04	7.77	27.92	
8	33	19.81	16.92	7.41	27.36	
9	36	19.80	16.46	6.79	27.82	
10	52	19.65	15.70	7.61	28.00	
11	55	19.60	15.50	5.32	26.20	
12	90	18.70	13.72	3.93	25.82	

 Table 1. Oxygen Concentration and Chroma Meter values

remaining beakers at regular intervals. The results in Table 1 clearly show that the oxygen concentration inside the beaker continued to decrease over time and that the surface color changed from red to brown as shown by the decline in the chroma value "a" indicating that oxygen had been consumed in the browning process. Since the changes in oxygen concentration and redness were small, separate sensitivity experiments were performed on the GC and the Chroma Meter to determine their respective instrument errors. This was done to verify that the measured changes were not the result of instrument imprecision alone.

To determine the precision of the GC, 50 samples were taken from still lab air using a syringe and analyzed. Precautions were taken to minimize the possibility of taking air samples contaminated by human or plant respiration. From the fifty air samples, only the maximum and minimum GC results for percent oxygen content were used to calculate the instrument error, defined here as half the range expressed as a percent of the average

$$\% \text{ ERROR} = \frac{\max - \min}{\max + \min} 100. \tag{3.1}$$

The instrument error for oxygen measurement was found to be 0.54%.

To determine the associated error for the Chroma Meter, thirty color measurements were taken at various locations on the surface of fresh ketchup. Again using only the maximum and minimum chroma "a" values in Eq. (3.1), the Minolta Chroma Meter instrument error was found to be 1.73%. This error may also include color non-homogeneity of ketchup.

3.2 Oxygen Diffusion

Having shown that oxygen is consumed by ketchup during browning, it is now necessary to determine the extent to which it reacts chemically with ketchup. It is entirely

possible that browning requires oxygen only as a catalyst and that oxygen consumption is the result of diffusion alone. It is more likely however that both diffusion and reaction take place simultaneously. In order to gauge the extent to which diffusion plays a role in the potentially combined diffusion/reaction process, pure diffusion was studied first. Oxygen molecules were assumed to diffuse through the ketchup with no direct involvement in a chemical reaction. Fick's law for diffusion in the downward direction (Figure 3) states that the flux of oxygen molecules through each layer of ketchup is proportional to the oxygen concentration gradient:

$$\phi = -D\frac{\partial c}{\partial x} \tag{3.2}$$

where ϕ is the flux (moles/s/m²), c(x,t) is the concentration of oxygen x (m) below the surface at time t (s), and D is the diffusion coefficient for oxygen in ketchup (m²/s). A mass balance for oxygen diffusing through a control volume fixed in space leads to the one-dimensional transient diffusion equation in a homogeneous substance [Holman, 1986],

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}.$$
(3.3)

Since glass and metal are impermeable to oxygen [Dow, 1984], the beakers used in the browning experiment allowed no oxygen to enter from the outside so that the assumption of one-dimensional diffusion is justified. The solution to Eq (3.3) for a prescribed constant concentration $c(0,t)=c_0$ at the boundary x=0 of the ketchup and no flux $(\partial c/\partial x=0)$ at the bottom (x=h) of the ketchup with an initial constant oxygen concentration $c(x,0)=c_i$ is given in Appendix A. At the bottom of the ketchup, the oxygen concentration c(t) is

$$\frac{c_o - c(t)}{c_o - c_i} = \frac{4}{\pi} \left(q - \frac{q^9}{3} + \frac{q^{25}}{5} - \frac{q^{49}}{7} + \dots \right)$$
(3.4)

where

$$q = \exp\left(\frac{-\pi^2 D t}{4h^2}\right). \tag{3.5}$$

Please see Appendix A for the derivation of Eq. 3.4.

The numerator on the left hand side of Eq (3.4) represents the change in oxygen concentration at time t needed to reach steady state and the denominator represents the change required from the start. Therefore, the left hand side will be denoted by f(t) and referred to as the instantaneous fractional change left to go to reach steady state. A value of f=1 then means that the diffusion process has just begun and corresponds to q=1 and t=0 while a value of f=0 means that steady state has been reached with q=0 and $t = \infty$. For values of t>0, Eq (3.5) gives q<1 so that the infinite series in brackets in Eq (3.4) is dominated by the first term q. Using only the first term on the right hand side with f(t) on the left hand side and solving for t from Eq (3.5) gives the time required to reach the fraction f left to achieve steady state,

$$t = \frac{4h^2}{\pi^2 D} \ln\left(\frac{4}{\pi f}\right). \tag{3.6}$$

Since ketchup is essentially hydrated cellulose (tomato pulp) held in suspension by water which accounts for at least 70% of the product by volume [Lamb, 1977], the diffusion coefficient for oxygen in water will be used [Geankoplis, 1983] as an estimate,

$$D = 3.25 \times 10^{-9} \qquad m^2 s^{-1} \tag{3.7}$$

In the oxygen consumption experiment (Figure 3), the beakers were filled with ketchup to a depth of 1 cm. With x=0.01 m, D=3.25 $\times 10^{-9}$ m²/s, and f=0.05 in Eq. (3.6), the time required to reach 95% of steady state is 40,370 s or 11.2 hours. In other words,

the ketchup should have been nearly saturated with oxygen through diffusion alone in about a half a day. This means that if oxygen had acted only as a catalyst in the browning reaction with the concentration of oxygen inside the ketchup controlled by diffusion alone, then the compositions of the headspace air in all of the beakers referred to in Table 1 should have been the same. The fact that they were not supports the conclusion that oxygen was actually consumed in a chemical reaction during browning. Of course this conclusion does not hold if the diffusion coefficient in Eq (3.7) is in error. Since the headspace air composition continued to change up to 90 days, the diffusion coefficient for oxygen in ketchup would need to be smaller than the value in Eq (3.7) by a factor of 90x24/11.2=193, or about two to three orders of magnitude in order to support the alternate conclusion that oxygen acts purely as a catalyst.

