STRESS-STRAIN PROPERTIES OF ELASTOMERS

by

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A Thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

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February, 1965.

ABSTRACT

After a brief review of the current ideas of the molecular structure of elastomers and an outline of the thermodynamic changes which occur when an elastomer is deformed, the generally accepted theories of rubber elasticity are reviewed in turn. This is followed by a more detailed discussion of the origin and development of the Kinetic theory of elasticity and some of the more important modifications. A discussion of the three main analyses of the thermodynamics of rubber elasticity and the assumptions and approximations involved in each completes the first part of this thesis.

The second part describes the experimental procedures used in this work and gives the results obtained. The thermodynamic results obtained do not contain any surprising features but values of the temperature coefficient of the mean square end-to-end length are obtained for two polymers, ethylene-propylene and polybutadiene which have not been previously attempted.

The results of this work are used to assess the principal theories of elasticity and it appears that no theory is satisfactory. An empirical equation is proposed which gives a better representation of the data obtained in this work but like the phenomenological equations at least one of the coefficients involved cannot be given any physical significance.

ACKNOWLEDGEMENTS

The author would like to thank:

1. Dr. J. A. Barrie for initiating and supervising the work.

2. Professor R. M. Barrer for his interest and encouragement.

3. The staff of the Department of Chemistry, Royal College of Science for many helpful discussions.

4. The technical staff of the Department of Chemistry, Royal College of Science for their willing help in constructing apparatus.

5. The staff of the University of London Computer Unit for their help in overcoming the difficulties of programme writing.

6. To Dunlop Rubber Company for a research scholarship enabling this work to be carried out.

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CHAPTER 1

1. Introduction

Elastomers are a group of materials whose mechanical properties differ quite markedly from other materials. When subjected to external forces, elastomers behave like viscous liquids in their ready deformation, but when the forces are removed they behave as solids in their rapid, almost instantaneous, return to their former shape. Some of these mechanical properties, for a lightly vulcanised natural rubber, are contrasted, in Table 1.1, with the properties of a typical normal solid, mild steel.

Table 1.1

Comparison of some mechanical properties of a typical elastomer (natural rubber) and mild steel

	Property	Elastomer	Mild Steel
1)	Young's Modulus	10^{7} dynes cm.$^{-2}$	10^{12} dynes cm.$^{-2}$
2)	Maximum extensibility	500 - 1000 %	.1 %
3)	$(\partial f/\partial T)_{\ell}$	+ve	-ve
4)	Internal Energy change	small	large
5)	Entropy change	large	small

2. Definitions

An Elastomer may be defined as a material which is capable of undergoing large, elastic, i.e. reversible, deformations. The first and best known of these materials is Natural Rubber hence the word

'rubber' is often used as a synonym of elastomer and will be so used in this thesis.

Stress (τ) is the name given to a deforming force acting on a body. It is normally defined in terms of force per unit area, where the area considered is that of a cross section perpendicular to the force vector. Thus $\tau = f/A$ where f is the resultant force acting on the sample and A is the cross sectional area of the sample at right angles to the direction of f. In rubber elasticity however, it is conventional to use units of mass per unit area so that the dimensions of the stress are ML^{-2} instead of $ML^{-1}t^{-2}$.

Strain (σ) is the deformation resulting from the application of a stress and is given as the fractional change in the dimensions of the strained body. For a one dimensional extension the strain is $(l - l_o)/l_o$ where l is the strained and l_o the unstrained length of the sample. In rubber elasticity it is conventional to use the extension ratio (α), where $\alpha = l/l_o = \sigma - 1$, as the measure of deformation.

A homogeneous strain is one in which the strain at any point is equal to the strain at any other point. Thus, lines which were parallel in the unstrained state are parallel also in the strained state.

Simple Elongation is a one dimensional extension α_x along the axis of elongation. As the value of Poisson's ratio for rubber is very close to 0.5, the rubber is assumed to be incompressible so the extension ratios α_y and α_z perpendicular to the direction of α_x are each equal to $\alpha_x^{-\frac{1}{2}}$ and the stresses normal to the direction of α_x are

equal to -p where p is the ambient pressure. This present investigation is concerned primarily with simple elongation.

Elastic Limit. In this work the elastic limit is defined as the maximum elastic deformation rather than as the point of departure from Hooke's law.

Chain Contour Length (L) is the overall length of a chain molecule. For a chain of n links each of length d the contour length is nd.

Chain displacement length (r) is the direct end-to-end distance of a chain in a particular configuration. For a chain of n freely jointed links of length d the most probable value of r is b^{-1} where $b^2 = \frac{3}{2} nl^2$. The instantaneous value will however vary between zero and L and the distribution of values of r about the most probable value for the chain described here is given by the Gaussian error function (1.11). Hence such chains are often termed 'Gaussian' chains.

3. Thermodynamics of Elasticity

An appreciation of the nature and origin of the retractive force in high elastic materials requires a study of the thermodynamics of elastic deformation. The earlier work has been reviewed by Treloar (2) and only the brief outline necessary for continuity will be reproduced here.

For any reversible isothermal process the internal energy (U) is related to the entropy (S) and to the work done on the systen (W) by:

$$dU = TdS + W \tag{1.1}$$

In general any stress can be resolved into a pure distortive stress and a compressive stress. Thus for a simple elongation the work done in stretching a piece of rubber by an amount dl is:

$$W = f\,dl - P\,dV \tag{1.2}$$

where P is the ambient pressure and dV is the change of volume resulting from the change of length dl. As elastomers are almost incompressible the PdV term is much less than the fdl term, at least if P does not exceed 100 atmospheres. Thus

$$W \simeq f\,dl \tag{1.3}$$

is always a good approximation and becomes an equality when P or dV = 0.

Elliott and Lippmann (13) were the first to point out that though $PdV \ll fdl$, any change in the volume of the sample alters the average interatomic distances and thus alters the internal energy. Thus the variations in internal energy and entropy with deformation will depend on whether the sample is held at constant volume or under constant pressure. The values obtained at constant volume, being independent of any effects due to changes in interatomic distances, offer the greater insight into the molecular processes involved in the deformation, whilst the values under constant pressure are far more accessible experimentally. In the remainder of this analysis constancy of volume is stipulated and hence the relationship expressed in

equation (1.3) is taken as an equality.

From the differential of the Helmholtz free energy F defined by:

$$dF = dU - TdS - SdT \tag{1.4}$$

and equations (1.1) and (1.3) we get:

$$dF = fdl - SdT \tag{1.5}$$

hence

$$f = (\partial F/\partial l)_{T.V.} \tag{1.6}$$

Combining equations (1.4) and (1.6) then gives:

$$f = (\partial U/\partial l)_{TV} - T(\partial S/\partial l)_{TV} \tag{1.7}$$

From equations (1.5) and (1.6) respectively we get:

$$\left[\frac{\partial}{\partial l}\left(\frac{\partial F}{\partial T}\right)\right]_V = -\left(\frac{\partial S}{\partial l}\right)_{TV} \tag{1.8}$$

and

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial l}\right)\right]_V = \left(\frac{\partial f}{\partial T}\right)_{lV} \tag{1.8a}$$

hence

$$(\partial f/\partial T)_{lV} = -(\partial S/\partial l)_{TV} \tag{1.9}$$

and substituting (1.9) into (1.7):

$$f = (\partial U/\partial l)_{VT} + T(\partial f/\partial T)_{Vl} \tag{1.10}$$

Thus measurement of f and $(\partial f/\partial T)_{V,l}$ at any extension is sufficient to allow the calculation of $(\partial U/\partial l)_{TV}$ and $(\partial S/\partial l)_{TV}$. In practice however the experimental difficulties involved in the measurement of

$(\partial f/\partial T)_{Vl}$ are too great so that the quantity measured is invariably $(\partial f/\partial T)_{Pl}$. It then becomes necessary to deduce some relationship between $(\partial f/\partial T)_{Vl}$ and $(\partial f/\partial T)_{Pl}$ so that the more useful one may be calculated from the more accessible. These relationships will be discussed in Chapter 3 of this thesis.

Equation (1.7) shows that the retractive force f may be resolved into internal energy and entropy components and though this analysis has used simple elongation, this result holds for any other type of deformation. In general, materials having a large entropy component show large elastic deformability and those having a large energy component have only limited elastic deformability. This generalisation may be rationalised in terms of the current theories of elasticity as discussed in subsequent sections of this chapter.

4. Theories of Elasticity

The early theories of elasticity assumed that the retractive force originates in interatomic forces, i.e. they assumed the energy term of equation (1.7) to be predominant. Typical of these early theories are those of Mack (47), Ostwald (58) and Fekentscher and Mark (22) all of which were specific to natural rubber and ignored the fact, first demonstrated by Gough (26) and confirmed by Joule (39), that the stretching of rubber is exothermic. From the first law of thermodynamics this indicates that at least part of the work of deformation is not used in increasing the internal energy of the material, and from the

second law of thermodynamics this evolution of heat is associated with a decrease in the entropy of the material. Lord Kelvin (40) in 1855 showed that an evolution of heat is associated with positive values of $(\partial f/\partial T)_l$. The development of synthetic elastomers led Meyer, von Susich and Valko (51) to suggest that the results of Gough and of Joule indicate that the entropy term, in equation (1.7), may be larger than the internal energy term. This suggestion was supported by the experimental results of Meyer and Ferri (50) and of Weigard and Snyder (86) which appeared to indicate that the energy term is in fact negligible or even zero. These results then led to the development of the kinetic theory of rubber elasticity by several independent groups of workers including Flory and Rehner (14), James and Guth (35, 36, 37, 38) Kuhn (44), Treloar (76) and Wall (83) by various methods. An outline of the general ideas and arguments and of the basic postulates used in this development is given in the next sections of this chapter.

5. Nature of Polymer Molecules

Though the idea that some molecules can be very large with molecular weights greater than 20,000 was not acceptable to many early physical chemists, it is now generally recognised, and such molecules have the generic name macromolecules. These macromolecules are often built up of large numbers of smaller units which are all identical and are linked together by primary valence bonds. Molecules of this type are called polymers and if the sub-units are linked head to tail to form

a single chain they are straight chain polymers. Most plastic materials and elastomers are formed from molecules of this type and though other forms of polymerisation are possible they will not be discussed here. It is commonly accepted (1, 2) that if some degree of rotation about the valence bonds within the chain is possible, then the molecules will not be fully extended but the thermal motion of the units of the chain will cause it to be continually changing its configuration. Over a period of time the displacement length (r) of a sufficiently long molecule will vary between zero and the contour length (L) of the molecule. The probability of finding the molecule with any particular value of r will be proportional to the number of configurations consistent with that value. Thus there will be some most probable displacement length (b^{-1}) for which the number of configurations is a maximum. Tchen (73a) has shown that provided a molecule is sufficiently long for the most probable value of the displacement length (b^{-1}) to be small compared with the contour length (L), then the probability $w(r)$ of finding the chain with a displacement length between r and r + dr is given by the Gaussian distribution function:

$$4\pi r\, w(r)\, dr = \frac{4b^3}{\pi^{\frac{1}{2}}}\, r^2\, e^{-b^2 r^2}\, dr \qquad (1.11)$$

Such chains are commonly termed 'Gaussian chains'.

From the known dependence (Eqn. 1.12) of entropy (S)

$$S = k \ln w \qquad (1.12)$$

on probability (w), the entropy associated with any displacement length

and hence the variation of entropy with displacement length can be shown to be:

$$(\partial S/\partial r)_{TV} = -2 k b^2 r \qquad (1.13)$$

If the chains are assumed to be iso-energetic, i.e. the internal energy is independent of the displacement length, then combination of equations (1.7) and (1.13) gives:

$$f = 2 k T b^2 r \qquad (1.14)$$

Though this equation has been derived for iso-energetic chains, Flory (19) has recently shown that the same equation may be derived for non-isoenergetic chains. This will be discussed more fully in Chapter 2 of this thesis.

6. Molecular Structure of Elastomers

Equation (1.14) shows the relationship between the retractive force and the displacement length of a single chain but this will be related to the retractive force in bulk elastomer only if the ends of the chain are fixed in relation to the rest of the material. The model used to describe an elastomer is based on a set of suggestions by Busse (5) and now generally accepted. An elastomer is regarded as being composed of a number of polymer chains, in which some degree of rotation about the interatomic bonds is possible, and linked together at comparatively few places called cross links. By this process the original polymer molecules loose their identity and become

parts of a large network molecule. The term 'network chain' will be used to denote any chain joining two contiguous crosslinks. A network formed from chains of finite length will have some loose ends or parts of the original chains which are attached to the network at one point only. These loose ends do not contribute to the retractive force generated when the network is deformed and thus only complicate the estimation of the number of effective network chains in any network. This estimation is further complicated by the possibility that two or more chains can be so entangled that the entanglement acts as a crosslink and thus apparently increases the number of effective chains. The difficulty of accurately assessing the number of effective chains in a network is a serious drawback in any attempt to evaluate a theory of elasticity, as the free energy of deformation of the network is assumed to be the sum of the corresponding free energies of its component effective chains.

7. Kinetic Theory of Rubber Elasticity

Assuming that an elastomer may be regarded as a network of chains as described in the preceding sections and further assuming that the deformation changes the components of the displacement length of each chain in the same ratio as the corresponding dimensions of the bulk rubber (affine deformation assumption) then as will be shown in Chapter 2 of this thesis the free energy of deformation (ΔF) of a network of ν chains is given by:

$$\Delta F = \overline{r^2} b^2 \frac{\nu kT}{3} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \qquad (1.15)$$

where α_x, α_y and α_z are the extension ratios along the Cartesian axes, $\overline{r^2}$ is the mean square end-to-end distance of the chains in the undeformed state, and $b^2 = \frac{2}{3} \overline{r_o^2}$ where $\overline{r_o^2}$ is the mean square end-to-end distance of the same set of chains in the absence of crosslinks. For the case of simple elongation $\alpha_y^2 = \alpha_z^2 = \alpha_x^{-1}$ and hence:

$$\Delta F = \overline{r^2} b^2 \frac{\nu kT}{3} (\alpha_x^2 + 2\alpha_x^{-1} - 3) \qquad (1.16)$$

At this point Flory and Rehner, Kuhn, Treloar and Wall assumed that the process of introducing crosslinks does not affect the value of the mean square end-to-end distance and hence $\overline{r^2} b^2 = 3/2$ and equation (1.16) becomes:

$$\Delta F = \frac{\nu kT}{2} (\alpha_x^2 + 2\alpha_x^{-1} - 3) \qquad (1.17)$$

and hence the retractive force $f = (\partial \Delta F / \partial l)_{T.V.} = \frac{1}{l_o} (\partial \Delta F / \partial \alpha)_{TV}$ can be written:

$$f = \frac{\nu kT}{l_o} (\alpha_x - \alpha_x^{-2}) \qquad (1.18)$$

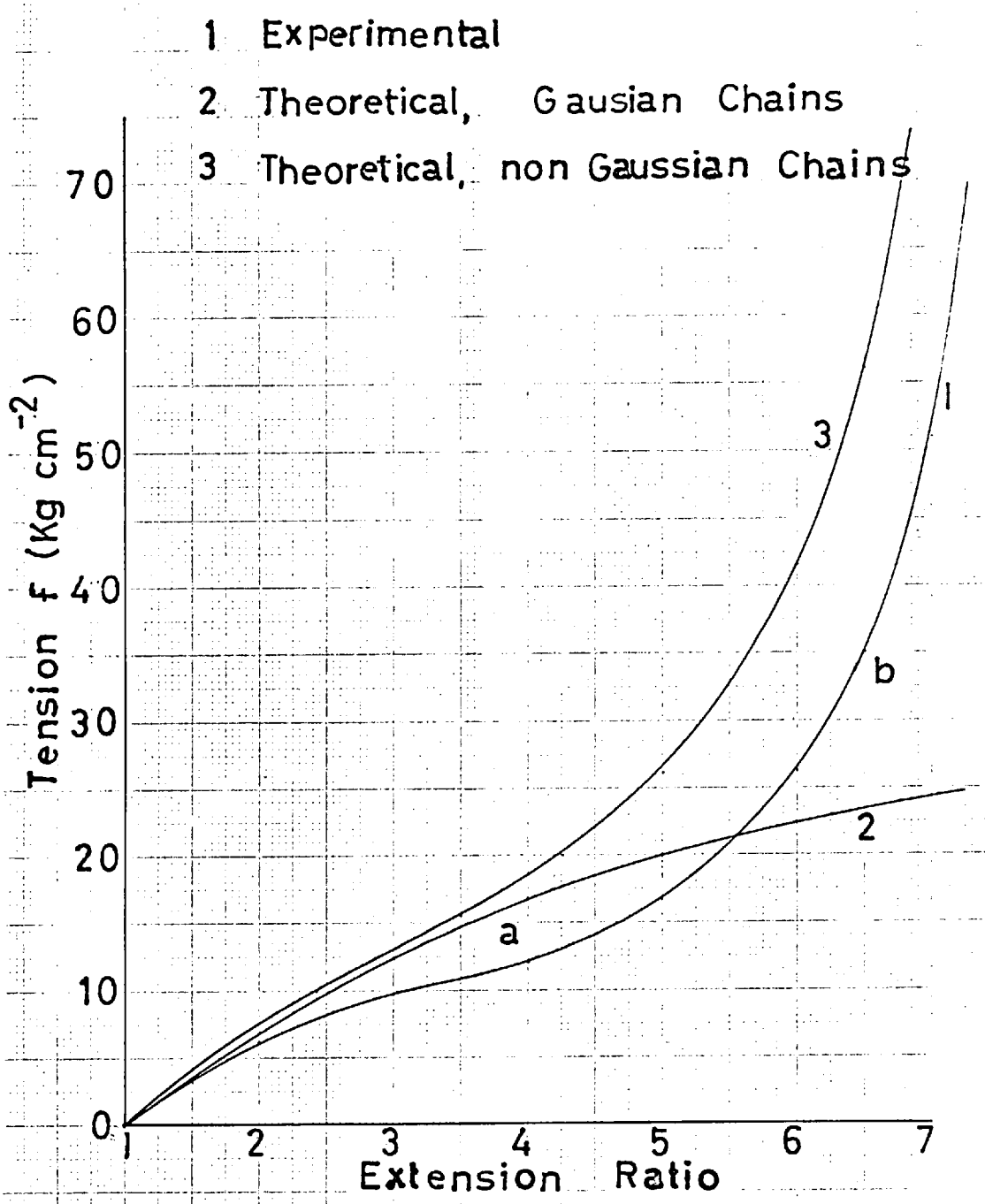
James and Guth (loc. cit.) and later, Tobolsky (27, 72) did not accept this assumption but insisted that $\overline{r^2} / \overline{r_o^2}$ be represented by the quantity ψ for which James and Guth (35) obtained a tentative value of 0.5.

8. Comparison with Experiment

The difficulty in assessing the value of ν discussed in

section 6 means that the value of ψ cannot be readily determined by experiment. However the main protagonist of the view that $\psi = 1$ has recently (17) accepted that this view is over-simplified and now agrees that $\psi \neq 1$.

A more serious discrepancy in this theory lies in the failure of the stress function $(\alpha_x - \alpha_x^{-2})$ adequately to describe the variation of stress with strain when the most suitable value of ν kT is chosen to fit the measured values of f and α_x at small extensions. Many experiments such as those of Gumbrell, Mullins and Rivlin (28) show that the stress function derived by the kinetic theory is valid only over a very small range of extension. The discrepancy is illustrated graphically in Figure 1.1. This diagram shows that there are two ranges of strain for which the experimentally measured stress deviates from the predicted values. In region b) the rubber is much harder than the kinetic theory predicts, whilst in region a) the rubber is softer than expected. It has been suggested (17a) that the rapid increase in the force required to increase the extension in region b) is caused partially by crystallisation of the oriented molecules. However, though all elastomers show this deviation, some do not show any other evidence of crystallisation whilst others show clear X-ray evidence that some crystallisation occurs on stretching. A more likely explanation of the deviation in region b) is that the displacement lengths of the network chains are no longer short compared with their contour lengths and so the use of the Gaussian distribution



Comparison of Experimental and Theoretical Stress-strain Curves

Figure 1-1

function is no longer valid to describe the distribution of displacement lengths. Several workers including Kuhn and Kuhn (45) and Kuhn and Grün (46) have avoided using the Gaussian function and have developed stress-strain relationships exemplified by line 3 of Figure 1.1.

