JOURNAL OF MATERIALS SCIENCE 26 (1991) 6–10

Absorption of silicone fluid in a silicone elastomer

D. E. MATHISON[‡], B. YATES, M. I. DARBY
Department of Pure and Applied Physics, University of Salford, Salford, M5 4WT, UK

Measurements have been made of the absorption properties of a silicone fluid in a silicone elastomer, Aircast 3700, at temperatures between 0 and 150 °C. It was found that the diffusivity could be described by Arrhenius' law. The saturation fluid content was 20% at 0 °C, decreasing to 17% at 120 °C. The swelling was large, up to 26% at saturation, and approximately equalled the volume of fluid absorbed. A "reverse thermal effect" was observed and an attempt has been made to explain it.

1. Introduction

While silicone elastomers are generally more expensive than organic rubbers, and have inferior mechanical strength, they have a number of unique characteristics which make them invaluable for certain applications, see for example [1, 2]. In particular they are thermally stable, showing little deviation in chemical, mechanical and electrical properties, over a much wider range of temperature than other elastomers, e.g. − 80 to 250 °C. In addition to their use as sealants, they are especially useful as electrical insulators at high temperatures, because they fail safer on burning than do organic polymers.

It is known [1, 3] that silicone elastomers can absorb significant amounts of some oils, leading to swelling of the material and degradation of their mechanical properties. It might be expected that silicone oils would enter the elastomer more readily than organic lubricants, but little qualitative work on the absorption properties has been reported. One aim of the present study was to characterize the absorption of a silicone fluid by a commercial elastomer, Aircast 3700, at temperatures in the range 0 to 150 °C.

It has been found that the rate of absorption of liquids into rubbers, characterized by the diffusivity D, depends inversely on the viscosity of the penetrating fluid [3]. It is also known that for a given fluid, D increases with increasing temperature. Hence, if a sample of elastomer is transferred from silicone oil at 80 °C to oil at 0 °C it might be expected that the rate of absorption would decrease. However, it is known that the opposite effect is observed for water absorption at comparable temperatures in some polymer resins, i.e. the rate of absorption increases on transferring to a lower temperature bath [4–7]. A second aim of the present investigation was to determine whether such a "reverse thermal effect" occurred for the absorption of a silicone fluid in a silicone elastomer.

2. Materials

The elastomer studied was a commercial two component modified RTV compound, Aircast 3700, manufactured by Airtech International Inc. It is mainly used as a flexible mould making material, e.g. for urethane foams. The silicone oil used was of type 47 V 100.

3. Experimental procedure

Samples of the elastomer were cut from a single block of material to an approximate size $25 \times 25 \times 3\ \text{mm}^3$. The dimensions of each sample were measured. All the samples were cleaned and degreased using propanone and they were dried in air at room temperature. Each sample was weighed using a microanalytical balance which had a sensitivity of $\pm 2 \times 10^{-4}$ g, and the volumes of the samples were determined using the Archimedian method.

Sets of four specimens were placed in one of six vessels containing silicone fluid held at temperatures of 0, 25, 60, 80, 120 and 150 °C, respectively. The temperatures of 0, 80, 120 and 150 °C were maintained by using constant temperature baths. The temperature of 25 °C was taken to be the ambient room temperature, and a temperature of 60 °C was maintained by using an air circulating oven.

The weights and volumes of all the samples were measured at various times following initial immersion. Before each measurement was made a specimen was wiped with tissue paper to remove surface oil. The specimens which were held at elevated temperatures were allowed to cool. The time interval between the removal of a sample from the fluid at an elevated temperature and its return was approximately 15 min.

The effects of a change in temperature on the absorption were investigated by preparing 24 fresh samples. Twelve samples were placed in silicone fluid at 0 °C, and the other twelve samples were immersed

---

[‡] *Present address*: Green Lane High School, Timperley, Altrincham, WA15 8QW, UK.