The case for oxygen being consumed in the browning reaction is further supported by examining the solubilities of oxygen in both ketchup and air. Again assuming that ketchup is essentially water, these room temperature solubilities under exposure to normal air are [Masterton and Slowinski, 1973]

$$S_k = 2.82 \times 10^{-4}$$
 moles oxygen per liter water (3.8*a*)
 $S_a = 86.9 \times 10^{-4}$ moles oxygen per liter air, (3.8*b*)

Therefore, the maximum amount of oxygen that can by absorbed by the 50 ml of ketchup is $(2.82 \times 10^4)(0.05)= 1.41 \times 10^{-5}$ moles. In comparison, the amount of available oxygen in the 390 ml headspace above the ketchup in the beaker is $(86.9 \times 10^4)(0.390)=$ 3.39 x 10⁻³ moles which says that the ketchup is capable of consuming only

$$\left(\frac{1.41 \times 10^{-5}}{3.39 \times 10^{-3}}\right) 100 = 0.42\%$$
(3.9)

of the available oxygen in the headspace by diffusion alone. However from Table 1, the ketchup did actually consume as much as

$$\left(\frac{0.214 - 0.187}{0.214}\right)100 = 12.6\% \tag{3.10}$$

of the available oxygen after 90 days which amounts to 12.6/0.42 = 30 times more than saturation by diffusion will allow. Therefore, diffusion alone without reaction does not account for the amounts of oxygen consumed. This can only mean then that oxygen is involved directly in the browning reaction. Moreover, because of the results in Eqs. (3.9) and (3.10), the evidence suggests that oxygen is consumed much faster than it can diffuse. This should halt the diffusion of oxygen altogether at some depth below the surface and confine browning to the surface layers only. The extent of the affected region is expected to be determined by a balance between the diffusion rate and the reaction rate. A quantification of this can be made only by studying diffusion and reaction together.

3.3 Combined Diffusion and Reaction

The fundamental differential equation for combined diffusion and reaction can be derived by first considering an element of ketchup in the form of a thin rectangular slab of ketchup as shown in Figure 4. The diffusion constant for oxygen in ketchup is assumed to be unaffected by the change in chemical makeup during the reaction. Oxygen can leave the slab in two different ways. The first is by a difference in fluxes at each face of the slab and the second is by consumption due to reaction. The net number of moles N_D of oxygen leaving the slab in time Δt by diffusion alone is

$$N_D = \left(\frac{\partial \Phi}{\partial x}\Delta x\right)(A \Delta t) \tag{3.11}$$

and the net number of moles N_c consumed in the browning reaction in time Δt is



Figure 4. Control Volume Used for Unsteady Diffusion and Reaction Analysis.

$$N_{c} = (k c^{n} \Delta t) (A \Delta x)$$
(3.12)

where the Labuza (1982) reaction rate from Eq (1.12) was used. Since the total amount of oxygen leaving the slab must equal the reduction in the amount of oxygen in the slab,

$$\frac{\partial \phi}{\partial x}(A \Delta x \Delta t) + kc^{n}(A \Delta x \Delta t) = -\frac{\partial}{\partial t}(c A \Delta x) \Delta t. \qquad (3.13)$$

Dividing each term by $A \Delta t \Delta x$, rearranging, and using Eq (3.2) gives

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - k c^n.$$
(3.14)

Since Eq (3.14) is a nonlinear partial differential equation, it is doubtful that it can be solved analytically. Fortunately, a steady state solution exists which provides the information sought. If steady-state conditions exist, then $\partial c/\partial t$ is zero everywhere, c becomes a function of x only, and Eq (3.14) reduces to

$$D\frac{d^2c}{dx^2} = kc^n. aga{3.15}$$

The solution to Eq (3.15) is obtained by introducing z=dc/dx so that

$$\frac{d^2c}{dx^2} = \frac{dz}{dx} = \frac{dz}{dc}\frac{dc}{dx} = z\frac{dz}{dc}.$$
(3.16)

Substituting this into Eq (3.15) gives

$$D z dz = kc^* dc \tag{3.17}$$

and integration leads to

$$D\frac{z^2}{2} = \frac{kc^{n+1}}{n+1} + constant.$$
(3.18)

Eq (3.18) shows that the steady state solution cannot be $c(x)=c_0$ as with pure diffusion alone since z=dc/dx must depend on c and is therefore nonzero. Since $z\leq 0$ in Eq (3.18) for obvious physical reasons and c starts out at c_o when x=0, the concentration must eventually reach zero at some location x_o presumably inside the ketchup. Beyond this point, there is no oxygen so that

for
$$x \ge x_o$$
, $c = 0$ and $\frac{dc}{dx} = 0$. (3.19)

Forcing Eq (3.18) to fit these internal boundary conditions requires the constant of integration to be zero so that

$$z = \frac{dc}{dx} = -\sqrt{\frac{2k c^{n+1}}{(n+1)D}}.$$
 (3.20)

Integrating and using the boundary condition that $c=c_o$ at x=0 gives

$$c^{(1-n)^2} = c_o^{(1-n)^2} + \frac{n-1}{2} \sqrt{\frac{2kx}{(n+1)D}}$$
(3.21)

or in terms of x_o,

$$\frac{c}{c_o} = \left(1 - \frac{x}{x_o}\right)^{2/(1-n)}$$
(3.22)

where

$$x_o = \frac{1}{1-n} \sqrt{\frac{2(n+1)D c_o^{(1-n)}}{k}}.$$
(3.23)