Evaluation of these non-Gaussian relationships is hindered by the excessive hysteresis always encountered at large strains. This indicates that a reasonable approach to equilibrium conditions has not been achieved and so the region of large deformations has been largely ignored and will not be treated further in this thesis.

No satisfactory explanation of the deviations in region a) has yet been advanced and some of the suggestions will be discussed in Chapter 2.

Though the Kinetic Theory is far from satisfactory, it is the only current theory which can even qualitatively relate the molecular structure of elastomers to their mechanical properties. This failure to eliminate the inadequacies of the Kinetic Theory either by modification to the original theory or by the substitution of a new one has led to the development of a number of stress-strain equations which are not based on any molecular model. These relationships are collectively referred to as phenomenological theories. They contribute little or nothing to the understanding of the molecular processes involved in the deformation of elastomers but they may provide a relationship between stress and strain which is of technological value. Further, by

emphasising the inadequacies of contemporary, genuine theories, they may indirectly lead to improvements in those theories. The more important of these phenomenological theories will be discussed in the next section.

9. Phenomenological Theories

(a) Mooney-Rivlin Equation

This is the most widely known of these equations and was derived by Mooney (52) and by Rivlin (60) by completely different methods. Though Mooney's derivation was the earlier, it may be regarded as a special form of Rivlin's equation, and it is the derivation of the more general form which will be outlined here.

Rivlin derived an expression for the stored energy or free energy ΔF of deformation in terms of some functions of the strain parameters called strain invariants. For a material which is isotropic in the unstressed state the strain invariants are symmetric functions of the extension ratios and Rivlin showed that all possible forms of ΔF can be represented by three invariants I_1, I_2 and I_3 which he defined by:

$$I_1 = \alpha_x^2 + \alpha_y^2 + \alpha_z^2 \qquad (1.19)$$

$$I_2 = \alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 + \alpha_x^2\alpha_z^2 \qquad (1.20)$$

$$I_3 = \alpha_x^2\alpha_y^2\alpha_z^2 \qquad (1.21)$$

If the material is incompressible there is no change of volume of the sample with strain and hence $I_3 = 1$,

thus:
$$I_1 = \alpha_x^2 + \alpha_y^2 + \alpha_x^{-2}\alpha_y^{-2} \tag{1.22}$$

$$I_2 = \alpha_x^2\alpha_y^2 + \alpha_x^{-2} + \alpha_y^{-2} \tag{1.23}$$

Rivlin then showed, by extending the classical theory of elasticity to include finite strains, that the most general form of the stored energy is the summation of a power series

$$\Delta F = \sum_{i,j=0}^{i,j=\infty} C_{ij}(I_1 - 3)^i(I_2 - 3)^j \tag{1.24}$$

The first non-zero term in this series, obtained by putting i = 1 and j = 0 gives:

$$\Delta F = C_{1,0}(I_1 - 3) \tag{1.25}$$

which, from the definition of I_1 given in equation (1.19), is equivalent to the equation (1.15) derived from the Kinetic Theory with $2C_{1,0} = \overline{r^2}\, b^2 \nu\, kT$. The second term, obtained when i = 0 and j = 1 does not correspond to any known material but the combination of these two terms gives an equation:

$$\Delta F = C_{1,0}(I_1 - 3) + C_{0,1}(I_2 - 3) \tag{1.26}$$

first derived by Mooney (52) by assuming a linear stress-strain relationship for an isotropic material in pure shear.

Mooney then proceeded to derive a stress strain equation for simple elongation assuming the constants $C_{1,0}$ and $C_{0,1}$ to be independent of strain. This equation, derived from equation (1.26) by an argument similar to that given on page 16, may be written:

$$f = 2(C_1 + C_2\alpha^{-1})(\alpha - \alpha^{-2}) \qquad (1.27)$$

Rivlin (60) however, derived a stress strain relationship for simple elongation of the form:

$$f = 2\left(\frac{\partial \Delta F}{\partial I_1} + \frac{1}{\alpha}\frac{\partial \Delta F}{\partial I_2}\right)(\alpha - \alpha^{-2}) \qquad (1.28)$$

In each of equations (1.27) and (1.28) f is the force per unit area of the unstrained sample and α the extension ratio in the direction of stretch.

Equation (1.27) indicates a linear relationship between $f/(\alpha - \alpha^{-2})$ and α^{-1} and this has been verified experimentally at least for values of α greater than 1.2 and less than 2.5 by many experimenters, particularly Gumbrell, Mullins and Rivlin (28) and Rivlin and Saunders (62). Though Rivlin and Saunders maintained that this linear relationship does not necessarily mean that $\partial\Delta F/\partial I_1$ and $\partial\Delta F/\partial I_2$ are individually constant, it has been generally accepted that $\partial\Delta F/\partial I_1$ is identical with C_1 and $\partial\Delta F/\partial I_2$ is identical with C_2. The contention of Rivlin and Saunders is, however, supported by the limited range of values of α for which the linear relationship is found experimentally to be valid.

Correlation of C_1 and C_2 with the Kinetic Theory

When $C_2 = 0$, equation (1.27) reduces to the kinetic theory equation (1.17) with $2C_1 = \bar{r}^2 b^2 \nu kT / l_o$. This led to speculation that the Mooney-Rivlin phenomenological equation may be regarded as the

kinetic theory equation plus an extra term. A detailed examination of the experimental results of Gumbrell Mullins and Rivlin gives some support to this idea. These authors found C_1 to be directly proportional to the degree of cross linking but independent of the degree of swelling or of the swelling agent used. C_2 however was found to be inversely proportional to the degree of swelling and independent of the degree of cross linking though a dependence of C_2 on the nature of the cross linking process was observed.

Though these and other similar experimental results support the equivalence of C_1 and the Kinetic theory modulus, no satisfactory physical interpretation of C_2 has yet been published. Flory and Ciferri (18) have recently suggested that C_2 is a spurious term arising from the failure of the sample to reach equilibrium but this suggestion is not borne out by the evidence quoted in its support.

(b) Holdaway and Carmichael Equation

The most recent phenomenological theory was developed from an extension of Mooney's approach by Holdaway and Carmichael (6) who obtained a stress strain equation for simple extension:

$$f = \alpha^{-1}\left[\psi(\alpha^2) - \psi(\alpha^{-1})\right] \qquad (1.29)$$

where

$$\psi(x) = \tfrac{1}{2}A \exp\left\{\beta(x^{\frac{1}{2}} - x^{-\frac{1}{2}})\right\} - B(x - x^{-1} - 2) \qquad (1.30)$$

where x is a dummy variable and A, B and β are constants. As no attempt has been made to attach any physical meaning to these three constants equation (1.29) is a three parameter equation and the most

suitable values of A, B and β may be chosen for any set of stress strain values. By this method Holdaway and Carmichael obtained good agreement between calculated and experimental values of f, the tensile force per unit area of unstrained cross section, for values of α between 0.4 and 7.5. Similar agreement was obtained over wide ranges of other types of strain.

(c) Other Phenomenological Equations

A number of equations have been suggested from time to time the most noteworthy being that due to Thomas (74), but they have all been largely ignored by other workers in this field and they do not offer any insight into the molecular processes of deformation. It is in fact comparatively easy to obtain an empirical relationship between stress and strain over a particular limited range of strain, and some phenomenological approaches offer little more than this. Consequently only the Mooney-Rivlin theory will be considered in subsequent chapters of this thesis.

10. Recent Developments

The two most important developments in rubber elasticity theory during the past decade have been the realisation that the energy term of equation (1.10) is not negligible and the suggestion by Flory and Ciferri (18) that the second term of the Mooney-Rivlin phenomenological theory is due to failure to attain equilibrium in the strained elastomers and is thus a spurious term. The first of these developments has

led several groups, notably those led by Vol'kenstein and Ptitsyn (80) by Flory (19) and Tobolsky (75) and by Krigbaum (43) to attempt to extend the Kinetic Theory to include variations in internal energy with extension.

11. Object of Present Work

This work was undertaken for two reasons:

(a) In an attempt to clarify the controversy regarding the validity of the second term of the phenomenological theory, in particular, to determine the dependence, if any, of the constant C_2 on temperature, and

(b) to evaluate the entropy and energy terms of equation (1.10) over as wide a temperature range as possible. To minimise the irreversible effects of oxidation which can be serious in unsaturated hydrocarbons above about 50°C the experimental measurements have been carried out under high vacuum (10^{-6} torr) conditions.

In addition, calculations have been carried out using the University's 'Mercury' computer to evaluate the magnitude of some suggested modifications to the simple Kinetic Theory.

CHAPTER 2

Kinetic Theory of Elasticity

The outline of the theory given in the preceding chapter indicated how a stress strain equation may be derived from the properties of an idealised network. The object of this chapter is to discuss, in more detail, the development of the Kinetic theory and the nature of the assumptions and approximations involved. The early stages of the development have been reviewed by Treloar (2) and so will not be treated here in the same detail as the more recent developments. The thermodynamic analysis in section 3 of Chapter 1 shows that the essential step in the development of a theory of elasticity is the derivation of an expression for the change of Helmholtz free energy with deformation, and further that this free energy change may be split into a component due to a change of entropy and one due to a change in internal energy.

1. Early Development

The original development of the kinetic theory stemmed from the contemporary interpretations of the experimental results of Meyer and Ferri (50) and of Weigand and Snyder (86) which appeared to indicate that there was no change of internal energy on deformation. The model used to represent an elastomer in these early theories was similar to that discussed in sections 5 and 6 of the preceding chapter. An individual chain in such a network will have a

displacement length r (with Cartesian components x, y and z) in the unstrained state, and in the strained state these will change to r', x', y' and z' respectively, where

$$x' = \alpha_x x; \qquad y' = \alpha_y y; \qquad z' = \alpha_z z ; \qquad (2.1)$$

provided that the coordinate axes are chosen to lie along the principal axes of strain.

Integration of equation (1.13) gives:

$$S = - k b^2 r^2 + C \qquad (2.2)$$

where S is the total entropy of the system and C is the integration constant. Thus in the undeformed state:

$$S = C - kb^2(x^2 + y^2 + z^2) \qquad (2.3)$$

and in the deformed state:

$$S' = C - kb^2\left[x^2\alpha_x^2 + y^2\alpha_y^2 + z^2\alpha_z^2\right] \qquad (2.4)$$

Thus the change of entropy S due to the deformation is given by:

$$S' - S = \Delta S = -kb^2\left[x^2(\alpha_x^2 - 1) + y^2(\alpha_y^2 - 1) + z^2(\alpha_z^2 - 1)\right] \qquad (2.5)$$

For an assembly of free (uncrosslinked) chains of this type the total entropy of the system is the sum of the entropies of the individual chains. The early theories of elasticity assumed that this summation would not be invalidated by the introduction of crosslinks so that the entropy of a network may be calculated as the sum of the individual chain entropies. A real network will consist of chains of differing

overall lengths and thus differing values of the parameter b. Such a network may be regarded as being composed of a number of sub-networks each composed only of chains characterised by a single value of b. The total change of entropy of a sub-network characterised by the particular value b_p is:

$$\Delta S_p = - kb_p^2\left[(\alpha_x^2 - 1)\sum x^2 + (\alpha_y^2 - 1)\sum y^2 + (\alpha_z^2 - 1)\sum z^2\right] \tag{2.6}$$

The components x, y and z in equation (2.6) refer to the undistorted, isotropic network and as for such a network all directions of the end to end vector are equally probable,

$$\sum x^2 = \sum y^2 = \sum z^2 = \tfrac{1}{3}\sum r^2 \tag{2.7}$$

Thus if this particular sub-network contains N_p chains, equation (2.6) can be rewritten:

$$\Delta S_p = - kb_p \frac{\overline{r_p^2}}{3} N_p\left[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3\right] \tag{2.8}$$

where $\overline{r_p^2} = \frac{1}{N_p}\sum r_p^2$.

The value of $b_p \overline{r_p^2}$ was the subject of some controversy but all agree that its value is not dependent on the chain length and hence the term can be represented by ψ so that equation (2.8) becomes:

$$\Delta S_p = - k\frac{\psi}{3} N_p\left[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3\right] \tag{2.8a}$$

and the total entropy ΔS for all such sub-networks is:

$$\Delta S = \frac{-k}{3}\sum \psi N_p \left[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3\right] \qquad (2.9)$$

which becomes:

$$\Delta S = \frac{-\nu k \psi}{3}\left[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3\right] \qquad (2.10)$$

where ν = total number of chains in the total network.

For an isothermal process the change of the Helmholtz free energy ΔF on deformation is:

$$\Delta F = \Delta U - T\Delta S \qquad (2.11)$$

and as the experimental results of Meyer and Ferri indicated that $\Delta U = 0$, then

$$\Delta F = -T\Delta S = \frac{\nu kT \psi}{3}\left[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3\right]$$

which is identical with equation (1.15) and the evaluation of the retractive force f then follows the outline given in section 7 of Chapter 1.

Though Flory (1) maintained for some time that the value of ψ should be unity, he later (17) deduced an equation:

$$f = \langle\alpha\rangle^2 \frac{\nu kT}{l_o}\left(\alpha - \alpha^{-2}\right) \qquad (2.12)$$

where $\langle\alpha\rangle^2 = \frac{\overline{r_i^2}}{\overline{r_o^2}} = \psi$, thus apparently arriving at the conclusion reached by James and Guth some years before. The derivation of equation (2.12) however included an allowance for the entropy of distribution of $\nu/2$ crosslinks through the volume of the rubber and hence includes any changes in this quantity due to volume changes on

deformation (see section 4 of this chapter). The paper is also important for the introduction of a particular reference state which has since been used by several other authors. The reference state defined here is that isotropic state where the distribution of mean square end to end lengths in the crosslinked material is identical to the distribution of mean square end to end lengths of the same assembly of free uncrosslinked chains, i.e.

$$\overline{r^2} = \overline{r_o^2} \tag{2.13}$$

The use of this reference state then shows $\langle\alpha\rangle^2$ to be a measure of the change in volume or the dilation of the network and hence $\langle\alpha\rangle^2$ is referred to as a dilation factor. Apart from these two useful introductions the derivation of equation (2.12) is very similar to the earlier derivations previously outlined and so will not be given here.

2. Modifications to Kinetic Theory

The comparison of the theoretical and experimental stress-strain curves shown in Figure 1.1 and discussed in section 8 of Chapter 1 indicate that the elementary kinetic theory gives a reasonable but not a perfect account of rubber like elasticity. The discrepancy between theory and experiment at large elongations may confidently be ascribed to the effects of the finite extensibility of real polymer chains but the discrepancy at fairly low elongations does not seem to be attributable to the neglect of any single factor in the development of the theory. Consideration of the model used in the Kinetic Theory

suggests that amongst possible contributing effects would be:

(a) An excluded volume effect due to the finite size of the chain segments;

(b) an extra entropy term due to the distribution of cross-links throughout the sample;

(c) due to the presence of crosslinks the entropy of a network may not be the same as that of the equivalent assembly of free chains;

(d) an extra term due to variation of the internal energy of chains with extension.

In addition Flory and Ciferri (18) have suggested that failure to attain equilibrium is the main cause of this discrepancy. These five factors will now be discussed in turn.

(a) Excluded volume effect

Di Marzio (12) states that the configurational entropy S of a network can be regarded as the sum of two components:

$$S = S_c + S_p \qquad (2.14)$$

where S_c is the entropy associated with the network chains when it is assumed, as in the kinetic theory, that the entropy is dependent only on the end-to-end distances of the corresponding assembly of free chains. S_p is the entropy of packing and arises from the competition for space between neighbouring chains. Thus this component has the effect of increasing the end-to-end distance to a value greater than

that of the identical but isolated chain and so decreasing the number of configurations available and decreasing the entropy. S_p is thus seen to be a negative quantity and its effect may be expected to decrease as the elongation of the chains increases. Di Marzio has calculated the value of S_p and its variation with chain elongation for a model in which the interchain segment bonds can lie only along the principal Cartesian axes and he shows that the effect of S_p is in fact reduced as chain orientation increases. Thus this effect will lead to a reduction of the retractive force below the value predicted by the simple Kinetic Theory. The use of this model is necessitated by the mathematical procedures available but Di Marzio justifies it by pointing out the analogy with the model used by James and Guth (35) to obtain a stress strain equation identical in form to the one obtained from a less restrictive model.

This theory depends only on entropy effects and so does not affect the validity of the linear relationship observed between the retractive force and the absolute temperature. Furthermore, it is to be expected that as swelling a network increases the separation between chains it will reduce the effect of competition for space between neighbouring chains and so any deviation from the Kinetic Theory predictions due to this effect will decrease as the elastomer is swollen. This is in agreement with the experimental evidence such as that of Gumbrell, Mullins and Rivlin (28), of Flory and Ciferri (18) and of Gee (22).

Quantitative comparison of the equation (2.15) finally derived from this theory with experimental evidence shows that the calculated correction term does in fact have the correct sign but is rather too small. Di Marzio considers that this is probably because the experimental observations were not made on systems in equilibrium. He dismisses by qualitative arguments the suggestion that a more exact network model could produce the required improvement, but this can only really be tested by the appropriate calculations.

$$f_p = \frac{kT\nu}{3}\left[2\alpha\left(1 + \frac{3\alpha^2}{n}\right)^{-\frac{1}{2}} + \frac{1}{\alpha^2}\left(1 + \frac{3}{n\alpha}\right)^{-\frac{1}{2}}\right] \ln\left[\frac{1 - \lambda}{1 - \frac{1}{2}(1 - \lambda)}\right] \qquad (2.15)$$

where f_p is the correction to the retractive force due to the entropy of packing;

n is the average number of links per chain

$$\lambda = \frac{1}{3} + \frac{2}{9}\left[\left(1 + \frac{3\alpha^2}{n}\right)^{\frac{1}{2}} - \left(1 - \frac{3}{n\alpha}\right)^{\frac{1}{2}}\right]$$

(b) Distribution of Crosslinks

All the early versions of the development of the kinetic theory implicitly regarded crosslinks as being fixed in space and hence the contribution to the total configurational entropy due to the possible distributions of the crosslinks was ignored. Kuhn and Grün (46) pointed out this omission and attempted to calculate the relevant quantity but Flory (14a) considers their result to be too large as they failed to allow for the necessity for chain ends to meet at a crosslink.

Flory (14a) recalculated the effect and derived the result:

$$S' = \frac{k\nu}{2} \ln V + \text{constant} \qquad (2.16)$$

where S' is the contribution to the entropy due to the distribution of $\frac{\nu}{2}$ crosslinks in a volume V. This equation is strictly valid only for tetra functional crosslinks and for any other type the quantity $\nu/2$ is replaced by $^{2}\nu/f$ where ν is the number of chains in the network and f the number of chains meeting at a crosslink.

This result has been generally accepted and shows that for deformations occurring at constant volume this factor does not contribute to the retractive force. Measurements of the volume changes associated with actual deformations of real rubbers by Gee, Stern and Treloar (24) and by Holt and McPherson (33) show that the change of volume is negligible hence this particular effect cannot make any appreciable contribution to the retractive force.

(c) Effect of crosslinks on chain entropy

This effect is quite distinct from that considered in section (b) but has something in common with Di Marzio's approach though it is not specifically mentioned by him. If competition for space between neighbouring chains results in a decrease in the number of configurations available to the chains, it may be expected that the confluence of several such chains at a single network junction point will restrict the number of configurations available to the end few segments even more severely. This must result in a further decrease in the number

of configurations available to the chains. Unfortunately the effect of this cannot be quantitatively assessed with present statistical techniques, but qualitative consideration indicates that the effect will become less pronounced as the chain orientation increases. Thus the effect on the retractive force should be qualitatively analogous to the packing effect discussed by Di Marzio and will have a similar effect on the retractive force. This effect, which is also a pure entropy of packing effect, may be one way in which the numerical value of Di Marzio's correction can be brought closer to the value required by the experimental evidence.