0022–2461/91 $03.00 + .12

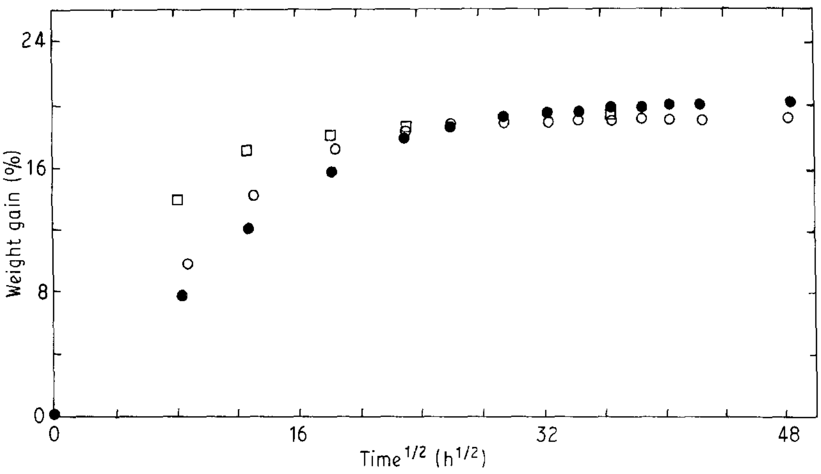

Figure 1 Fractional weight increase as a function of the square root of time (● 0 °C, ○ 25 °C, □ 60 °C).

in fluid at 80 °C. When all the samples appeared to be saturated with fluid, sets of four samples were transferred from the fluid at 0 °C to fluid at 20, 60 and 80 °C, respectively. Sets of four samples were also transferred from the fluid at 80 °C to fluid at 0, 20 and 60 °C, respectively. The resulting changes in the weights and volumes of the specimens were measured as functions of time.

In a separate experiment, four samples were placed in silicone fluid at 150 °C and held there until they appeared to be saturated. The samples were then transferred to fluid at 80 °C and they remained there until a new saturation, equilibrium level was attained. This procedure was repeated, samples being transferred to lower temperature fluid when a new equilibrium was reached, until a final temperature of 0 °C was attained.

4. Results

4.1. Isothermal absorption

The variations of the percentage weight gain of the specimens with the square root of time t are displayed in Figs 1 and 2 for each temperature studied. Each point was obtained as an average of measurements on four specimens.

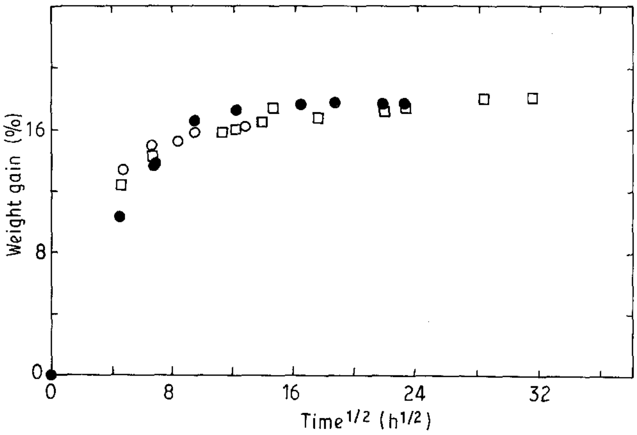

Figure 2 Fractional weight increase as a function of the square root of time (● 80 °C, ○ 120 °C, □ 150 °C).

TABLE I Saturation fluid content and diffusivity

Temperature (°C)	Saturation fluid content (%)	Diffusivity ($\times 10^{-5}$ mm^2 sec^{-1})
0	19.88	1.10
25	20.00	1.48
60	18.66	3.61
80	18.45	5.29
120	16.71	9.49
150	18.34	9.88

It can be seen from Figs 1 and 2, and more clearly from the values given in Table I, that in general the fluid saturation level M_m decreases slightly with increasing temperature. However, the situation at 150 °C appears to be anomalous.

Assuming that the initial sections of the curves were linear, corresponding to classical Fickian diffusion, the diffusivities D were calculated from the slopes $\Delta M/\Delta t^{1/2}$ near $t = 0$ using the relationship

$$D = \frac{\pi}{C^2}\left[\frac{h}{4M_\mathrm{m}}\right]^2\left[\frac{\Delta M}{\Delta t^{1/2}}\right]^2 \qquad (1)$$

where h is the thickness of a specimen and the edge correction factor C is given by [8]

$$C = 1 + \frac{h}{l} + \frac{h}{q} \qquad (2)$$

where l and q are the other dimensions of a specimen. Values of the calculated diffusivities are presented in Table I.