As expected, Eq. (3.23) predicts a decrease in the penetration distance as the reaction rate k increases relative to the diffusion rate D. In addition, this steady state solution makes physical sense only for n < 1, since x_0 would otherwise be negative and the concentration would increase with depth into the ketchup. Because the browning reaction is known to be complex, a fractional order of reaction n < 1 is expected [Latham, 1964]. Using n= 0.5 for example, D= 3.25 x 10⁻⁹ m²/s from Eq (3.7), $c_0 = 0.282$ moles/m³ from Eq (3.8) and the fact that in each browning experiment, the discolored portion was found to be confined to a thin surface layer approximately 1 mm thick regardless of exposure time, Eq (3.23) gives $k= 0.021 \text{ moles}^{0.5}/\text{m}^{1.5}/\text{s}$ as an estimate of the oxidation reaction rate. Used in this way, Eq (3.23) may be viewed as a relationship between n and k involving ketchup properties D and c and a measurable quantity x_0 . Unfortunately, this appears to be as far as the results of the browning experiment will allow the analysis to go and falls somewhat short of the desired goal of finding n and k separately. However, even if n and k could be determined individually by some experiment, the interpretation of the results would be difficult since both may change values during the different stages of the browning reaction depending on whether separate reactions occur in sequence (series reactions) or several reactions occur concurrently (parallel reactions). The browning reaction probably involves both series and parallel reactions and for this reason, n and k in Eq (3.23) are most likely weighted averages of the individual n's and k's for the separate reactions.

The preceding analysis has shown that browning is essentially a surface phenomenon and that n and k in the context of Eq (1.12) may be too complex in meaning to be of any real value. A simpler approach based on the collision theory of reaction rates [Frost, 1961] will be used to produce a more practical version of the reaction rate equation. Consider a volume of pure ketchup with an exposed surface area A that has not yet absorbed any oxygen as shown in Figure 5. Of all the molecules of oxygen immediately surrounding the surface of the ketchup, only 1/6 of these are expected to hit the surface since on the average there are equal numbers of molecules moving in six perpendicular directions, one of which may be considered to be directed toward the surface. Since the average speed of a molecule is [Frost, 1961]



Figure 5. Volume of Ketchup Used for Collision Theory of Reaction Rates.

$$\overline{u} = \sqrt{\frac{3RT}{M}}$$
(3.24)

where T is the absolute temperature (°R), R is the universal gas constant (45.61 ml-atm/mole-°R), and M is the molecular weight (grams/mole), the number of moles that hit per unit time is

$$\frac{1}{6} \frac{\text{concentration x volume}}{dt} = \frac{1}{6} \frac{c(A\overline{u} dt)}{dt} = \frac{1}{6} c A \overline{u}.$$
(3.25)

Of these, only a fraction, f, is expected to adsorb and react with the ketchup with the fraction (1-f) rebounding back into the surrounding air. Since molecular speeds are distributed normally with \overline{u} as the average, and since the browning reaction is expected to take place only if the kinetic energy of an individual oxygen molecule equals or exceeds the required activation energy E_A [Frost, 1961], f should be related most strongly to the distribution of speeds. For example, if E_A just equals $m\overline{u}^2/2$ with m the mass of an oxygen molecule, then f should be about 0.5. Even with the required activation energy however, an impacting oxygen molecule may still not cause a reaction simply because of a deficiency in the number of favorable impact sites on the surface of the ketchup which would allow the molecule to adsorb. This suggests that f may be dependent on the oxygen concentration as well since increasing c would have the net effect of positioning more molecules over favorable impact sites. From Eq (3.25) then, the flux of oxygen molecules reacting with the ketchup is

$$\phi = \frac{1}{A} \frac{dn}{dt} = \beta c \tag{3.26}$$

where $\beta = f\overline{u}/6$ is a function of temperature through \overline{u} and possibly c through f. This result is similar in structure to the defining equation for heat transfer by convection [Holman, 1986] with ϕ analogous to the heat flux, c to temperature, and β to the average surface heat transfer coefficient. Since the browning experiment was performed at constant temperature, β was taken as a function of c alone with $\beta = kc^{n-1}$ so that the modified reaction rate equation becomes

$$\phi = kc^n \tag{3.27}$$

where k now is the reaction rate and n is the order of the reaction.

The reaction constants in Eq (3.27) were determined by fitting this relationship to the observed data in Table 1. Substituting n=cV into Eqs (3.26) and (3.27) gives

$$\phi = \frac{1}{A}\frac{dn}{dt} = -\frac{V}{A}\frac{dc}{dt} = kc^n$$
(3.28)

with V the headspace air volume. Integrating the last equality gives

$$\frac{c}{c_o} = (1-zt)^p \tag{3.29}$$

where

$$z = \frac{(1-n)kA}{Vc_o^{(1-n)}}$$
(3.30*a*)

$$p = \frac{1}{1-n} \tag{3.30b}$$

and $c_o = initial oxygen concentration = 8.85 moles/m³.$

After taking the natural log of both sides of this equation, p and z were chosen so that the overall difference between the actual and the predicted results (the variance) was a minimum,

VAR =
$$\sum_{i=1}^{N} \left(\ln \frac{c_i}{c_o} - p \ln (1 - zt_i) \right)^2$$
 = minimum (3.31)

where (t_i, c_i) are the N actual data. Differentiating VAR with respect to p and z then setting the derivatives equal to zero for a minimum results in two independent equations for p in terms of z,

$$p = \frac{\sum_{i=1}^{N} \ln \frac{c_i}{c_o} \ln (1 - zt_i)}{\sum_{i=1}^{N} \ln^2 (1 - zt_i)} = \frac{\sum_{i=1}^{N} \frac{t_i \ln \frac{c_i}{c_o}}{1 - zt_i}}{\sum_{i=1}^{N} \frac{t_i \ln (1 - zt_i)}{1 - zt_i}}.$$
(3.32)

The computer program in Appendix B calculates c_i/c_o from the data in Table 1 as the ratio of percent compositions and uses Eq. (3.32) to obtain the solution for p and z by trial and error. The results of the fit are p=-0.983 and z=-0.00191 day⁻¹. With V=390 ml = $3.9 \times 10^{-4} \text{ m}^3$ and A=3.96 x 10^{-3} m^2 from Figure 3, the order of the reaction and the reaction rate are found from Eq (3.30) to be n=2 and k=2.15 x 10^{-5} m^4 /day/mole. Since these results apply to the modified Labuza reaction rate equation in Eq (3.27) instead of Eq (1.12), a fractional order for n should not necessarily have been expected.