3. Effect of variations of Internal Energy with Extension

So far, discussion of the kinetic theory of elasticity has assumed that the origin of the retractive force is purely an entropy effect. This assumption was justified by the experimental results of workers such as Meyer and Ferri (50), Wiegand and Snyder (86) and Gee (22), all of which appeared to suggest that the variation of the internal energy on isothermal stretching at constant volume is zero. Reinterpretation of these results on the basis of more recent thermodynamic analysis to be discussed in Chapter 3 has shown that in fact variations in internal energy contribute about 20% of the total retractive force at moderately low extensions.

Efforts have been made to incorporate internal energy changes in models of polymer chains by several groups of workers including

Vol'kenstein and Ptitsyn (80), Krigbaum and Kaneko (43), Tobolsky, Carlson and Indictor (75), and Flory, Hoeve and Ciferri (19). These treatments will be discussed in turn.

(a) Volkenstein and Ptitsyn (80) obtained an expression for the configuration integral of a chain subjected to an external force f which may be written:

$$Z_f = \int \cdots \int \exp\left(\vec{r}\,\vec{f} - \epsilon\{l\} \right)/kT \; d\vec{l}_1 \cdots d\vec{l}_n \qquad (2.17)$$

where $\vec{l}_i$ and $d\vec{l}_i$ represent the i^{th} bond vector and its differential, $\epsilon\{l\}$ is the potential energy for the particular configuration represented by the set of bond vectors $\{l\}$ and $\vec{r}$ is the end to end distance vector.

For a chain with a specified end-to-end length vector $\vec{r}$ Volkenstein and Ptitsyn obtain the intrgral:

$$Z_r d\vec{r} = \int_r \cdots \int \exp(-\epsilon\{l\}/kT) \; d\vec{l}_1 \cdots d\vec{l}_n \qquad (2.18)$$

and showed that Z_f and Z_r are related by the equation:

$$Z_f = \int Z_r \exp\left(\vec{r}\,\vec{f}/kT \right) d\vec{r} \qquad (2.19)$$

unfortunately Z_f can be evaluated for only very simple models such as the freely jointed random chain whilst Z_r has not been evaluated for any model at all.

However, the probability distribution $W_o(r)$ for the unperturbed chain, i.e. where f = 0, may be expressed by:

$$W_o(r) = 4\pi r^2 Z_r/Z_o \qquad (2.20)$$

and by substituting equation (2.20) into (2.19) Z_f can be obtained as a function of Z_o:

$$Z_f = Z_o \overline{(rf/kT)^{-1} \sinh(rf/kT)} \qquad (2.21)$$

where according to custom the bar denotes an average value of the appropriate function. This average is taken, in this case, over the unperturbed distribution.

Volkenstein and Ptitsyn then used equation (2.21) to obtain the power series:

$$\langle \vec{r}_f \rangle = (f/kT)(\overline{r_o^2}/3) + (f/kT)^3 \left[\overline{r_o^4}/30 - (\overline{r_o^2})^2/18 \right] + \ldots . \qquad (2.22)$$

where $\langle \vec{r}_f \rangle$ denotes the avergge value of the vector $\vec{r}$ in the direction of the applied force. The first term of this equation is identical with that obtained from classical kinetic theory, hence Volkenstein's treatment corresponds to the evaluation of a correction term to this simple theory. Unfortunately no evidence has so far been produced to allow the value of equation (2.22) to be assessed.

(b) Krigbaum and Kaneko used a cubic lattice model in which the sequence of successive links is always for example $x \rightarrow y \rightarrow z \rightarrow x \rightarrow y \rightarrow z$ where x, y and z are the Cartesian axes of the lattice. Thus any individual link has only two choices of direction (say) +x or -x. For a chain of N links there will be N/3 links along each axis and those along the x axis may be numbered $x_1, x_2 \ldots . x_i \ldots . x_{N/3}$ and similarly for the links along the y and

z axes. The transition $x_i \rightarrow x_{i+1}$ is then equivalent to the same transition in a one dimensional chain save that 3 steps are involved instead of one. Krigbaum and Kaneko were able to show that this particular model is mathematically equivalent to three one-dimensional chains and in consequence the partition function Z_f, for a fixed extending force f, is given by:

$$Z_f = Z_{f_x} Z_{f_y} Z_{f_z} \tag{2.23}$$

where Z_{f_x} etc. are the corresponding partition functions for the one dimensional chains. Similarly the partition function Z_r for a fixed end to end length r is given by:

$$Z_r = Z_{r_x} Z_{r_y} Z_{r_z} \tag{2.24}$$

and as these partition functions for the one dimensional chains had been already evaluated the results for the cubic lattice model were immediately available. The network model postulated by Wang and Guth (85) for non-Gaussian chains was then used to derive expressions for the change in free energy on stretching and hence the stress-strain equations. The reference state chosen by Krigbaum and Kaneko is identical to that used by Flory, Hoeve and Ciferri (19). The material in this reference state is considered to be isotropic and to have a volume V_o such that the mean square end-to-end length of the network chains is the same as the mean square end-to-end length $\overline{r_o^2}$ of the same set of chains in an uncrosslinked state. The network postulated by Krigbaum and Kaneko also has all its chains of the same length having N

links of length b. For this network the equation derived for the change of free energy with deformation is:

$$\Delta F = \nu kT\left[\left(\frac{V}{V_o}\right)^{\frac{2}{3}}\frac{I_1}{2} + \frac{9}{40N}\left(\frac{V}{V_o}\right)^{\frac{4}{3}}(3e^{2K} - e^{-2K})(I_1^2 - \frac{4}{3}I_2) + \frac{27}{112N^2}\left(\frac{V}{V_o}\right)^{2}(15e^{4K} - 10 + 3e^{-4K})(I_1^3 - \frac{12}{5}I_1I_2) + \ldots.\right] \quad (2.25)$$

where ν is the number of chains in the lattice, I_1 and I_2 are the Rivlin strain invariants (Chapter 1, section 8a), and $K = \frac{\Delta\epsilon}{2kT}$. $\Delta\epsilon$ is the difference in energy between the two possible choices for the positioning of any link on the lattice. V is the volume of the strained sample.

From this equation, Krigbaum and Kaneko derived:

$$f = \nu kT \frac{V^{\frac{1}{3}}}{V_o^{\frac{2}{3}}}(\alpha - \alpha^{-2})\,Q \quad (2.26)$$

for simple elongation. f is the retractive force, α the extension ratio and Q a function:

$$Q = \left[1 + \frac{9}{10N}\left(\frac{V}{V_o}\right)^{\frac{2}{3}}(3e^{2K} - e^{-2K})(\alpha^2 + \frac{4}{3\alpha}) + \frac{81}{56N^2}\left(\frac{V}{V_o}\right)^{\frac{4}{3}}(15e^{4K} - 10 + 3e^{-4K})(\alpha^4 + \frac{8\alpha}{5} + \frac{8}{5\alpha}) + \ldots..\right] \quad (2.27)$$

where the various quantities have the same meaning as in equation (2.25). Equation (2.26) is seen to be simply the simple Kinetic theory equation modified by the factor Q which contains the energy dependent terms.

Comparison with Experiment

Equation (2.26) has been evaluated by its authors for a range of values of α and several values of K using suitable values of ν, N and V/V_o. They found that when K = +1 or 0 the calculated values of the retractive force f are higher than the values calculated from the kinetic theory equation for all values of α. When K = -1 however the values of f for the cubic lattice model are lower than those from the kinetic theory in the range $\alpha = 1.5 \rightarrow 4$. Thus when K = -1 the shape of the stress strain curve is very similar to that of the experimental curve of Figure 1.1. Negative values of K indicate that coiled configurations are energetically preferred to more extended configurations and thus the process of stretching is opposed by both the entropy and the internal energy effects. Ciferri (10) has recently shown that the variation of $\overrightarrow{r_o^2}$ with temperature indicates that coiled configurations are preferred both for natural rubber and for polydimethyl siloxane. Unfortunately the value of K calculated from Ciferri's results is numerically smaller by one order of magnitude than the value predicted by the cubic lattice treatment.

Krigbaum and Kaneko consider that the extensive simplifications involved in the cubic lattice treatment may be largely responsible for this lack of quantitative agreement and it should be interesting to see a similar treatment for a more realistic model.

(c) Tobolsky, Carlson and Indictor (75) used a one dimensional chain as a model to derive an equation incorporating internal energy

effects. They point out that though this model is apparently very artificial it can be regarded as the projection along a major axis of a three dimensional chain. Scott and Tobolsky (72) had previously shown that the one dimensional chain corresponds to a polymethylene chain where the trans and gauch configurations have unequal energies. The model used consists simply of a chain of N links of length b where any link may be in the same direction or the opposite direction as its predecessor. The difference in energy between these possibilities is $\Delta\epsilon$ and as in Krigbaum's model the more negative energy is associated with two successive links pointing in opposite directions. Tobolsky et al. derive an equation:

$$f_c = k\,T\,e^{-2K(1/Nr^2)} \qquad (2.28)$$

where f_c is the force required to maintain the chain at a length l and K is again $\frac{\Delta\epsilon}{2kT}$.

Incorporating this result into a network of ν such chains and assuming affine deformation of the crosslinks, Tobolsky et al. were able to derive:

$$f = \frac{\psi}{e^{2K}}\,\nu\,kT(\alpha - \alpha^{-2}) \qquad (2.29)$$

where ψ is the quantity introduced in section 7 of Chapter 1 as the ratio of the mean square end to end distances of the same set of chains in the presence and absence of cross linkages. Equation (2.29) differs from the equation derived by Tobolsky (72) for a network without any internal energy changes only by the factor $\frac{1}{e^{2K}}$.

In this respect his conclusion is analogous to that of Krigbaum and Kaneko though the latter obtain a more complicated modification factor.

Tobolsky et al. used equation (2.29) to analyse the stress strain data for a number of polyacrylate and methacrylate esters but contented themselves with showing that the factor $\Psi/\exp(2K)$ is not unity even when $K = 0$. They do not give enough evidence to allow an assessment of the value of equation (2.29) as a stress strain relationship. However if K is constant for different extensions of any given polymer, then the term $1/\exp(2K)$ is also constant and the retractive force calculated from this equation will always be greater or always smaller than the force calculated from the simple kinetic theory. In no case can this equation lead to the variation of the retractive force with extension required by the experimental curve of Figure 1.1.

(d) Flory, Hoeve and Ciferri (19) start by accepting the expressions of Vol'kenstein and Ptitsyn (80) for the configuration integrals for a chain subjected to a specified force $\vec{f}(Z_{\vec{f}})$ and for a chain with a specified end to end length $\vec{r}(Z_{\vec{r}})$ but point out that $Z_{\vec{f}}$ and $Z_{\vec{r}}$ cannot be calculated for real polymer chains with specified bond angles and lengths and with potential barriers hindering free rotation about the chain bonds. Thus the calculation of the probability of finding a chain with any end to end length $\vec{r}$ under the action of a force $\vec{f}$ cannot be rigorously derived since the

probability distribution $W_f(\vec{r})$ is given by:

$$W_f(\vec{r}) = \frac{Z_{\vec{r}}}{Z_f} \exp\left(\frac{\vec{r}\,\vec{f}}{kT}\right) \qquad (2.30)$$

However the basis of the 'Equivalent Random Chain' first suggested by Kuhn (44) is the idea that any chain will obey gaussian distribution if the total length is long compared with the end to end length. This has since been confirmed by Tchen (73a) by rigorous analysis and by Treloar (78) by numerical calculations for chains where the end-to-end length is not greater than 0.5 times the overall length. Thus the gaussian distribution should be valid for any real chains at reasonably low extensions and certainly should be valid for natural rubber at extensions of less than 400%. It is hardly surprising that after reaching this conclusion Flory et al. then derive the same expressions for the elastic free energy and for the retractive force as were derived earlier by Flory (17) for networks whose elasticity was considered to be due only to changes in configurational entropy. For the case of simple extension the stress-strain equation is given by equation (2.12):

$$f = \frac{\nu kT}{l_i} \langle\alpha\rangle^2 (\alpha - \alpha^{-2}) \qquad (2.12)$$

The contribution f_e to the total retractive force f due to internal energy changes is given by equation (1.10):

$$f_e = \left(\frac{\partial U}{\partial l}\right)_{VT} = f - T\left(\frac{\partial f}{\partial T}\right)_{Vl} \qquad (1.10)$$

which may be rewritten:

$$f_e = f\,T\left[\frac{\partial \ln (f/T)}{\partial T}\right]_{V1} \qquad (2.31)$$

Differentiation of equation (2.12) in this way yields:

$$f_e = f\,T\left[\frac{\partial \ln \langle\alpha\rangle^2}{\partial T}\right]_{V1} \qquad (2.32)$$

The definition of $\langle\alpha\rangle^2$ as $\overline{r_i^2} / \overline{r_o^2}$ clearly shows that $\langle\alpha\rangle^2$ will depend on T in the same way as $\overline{r_o^2}$ since at constant volume $\overline{r_i^2}$ is constant, hence:

$$f_e = f\,T\left[\frac{\partial \ln \overline{r_o^2}}{\partial T}\right] \qquad (2.33)$$

This equation relates the energy contribution to the retractive force with the temperature coefficient of the unperturbed end to end length and as this quantity can be obtained (1) from viscosity studies on dilute solutions of polymers, a useful independent check on elasticity theory is available. A comparison of values of $\partial \ln \overline{r_o^2} / \partial T$ obtained in these two distinct ways is given later in this section (Table 2.1).

A further advantage of equation (2.33) is that it allows evaluation of the energy difference $\Delta\epsilon$ between the trans and gauche rotational isomers of simple chains such as polymethylene or linear polyethylene. Flory et al. calculate $\Delta\epsilon$ for a sample of polyethylene cross linked by γ-radiation and obtain good agreement between the values at several extensions up to 100%. The average of their

values is 540 ± 100 cals. per mole which is in quite good agreement with the values of 520 ± 70 and 450 ± 60 cals./mole obtained for n-hexane and n-pentane respectively by Sheppard and Szasz (72a) from Raman spectroscopy studies and also with the value of 700-800 cals./mole obtained for uncrosslinked polyethylene by Novak (56a) from infrared spectroscopy.

The crucial step in this treatment is the adoption of Tchen's result that any chain, if sufficiently long, will obey gaussian statistics. It can hardly be disputed that this will be true for chains having some potential barrier to rotations between rotational isomers of equal or approximately equal energies, but it need not be true for chains of finite length with large energy differences between rotational isomers. Unfortunately, Tchen makes no estimate of what constitutes a sufficiently long chain and Treloar's numerical calculations do not involve consideration of rotational isomers of different energies.

Consider two chains, A and B, which are identical except that in chain A the gauche isomer is more stable by an amount of energy $\Delta\epsilon$ whilst in chain B the trans isomer is more stable by the same amount. As the value of $\Delta\epsilon$ increases, the fraction of units in the more stable isomer will also increase according to equation (2.34):

$$n_o = n \exp \Delta\epsilon/kT \qquad (2.34)$$

where n is the number of units in the less stable and n_o the number

of units in the more stable configuration. For chain A this means that the number of links in the more coiled gauche configuration will increase and the chain will become more tightly coiled. This is clearly equivalent to reducing the length of the 'equivalent random link'. For chain B however, the more extended trans isomer will become increasingly predominant with a resulting increase in the end to end distance, i.e. the length of the equivalent random link will be increased. As the length of the equivalent random link increases the number of such links in a chain of finite length must decrease. Treloar's calculations have already shown that a chain with a small number of links does not obey gaussian statistics. This qualitative argument suggests that the treatment of Flory et al. may be inapplicable to polymers in which the trans isomer is too heavily favoured, but the question of what is meant by 'too heavily favoured' must be left open, perhaps until sufficient experimental evidence on a variety of polymers covering a range of values of $\Delta\epsilon$ is available. This restriction is, of course, additional to the restriction specified by Flory et al. that the change of energy on stretching should be due only to intra-molecular interactions.

The difficulty in calculating values of $\Delta\epsilon$ from the elasticity measurements for any but very simple chains means that the easiest method of verifying this treatment is to compare the values of $\frac{\partial \ln(\bar{r_o^2})}{\partial T}$ obtained from elasticity measurements with values obtained by other independent methods such as dilute solution

viscometry. A comparison of some of the reported values is given in Table 2.1.

Comparison with Experiment

The stress-strain equation derived in this treatment (eqn. 2.12) is identical with that derived in the simple kinetic theory and so cannot give a better representation of the experimental evidence. However the theory also gives a relationship between the temperature coefficient of the unperturbed mean square end to end distance $(\partial \ln \bar{r}_o^2 / \partial T)$ and the temperature coefficient of the retractive force $\left[\frac{\partial \ln (f/T)}{\partial T}\right]_{Vl}$. In the original development of their theory Flory, Hoeve and Ciferri used the equation:

$$\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{Vl} = \left[\frac{\partial \ln(f/T)}{\partial T}\right]_{P\alpha} \qquad (2.35)$$

which Flory (20) has since shown should be replaced by:

$$\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{Vl} = \left[\frac{\partial \ln(f/T)}{\partial T}\right]_{Pl} + \frac{3\lambda}{\alpha^3 - 1} \qquad (2.36)$$

where λ is the linear coefficient of thermal expansion of the polymer. The origins of these two equations will be discussed in Chapter 3, but meanwhile the results quoted in support of this treatment will be calculated on the basis of equation (2.36).

The theory of Flory, Hoeve and Ciferri does not evaluate theoretical values for the quantity $\partial \ln \bar{r}_o^2 / \partial T$ and in fact Ciferri (8) shows that the value and even the sign will depend on the

precise nature of the individual polymer. Some idea of the validity of the theory, however, can be obtained by comparing the values of $\partial \ln \overline{r_o^2} / \partial T$ calculated from elasticity measurements with those obtained by dilute solution viscometry on the uncrosslinked polymer. Some of the values so far published are collected in Table 2.1.

Table 2.1

Comparison of values of $\partial \ln \overline{r_o^2} / \partial T$ from network elasticity and from dilute solution viscometry

Polymer	$\partial \ln \overline{r_o^2} / \partial T$ Network Elasticity	Dilute Solution	Reference
Natural Rubber	0.55		(10)
Swollen Natural Rubber	0.56		(10)
Natural Rubber	0.41 ± 0.04		(11)
Polyethylene	-0.97 ± 0.1		(11)
Polyisobutylene	-0.08 ± 0.06	+1.1 ± 0.5	(11)
Polydimethylsiloxane	0.45 ± 0.15	0.33 ± 0.05	(9)

As positive values of $\frac{\partial \ln \overline{r_o^2}}{\partial T}$ indicate the trans isomer to have the higher potential energy these results are rather inconclusive. The poor correlation in the values for polyisobutylene may be explained if this polymer had a large value of $\Delta\epsilon$ so that the theory does not apply. However polyethylene would seem to have an even heavier favouring of the trans isomer and the values of $\Delta\epsilon$ deduced are in good agreement with those obtained from spectroscopy. Flory himself (11) attributed the lack of correlation to the low accuracy of the solutiom measurements and this, though not very satisfactory, may well be the case.

CHAPTER 3

Thermodynamic Analysis

The outline of the basic thermodynamics of rubber elasticity given in section 3 of Chapter 1 indicated that the retractive force may be divided into an entropy component and an internal energy component. It was also shown that these two components may each be evaluated from a knowledge of the quantity $(\partial f/\partial T)_{l.V}$. A similar analysis would indicate that the quantity $(\partial f/\partial T)_{lP}$ may be used to evaluate the entropy and enthalpy components $(\partial S/\partial l)_{P.T}$ and $(\partial H/\partial l)_{PT}$. Though $(\partial f/\partial T)_{lP}$ is much more easily measured than the corresponding coefficient at constant volume, the resulting thermodynamic quantities do not offer so good an insight into the molecular processes involved in rubber elasticity. Hence it has become customary to derive the thermodynamic quantities $(\partial S/\partial l)_{T.V.}$ and $(\partial U/\partial l)_{T.V}$ from the experimentally accessible quantity $(\partial f/\partial T)_{l.P}$ by the use of suitable relationships. The development of the three most important relationships due to (a) Elliott and Lippmann, (b) Gee, and (c) Flory, and a discussion of the assumptions made in their derivation is the subject of this chapter.