The variation of D with temperature was found to be well represented by the Arrhenius relationship

$$D = D_0 \exp(-Q/T) \qquad (3)$$

with T in Kelvin, and $D_0 = 3.0 \times 10^{-3}$ mm^2 sec^{-1}, $Q = 2236$ K.

4.2. Swelling

The results for the percentage change in volume of the elastomer on absorbing the fluid are displayed in Figs 3 and 4 as functions of the percentage volume of fluid absorbed. Each point represents the average of four measurements. A linear relationship between the volume changes in elastomer and fluid absorbed was found at all the temperatures studied. The broken

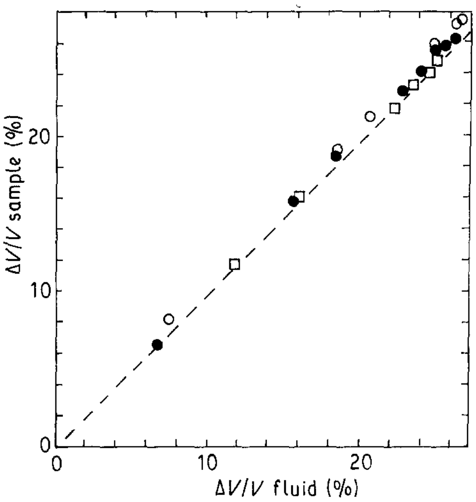

Figure 3 Fractional increase in the volume of a specimen as a function of the fractional increase in the volume of fluid absorbed (● 0 °C, ○ 25 °C, □ 60 °C). The broken line has slope unity for comparison.

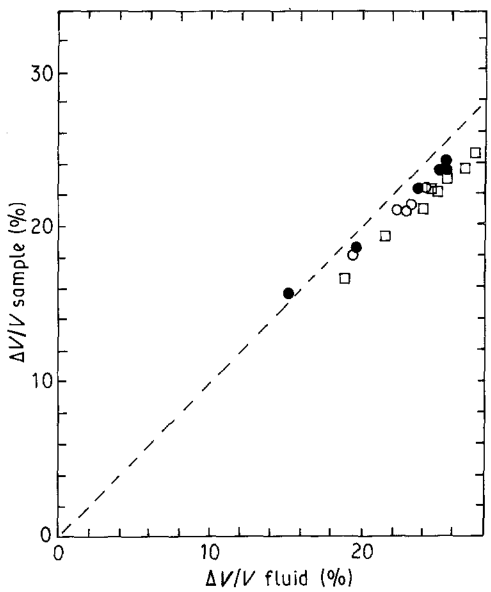

Figure 4 Fractional increase in the volume of a specimen as a function of the fractional increase in the volume of fluid absorbed (● 80 °C, ○ 120 °C, □ 150 °C). The broken line has slope unity for comparison.

lines correspond to the fraction volume increase in the elastomer being equal to the fractional volume of fluid absorbed.

At 0 °C the percentage increase in the volume of the elastomer is greater than the percentage increase in the volume of fluid absorbed. At temperatures above 20 °C the fractional change in volume of the elastomer decreases with increasing temperature for a fixed volume of fluid absorbed.

4.3. Reverse thermal effect

Fig. 5 displays the effects on the moisture absorption of transferring specimens initially maintained at 80 °C to fluid at either 0 or 60 °C. The transfers were made 13 h after the initial immersion, at which time the fluid had reached on equilibrium level in the elastomer. Each point in the figure represents an average of measurements on four samples. The curve for the situation when a sample is transferred to fluid at 25 °C is almost the same as that for transfer to fluid at 0 °C, and is not shown.

Fig. 6 illustrates the results of transferring samples saturated with fluid at 0 °C to fluid at either 25 or 80 °C. The transfers were made after 62 h and again each point is the average of four measurements. The curve obtained on transferring to fluid at 60 °C was found to be almost identical with that for transfer to fluid at 80 °C, and it is not shown.

It was found that transfer from 80 °C to a lower temperature resulted in an increase in the moisture absorption, the magnitude of the increase being larger the greater the change in temperature. When transfer was from fluid at 0 °C to fluid at a higher temperature, the absorption decreased, the magnitude of the decrease being larger the greater the temperature change. In both cases the changes in absorption are not those expected, and they are characteristic of a "reverse thermal effect", such as is observed for moisture absorption in some polymers [4–7].