The specific information required for shelf life calculations is the relationship between redness and the amount of oxygen consumed. The amount of oxygen consumed is determined from Table 1 as the reduction in oxygen concentration $c_o - c(t)$ converted into a reduction in oxygen partial pressure and then into the number of moles using the gas law. For example, after 33 days of exposure to headspace air at room temperature (sample 8 in Table 1), the number of moles of oxygen consumed was

$$n = \frac{(0.214 - 0.1981)(390)}{(45.61)(530)} = 2.57 \times 10^{-4} \text{ moles.}$$
(3.33)

Since this amount was consumed only by the exposed surface whose area was $3.96 \times 10^{-3} \text{ m}^2$, the consumption rate required to produce a corresponding redness of 16.92 from Table 1 is 0.065 moles/m². This procedure was applied to the remaining data and ketchup

surface redness was graphed against moles/ m^2 of oxygen consumed in Figure 6. After 52 days, the exposed surface of the ketchup developed a redness of 15.7. This color level was chosen by a small test panel to be the minimum level required for an acceptable surface color when compared to fresh ketchup. Therefore, from Figure 6,

$$Q = 0.072 \frac{\text{moles oxygen}}{m^2 \text{ surface}}$$
(3.34)

must be absorbed by the ketchup before its color can be considered unacceptable.



Figure 6. Ketchup Redness Versus Number of Moles of Oxygen Consumed.

4 PERMEABILITY AND SHELF LIFE ESTIMATION 4.1 Gamma Bottle Permeability

The two processes by which gas and vapor move through packaging materials are flow through imperfections like pinholes and cracks in the package and diffusion through the pore structure of the material itself. Since the mouth of a Gamma bottle is sealed with foil after it is filled with ketchup, diffusion through the exposed surface of the bottle is the only way that oxygen can reach the ketchup. In general, diffusion through a barrier is driven by a difference in concentration in gas or vapor molecules across the barrier. Molecules adsorb on the surface of higher concentration, diffuse through the barrier toward the side of lower concentration, and then desorb as shown in Figure 7. Fick's Law in Eq. (3.2) may be used to describe gas transport through the bottle with D now the diffusion coefficient for oxygen in the Gamma material (m^2/day). If D is constant and the bottle wall thickness is small, then the concentration gradient may be expressed as a finite difference and Fick's law for the diffusion rate in moles/s becomes

$$\frac{dn}{dt} = D A \frac{(c_1 - c_2)}{\Delta x}$$
(4.1)

where c_1 and c_2 are the surface oxygen concentrations inside and outside the bottle, A is the bottle surface area, and Δx is the wall thickness. Since c_1 and c_2 are usually difficult to measure experimentally, the concentrations in Eq. (4.1) may be related to the gas partial pressures through Henry's law [Tobolsky, 1971]

$$c = S p \tag{4.2}$$

where S is the equilibrium solubility constant for a given gas-polymer system in cm³ (gas at STP)/cm³ (polymer)/atm and p is the gas partial pressure in atm. Substituting Eq. (4.2) into Eq. (4.1) gives the permeability equation [Dow, 1984]



Figure 7. Diffusion Through a Barrier.

$$\frac{dn}{dt} = C A \frac{(p_1 - p_2)}{\Delta x}$$
(4.3)

where C = DS is the permeability constant for a given gas-polymer system.

To experimentally determine the oxygen permeability constant for the Gamma material, twelve empty bottles were flushed with 100% nitrogen at 1 atm, sealed, and stored under standard conditions (22.8°C, 1 atm, 21% O₂ and 50% RH.). The bottles were flushed for a period of three hours before they were sealed. After 49 days, a gas sample was extracted from each bottle with a syringe and analyzed on the same gas chromatograph used in the browning experiment to determine the percent oxygen content. This result was then converted into an equivalent volume of oxygen under standard reporting conditions of 1 atm and 22.8°C using the gas law and the measured bottle volume of 720 ml. For example, if after 49 days the GC measured an oxygen content of 3.5% inside the bottle, then the oxygen partial pressure was 3.5% of 1 atm = 0.035 atm and the equivalent STP volume of oxygen was 3.5% of 728 ml = 25.5 cc since the experiment was already conducted under STP conditions. Since the bottle was initially flushed with nitrogen, this volume of oxygen also represents the amount of oxygen which had permeated into the bottle, and the oxygen transmission rate under standard conditions was 25.5 ml/49 days = .52 cc/day. The actual oxygen transmission rates for the 12 bottles tested are shown in Table 2. The average oxygen transmission rate was found to be

$$OTR = 0.56cc/day.$$
 (4.4)

The oxygen transmission rate in moles/day may be obtained from the rate in cc/day using the gas law result that one mole = 24,173 cc at STP. It is more common, however, to find the permeability equation in Eq (4.3) written as [Dow, 1984]