1. Elliott and Lippmann's Analysis (13)

It is clear that the required thermodynamic quantities may be calcuated either by correcting the measured $(\partial f/\partial T)_{lP}$ to give $(\partial f/\partial T)_{lV}$ or by calculating $(\partial U/\partial l)_{TP}$ and $(\partial S/\partial l)_{TP}$ and then

applying a suitable correction to give the corresponding constant volume coefficients. Elliott and Lippmann adopted the latter approach and confined their attention to the evaluation of $(\partial U/\partial l)_{T.V.}$.

Starting with the standard thermodynamic identity:

$$\left(\frac{\partial U}{\partial l}\right)_{T.V} = \left(\frac{\partial U}{\partial l}\right)_{TP} + \left(\frac{\partial U}{\partial P}\right)_{Tl}\left(\frac{\partial P}{\partial l}\right)_{TV} \tag{3.1}$$

Elliott and Lippman expanded the terms on the right hand side according to equations (3.2) to (3.4):

$$\left(\frac{\partial U}{\partial l}\right)_{TP} = f - T\left(\frac{\partial f}{\partial T}\right)_{Pl} - P\left(\frac{\partial V}{\partial l}\right)_{TP} \tag{3.2}$$

$$\left(\frac{\partial U}{\partial P}\right)_{Tl} = -P\left(\frac{\partial V}{\partial P}\right)_{Tl} - T\left(\frac{\partial V}{\partial T}\right)_{Pl} \tag{3.3}$$

$$\left(\frac{\partial P}{\partial l}\right)_{TV} \backsimeq \frac{MA}{3V} \quad \text{provided} \quad \frac{YA^2}{K} \gg 9 \tag{3.4}$$

The quantities M, K and Y are moduli defined by equations (3.5):

$$\left.\begin{array}{lll} \text{Stress-strain modulus} & M = l\left(\frac{\partial f}{\partial l}\right)_{PT} \\ \text{Bulk modulus} & K = -V\left(\frac{\partial P}{\partial V}\right)_{fT} \\ \text{Young's Modulus} & Y = \frac{Ml}{V} \end{array}\right\} \tag{3.5}$$

and A is an anisotropy factor defined by equation (3.6):

$$A = \frac{3V}{l}\left(\frac{\partial l}{\partial V}\right)_{fT} \tag{3.6}$$

Two coefficients of thermal expansion β_1 and β_2 defined by equations (3.7) and (3.8)

$$\beta_1 = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_{Pl} \qquad (3.7)$$

$$\beta_2 = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_{PD} \qquad (3.8)$$

were also used. D, the deformation, is the ratio of two perpendicular lengths, one parallel to the direction of elongation. Elliott and Lippmann then showed that when $\frac{YA}{K} \ll 9$ these two thermal expansion coefficients are approximately equal. For rubbery materials Y/K varies between 10^{-3} and 10^{-4} so that the conditions $\frac{YA}{K} \ll 9$ and $\frac{YA^2}{K} \ll 9$ are both satisfied unless $A \gg 10$.

The exact value of A is difficult to determine but it was shown (13) to be unity for an isotropic material such as unstrained rubber and the value decreases as the anisotropy increases. Thus A is never greater than unity and the equivalence of β_1 and β_2 and the validity of equation (2.4) may be regarded as established.

Combination of equations (3.1) to (3.8) gives equation (3.9):

$$\left(\frac{\partial U}{\partial l}\right)_{TV} = f - T\left(\frac{\partial f}{\partial T}\right)_{Pl} - MAT\beta_2 \qquad (3.9)$$

which Elliott and Lippmann used to re-evaluate the results obtained by Meyer and Ferri (50) assuming that A = 1 for the deformations used. In this way they showed that for extensions up to 166% in natural rubber, the energy component $(\partial U/\partial l)_{TV}$ is zero. These authors pointed out that this conclusion indicates that changes in valence angles do not contribute to either the elastic stored energy or to the mechanism of deformation. Meyer and Ferri (50) in their

paper had suggested the criterion $(\partial U/\partial l)_{TP} = 0$ as the definition of an 'ideal' rubber but in view of their own analysis Elliott and Lippmann suggested that $(\partial U/\partial l)_{TV} = 0$ would be better. This suggestion was later supported by both Gee (23) and by Flory (20).

2. Gee's Analysis (23)

Shortly after the publication of their analysis by Elliott and Lippmann, Gee published a rather different analysis of the same problem which, however, gave substantially the same results as Elliott and Lippmann's.

The analogue of equation (1.10) for constant pressure conditions may be written:

$$\left(\frac{\partial H}{\partial l}\right)_{TP} = f - T\left(\frac{\partial f}{\partial T}\right)_{lP} \qquad (3.10)$$

then combination of equations (1.10) and (3.10) gives:

$$\left(\frac{\partial H}{\partial l}\right)_{TP} - \left(\frac{\partial U}{\partial l}\right)_{TV} = T\left[\left(\frac{\partial f}{\partial T}\right)_{Vl} - \left(\frac{\partial f}{\partial T}\right)_{Pl}\right] \qquad (3.11)$$

leading to the identity of equation (3.12):

$$\left(\frac{\partial H}{\partial l}\right)_{TP} - \left(\frac{\partial U}{\partial l}\right)_{TV} = \frac{T\left(\frac{\partial f}{\partial l}\right)_{PT}\left(\frac{\partial l}{\partial V}\right)_{fT}\left(\frac{\partial V}{\partial T}\right)_{Pl}\left(\frac{\partial V}{\partial P}\right)_{fT}}{\left(\frac{\partial V}{\partial P}\right)_{lT}} \qquad (3.12)$$

Though equation (3.12) is exact not all the coefficients on the right hand side are readily measurable so Gee had to make a number of assumptions in order to simplify the relationship. These assumptions may

conveniently be expressed as equations (3.13) - (3.15):

$$\left(\frac{\partial \frac{1}{V}}{\partial f}\right)_{fT} = \frac{1}{3V} \tag{3.13}$$

$$\left(\frac{\partial \frac{V}{P}}{\partial f}\right)_{fT} = \left(\frac{\partial V}{\partial P}\right)_{lT} \tag{3.14}$$

$$\left(\frac{\partial \frac{V}{T}}{\partial f}\right)_{Pl} = 3\beta V \tag{3.15}$$

where $$\beta = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_{P,f=0}$$

Equation (3.13) implies that the stretched rubber is isotropic in its response to compression. In fact this is strictly true only for unstretched rubber and $\frac{1}{3V}$ is the limiting value of $(\partial l/\partial V)_{f,T}$ as $f \rightarrow 0$. For an anisotropic material the value of $(\partial l/\partial V)_{fT}$ is less than this limiting value.

Equation (3.15) implies that the volume coefficient of thermal expansion is the same for stretched as for unstretched rubber. If this assumption is valid then the quantity β defined by Gee is identical with the β_1 defined by Elliott and Lippmann.

Equation (3.14) is a consequence of Gee's demonstration that the retractive force f is almost independent of V when the length and temperature of the sample are held constant.

Combination of equation (3.12) with (3.13) to (3.15) gives:

$$\left(\frac{\partial H}{\partial l}\right)_{PT} - \left(\frac{\partial U}{\partial l}\right)_{VT} = \beta l T\left(\frac{\partial f}{\partial l}\right)_{PT} \tag{3.16}$$

Defining the extension ratio α as l/l_o the ratio of the stretched to

the unstretched length at a temperature T then from the properties of partial differentials:

$$\left(\frac{\partial \frac{f}{T}}{\partial T}\right)_{P\alpha} = \left(\frac{\partial \frac{f}{T}}{\partial T}\right)_{Pl} + \left(\frac{\partial \frac{f}{T}}{\partial l}\right)_{PT}\left(\frac{\partial \frac{l}{T}}{\partial T}\right)_{P\alpha} \Bigg\} \qquad (3.17)$$

and $$\left(\frac{\partial \frac{f}{T}}{\partial T}\right)_{P\alpha} = \alpha\left(\frac{\partial \frac{l_o}{T}}{\partial T}\right)_{P\alpha} = \beta\, l$$

Thus combination of equations (3.16) and (3.17) gives:

$$\left(\frac{\partial \frac{H}{T}}{\partial l}\right)_{PT} - \left(\frac{\partial U}{\partial l}\right)_{VT} = T\left[\left(\frac{\partial \frac{f}{T}}{\partial T}\right)_{P\alpha} - \left(\frac{\partial \frac{f}{T}}{\partial T}\right)_{Pl}\right] \qquad (3.18)$$

Comparison of equations (3.11) and (3.18) shows that this analysis implies the identity expressed in equation (3.19):

$$\left(\frac{\partial \frac{f}{T}}{\partial T}\right)_{lV} = \left(\frac{\partial \frac{f}{T}}{\partial T}\right)_{P\alpha} \qquad (3.19)$$

Thus the validity of this identity which has been widely used by most workers in this field, rests on the validity of the assumptions expressed in equations (3.13) to (3.15).

In his own discussion of the validity of these assumptions Gee points out that equation (3.13) is equivalent to Elliott and Lippmann's assumption that A = 1 and is similarly valid only for infinitessimally small deformations. The third approximation expressed in equation (2.15) is justified by the experimental data of Holt and McPherson (33) for natural rubber which showed a negligible variation of $(\partial V/\partial T)_{Pl}$ with extension ratio for extensions of up to 100%.

To examine the validity of the approximation expressed in

equation (3.14), Gee considered the effect of applying a hydrostatic pressure P to a strip of rubber whose volume had increased from V_o to $V_o + \Delta V$ when the rubber was stretched from l_o to l. P is the pressure required to compress the sample to the original volume V_o whilst the tensile force is increased to maintain the length constant at l. The increase in the tensile force is then given by equation (3.20):

$$\Delta f = -\left(\frac{\partial f}{\partial V}\right)_{l,T} \Delta V = \left(\frac{\partial f}{\partial l}\right)_{V,T} \left(\frac{\partial l}{\partial V}\right)_{fT} \Delta V \qquad (3.20)$$

For infinitessimally small extensions $(\partial f/\partial l)_{VT} = (\partial f/\partial l)_{PT}$ and $(\partial l/\partial V)_{fT} = \frac{l}{3V}$ so that:

$$f = \left(\frac{\partial f}{\partial l}\right)_{PT} \frac{l}{3} \frac{\Delta V}{V} \qquad (3.21)$$

Using values of $(\partial f/\partial l)_{PT}$ obtained by Gee and of $\frac{\Delta V}{V}$ obtained by Holt and McPherson, Gee then showed that $\frac{f}{\Delta f}$ for natural rubber is about 0.007. Thus Δf may be regarded as negligible and the value of f may be considered to be independent of whether the extension occurs at constant pressure or constant volume.

From this independence of f on V at constant l, it follows that the quantities $(\partial V/\partial P)_{Tf}$ and $(\partial V/\partial P)_{Tl}$ are identical as required by equation (3.14). Further the same independence is seen to be the assumption made in obtaining equation (3.11) and consideration of this equation indicates that the tensile force is independent of the volume if the change of energy with volume is balanced by a change in the entropy. This change of entropy on dilation is due to the increase

in the number of configurations made possible by an increase in the volume of the sample.

Analysis of his own experimental results using equation (3.19) to evaluate $(\partial f/\partial T)_{lV}$ led Gee to conclude, as had Elliott and Lippmann, that $(\partial U/\partial l)_{VT} = 0$.

As was originally indicated by the respective authors, the analyses of Elliott and Lippmann and of Gee are applicable only at infinitessimally small strains when their assumptions are valid. A more remarkable feature of Gee's analysis is his demonstration that the retractive force f in a piece of deformed rubber is independent of the volume of the rubber. Though the explanation of this is reasonable it is difficult to reconcile this result with the accepted non-equality of the quantities $(\partial f/\partial T)_{lV}$ and $(\partial f/\partial T)_{lP}$.

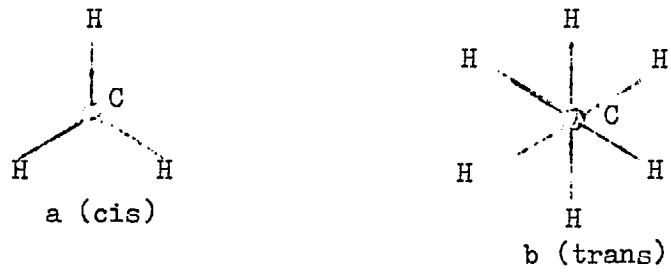
Despite these drawbacks the simplicity of equation (3.19) led to its general acceptance and an independent proof was given by Flory in his classic textbook (1). A further advantage of these two analyses was their support of the basic assumption of the Kinetic Theory by indicating that, at least for natural rubber, $(\partial U/\partial l)_{VT} = 0$.

3. More recent Thermodynamics

However, though this result is essential to justify the kinetic theory of elasticity, more recent studies (16) of dilute solution properties of polymers have indicated that in general, the mean square end to end distance $\overline{r_o^2}$ of a polymer chain is temperature dependent.

Volkenstein and Ptitsyn (80) have shown that this implies a dependence of the internal energy of the chain on its end to end length and this is turn implies that for a network of such chains the internal excess will be dependent on the extension. Taylor (73) has suggested that this effect may be due to different rotational isomers being associated with different potential energies.

A consideration of the rotation of one methyl group in ethane with respect to the other and about the carbon-carbon bond, shows that there are three positions in which interference of the hydrogen atoms is maximised and three positions in which it is minimised. This is illustrated in Figure 3.1. As the molecule is symmetrical about the



Diagrammatic view of ethane molecule viewed along the carbon-carbon bond.

Figure 3.1

carbon-carbon bond the three positions giving maximum interference are indistinguishable as are the three positions giving minimum interference. The variation of the potential energy, $V(\phi)$ with the angle

of rotation ϕ for ethane is shown in Figure 3.2a. ϕ is taken as zero at any potential minimum and $V(\phi) = 0$ when $\phi = 0$. For a less symmetrical molecule than ethane the three potential minima need not have the same value of $V(\phi)$. Possible forms are shown in Figure 3.2 b, c and d. When all three minima are unequal as in Figure 3.2d the absolute minimum may or may not be at $\phi = 0$. It should be emphasised that steric interference is not the only cause of variations in $V(\phi)$ with ϕ but has simply been chosen as giving a readily illustrated model.

It has been shown (73a) that neither the existence of potential barriers nor of a temperature dependent $\overline{r_o^2}$ will prevent a sufficiently long chain from showing a Gaussian distribution of end to end distances. Flory (19) has based his derivation of a stress strain equation for a network of chains whose energy depends on their end to end lengths (non iso-energetic chains) which is identical with that obtained for isoenergetic chains on this point. The validity of this procedure has been discussed in section 6d of Chapter 2. However, having shown that his stress strain equation is valid for non-energetic chains, Flory (20) has been able to use the kinetic theory to develop interesting relationships between $(\partial f/\partial T)_{Pl}$, $(\partial f/\partial T)_{P:}$ and $(\partial f/\partial T)_{Vl}$. The derivation of these relationships is discussed in the next section.

4. Flory's Thermodynamic Analysis (20)

Like both Elliott and Lippmann, and Gee, Flory starts from a

Variation of $V(\psi)$ with ψ

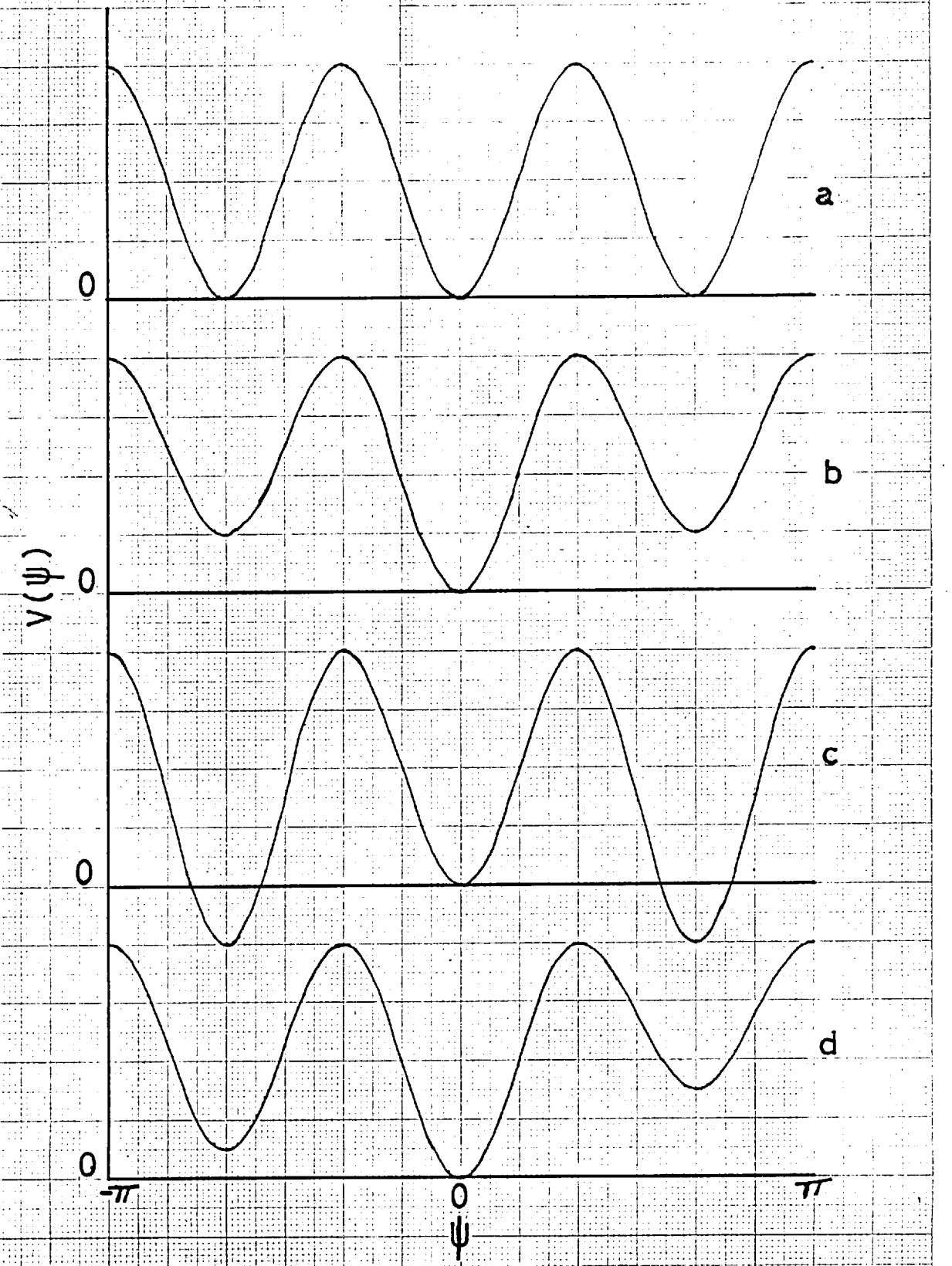


Figure 3·2

standard partial differential identity in this case the one given in as equation (3.22):

$$\left(\frac{\partial f}{\partial T}\right)_{Pl} = \left(\frac{\partial f}{\partial T}\right)_{Vl} - \left(\frac{\partial P}{\partial T}\right)_{Vl}\left(\frac{\partial V}{\partial l}\right)_{TP} \qquad (3.22)$$

and defines a set of moduli as in equations (3.23) - (3.26):

dilation coefficient $$\eta = \frac{l}{V}\left(\frac{\partial V}{\partial l}\right)_{TP} = \left(\frac{\partial \ln V}{\partial \ln l}\right)_{TP} \qquad (3.23)$$

compressibility $$K_l = -\frac{l}{V}\left(\frac{\partial V}{\partial P}\right)_{Tl} \qquad (3.24)$$

thermal expansion $$\beta_l = \frac{l}{V}\left(\frac{\partial V}{\partial T}\right)_{Pl} \qquad (3.25)$$

stress-strain modulus $$M = \frac{l^2}{V}\left(\frac{\partial f}{\partial l}\right)_{TV} = \frac{\alpha l}{V}\left(\frac{\partial f}{\partial \alpha}\right)_{TV} \qquad (3.26)$$

then substitution of equations (3.23) - (3.25) into (3.22) gives:

$$\left(\frac{\partial f}{\partial T}\right)_{P,l} = \left(\frac{\partial f}{\partial T}\right)_{Vl} - \frac{V\eta\beta_l}{l K_l} \qquad (3.27)$$

Similarly, starting from the equation (3.28) connecting $(\partial f/\partial T)_{P\alpha}$ with $(\partial f/\partial T)_{Vl}$,

$$\left(\frac{\partial f}{\partial T}\right)_{P\alpha} = \left(\frac{\partial f}{\partial T}\right)_{Vl} + \left(\frac{\partial f}{\partial V}\right)_{T\alpha}\left(\frac{\partial V}{\partial T}\right)_{P\alpha} \qquad (3.28)$$

substitution of equations (3.23) - (3.26) leads to:

$$\left(\frac{\partial f}{\partial T}\right)_{P\alpha} = \left(\frac{\partial f}{\partial T}\right)_{Vl} + \frac{V\beta_\alpha}{l}\left(\frac{M}{3} - \frac{\eta}{K_l}\right) \qquad (3.29)$$

where $$\beta_\alpha = \frac{l}{V}\left(\frac{\partial V}{\partial T}\right)_{P\alpha} = \frac{\beta_l}{(1 - \eta/3)} \simeq \beta_l$$

Thus Gee's suggestion that $(\partial f/\partial T)_{P\ell} = (\partial f/\partial T)_{Vl}$ is true only if $\frac{M}{3} = \frac{\eta}{K_1}$. Flory showed that this identity holds for infinitessimally small strains since from the classical theory of elasticity for isotropic solids the application of a tensile stress t must be accompanied by an increase in the hydrostatic pressure $\Delta P = \frac{t}{3}$ if the volume is to be kept constant. Since t = fl/V, then:

$$\left(\frac{\partial P}{\partial f}\right)_{TV} = \frac{l}{3V} \qquad (3.30)$$

Rewriting equation (3.23) as:

$$\eta = -\frac{l}{V}\left(\frac{\partial V}{\partial P}\right)_{Tl}\left(\frac{\partial P}{\partial l}\right)_{TV} \qquad (3.31)$$

and substituting equations (3.24), (3.26) and (3.30) into (3.31) gives: $\eta = \frac{MK_1}{3}$. Thus the identity $(\partial f/\partial T)_{P\alpha} = (\partial f/\partial T)_{Vl}$ is valid over the range of applicability of the classical theory of elasticity.