For transfers to a lower temperature fluid a new, higher equilibrium level in the elastomer was attained after approximately four days. However, on changing from a lower to a higher temperature fluid, with a resulting sudden decrease in the fluid absorbed in the elastomer, the fluid absorption subsequently began to rise again slowly, as illustrated in Fig. 6.

The effects on the absorption of one sample of a series of transfers to lower temperatures are illustrated in Fig. 7. The results are consistent with those expected from the single transfer experiments.

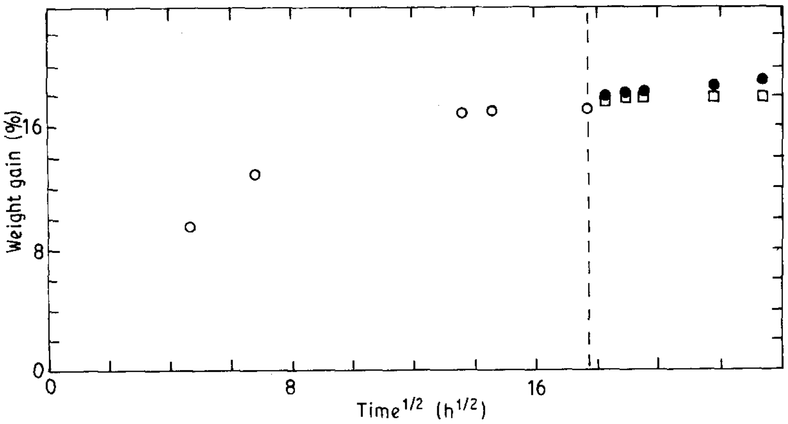

Figure 5 Fractional weight increase as a function of the square root of time (○ 80 °C, ● 0 °C, □ 60 °C). The broken line indicates the time of the temperature changes.

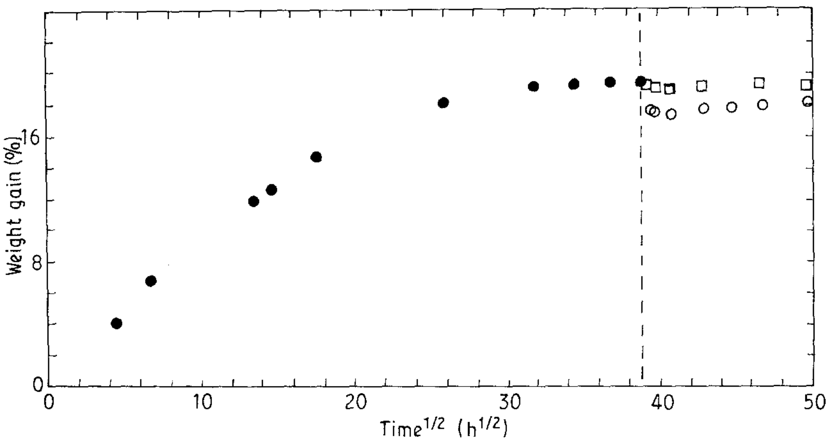

Figure 6 Fractional weight increase as a function of the square root of time (● 0 °C, ○ 80 °C, □ 25 °C). The broken line indicates the time of the temperature changes.

5. Discussion

The present results indicate that the diffusivity D of silicone fluid in the silicone elastomer Aircast 3700 increases with increasing temperature in accordance with Arrhenius' law.

Under isothermal conditions the fluid saturation level M_m in the elastomer is approximately 20% at 0 °C and decreases slowly with increasing temperature between 0 and 120 °C, as can be seen from Table I, but the saturation level appears to be slightly higher at 150 °C.

The determined values of D and M_m have been used in an analytical solution of the Fickian diffusion equation [8, 9] to predict the variation of fluid absorption M as a function of the square root of time

$$\frac{M}{M_m} = 1 - \frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^2} \times \exp\left[-(2j+1)^2\pi^2\left(\frac{Dt}{h}\right)\right] \qquad (4)$$

A typical result of this analysis, for a sample at 0 °C, is compared with the corresponding experimental data in Fig. 8. The good agreement indicates that the diffusion of the fluid into the elastomer is well described by Fickian theory.