Bottle	% O ₂ from	cc/day	<u><u><u></u><u>d</u><u>A</u></u></u>	С
Number	GC		Jdx	cc-mil/m²-day-atm
	after 49 days		m²/mil	
1	6.30	0.94	0.00124	3581
2	4.97	0.74	0.00133	2646
3	2.10	0.31	0.00141	1052
4	2.45	0.36	0.00126	1371
5	5.88	0.87	0.00100	4160
6	6.58	0.98	0.00129	3608
7	3.01	0.45	0.00142	1500
8	2.87	0.43	0.00122	1665
9	2.24	0.33	0.00121	1314
10	4.55	0.68	0.00129	2494
11	2.38	0.35	0.00117	1434
12	2.17	0.32	0.00126	1214
Average	3.79	0.56	0.00126	2170
Std. Dev.	1.67	0.25	0.00011	1046

 Table 2. Oxygen Permeability Data for the Gamma Bottle

$$\frac{cc}{day} = C A \frac{\Delta p}{x}$$
(4.5)

where Δp is the difference in oxygen partial pressures (atm) inside and outside the bottle, x is the wall thickness of the bottle (mil), A is the exposed surface area of the bottle (m²), and C is the permeability constant (cc-mil/m²-day-atm) for oxygen in the Gamma material. When the thickness varies over the surface of the bottle, the permeability equation is replaced by

$$\frac{cc}{day} = C \Delta p \oint \frac{dA}{x}$$
(4.6)

where $\oint dA/x$ is the integral over the exposed surface of the bottle. The integral was estimated by cutting the bottle into thin bands as shown in Figure 8. Four thickness measurements, x, at the center of each band were taken at locations A, B, C and D using a vernier caliper along with the four corresponding slant heights S and the perimeters L of the top and bottom of the band. The measurements for a single bottle are given in Appendix C. The contribution of each band to the total integral was then approximated by

$$\int_{band} \frac{dA}{x} = \frac{\left(\frac{L_{top} + L_{bottom}}{2}\right) \left(\frac{S_A + S_B + S_C + S_D}{4}\right)}{\left(\frac{x_A + x_B + x_C + x_D}{4}\right)}.$$
(4.7)

The individual results for each band were added to obtain $\oint dA/x$ for the entire bottle. Eq (4.7) was also used for the base of the bottle by taking the bottom L equal to zero, the top L equal to the circumference, and the slant heights as the radii. The results for the 12 bottles cut and measured are given in Table 2. The average value for the integral is 12.639 cm²/mil.



Figure 8. Measurement Types and Positions Taken on a Typical Band cut from the Gamma Bottle.

The final quantity in Eq (4.6) required for the calculation of the permeability constant C is Δp . Since the oxygen partial pressures found in the bottles after 49 days were on the order of a fraction of a percent, the partial pressure difference was essentially constant at $\Delta p = 0.21$ atm. Using Eq (4.6), the results for the permeability constant are shown in the last column of Table 2. The Gamma material is primarily polypropylene (PP) for structure with a thin layer of ethyl vinyl alcohol (EVAL) to provide barrier properties. The permeability constant was expected to be a weighted average of the permeability constants for oxygen in PP and oxygen in EVAL, respectively. The reported permeability constant for oxygen in PP is C = 1,300 to 6,400 cc-mil/m²-day-atm [Packaging Encyclopedia, 1985] and for oxygen in EVAL is C = 0.16 to 1.4 cc-mil/m²-day-atm [Dow, 1984]. Since the average permeability constant obtained for the Gamma copolymer in Table 2 is much closer to that for PP than for EVAL, the thickness of the EVAL layer was probably very small.

The variations in data found in Table 2 are due both to measurement errors and manufacturing differences between bottles. Because of precision of the GC, the concentrations of oxygen found in the bottles after 49 days and therefore the oxygen transmission rates may be in error by as much as 0.54% from an earlier calculation. Another source of error in the area integral is the measurement of the band dimensions in Figure 8. Using a vernier caliper with a sensitivity of 1 mil, the average thickness taken over the various band locations was found to be about 50 mil so that an error of +/-1% may be attached to each thickness measurement in Table 2. The measurement errors associated with the slant heights and perimeters are much smaller on a percent basis since the measurements themselves are much bigger. Possibly the greatest source of error is the approximation itself in Eq (4.7), because average values for L, S, and x were used. This error is difficult to quantify because it depends on how S and x vary between

measurement locations. More importantly, within this approximation there was an additional error due to the way in which the band areas (numerator in Eq (4.7)) were calculated. After the bottle was sectioned into bands, the bands were cut and unfolded into flat strips as shown in Figure 9. Inevitably, the long sides of the band were rough and jagged. The maximum error associated with the length measurement in Figure 9 was 0.51 cm and the maximum error on width was 0.191 cm. The length and width measurements are

$$L = 20.45 \pm 0.51 \,\mathrm{cm} \tag{4.8a}$$

$$W = 1.27 \pm 0.191 \,\mathrm{cm} \tag{4.8b}$$

so that the band area A = LW is bounded between 21.52 cm^2 and 30.62 cm^2 , or

$$A = 26.07 \pm 4.55 \, cm^2. \tag{4.9}$$

Using the error in the measurement of band dimensions, the total error associated with the calculation of $\oint dA/x$ was less than 20%. This explains part but not all of the variation in the calculated permeability constant in Table 2. The rest is attributed to material composition and manufacturing differences.