In order to reduce equations (3.27) and (3.29) to more useful expressions without losing their general applicability, Flory then introduced some of the relationships given by the Kinetic Theory. This procedure is justified to some extent by Flory (19) having previously shown that the form of the stress strain equation is the same for both iso-energetic and non iso-energetic networks. It does however mean that any resulting equations will be valid only in so far as the kinetic theory is applicable under any given circumstances. In so far as the kinetic theory is a considerable improvement on the classical theory, the resulting equations should be of more value than those of Gee and of

Elliott and Lippmann but it must be emphasised that they will no longer have the general validity of purely thermodynamic equations such as (3.27).

The outline of the kinetic theory given by Flory for this analysis does not contain any new postulates or definitions so only the final equations of state will be given here. These may be written:

$$f = G\left(\frac{V}{V_o}\right)^{\frac{2}{3}} \frac{1}{l_i}\left(\alpha - \alpha^{-2}\right) \qquad (3.32)$$

$$P = P^{*} + \frac{G}{2V} - \frac{G}{V^{\frac{1}{3}}V_o^{\frac{2}{3}}\alpha} \qquad (3.33)$$

where $G = \nu kT$, f is the tensile force, l_i is the unstrained length of the sample when dilated to the volume V obtaining in the strained state, $\alpha = \frac{l}{l_i}$, P is the ambient pressure and V_o the volume of the sample in the reference state defined in Chapter 2. The quantity P^{*} is the contribution to the pressure from intermolecular interactions such as are found in simple liquids and hence depends only on the temperature and volume of the sample but not on its state of strain.

Differentiation of equation (3.32) gives:

$$\left(\frac{\partial f}{\partial \alpha}\right)_{T,V} = \frac{G}{l_i}\left(\frac{V}{V_o}\right)^{\frac{2}{3}}\left(1 + 2\alpha^{-3}\right) \qquad (3.34)$$

and substituting for G from equation (3.32) then gives:

$$\left(\frac{\partial f}{\partial \alpha}\right)_{T,V} = f\,\frac{\left(1 + 2\alpha^{-3}\right)}{\left(\alpha - \alpha^{-2}\right)} \qquad (3.35)$$

Hence

$$M = \frac{fl}{V}\,\frac{\left(\alpha^3 + 2\right)}{\left(\alpha^3 - 1\right)} \qquad (3.36)$$

By a similar procedure starting from equation (3.33):

$$\eta = \frac{K_1 f 1}{V(\alpha^3 - 1)} \tag{3.37}$$

and substituting equation (3.37) into (3.27) gives:

$$\left(\frac{\partial f}{\partial T}\right)_{P1} = \left(\frac{\partial f}{\partial T}\right)_{V1} - \frac{f \beta_1}{\alpha^3 - 1} \tag{3.38}$$

and similarly substitution of equations (3.36) and (3.37) into (3.29) gives:

$$\left(\frac{\partial f}{\partial T}\right)_{P\alpha} = \left(\frac{\partial f}{\partial T}\right)_{V1} - \frac{f \beta_\alpha}{3} \tag{3.39}$$

These equations may be rewritten in the more useful form:

$$\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{V1} = \left[\frac{\partial \ln(f/T)}{\partial T}\right]_{P1} + \beta_1(\alpha^3 - 1)^{-1} \tag{3.40}$$

$$\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{V1} = \left[\frac{\partial \ln(f/T)}{\partial T}\right]_{P\alpha} + \frac{\beta_\alpha}{3} \tag{3.41}$$

In practice it is usually assumed that β_1 and β_α are equal to the volume coefficient of expansion 3λ where $3\lambda = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$.

Combination of equations (1.10) and (2.31) gives:

$$\left[\frac{\partial \ln(f/T)}{\partial T}\right] = \frac{1}{T} - \frac{1}{f}\left(\frac{\partial f}{\partial T}\right) \tag{3.42}$$

indicating how this differential may be evaluated. Section 6d of Chapter 2 also indicated how the quantity $\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{V1}$ is related to the temperature coefficient of the unperturbed chain dimensions.

It is interesting to note that whilst the difference between $(\partial f/\partial T)_{P\alpha}$ and $(\partial f/\partial T)_{Vl}$ is zero for infinitessimally small strains and becomes progressively larger as the stress (or strain) increases, the reverse is true of the difference between $(\partial f/\partial T)_{Pl}$ and $(\partial f/\partial T)_{Vl}$ which equation (3.38) shows to be infinite at zero strain and becomes progressively smaller as the strain increases.

5. Summary

From this discussion of the three principal thermodynamic analyses, it is clear that all of the final equations are limited by the need to introduce some approximations in order to evaluate the correction terms. As the analyses of Elliott and Lippmann and of Gee are limited by their approximations to the region of infinitessimal strain whilst Flory's analysis is limited only to the region in which the Kinetic theory is valid, it might be expected that equations (3.38) to (3.41) would be the most valuable. In fact, analysis of experimental results on the basis of these equations generally leads to the conclusion that $(\partial U/\partial l)_{V.T} \neq 0$ which is in agreement with the results obtained from studies of dilute solutions of polymers. Work now in progress is aimed at evaluating the correction term in equation (3.22) directly by measurement of the partial differentials involved and this will then be compared with the correction term derived by Flory and expressed in equation (3.38).

CHAPTER 4

Experimental

1. Materials used

The six elastomers used in this work were chosen for their particular chemical composition. The original intention to include halogenated hydrocarbon rubbers was abandoned when it was found to be impossible to obtain a satisfactory vulcanisate of these polymers without the introduction of inert solid material. The method of preparation of the elastomers used was as follows.

(a) Natural Rubber supplied and vulcanised with 2% dicumyl peroxide (D.C.P.) for 60 minutes at 140°C by the Natural Rubber Producers Research Association.

(b) Synthetic cis poly isoprene supplied by Shell Chemical Co. Ltd. and vulcanised with 2% D.C.P. for 60 minutes at 140°C by the Natural Rubber Producers Research Association.

(c) Poly dimethyl siloxane of initial molecular weight 650,000 supplied by Midland Silicones Ltd., extracted by the procedure described by Osthoff, Bueche and Grubb (57) and vulcanised with 2% dibenzoyl peroxide for 30 minutes at 141°C by the Natural Rubber Producers Research Association.

(d) Polydimethyl siloxane with one vinyl side group per 100 silicon atoms, supplied, extracted by the method of Osthoff, Bueche and Grubb to remove any residual catalyst and vulcanised with 0.05% D.C.P. for 20 minutes at 150°C by Midland Silicones Ltd.

(e) Ethylene propylene rubber (Enjay 404) vulcanised with 5.5% D.C.P. for 45 minutes at 153°C.

(f) Poly butadiene (Phillips cis 4) vulcanised with 1.5% D.C.P. for 45 minutes at 153°C.

Elastomers 'e' and 'f' were supplied and vulcanised by the Rubber and Plastics Research Association of Great Britain.

All the elastomers were supplied as sheets 6 inches square and of thicknesses varying from 1 to 4 mm. Preliminary experiments were carried out on each elastomer to determine the cross-sectional area required to give an extension ratio of two with a load of 100-150 g. A number of strips of this cross-sectional area and about 3 cms. long were then cut and extracted for 8 hrs. with hot acetone under a nitrogen atmosphere in a Soxhlet extractor. After this extraction, carried out to remove any residual traces of vulcanising agents, accelerators or antioxidants etc., the strips were outgassed for several days at a pressure of 10^{-6} torr and at room temperature. After about 4 days no evidence of volatile material could be detected with a McLeod gauge attached to the vacuum line.

2. Vacuum System

This consisted of a two stage mercury diffusion pump backed by a 'Speedivac' rotary oil pump. A cold finger condenser cooled in liquid nitrogen prevented ingress of mercury vapour into the evacuated system. A McLeod gauge on the high vacuum side of the diffusion pump enabled the pressure in the apparatus to be measured. The whole

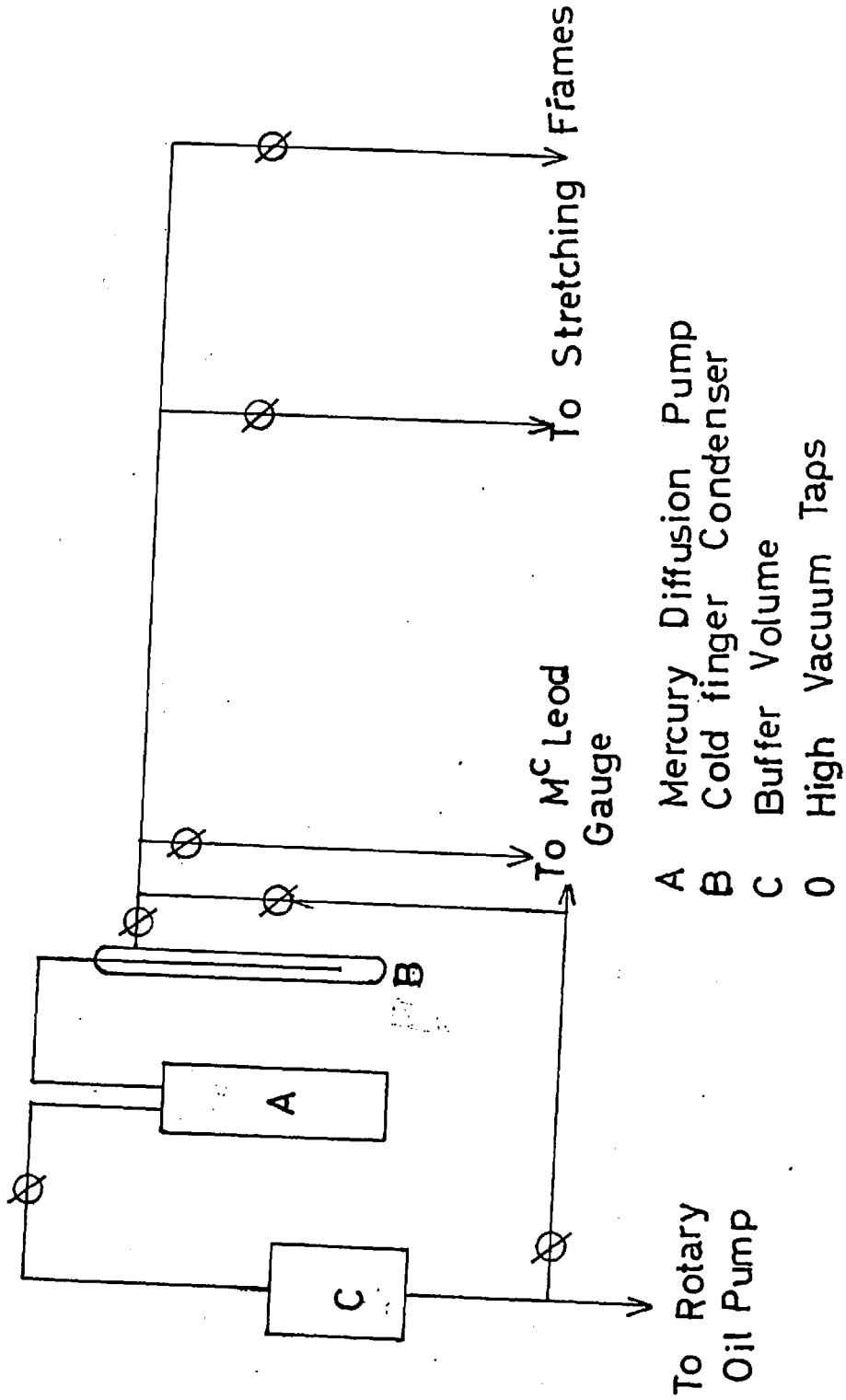


Diagram of Vacuum System

Figure 4·1

system is shown in diagrammatic form in Figure 4.1.

3. Thermostat Baths

The two thermostatic baths used in this work were identical and were made in the departmental workshops. A rectangular tank 12" x 12" x 15" deep made of sheet copper with silver soldered seams was fitted with a $\frac{1}{4}$" thick plate glass window 5" wide by 10" deep on one side. This tank was fitted inside a sheath made of $\frac{1}{4}$" thick 'Syndanio' with a rectangular hole in one wall in juxtaposition to the window in the copper tank. The two inch space between the tank and sheath was then filled with asbestos wool. The tank was filled with Midland Silicone MS 200 silicone fluid and no lid or cover over the fluid was found necessary.

The main heating unit consisted of two 600 watt Bray 'Tubalox' immersion heaters permanently fixed near the bottom of the tank and connected, in parallel, to the mains via a variable transformer. Thus full power could be used to achieve a heating rate of 3-4 Centigrade degrees per minute when changing the temperature of the bath and then the power was reduced to just below the value required to maintain the desired temperature. Accurate temperature control was then achieved by a 100 watt candle lamp operated through a 'Sunvic' relay by an adjustable bimetallic switching unit. Adequate stirring was provided by a set of three turbine paddles of three inches diameter, mounted on a common shaft and driven by a small electric motor. The baths could be maintained at any temperature up to 140°C with an accuracy of 0.01°C

for several hours. The temperature was measured to 0.05°C by a mercury in glass thermometer calibrated in units of 0.1°C and checked by the manufacturers against an N.P.L. calibrated thermometer.

4. Experimental Procedure

A self-explanatory diagram of the stretching apparatus is given as Figure 4.2. An extracted and outgassed strip of elastomer was cut to a standard length and weighed and the unstrained cross-sectional area was calculated from these two measurements and the density of the material. The strip was then fixed between the two clamps and a load, greater than the maximum to be used in the measurements, was attached to the lower clamp. The glass envelope was then put in place and the whole unit connected via a standard cone and socket joint to the vacuum line and clamped in position in the oil bath. The stretching vessel was then evacuated to 10^{-6} torr and the sample left overnight at room temperature. The system was then raised over about 3 hrs. to 5°C above the maximum temperature to be used in the measurements, held at that temperature for 2 hrs., then cooled to 25° over 5 hrs. After leaving overnight at 25°C the cycle was repeated until the length of the sample at 25° was constant to within 0.01 cms. on two successive days. The load was then reduced to the maximum to be used in the measurements, the system reconnected to the vacuum line and evacuated and held at 25°C for 24 hrs. The length of the sample at 25°C was then measured by a cathetometer to ± 0.004 cms. and the temperature raised to about 35°C. After a wait of 45 mins. to allow the sample to

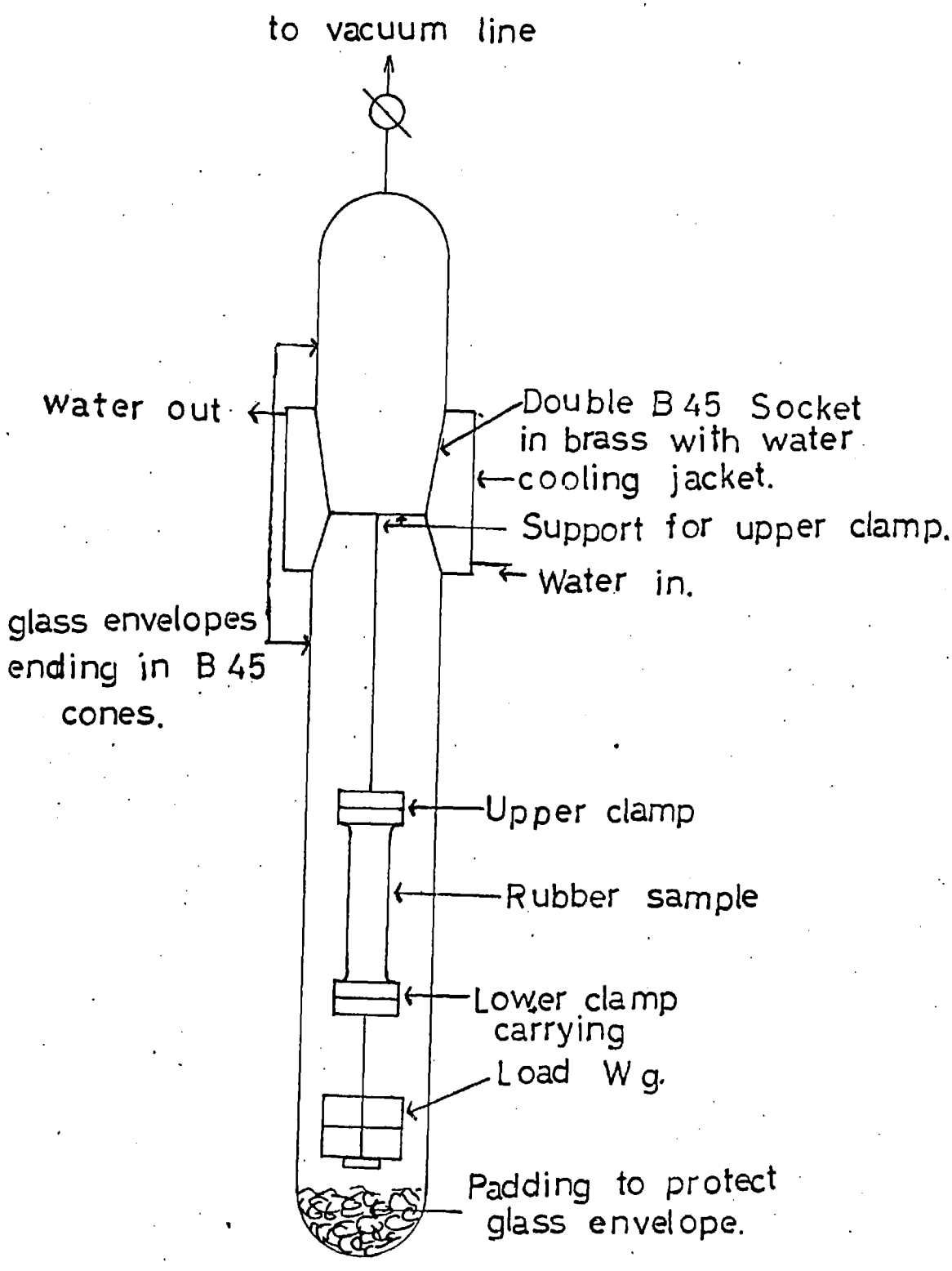


Diagram of Stretching Apparatus

Figure 4·2

attain equilibrium the length was again recorded. This procedure was repeated with temperature increases of 10°C to a maximum value of 75°C and then the temperature was reduced to 70°C and then in steps of 10°C to 30°C and finally returned to 25°C. The length of the sample was recorded at each stage. The maximum temperature of 75°C was used because it was found to be impossible to attain any equilibrium with temperatures of 85°C or over for samples a, b, c and d. Samples e and f were however stable up to a temperature of about 120°C and so the measurements were repeated on sample e using a fresh specimen over a temperature range of 50°C to 100°C. Sample f was used over a range of 40°C 100°C.