The swelling data indicate that the fractional increase in the volume of the elastomer is approximately equal to the fractional increase in the volume of the fluid absorbed. The deviations from this equality depend on temperature, showing a greater fractional increase in the volume of the elastomer at temperatures at and below 60 °C, and a smaller fractional increase in volume at higher temperatures. An explanation for a similar type of behaviour to that observed here at the higher temperatures, in the case of water absorption in polymers [5], is that some of the absorbed fluid enters free volume in the polymer, and therefore does not contribute to the swelling. However, the behaviour observed here at lower temperatures suggests that free volume arguments are not valid for the absorption of silicone fluid into a silicone elastomer.

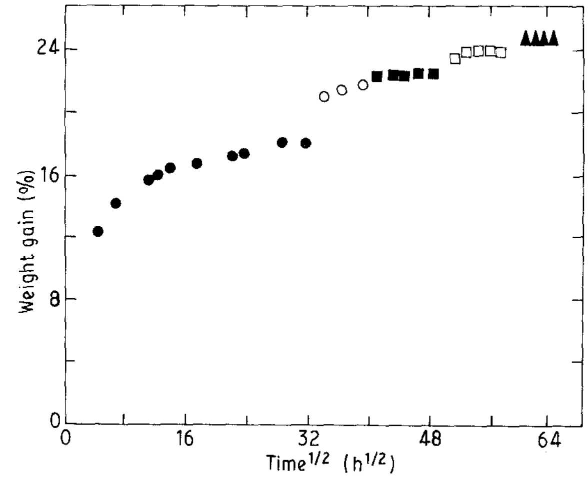

Figure 7 Fractional weight increase as a function of the square root of time showing the effect of a sequence of transfers to lower temperatures (● 150 °C, ○ 80 °C, ■ 60 °C, □ 25 °C, ▲ 0 °C).

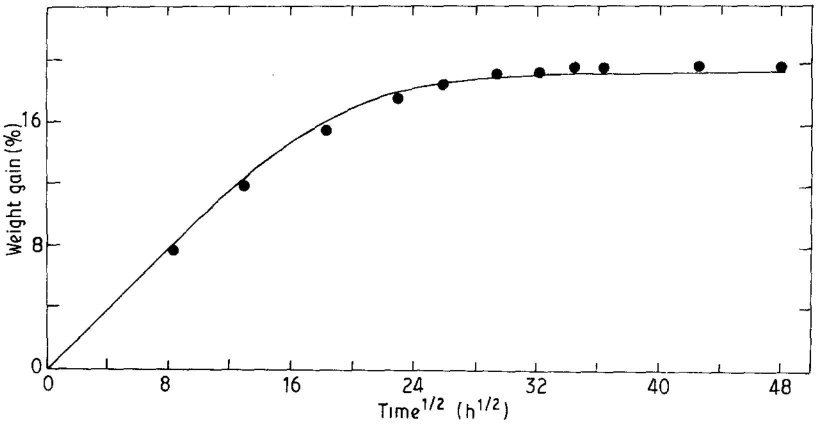

Figure 8 Fractional weight increase as a function of the square root of time at 0 °C (● experiment, —— theory).

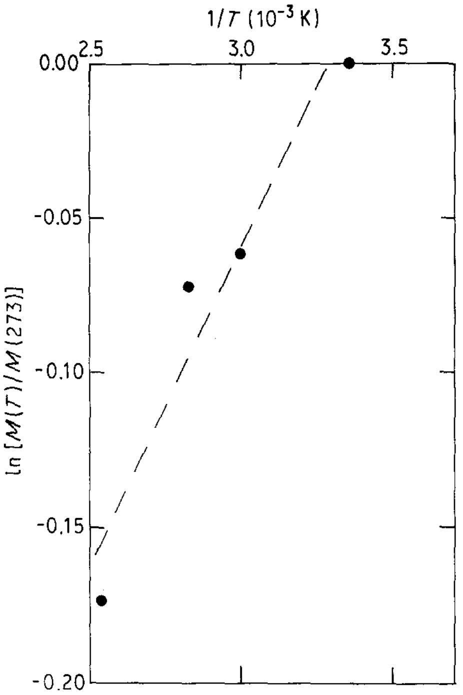

Figure 9 Variation of the fractional saturation weight increase with inverse temperature.

It should be noted that because the absorption of the fluid is large at saturation, the magnitude of the swelling is corresponding large, e.g. approximately 26%.