4.2 Ketchup Shelf Life Estimation

Shelf life is defined as the period between manufacture and retail purchase during which the product is of satisfactory quality [Eckerle et al., 1984]. In order to estimate the shelf life of ketchup with respect to color degradation when packaged in a Gamma bottle, certain results from the browning and permeability experiments described in this and the previous chapter are required. For convenience, they have been summarized below. Gamma bottle oxygen permeation rate and relevant data are:

permeation rate =
$$R_p = C \Delta p \oint \frac{dA}{x}$$
 (4.10*a*)



Figure 9. Error Analysis of dA on a Typical Band Cut.

$$\Delta p = O_2 \text{ partial pressure difference (atm)}$$
(4.10b)

$$C = 2170 [cc - mil] day^{-1}m^{-2}atm^{-1} = \text{permeability constant} \qquad (4.10c)$$

$$\oint \frac{dA}{x} = 0.00126 \, m^2 m i l^{-1} = \text{area integral} \tag{4.10d}$$

$$A = 0.067 m^2 = \text{exposed bottle surface area.}$$
(4.10e)

For ketchup, the oxygen consumption rate and related adsorption data are:

Consumption rate =
$$R_c = k A c^n$$
 (4.11*a*)

$$c = O_2$$
 concentration in surrounding air (moles m^{-3}) (4.11b)

$$k = 2.15 \times 10^{-5} m^{4} [mole - day]^{-1} = \text{reaction rate}$$
(4.11c)

$$n = 2 = \text{order of reaction}$$
 (4.11d)

$$A = 0.067 m^2 = \text{exposed ketchup surface area}$$
 (4.11e)

$$S_k = 2.82 \times 10^{-4}$$
 moles/liter = solubility of oxygen in ketchup (4.11f)

$$S_a = 86.9 \times 10^{-4}$$
 moles/liter = solubility of oxygen in air (4.11g)

$$Q = 0.072$$
 moles m^2 = critical oxygen consumption for browning. (4.11*h*)

Under actual storage conditions, the rate at which ketchup adsorbs oxygen is limited by the rate at which the bottle allows oxygen to permeate inward. From Eq (4.10), the bottle permeation rate is determined by Δp alone since the remaining quantities are fixed bottle properties. The maximum possible R_p is obtained by using an inside oxygen partial pressure of zero. Therefore, the maximum R_p (in mol/day) is

$$R_{p} = (2170)(0.21 - 0)(0.00126) = 0.57 \ cc/day = 2.38x \ 10^{-5}$$
(4.12)

where the conversion 1 mole = 24,173 cc at STP has been used. Now assume that the actual inside oxygen partial pressure is in fact zero. Then the oxygen concentration c_i at the interface between the ketchup and bottle must also be zero which makes the consumption rate $R_c = 0$ from Eq (4.11). But this cannot happen because oxygen entering the bottle through permeation is forced to react with the ketchup as soon as it appears at the interface. The ketchup has nowhere else to go. The true interface concentration must therefore be chosen so that R_p and R_c are equal, which means that c_i cannot be zero.

The permeation rate when c_i is not zero is most easily obtained by converting Δp in Eq (4.10) back into a concentration difference using the ideal gas law. This in essence amounts to reverting back to Fick's Law. Using p = (n/V)RT = cRT,

$$R_{p} = C R T (c_{o} - c_{i}) \oint \frac{dA}{x}$$
(4.13)

where R= 45.61 ml-atm/mole-°R is the universal gas constant, T= 530 °R is the assumed absolute storage temperature, $c_o = S_a = 86.9 \times 10^{-4}$ moles/liter is the outside oxygen concentration, and c_i = is the unknown interface concentration. Substituting the required quantities into Eq (4.13) and making the appropriate conversions gives

$$R_{p} = \frac{2170}{24173} \frac{45.61}{1000} (530) (86.9 \times 10^{-4} - c_{i}) (0.00126)$$
(4.14*a*)

or

$$R_{p} = (2.38 \times 10^{-5} - 0.00273c_{i}) \text{ moles/day}$$
(4.14b)

provided that c₁ is in moles/liter. The corresponding consumption rate is

$$R_c = 2.15 \times 10^{-4} (0.067) (1000 c_i)^2$$
(4.15a)

or

$$R_c = 1.44 c_i^2 \tag{4.15b}$$

again with c_i in moles/liter. The condition that $R_p = R_c$ leads to a quadratic equation in c_i

$$c_i^2 + 1.9 \times 10^{-3} c_i - 1.65 \times 10^{-5} = 0.$$
(4.16)

The solution to Eq (4.16) gives the interface concentration

$$c_i = 32.2 \times 10^{-4} \text{ mole/liter}$$
 (4.17)

which when substituted back into either Eq (4.14b) or Eq (4.15b) gives the true permeation and consumption rates:

$$R_p = R_c = 1.5 \times 10^{-5} \text{ moles/day.}$$
 (4.18)

The actual permeation rate is less than the maximum rate in Eq (4.12) as expected but the predicted interface oxygen concentration in Eq (4.17) is greater than the assumed solubility of oxygen in ketchup (water), $S_k = 2.82 \times 10^{-4}$ moles /liter. One possible explanation of this result is that ketchup is capable of holding much more oxygen than previously assumed, about 32.2/2.82 = 11.4 times more. This is the situation if a volume property such as solubility can even be considered to apply to a surface phenomenon. The more likely explanation which is consistent with oxidation and browning as a surface effect is simply that the browning reaction dictates this concentration based on supply and demand, regardless of solubility. In any case, Eq. 4.17 must be true since the permeation and consumption must be equal.

The shelf life for browning may now be deduced from the oxygen consumption rate in Eq. 4.18 and the ketchup properties in Eq. (4.11e) and Eq. (4.11h). The calculation gives

Shelf life =
$$\frac{QA}{R_c}$$
 = $\frac{(0.072)(0.067)}{1.5 \times 10^{-5}}$ = 320 days. (4.19)

5 DISCUSSION

The actual shelf life of ketchup in the Gamma bottle could not be measured directly due to difficulties encountered in the color measurement process. The average shelf life of 320 days is based on an unacceptable redness level of 15.7 for ketchup by itself, not for ketchup packaged in the translucent Gamma bottle. This was done because both the measured and perceived redness of the ketchup is altered considerably when viewed through the bottle. The true color quality of the ketchup can be evaluated only when the bottle is opened and some ketchup is removed. But this process alters the color since browning is a surface defect and the act of removing ketchup from the bottle by whatever means tends to mix surface ketchup with fresh red ketchup underneath. The result is a mixture whose surface redness measurement varies too much with location to be of any real value.