On the completion of a temperature cycle the load was changed to the next value, the system re-evacuated and left overnight at the lowest temperature used in the cycle. A total of between 9 and 15 different loads was used on each specimen and to detect any irreversible changes in the specimen the load was first reduced and then increased. A typical sequence of loads was:-

111, 86, 61, 36, 11, 21, 46, 71, 96, 106 g.

No explanation of the degradation of the poly isoprene and poly siloxane networks at moderately high temperatures is offered here but the most probable causes are oxidation and hydrolysis respectively. This degradation of networks under vacuum could well form the subject of a separate study.

CHAPTER 5

Analysis of Results

1. All calculations were carried out on the Ferranti 'Mercury' computer of the London University Computer unit or on the 'Atlas' computer of Manchester University. The programmes used were developed by the author using a modified version of the 'Autocode' programming language. Two main programmes were used, one to calculate thermodynamic quantities and the other to calculate the various constants used in the stress-strain relationships.

For the thermodynamic calculations the stress used was the total force applied to the sample but to facilitate comparison of samples of different cross-sectional area, the force in kilograms was divided by the unstrained cross-sectional area of the sample at 25°C (A_{25}). As this is a constant factor for all weights and all temperatures it does not affect the values of $\partial \ln \bar{r_o}^2 / \partial T$ but has the effect of giving $(\partial f/\partial T)_{Vl}$ and hence $T(\partial S/\partial l)_{VT}$ and $(\partial U/\partial l)_{VT}$ in terms of kilograms per unit area. The dimensions of $T(\partial S/\partial l)_{VT}$ and $(\partial U/\partial l)_{VT}$ being ML^{-2} the results may be converted to calories per cubic centimetre by use of the relation

$$1 \text{ kg./cm.}^2 = 0.023438 \text{ cal./cm.}^3 \qquad (5.1)$$

For the stress-strain isotherms the stress is defined as force per unit unstrained cross-sectional area (A_T) at the temperature T of the isotherm and A_T is defined by:

$$A_T = A_{25}\left[1 + 2\beta(T - 25)\right] \qquad (5.2)$$

where β is the linear coefficient of thermal expansion.

Because of this difference in the definition of stress it was found to be convenient to carry out the thermodynamic and the stress-strain calculations in two separate programmes. The complete programmes are given as programmes 1 and 2 respectively in Appendix 1. The first stages of these two programmes are identical and this common portion will be discussed first.

2. Evaluation of l_o

The first step in each of programmes 1 and 2 computed, by the method of least squares, the coefficients a, b, c and d in the polynomial:

$$l = a + bt + ct^2 + dt^3 \qquad (5.3)$$

for the sets of length and temperature values obtained at each applied load. l is the length of the sample at $t^\circ C$. The primary data were then culled to eliminate any individual points which deviated by more than 2.5 times the standard deviation from the appropriate polynomial and a new set of coefficients was then evaluated for the remaining data. The standard deviation (δ) for any polynomial was defined by:

$$\delta = \left[\frac{1}{N}\sum_{i=1}^{N}(y_i - a - bx_i - cx_i^2 - dx_i^3)^2\right]^{\frac{1}{2}} \qquad (5.4)$$

where x and y are dummy variables.

Usually all the experimental points satisfied this culling criterion and in no case was more than one point rejected in any set of

twelve. The number of points rejected from each isobar of typical samples is given in Table 5.1 and values of δ for the culled isobars of the same samples are given in Table 5.2. These isobars are also displayed in Figure 5.1.

Table 5.1

No. of points rejected from each isobar of typical samples

Sample 10

Load	1	2	3	4	5	6	7	8	9
n° rejected	0	0	0	0	0	0	0	0	0

Sample 16

Load	1	2	3	4	5	6	7	8	9	10	11
n° rejected	0	0	0	0	0	0	0	0	0	0	0

Table 5.2

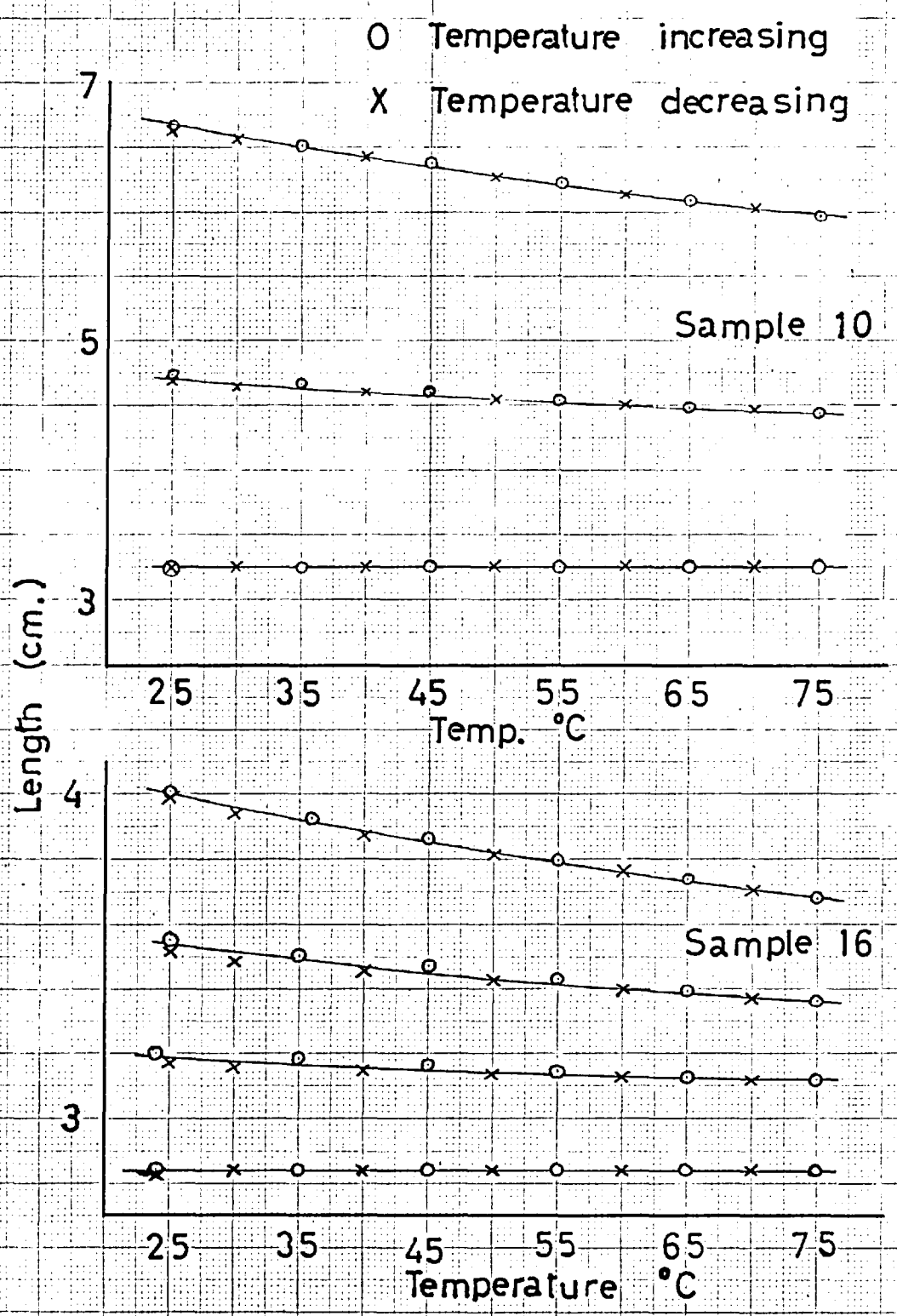
Values of standard deviation (δ) of culled data of each isobar of typical samples.

Sample 10

Load	1	2	3	4	5	6	7	8	9
δ	1.48 x10^{-2}	1.72 x10^{-2}	4.46 x10^{-3}	2.56 x10^{-3}	5.60 x10^{-3}	8.07 x10^{-3}	1.70 x10^{-2}	1.38 x10^{-2}	6.85 x10^{-6}

Sample 16

Load	1	2	3	4	5	6	7	8	9
δ	1.13 x10^{-2}	1.81 x10^{-2}	1.40 x10^{-2}	8.81 x10^{-3}	4.36 x10^{-3}	4.05 x10^{-3}	6.48 x10^{-3}	1.30 x10^{-2}	7.40 x10^{-3}
Load	10	11							
δ	1.49 x10^{-2}	1.23 x10^{-2}							



Typical Graphs of Length. vs. Temperature

Figure 5.1

Values of l for several 'standard' temperatures were then obtained by interpolation from the length-temperature polynomials. The standard temperatures were 25, 40, 55, 70, 85 and 100°C and as many of these as were included in the experimental range of temperature were used. The interpolated values of l were then used to evaluate similar polynomials for the load-length isotherms and the value of the unstretched length l_o at each standard temperature was obtained by extrapolation to zero load. These values of l_o at different temperatures were used to estimate the linear coefficient of thermal expansion λ for the rubber. λ is a quantity defined by:

$$\lambda = \frac{1}{l_{o,t_1}} \left[(l_{ot_2} - l_{ot_1})(t_2 - t_1)^{-1} \right] \qquad (5.5)$$

where l_{ot_1} is the unstretched length at the lowest standard temperature t_1 and l_{ot_2} is the same quantity at the highest standard temperature t_2. Values of λ evaluated from equation 5.5 are compared with the generally accepted values in Table 5.3.

The values of l_o were also used to convert the values of l to α by the relation $\alpha = l/l_o^{-1}$ and load-elongation isotherms were evaluated as cubic polynomials. Typical values of δ for these two sets of isotherms are listed in Tables 5.4 and 5.5 respectively.

Table 5.3

Rubber	Sample	$\lambda \times 10^4$ from 5.5	$\lambda \times 10^4$ accepted
Synth. cis poly isoprene	1	3.09	2.2
	2	2.06	"
	3	2.87	"
Natural Rubber	4	2.74	2.2
	5	2.82	"
	6	2.27	"
Poly dimethyl siloxane	7	3.86	3.2
	8	4.41	"
Poly dimethyl siloxane	10	4.11	3.2
	11	3.63	"
Ethylene propylene rubber	17	2.12	1.8
	17	2.12	"
Poly butadiene rubber	18	2.67	1.8 ?

Table 5.4

Values of standard deviation δ for the length-load isotherms of typical samples

Sample 4				
Temp. °C	25	40	55	70
$\delta \times 10^2$	2.23	2.11	1.93	1.80
Sample 10				
Temp. °C	25	40	55	70
$\delta \times 10^2$	1.99	1.92	1.89	1.85

Table 5.5

Values of standard deviation δ for the extension ratio-load isotherms of typical samples

Sample 4				
Temp. °C	25	40	55	70
$\delta \times 10^2$	2.23	2.11	1.93	1.80
Sample 10				
Temp. °C	25	40	55	70
$\delta \times 10^2$	1.99	1.92	1.89	1.85

3. Calculation of Thermodynamic quantities

Values of the load at values of the extension ratio α ranging from 1.1 to 2.0 in steps of 0.1 were obtained by interpolation from the load-extension isotherms and these were divided by the cross-sectional area of the sample at 25°C to facilitate comparison of different samples. These reduced values of the load are subsequently referred to as stress values (f). Values of $(\partial f/\partial T)_{P\alpha}$ were then obtained assuming a linear stress-temperature relationship, i.e. by assuming that:

$$\left(\frac{\Delta f}{\Delta T}\right)_{P\alpha} \equiv \left(\frac{\partial f}{\partial T}\right)_{P\alpha} \qquad (5.6)$$

Equation (5.6) was justified by graphical checking of the stress-temperature values and in all cases the relationship was seen to be linear as illustrated by the typical example shown in Figure 5.2.

Values of $\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{V1}$ were then obtained using the relationship derived by Flory (20):

$$\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{V1} = T^{-1} - f^{-1}\left(\frac{\partial f}{\partial T}\right)_{P\alpha} \ldots \lambda \qquad (5.7)$$

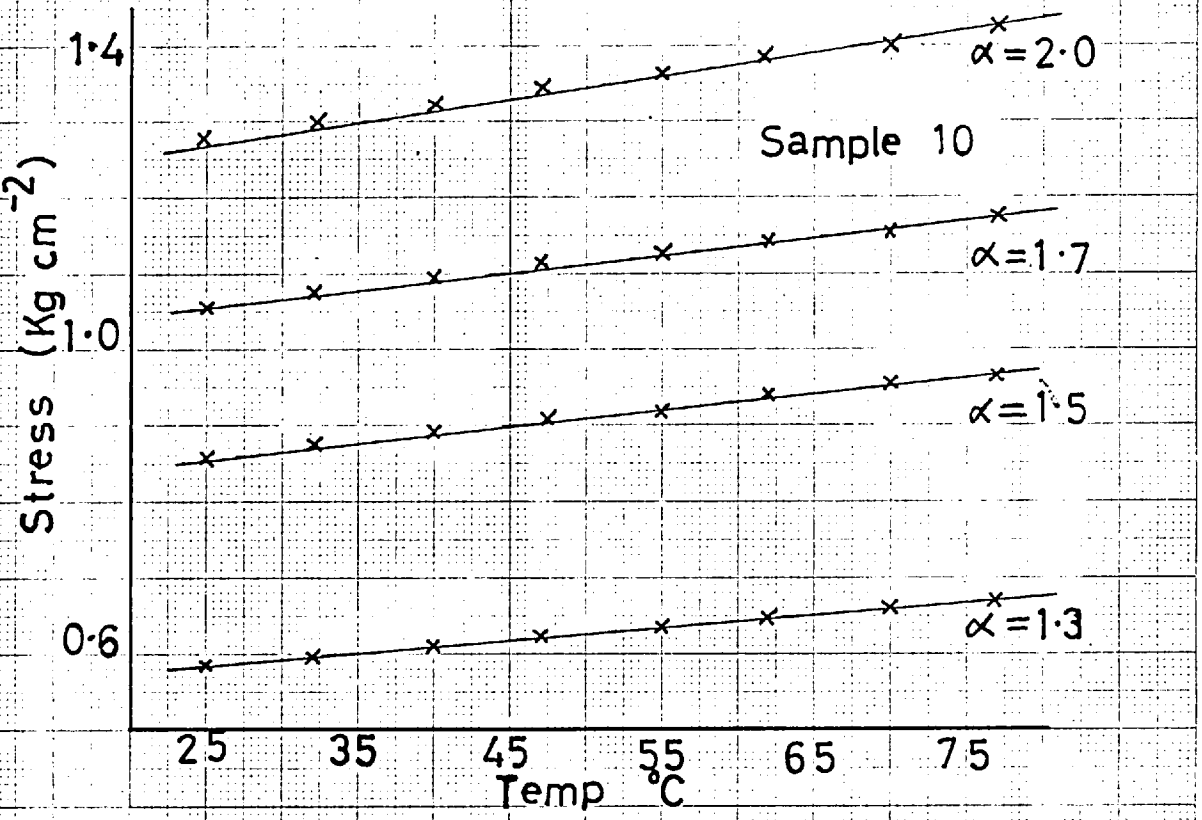
where f is the stress at extension ratio α and temperature T°A. This quantity $\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{V1}$ is numerically equal to $\frac{-\partial \ln \bar{r}_o^2}{\partial T}$ and the values obtained are listed in Chapter 6 (Table 6.1) under the latter heading. The quantities $\left(\frac{\partial U}{\partial l}\right)_{TV}$ and $T\left(\frac{\partial S}{\partial l}\right)_{TV}$ were evaluated by the equations:

$$\left(\frac{\partial S}{\partial l}\right)_{TV} = -\left(\frac{\partial f}{\partial T}\right)_{lV} = f\left[T^{-1} + \frac{\partial \ln \bar{r}_o^2}{\partial T}\right] \qquad (5.8)$$

and:

Typical Graph of stress vs temperature at constant α

Figure 5·2



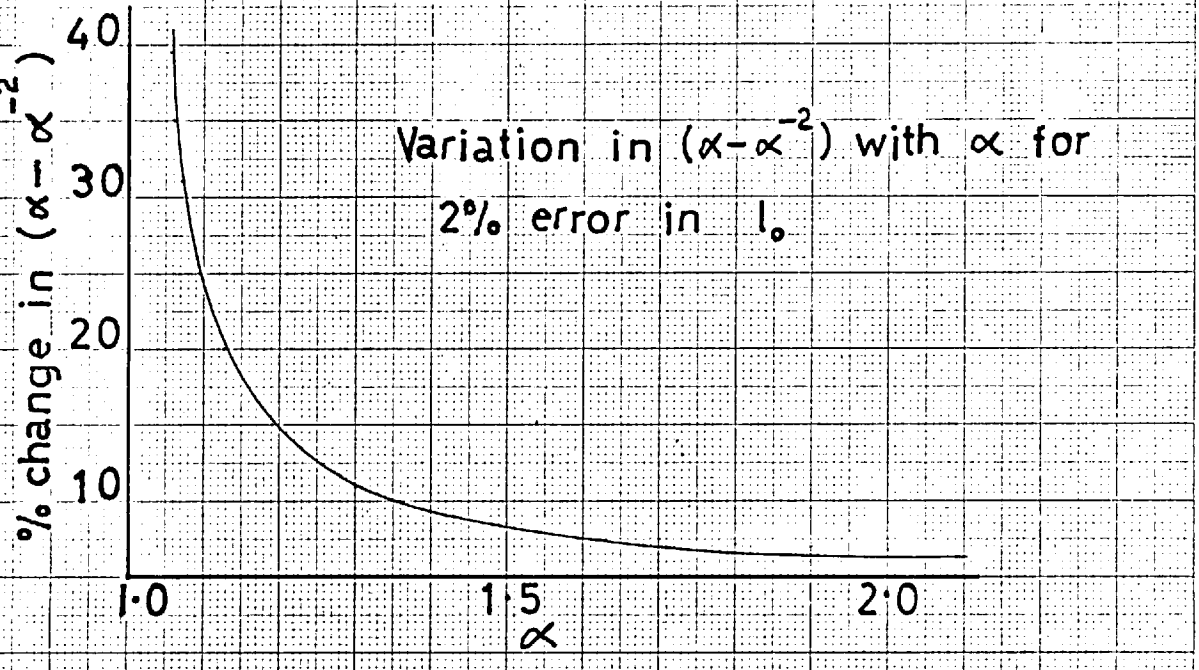


Figure 5·3

$$\left(\frac{\partial U}{\partial l}\right)_{TV} = f + T\left(\frac{\partial S}{\partial l}\right)_{TV} \qquad (5.9)$$

and are also given in Chapter 6 (Table 6.1).

4. Stress-Strain calculations

(a) Evaluation of the Kinetic Theory constants

Though the kinetic theory predicts a linear relationship between the retractive force f and the quantity $\phi(=\alpha - \alpha^{-2})$, preliminary calculations showed that over the range of values of α used, the actual relationship is approximately quadratic. Hence the coefficients a, b and c of the equation:

$$f = a + b\phi + c\phi^2 \qquad (5.10)$$

were evaluated by the method of least squares. From the definition of α given in Chapter 1, f must be zero when $\alpha = 1$, i.e. when $\phi = 0$ hence the constant a of equation (5.10) should be zero, and the constants b and c may be related to physical quantities, b being the quantity ($\psi \nu kT$) derived by the kinetic theory (equation 2.12) and c being a measure of the deviation from this equation. The constants b and c are thus subsequently referred to as C_o and C_1 respectively.