The observation of a reverse thermal effect for the absorption of a silicone fluid into a silicone elastomer is of considerable interest. While a similar effect has been noted by several workers [4–7] for water absorption in polymers, it does not appear to have been reported previously for any other absorbant fluid. The fact that the effect occurs for different absorbant–absorber systems suggests that the phenomenon does not depend on the detailed chemical mechanisms involved, and it may therefore be explained in terms of thermodynamics. In an earlier paper [7] it was proposed that the reverse thermal effect observed for moisture absorption in epoxy resins could be understood qualitatively in terms of Le Chatelier's principle, assuming that the water enters the polymer exothermically. Further, treating the absorbant fluid as a dilute solution in the polymer, it was suggested that the change in fluid content ΔM accompanying a temperature change of ΔT was given by

$$\frac{\Delta M}{M_m} = \frac{L}{RT^2}\Delta T \qquad (5)$$

where L is the molar heat of solution, R the gas constant and T in Kelvin. For an exothermic reaction L is negative, and in this case Equation 5 predicts that ΔM is positive when ΔT is negative, and vice-versa, which are the essential features of the reverse thermal effect. Equation 5 also predicts that ΔM is smaller at higher temperatures. The data illustrated in Figs 5 and 6 support this conclusion, indicating that ΔM is larger when the transfer is from 0 to 80 °C than when it is from 80 to 0 °C.

Taking L as a constant, integration of Equation 5 gives an expression for the variation of M_m with temperature, namely

$$M_m(T) = M_m(0)\exp(-L/RT) \qquad (6)$$

For a negative L value this expression implies that the fluid saturation level decreases with increasing temperature. Except for the results at 150 °C, the data presented in Table I for M_m show this behaviour. Taking logarithms of Equation 6 a plot of $\ln(M_m(T)/M_m(273))$ against $T^{-1}(\mathrm{K}^{-1})$ should be a straight line with slope $(-L/R)$. Such a graph is shown in Fig. 9 using data for 25, 60, 80 and 120 °C. Given the uncertainties in the measurements, and the relatively small sizes of the variation in M_m with temperature, a straight line is a reasonable fit to the data points. The slope of the line gives $L = -200R$, which is the heat evolved when one mole of the fluid is absorbed by the elastomer. Clearly it would be invaluable to have an independent measurement of L.

6. Conclusions

The absorption of silicone fluid into the silicon elastomer Aircast 3700 was found to be characterized by a diffusivity which increased with increasing temperature in accordance with Arrhenius' law, and a saturation level of approximately 20% at 0 °C which decreased to approximately 17% at 120 °C.

The swelling of the elastomer was large, up to 26% at saturation, and it was approximately equal to the volume of fluid absorbed. It decreased slightly with increasing temperature.

A reverse thermal effect was observed, similar to that observed for water absorption in some other polymers. It is suggested that the phenomenon can be understood using thermodynamic arguments. It is found that many characteristics of the reverse thermal effect can be explained using dilute solution theory.

References

1. E. L. WARRICK, O. R. PIERCE, K. E. POLMANTEER and J. C. SAAM, *Rubber Chem. Technol.* **52** (1979) 437.
2. C. M. BLOW and C. HEPBURN (eds) "Rubber Technology and Manufacture", 2nd Edn (Plastics and Rubber Institute, Butterworth, London, 1982).
3. E. SOUTHERN, "Use of Rubber in Engineering," edited by P. W. Allen, P. B. Lindley and A. R. Payne (Maclaren and Sons, London, 1967) pp 49–55.
4. A. APICELLA, L. NICOLAIS, G. ASTARTIS and E. DRICOLI, *Polymer* **20** (1979) 1143.
5. M. J. ADAMSON, *J. Mater. Sci.* **15** (1980) 1736.
6. V. N. KANELLOPOULOS, G. H. WOSTENHOLM and B. YATES, *ibid* **20** (1985) 2503.
7. L. EL-SA'AD, M. I. DARBY and B. YATES, to be published.
8. C. H. SHEN and G. S. SPRINGER, *J. Compos. Mater.* **10** (1976) 2.
9. H. S. CARSLAW and J. C. JAEGER, "Conduction of Heat in Solids", 2nd Edn (Oxford, Clarendon Press, 1959).

Received 26 July 1989
and accepted 19 February 1990