This was the case with several new unopened bottles placed in storage at room temperature at the beginning of the browning experiment. After six months, the bottles were opened and some ketchup was removed by simply pouring it out into a dish. The measured redness levels varied with surface location and were anywhere from about 16 to 19. It is difficult to conclude on the basis of these measurements that the predicted shelf life is correct. In support of this conclusion is the unwritten industry standard for ketchup and many similar perishable products that the package be designed to give the product a shelf life of at least one year [Heinz, 1988]. Whether or not it was the intention of the Heinz Company to adhere to this standard when considering color quality is not known since performance data related to the Gamma bottle was never released. It was found in the permeability experiment, however, that the Gamma bottle was adequate for this purpose. It was also found that the effectiveness of the EVAL layer in the

predominantly PP bottle wall as a barrier improvement is questionable since the overall permeability constant for the Gamma copolymer was well within the range of permeability constants for PP alone.

Some environmental factors not studied in this research which may influence the color degradation of ketchup in a Gamma bottle are temperature, humidity, exposure to light, and age. Storage temperature is expected to effect both the oxygen transmission rate through the bottle and the consumption rate by ketchup. Increased temperature typically increases permeation through a material by expanding the pore structure of the material [Karel, 1974]. In terms of the parameters which determine the permeation rate in Eq (3.6), the permeability constant C = DS increases primarily because the oxygen solubility S increases. Increased temperature will most likely also increase the oxygen consumption rate of ketchup by increasing the activation energy of the oxygen molecules consumed in the browning reaction. It would appear that increasing the storage temperature should reduce the shelf life considerably.

Humidity is known to affect permeability in a number of ways. For most packaging materials, absorbed moisture may either reduce the oxygen transmission rate by blocking pathways through the material or increase it by making oxygen more soluble in the hydrated material [Karel, 1974]. In reality, absorbed moisture probably does both simultaneously and the net increase or decrease in permeation rate with environmental humidity is determined by pore size and structure. For the Gamma bottle, the effect of humidity on permeability is not known.

Exposure to light is another factor which may affect the color of ketchup in opposite ways. Radiation delivering heat to the surface will most likely accelerate the browning process for reasons mentioned above and at the same time may whiten the surface by bleaching. The extent to which the separate effects occur is expected to depend on the

type of light the ketchup is exposed to and the exposure time. The effect of exposure to fluorescent store lighting over the duration of its shelf life in a Gamma bottle is not known but the shelf life under these conditions may not be very much different from the calculated value of 320 days since both the permeability and browning experiments were conducted under lab lighting which is very similar to storage conditions.

Color deterioration due to age alone is the final factor not accounted for in this study. The very first browning experiment performed in this research was done to establish that oxygen was required for browning. As described in the beginning of Chapter 3, sealed glass bottles full of ketchup were stored in a dark cabinet at room temperature for one month. The redness value was found to change from 19.6 to 19.5 in spite of the fact that the ketchup was deprived of oxygen, moisture, and light. This color change can only be due to age and if it is assumed for simplicity that the rate of aging is constant, then the change in redness over the 320 day shelf life would be $(19.6 - 19.5) \times (320/30) = 1.07$ due to age alone. Since the total change in redness required to turn the ketchup brown is 19.67 - 15.5 = 3.97 from Table 1, age must then be considered to account for $(1.07/3.97) \times 100$ = 27% of the change in color over the 320 day shelf life and the combined effects of oxidation, light, and heat, the rest. Even though this analysis is somewhat simplistic, it does identify aging as an important factor related to color deterioration which should be studied in future research.

6 CONCLUSIONS

The oxygen transmission rate through a Gamma bottle and the effect of oxygen consumption on the surface color of ketchup were studied separately. The relationship between surface redness and the amount of oxygen consumed along with the separate oxygen transmission and consumption rates for the bottle and ketchup were used to predict the shelf life for ketchup packaged in a Gamma squeeze bottle. It was found that browning was confined to a thin surface layer of ketchup and that the consumption of 0.072 moles of oxygen per square meter of exposed surface reduced the redness level of fresh ketchup from 19.67 to 15.7 as measured by a Minolta chroma meter. This level was found by a small test panel to be the color quality limit for consumer appeal. When packaged in a Gamma bottle and stored at room temperature, the shelf life of ketchup, defined as the time required to reach the brown color limit of 15.7, was calculated to be 320 days.

7 APPENDIX A

SOLUTION TO THE TRANSIENT DIFFUSION EQUATION

The transient diffusion equation in one direction is

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \tag{A-1}$$

and the boundary and initial conditions for the problem in Figure 3 are

$$c(0,t) = c_o = \text{constant} \qquad (A-2)$$

$$\frac{\partial c}{\partial x}(h,t) = 0 \tag{A-3}$$

$$c(x,0) = c_i = \text{constant.} \qquad (A-4)$$

Use of the separation of variables technique [Powers, 1979] with c(x,t)=X(x)T(t) in Eq (A-1) leads to the following ordinary differential equations,

$$\frac{d^2X}{dx^2} + p^2 X = 0 (A-5)$$

$$\frac{dT}{dt} + p^2 DT = 0 \tag{A-6}$$

where the constant p is an eigenvalue to be determined from the boundary conditions. Solving Eq (A-5) for X and Eq (A-6) for T and using a series of products to obtain X(x)T(t) gives

$$c(x,t) = c_o + \sum_p (A_p \sin(px) + B_p \cos(px)) \exp(-p^2 Dt)$$
 (A-7)

where part of the zero eigenvalue solution c_o has been added and the A_p and B_p are arbitrary constants. The boundary condition in Eq (A-2) requires that $B_p = 0$ and the boundary condition in Eq (A-3) requires that $\cos(ph) = 0$ which gives

$$p = \frac{\pi \left(n + \frac{1}{2}\right)}{h} \quad n = 0, 1, 2...$$
 (A-8)