(b) Calculation of Mooney-Rivlin constants

The equation (1.27) derived from the phenomenological theories of Mooney and of Rivlin may be written:

$$f(\alpha - \alpha^{-2})^{-1} = 2C_1 + 2C_2\alpha^{-1} \qquad (5.11)$$

indicating a linear relationship between the quantities $f(\alpha - \alpha^{-2})^{-1}$ and α^{-1}. Values of $2C_1$ and $2C_2$ were evaluated by the method of least squares. Typical graphs of $f(\alpha - \alpha^{-2})^{-1}$ vs. α^{-1} are shown in Figure 6.6.

5. Validity of Equations (5.10) and (5.11)

The values of the constant a of equation (5.10) are given in column 1 of Table 5.6 and examination of these values shows that, though small, they are not negligible. Further, examination of the typical Mooney-Rivlin plots given in Figure 6.6 shows that the predicted linear relationship is not obeyed. The experimental quantities used in the evaluation of equations (5.10) and (5.11) were l, l_o and f, and of these l_o is the least reliable as it has to be obtained by extrapolation. As any error in l_o will affect all values of α to the same degree it may be thought that errors in l_o are comparatively unimportant. This is not so as the function of α used in equations (5.10) and (5.11) is affected more seriously at low than at high values of α. This is demonstrated in Figure 5.3 which shows the percentage change in ϕ over a range of values of α for a 2% change in l_o. It was thus considered worth while to investigate the effect of a systematic variation in l_o. To this end a quantity $\alpha' = \alpha\gamma$ was defined where γ is a number which was varied from 1.005 to 0.976 in steps of 0.001. In effect this is the equivalent of changing l_o in steps of 0.1% from 0.5% below to 2.4% above the original extrapolated value.

Using each value of γ in turn values of a, C_o, C', C_1 and C_2, both for all values of α and for values of $\alpha \geqslant 1.095$, were calculated by the method of least squares. The value of γ giving the lowest value of a and those giving the best straight lines for all values of α and for $\alpha \geqslant 1.095$ were then selected. These values of γ are listed in columns 1, 2 and 3 respectively of Table 5.7, and the corresponding values of a are listed in columns 2, 3 and 4 of Table 5.6. The values of C_o, C', C_1 and C_2 obtained by these methods are tabulated in Chapter 6 (Tables 6.4 to 6.11 and 6.13 to 6.16).

Examination of Table 5.7 shows that different values of γ are required to satisfy the condition f = 0 when $\alpha = 1$ and to give a good straight line on a Mooney-Rivlin plot. This indicates that the equations (5.10) and (5.11) require slightly different values of 'l_o', and the question of which value corresponds to the true unstretched length is considered in Chapter 6.

The samples labelled 17R and 17C in the following tables refer to results obtained by measuring between marks on the rubber and marks on the clamps respectively of a single sample. The two sets of values for sample 17C refer to results obtained on a single sample over two separate ranges of temperature.

Table 5.6

Values of $|f_o|$ obtained by 4 standard methods:

1) Original value of l_o.
2) l_o adjusted to give minimum value of $|f_o|$.
3) l_o adjusted to give best fit to Mooney-Rivlin plot.
4) As 3) but using only values of $\alpha \geq 1.095$.

Sample	Temp. °C	Value of $\|f_o\|$ (Kg. cm.$^{-2}$ x 10^3) 1	2	3	4
1	25	42.26	2.006	6.85	24.44
	40	42.59	3.521	5.70	30.57
	55	35.91	2.348	7.21	51.02
	70	26.88	2.814	7.08	54.81
2	25	8.12	1.149	10.42	69.01
	40	22.99	3.323	3.32	56.04
	55	28.70	2.114	8.15	42.31
	70	27.38	4.551	6.09	25.69
3	25	33.49	3.587	13.55	53.84
	40	29.41	1.486	1.49	61.14
	55	24.66	3.336	7.32	57.26
	70	18.33	3.656	7.33	37.66
4	25	190.1	0.354	54.00	54.00
	40	181.7	1.757	58.48	58.48
	55	186.3	0.508	68.17	47.89
	70	186.6	3.201	74.37	54.24
5	25	37.09	0.952	19.01	11.61
	40	42.17	4.498	13.91	19.91
	55	36.10	2.719	16.68	16.99
	70	27.69	2.312	17.68	0.73
6	25	60.72	1.289	18.26	16.47
	40	61.74	0.092	17.56	7.66
	55	59.55	4.443	22.80	29.75
	70	56.78	0.102	18.85	25.79
18	40	54.77	9.467	22.64	24.00
	55	48.64	15.58	15.58	16.41
	70	9.55	9.553	9.55	6.67
	85	44.92	9.57	25.81	51.54
	100			149.6	284.8

Table 5.6 (Contd.)

Values of $|f_o|$ obtained by 4 standard methods

Sample	Temp. °C	Value of $\|f_o\|$ (Kg. cm.$^{-2}$ x 10^3) 1	2	3	4
7	25	15.94	0.029	1.62	9.02
	40	13.08	0.050	1.59	6.89
	55	12.52	0.605	4.01	3.98
	70	10.72	0.181	1.94	7.43
8	25	7.27	0.558	2.80	12.84
	40	5.12	0.060	1.79	12.35
	55	7.20	0.007	3.61	11.02
	70	4.20	0.505	1.34	9.09
10	25	1.29	1.294	33.61	33.61
	40	0.36	0.362	28.58	28.58
	55	3.77	1.001	26.68	26.68
	70	1.34	1.335	24.56	24.56
11	25	2.94	0.473	19.29	19.29
	40	4.62	0.545	13.45	39.98
	55	5.14	0.229	10.97	33.53
	70	6.55	0.964	10.21	28.81
17R	25	40.38	3.432	65.01	198.9
	40	65.55	26.59	65.55	209.5
	55	91.09	50.31	91.09	769.5
	70	59.10	0.983	88.13	775.9
17C	25	22.27	2.864	72.52	20.19
	40	7.262	6.134	74.18	198.5
	55	41.34	1.039	55.45	803.7
	70	41.61	2.563	26.89	881.8
17C	55	22.29	5.835	33.94	393.1
	70	28.25	1.081	15.73	434.9
	85	0.646	0.646	14.82	416.7
	100	21.31	5.032	43.75	387.7

Table 5.7

Values of γ obtained by 3 standard methods:

1) l_o adjusted to give minimum $|f_o|$.

2) l_o adjusted to give best fit to Mooney-Rivlin plot.

3) as 2) but using only values of $\alpha \geq 1.095$.

Sample	Temp. °C	Value of γ 1	2	3
1	25	0.994	0.995	0.990
	40	0.994	0.995	0.990
	55	0.995	0.996	0.989
	70	0.996	0.997	0.990
2	25	0.998	0.997	0.992
	40	0.997	0.997	0.991
	55	0.996	0.997	0.991
	70	0.996	0.997	0.993
3	25	0.996	0.997	0.989
	40	0.996	0.997	0.991
	55	0.997	0.996	0.992
	70	0.997	0.998	0.993
4	25	0.979	0.985	0.985
	40	0.981	0.987	0.987
	55	0.981	0.988	0.981
	70	0.982	0.989	0.982
5	25	0.995	0.997	0.991
	40	0.995	0.996	0.991
	55	0.995	0.997	0.991
	70	0.996	0.998	0.994
6	25	0.993	0.995	0.989
	40	0.993	0.995	0.990
	55	0.994	0.996	0.987
	70	0.994	0.996	0.988
18	40	0.998	0.999	1.002
	55	0.999	0.999	1.002
	70	1.000	1.000	1.001
	85	1.001	1.002	1.001
	100	1.001	1.005	0.999

Table 5.7 (Contd.)

Values of γ obtained by 3 standard methods

Sample	Temp. °C	Value of γ 1	2	3
7	25	0.989	0.990	0.979
	40	0.991	0.992	0.983
	55	0.992	0.994	0.985
	70	0.993	0.994	0.986
8	25	0.995	0.993	0.987
	40	0.996	0.995	0.988
	55	0.995	0.993	0.990
	70	0.997	0.996	0.992
10	25	1.000	0.987	0.987
	40	0.999	0.988	0.988
	55	0.998	0.988	0.988
	70	0.999	0.990	0.990
11	25	0.998	0.990	0.990
	40	0.997	0.992	0.985
	55	0.997	0.993	0.987
	70	0.997	0.993	0.989
17R	25	1.003	0.998	0.976
	40	1.003	1.000	0.979
	55	1.003	1.000	0.976
	70	1.004	0.998	0.976
17C	25	1.002	0.996	0.976
	40	1.001	0.995	0.976
	55	1.003	0.999	0.976
	70	1.003	1.001	0.976
17C	55	0.998	0.996	0.976
	70	0.998	0.997	0.976
	85	1.000	0.999	0.976
	100	0.999	0.996	0.976

Table 5.8

Values of $(\partial f/\partial T)_{P\alpha}$

$(\partial f/\partial T)_{P\alpha} \times 10^3$ (Kg./°C)

Sample	1	2	3	4
α				
1.1	2.91	2.32	3.11	2.17
1.2	4.74	4.20	5.20	4.06
1.3	6.18	5.73	6.74	5.67
1.4	7.35	6.97	7.97	6.99
1.5	8.34	8.00	9.08	8.00
1.6	9.26	8.86	10.30	8.72
1.7	10.20	9.64	11.84	9.13
1.8	11.27	10.38	13.92	9.23
1.9	12.57	11.17	16.74	9.00
2.0	14.21	12.07	20.53	8.45

Sample	5	6		18
α			α	
1.1	2.72	2.24	1.02	2.65
1.2	4.70	4.01	1.04	4.53
1.3	6.12	5.41	1.06	6.31
1.4	7.22	6.51	1.08	7.94
1.5	8.18	7.42	1.10	9.39
1.6	9.22	8.22	1.12	10.63
1.7	10.54	9.02	1.14	11.62
1.8	12.34	9.87	1.16	12.34
1.9	14.84	10.90	1.18	12.75
2.0	18.24	12.18	1.20	12.83

Table 5.8 (Contd.)

Values of $(\partial f/\partial T)_{P\alpha}$

$(\partial f/\partial T)_{P\alpha} \times 10^3$ (Kg./°C)

Sample	7	8	10	11
α				
1.1	0.44	0.51	0.87	0.71
1.2	0.80	0.91	1.54	1.28
1.3	1.08	1.20	2.04	1.72
1.4	1.30	1.41	2.39	2.08
1.5	1.48	1.57	2.65	2.37
1.6	1.64	1.72	2.84	2.62
1.7	1.79	1.88	2.99	2.87
1.8	1.94	2.09	3.16	3.14
1.9	2.11	2.38	3.36	3.46
2.0	2.32	2.78	3.64	3.87

Sample	17C	17R	17C	17R
α				
1.1	5.35	5.59	5.93	5.27
1.2	9.48	9.21	9.37	10.10
1.3	11.95	11.85	12.15	11.91
1.4	13.71	14.17	14.69	12.93
1.5	15.74	16.80	17.41	15.40
1.6	19.02	20.39	20.72	21.56
1.7	24.50	25.58	25.04	33.66
1.8	33.17	33.01	30.79	53.92
1.9	46.00	43.33	38.38	84.60
2.0	63.96	57.19	48.22	127.9

Table 5.9

Comparison of $(\partial \ln r_o^2/\partial T)$ with published values

	$(\partial \ln r_o^2/\partial T) \times 10^4$			
	This work	Previous work		
		Value	Ref.	Value	Ref.
Natural Rubber	5.4	5.5	10	6.0	65
		5.6	10		
Synth. cis poly isoprene	4.8	Should be same as Natural rubber.			
poly dimethyl siloxane	5.7	4.7	9		
poly dimethyl siloxane + 1% vinyl side gps.	4.7	None available. Should be very similar to poly dimethyl siloxane.			
Ethylene-propylene	-21.4	None available.			
Polybutadiene	- 1.26	None available.			

Accuracy of Results

The typical values of the standard deviation δ for the length-temperature isobars given in Table 5.2, together with the small number of individual points found to deviate from the 'best' curve by more than 2.5δ (Table 5.1) indicates that these experimental measurements were made on systems which were very close to equilibrium. The

typical graphs of length vs. temperature shown in Figure 5.1 confirm this. These values of δ indicate that the interpolated lengths subsequently used may be expected to be accurate to better than 0.1 mm. which compares quite well with the maximum accuracy of 0.04 mm. obtainable with the cathetometers used.

The typical values of δ for the load length and load extension isotherms given in Tables 5.4 and 5.5 together with the sample Mooney-Rivlin graphs given in Figure 5.4 further indicate that the interpolated lengths at different loads are mutually consistent. As the loads (in g.) for sample 6 were applied in the order:

131, 106, 81, 56, 31, 11, 36, 61, 86, 111, 121, 96, 71, 46, 21,

this is taken as an indication that irreversible effects such as chain scission were largely absent. If this were not so the points in Fig. 5.4 corresponding to (for example) 106 g. and 96 g., which were taken 10 days apart, would not be in such good agreement, and each line of Figure 5.4 would be resolvable into two or three component lines. This lack of hysteresis is in marked contrast to the results given by Flory and Ciferri (18) and illustrated by Figure 5 of that paper, and would seem to indicate that any divergence of the stress-strain results from the kinetic theory equation cannot be ascribed to non-equilibrium effects.

As the values of δ given in Table 5.4 are about 0.02 kg. the maximum probable error in any value of f is 0.02 kg. and as the temperature difference between the upper and lower isotherms is about

50°C the maximum error in $\Delta f/\Delta T$ is $\frac{2 \times 0.02}{50} = 0.0008$ Kg./°C. This is a small fraction of the values obtained for $(\partial f/\partial T)_{P\alpha}$ given in Table 5.8 but it is comparable with the magnitude of the correction factor $f\lambda$ required by equation (3.39) to evaluate $(\partial f/\partial T)_{V1}$. This would seem to suggest that a differential method of measuring $(\partial f/\partial T)_{P\alpha}$ is essential if sufficient accuracy is to be achieved. Financial limitations however necessitated the adoption of the procedure used in this work.

Values of the quantity $\frac{\partial \ln \bar{r}_o^2}{\partial T}$ were obtained from $(\partial f/\partial T)_{P\alpha}$ by use of equations (3.41) and (3.42)

$$\frac{\partial \ln \bar{r}_o^2}{\partial T} = \frac{1}{T} - \frac{1}{f}\left(\frac{\partial f}{\partial T}\right)_{P\alpha} + \lambda$$

where $\frac{1}{T}$ is about $0.003°A^{-1}$ and $\frac{1}{f}$ is about 0.25 kg.$^{-1}$.

Thus the maximum error in $\frac{1}{f}\left(\frac{\partial f}{\partial T}\right)_{P\alpha}$ is about 6% and will vary between 1×10^{-4} at $\alpha = 1.1$ and 3×10^{-4} at $\alpha = 2.0$. These values are small compared with the magnitude of $\frac{1}{T}$ but are again comparable with λ and suggest that the error in $\partial \ln \bar{r}_o^2/\partial T$ will be about 50%. Though high, this value is not unreasonable when compared with the scatter in reported values for this quantity, e.g. references 9, 10, and as shown in Table 5.9 the values in this work are in good agreement with those previously published.

CHAPTER 6

Results and Discussion

1. Thermodynamics

Values of $\frac{\partial \ln \bar{r_o^2}}{\partial T}$, $\left(\frac{\partial U}{\partial l}\right)_{TV}$ and $-T\left(\frac{\partial S}{\partial l}\right)_{TV}$ at each value of the extension ratio α and each standard temperature are listed in Table 6.1 and the entropy and energy components of the retractive force are displayed for an example of each rubber in Figure 6.1. Values of $\frac{\partial \ln \bar{r_o^2}}{\partial T}$ and $\left(\frac{\partial U}{\partial l}\right)_{TV}$ averaged over all values of α at a particular temperature are given in Tables 6.2 and 6.3.

In all cases the values of $T\left(\frac{\partial S}{\partial l}\right)_{TV}$ are, as required by the kinetic theory, large and negative but the typical graphs of $-T\left(\frac{\partial S}{\partial l}\right)_{TV}$ vs. $(\alpha - \alpha^{-2})$ shown in Figure 6.2 are not linear. This would seem to indicate that the deviations from the kinetic theory are not wholly due to non-zero energy contributions but that some effects which influence the entropy change on deformation have been neglected in that treatment. This may be taken as qualitative support for the suggestion of Di Marzio (12) discussed in Chapter 2.

Quantitative evaluation of Di Marzio's suggestion is made difficult by the fact that the average number of links in a network chain cannot be reliably and independently estimated but the magnitude of the deviation (20%) of the values found in this work from those predicted by the kinetic theory are much larger than the 5% calculated by Di Marzio.

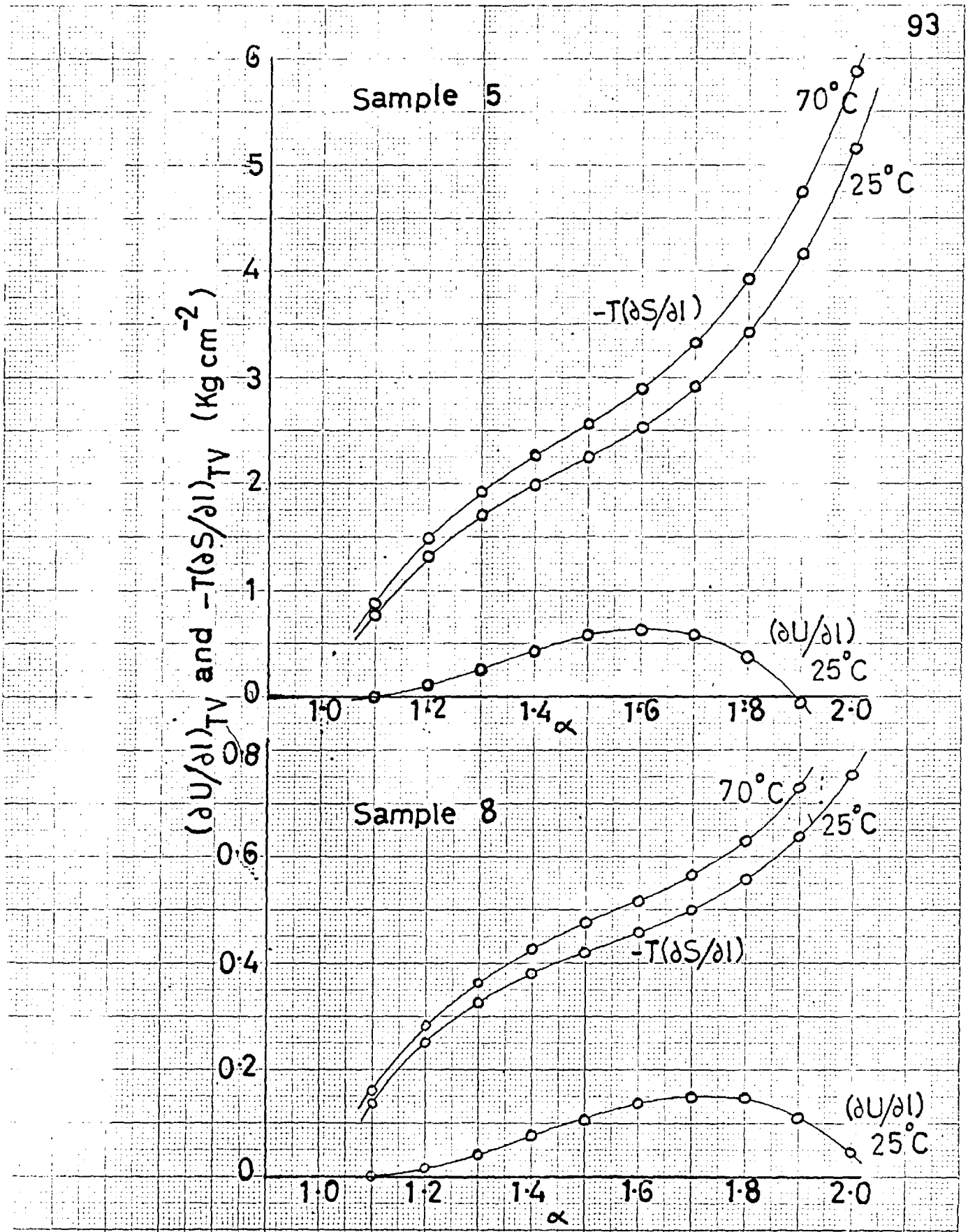

Sample 5
70°C
25°C
-T(∂S/∂l)
(∂U/∂l)
25°C
(∂U/∂l)TV and -T(∂S/∂l)TV (Kg cm-2)
α
Sample 8
70°C
25°C
-T(∂S/∂l)
(∂U/∂l)
25°C
α