Therefore, the solution in Eq (A-7) can now be written as

$$c(x,t) = c_{o} + \sum_{n=0}^{\infty} E_{n} \sin\left[\frac{\pi \left(n + \frac{1}{2}\right)x}{h}\right] \exp\left[\frac{-\pi^{2} D\left(n + \frac{1}{2}\right)^{2}x}{h^{2}}\right]$$
(A-9)

where the E_n are arbitrary constants. Finally, the initial condition in Eq (A-4) leads to the Fourier series

$$c_i - c_o = \sum_{n=0}^{\infty} E_n \sin\left[\frac{\pi \left(n + \frac{1}{2}\right)x}{h}\right]$$
 (A-10)

which requires that the E_n be

$$E_{n} = \frac{2}{h} \int_{0}^{h} (c_{i} - c_{o}) \sin \left[\frac{\pi \left(n + \frac{1}{2} \right) x}{h} \right] dx = \frac{-2}{\pi} \frac{c_{i} - c_{i}}{n + \frac{1}{2}}.$$
 (A-11)

Therefore, using these in Eq (A-9), the solution to Eqs. (A-1), (A-2), (A-3) and (A-4) is

$$c(x,t) = c_o - \frac{2}{h} (c_o - c_i) \sum_{n=0}^{\infty} \frac{\sin\left[\frac{\pi(n+\frac{1}{2})x}{h}\right]}{(n+\frac{1}{2})} \exp\left[\frac{-\pi^2 D(n+\frac{1}{2})^2 t}{h^2}\right].$$

At the bottom of the ketchup in Figure 3, x = h and Eq (A-12) reduces to

$$\frac{c_o - c(h, t)}{c_o - c_i} = \frac{4}{\pi} \left(q - \frac{q^9}{3} + \frac{q^{25}}{5} - \frac{q^{49}}{7} + \dots \right)$$
 (A-13)

where

$$q = \exp\left(\frac{-\pi^2 D t}{4h^2}\right), \qquad (A-14)$$

8 APPENDIX B

LIST OF PROGRAM TO CALCULATE REACTION RATE CONSTANTS

10	DIM T(10),C(10)
20	CO = 21.4
30	FOR I = 1 TO 10
35	READ T(I),C(I)
40	NEXT
50	INPUT Z
60	$\mathbf{P} = 0$
70	Q = 0
80	$\mathbf{R} = 0$
90	S = 0
100	FOR I = 1 TO 10
110	L1 = LOG (C(I) / CO)
120	L2 = LOG (1 - Z * T(I))
130	P = P + L1 * L2
140	Q = Q + T(I) * L1 / (1 - Z * T(I))
150	$\mathbf{R} = \mathbf{R} + \mathbf{L}1 * \mathbf{L}1$
160	S = S + T(I) * L2 / (1 - Z * T(I))
170	NEXT
180	$\mathbf{E} = \mathbf{P} * \mathbf{S} - \mathbf{R} * \mathbf{Q}$
190	PWR = Q / S
200	PRINT E
210	PRINT Z,PWR
220	FOR I = 1 TO 10
230	$CP = CO * (1 - Z * T(I)) ^ PWR$
240	PRINT CP,C(I)
250	NEXT
260	GO TO 50
270	DATA 3,21.102,6,20.972,10,20.885,17,20.7,27,19.975,
	30,19.9,33,19.81,36,19.803,52,19.65,55,19.6,
	90,18.7

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9 APPENDIX C

BAND MEASUREMENTS TAKEN FROM A TYPICAL GAMMA BOTTLE*.

Band**	\mathbf{L}_{top}	L _{bottom}	S _A	S _B	S _c	S _D	X _A	X _B	Xc	XD
1	11.89	12.01	1.37	1.29	1.35	1.25	54	53	59	48
2	12.06	13.50	1.40	1.25	1.37	1.25	57	62	62	55
3	13.49	14.61	1.40	1.32	1.45	1.25	57	54	58	46
4	14.61	15.24	1.42	1.30	1.45	1.25	56	53	60	44
5	15.24	15.88	1.45	1.25	1.45	1.25	52	46	47	41
6	15.88	17.15	1.52	1.29	1.45	1.25	45	46	47	41
7	17.15	18.42	1.51	1.31	1.47	1.32	34	39	39	32
8	18.42	18.73	1.50	1.29	1.49	1.32	29	38	34	30
9	18.73	25.40	1.47	1.29	1.45	1.25	32	52	27	36
10	25.40	26.03	1.42	1.35	1.42	1.27	32	59	29	46
11	26.04	27.31	1.55	1.32	1.58	1.29	30	56	30	43
12	27.31	27.62	1.55	1.25	1.58	1.58	30	56	32	46
13	27.62	27.62	1.52	1.25	1.55	1.25	29	56	30	45
14	27.62	27.31	1.37	1.25	1.32	1.25	30	53	30	43
15	27.31	26.04	1.39	1.29	1.37	1.37	27	50	28	40
16	26.04	25.88	1.35	1.25	1.32	1.25	27	38	29	29
17	25.88	25.88	1.35	1.30	1.35	1.30	25	28	26	19
18	25.88	0.0	0.31	0.79	0.31	0.79	27	27	27	27

*See Fig 8. L= cm, S= cm, and x= mil. **Band 1 is at the top; band 18 is at the bottom.

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