Figure 6.1

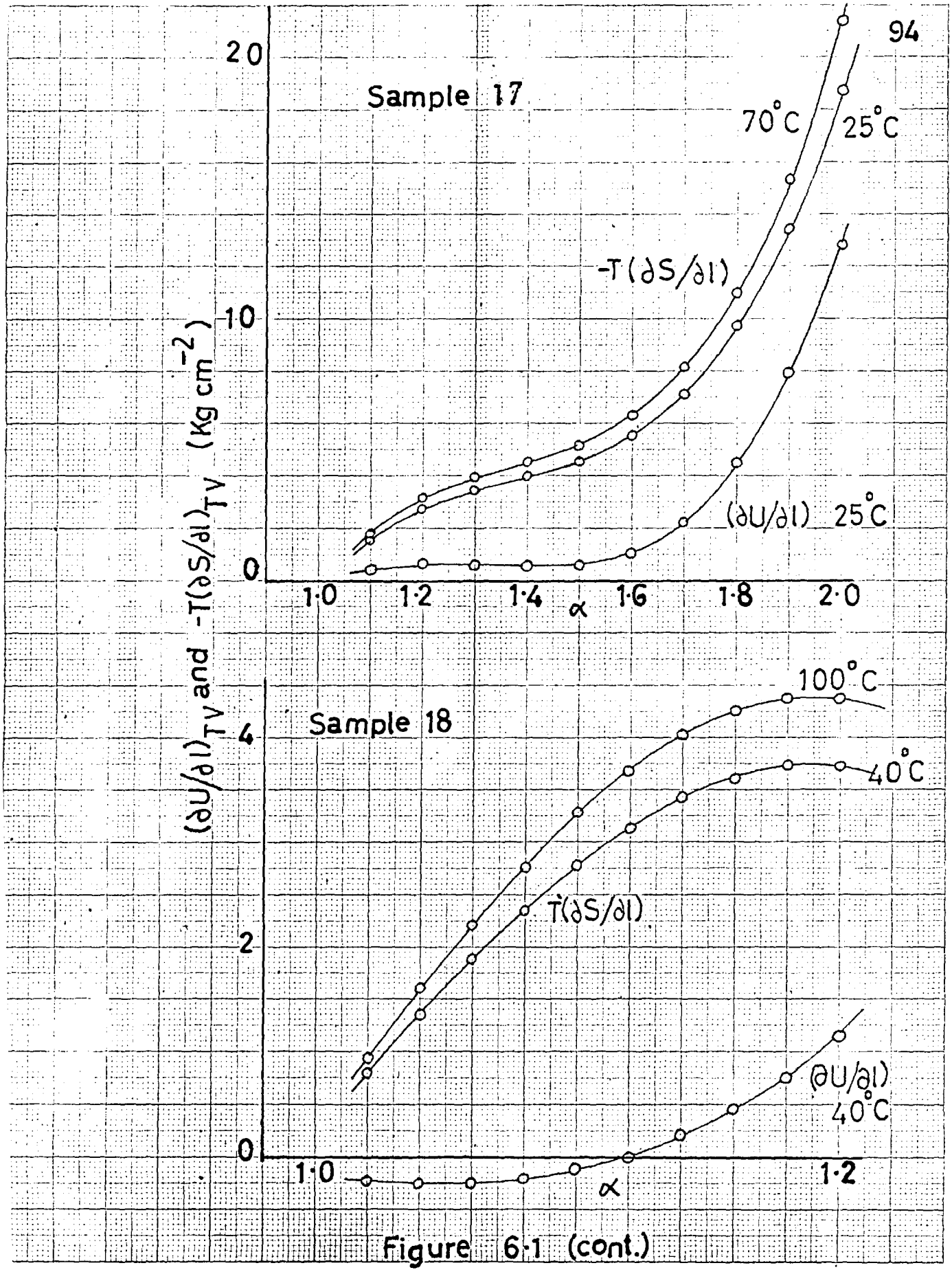


Figure 6·1 (cont.)

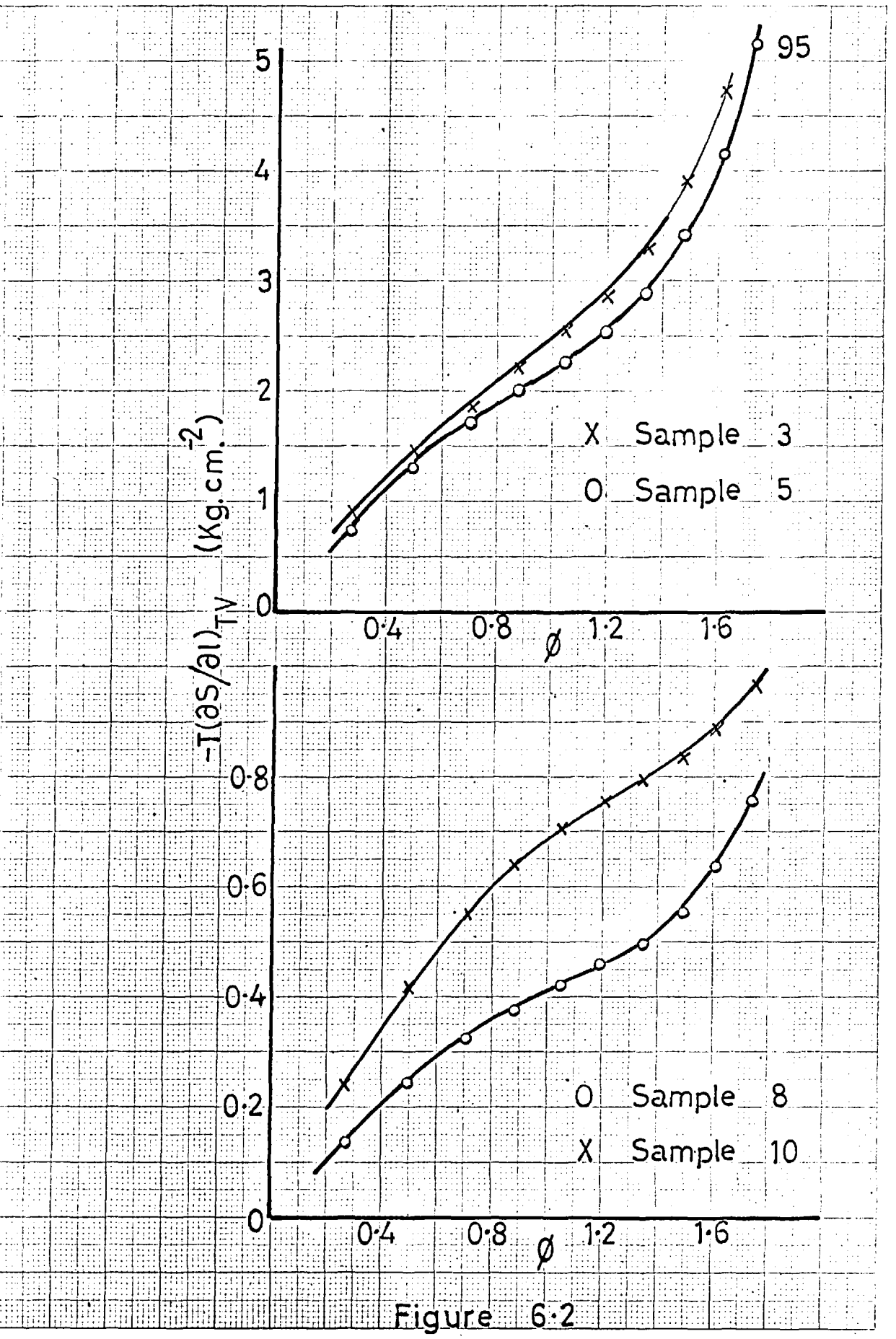

95
5
4
3
2
1
0
X Sample 3
O Sample 5
0·4
0·8
1·2
1·6
ϕ
$-T(\partial S/\partial l)_{TV}$ (Kg.cm.$^{-2}$)
0·8
0·6
0·4
0·2
0
O Sample 8
X Sample 10
0·4
0·8
1·2
1·6
ϕ

Figure 6·2

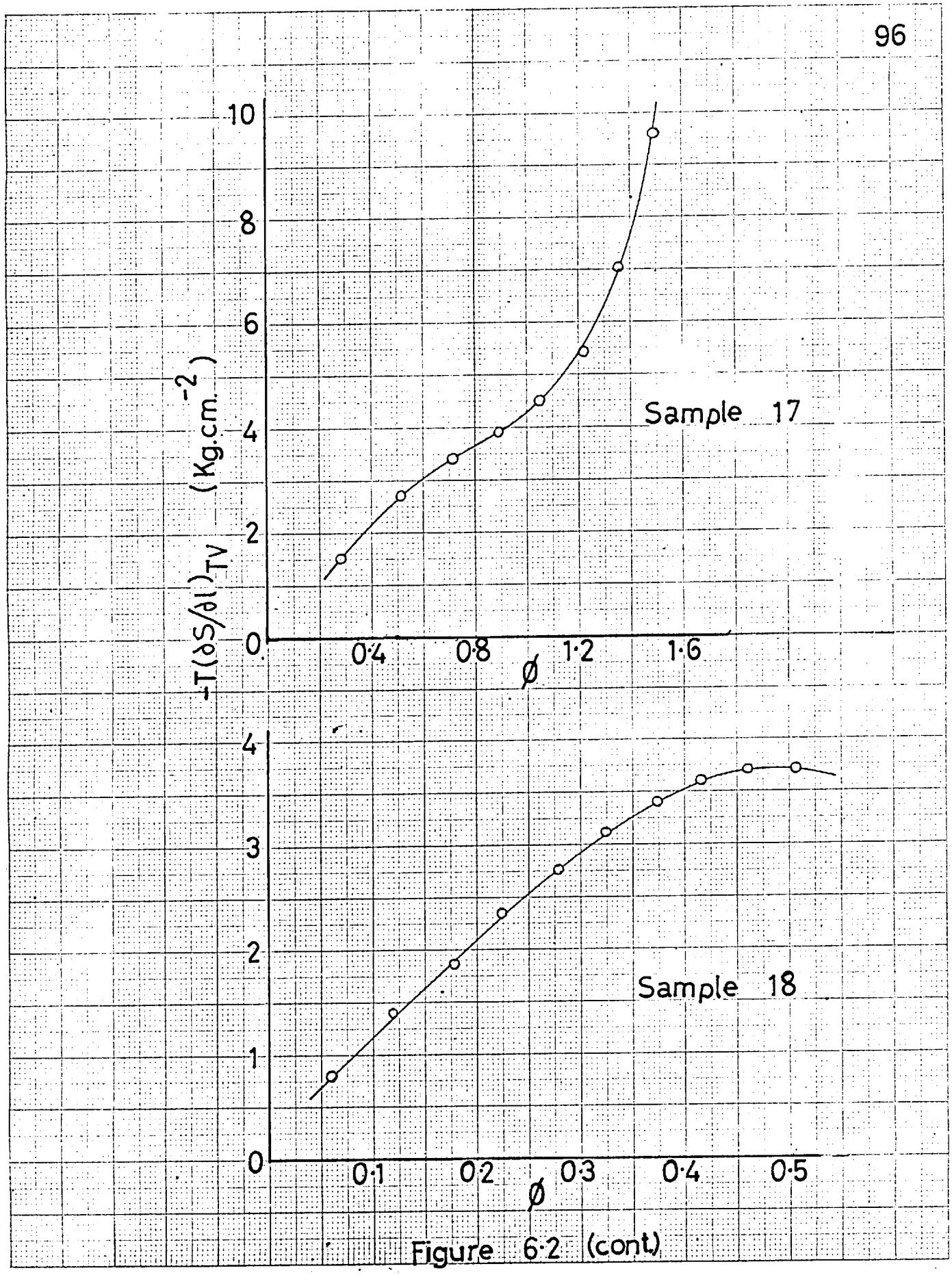
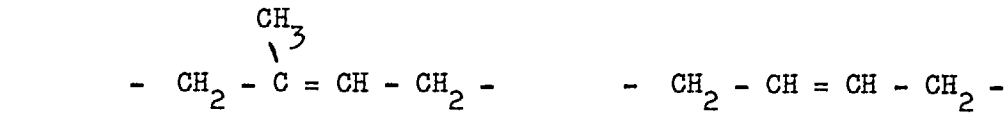


Figure 6·2 (cont)

The values of $\left(\frac{\partial U}{\partial l}\right)_{TV}$ for the poly isoprenes and poly dimethyl siloxanes are in good agreement with previously published values and the sign of this quantity indicates that coiled configurations are energetically more favoured than the extended configurations. For the ethylene propylene rubber however the energy term is negative, indicating that the extended configurations are energetically more favoured. This is in agreement with the effect observed for nearly all polymers. The values for poly buta diene are probably the most interesting as they change from negative at low extensions to positive at higher extensions. If this is true then poly buta diene joins the poly isoprenes and silicones in the small group of polymers with positive energy components to the retractive force. In view of the chemical similarity between the poly isoprene and poly-buta diene shown in Figure 6.3, this should not be unexpected.



isoprene buta diene

Fig. 6.3

Unfortunately the sample of poly buta-diene used in this work was very weak and reliable results were obtained on only one sample and then only for extension ratios less than 1.2. It is thus not certain whether the energy component of the retractive force does change sign, and thus the sign of this component is also uncertain.

The quantity $\frac{\partial \ln \overline{r_o^2}}{\partial T}$ is perhaps the most interesting of

these thermodynamic quantities as, unlike the entropy and internal energy components of the retractive force, it should not be dependent on the degree of crosslinking in the network but should be solely a function of the nature of the polymer chains.

Again the values obtained for the poly isoprenes are in good agreement with previously published values and the agreement between the average values for all samples of natural rubber and all samples of synthetic cis poly isoprene is particularly satisfying.

The results obtained for the two types of poly dimethyl siloxane however are rather more puzzling. Samples 7 and 8 were made from polymer having a small (1%) proportion of vinyl side groups replacing some of the methyl groups and crosslinking, by dicumyl peroxide, was via these larger side groups. Samples 10 and 11 were from poly dimethyl siloxane crosslinked through the methyl groups by di-benzoyl peroxide. Thus chemically the only difference is that the crosslinks of samples 7 and 8 are rather longer than those of samples 10 and 11. Despite this similarity the values of $\frac{\partial \ln \overline{r_o^2}}{\partial T}$ for the polymer containing the vinyl side groups is about 40% lower than the corresponding values for the polymer without vinyl side groups and though this difference is within the estimated maximum error, it is rather larger than the differences between individual samples of either type. No satisfactory reason is offered for this apparent difference and the effect may be spurious by being caused by some difference in the action of the two crosslinking agents used. For instance as both

these agents act via a free radical mechanism the number of crosslinks produced per molecule of peroxide decomposed may be quite different in the two cases and as all the crosslinks produced by a single radical may be expected to be close together this would lead to differences in the distribution of crosslinks through the medium. Though this effect should not influence a true estimate of the quantity $\frac{\partial \ln \bar{r}_o^2}{\partial T}$ the present estimate is based on the applicability of the Kinetic Theory which postulates a random distribution of crosslinks throughout the material. If failure to achieve such a distribution invalidates the applicability of the kinetic theory to the network then it presumably also invalidates the resulting estimate of $\frac{\partial \ln \bar{r}_o^2}{\partial T}$.

This suggestion that the apparent differences in the two rubbers are spurious is reinforced by the similarity between the values $\frac{\partial \ln \bar{r}_o^2}{\partial T}$ obtained in this work for the rubber containing 1 mole % vinyl side groups and the values obtained by Ciferri (9), see Table 5.9, for poly dimethyl siloxane crosslinked with di benzoyl peroxide.

The values of $\frac{\partial \ln \bar{r}_o^2}{\partial T}$ obtained for the ethylene propylene rubber are large and negative as would be expected from the values of $\left(\frac{\partial U}{\partial l}\right)_{TV}$. Though literature values are not available for poly ethylene - propylene the negative values obtained here would be expected from the negative values (-11.0) obtained by Flory, Hoeve and Ciferri (19) for poly ethylene as the substitution of some of the hydrogen atoms of poly ethylene by methyl groups should not have a very marked effect on the position and relative size of the rotational

minima. The introduction of these methyl groups does however have a considerable influence on the crystallinity of the polymer as the measurements in this work show that the copolymer is elastic at 25°C whilst pure poly ethylene does not show rubber elasticity until above 120°C when the material becomes amorphous.

The good agreement between the values obtained for the two temperature ranges and between the values obtained from observing marks on the rubber and on the clamps is indicative that the accuracy of these results is rather better than the estimated maximum error suggests.

The values of $\frac{\partial \ln \bar{r}_o^2}{\partial T}$ obtained for poly buta diene show the same change of sign with α as was observed in the values of $\left(\frac{\partial U}{\partial l}\right)_{TV}$. Whilst this is to be expected, it casts some doubt on the validity of the values as there appears to be no good reason why this change of sign should occur.

Though the amount of crosslinking agent used was very small, 1.5% dicumyl peroxide, these rubbers were very stiff and had a low maximum elongation. This suggests that a large number of crosslinks are formed from each initiating free radical. The combination of a large number of crosslinks, not randomly distributed would mean that the kinetic theory is not applicable particularly at extensions near the maximum when an appreciable number of chains will be fully extended. This line of reasoning suggests that the values obtained at the lowest extension ratios should be the most reliable in which case the negative values obtained indicate that for poly buta diene,

like most other polymers, the extended configurations have the lower potential energy. This contrast with natural rubber may, in view of their chemical similarity as shown in Figure 6.3, be regarded as rather surprising. However in view of the doubtful validity of applying this analysis to this particular polymer any speculation as to why poly isoprene and poly buta-diene appear to differ so markedly is somewhat pointless. In this connection work now in progress to attempt an experimental evaluation of the accuracy of Flory's analysis and the direct determination of the terms $\left(\frac{\partial P}{\partial T}\right)_{Vl}$ and $\left(\frac{\partial f}{\partial P}\right)_{Tl}$ used in equation (3.22),

$$\left[\left(\frac{\partial f}{\partial P}\right)_{Tl} = \left(\frac{\partial V}{\partial l}\right)_{TP}\right]$$

should be particularly interesting.

Table 6.1

Thermodynamic Quantities

Sample 1. Synthetic cis polyisoprene

	α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T}$ x 10^4	1.1	-3.365	-2.791	-2.733	-1.912
	1.2	+1.585	+1.681	+1.545	+1.737
	1.3	3.828	3.710	3.462	3.437
	1.4	5.225	4.972	4.648	4.511
	1.5	6.039	5.753	5.383	5.184
	1.6	6.484	6.099	5.712	5.489
	1.7	6.375	5.988	5.617	5.404
	1.8	5.715	5.374	5.060	4.891
	1.9	4.450	4.212	4.001	3.914
	2.0	2.538	2.472	2.419	2.456
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	0.818	0.856	0.895	0.931
	1.2	1.321	1.382	1.444	1.504
	1.3	1.716	1.796	1.876	1.954
	1.4	2.033	2.128	2.222	2.315
	1.5	2.302	2.409	2.516	2.621
	1.6	2.552	2.671	2.789	2.906
	1.7	2.812	2.944	3.074	3.202
	1.8	3.113	3.259	3.403	3.545
	1.9	3.485	3.647	3.809	3.968
	2.0	3.955	4.140	4.323	4.504
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10	1.1	-0.746	-0.688	-0.736	-0.573
	1.2	+0.655	+0.769	+0.771	+0.953
	1.3	2.211	2.361	2.404	2.613
	1.4	3.752	3.924	4.000	4.240
	1.5	5.110	5.294	5.398	5.672
	1.6	6.116	6.305	6.434	6.744
	1.7	6.601	6.793	6.947	7.291
	1.8	6.395	6.594	6.776	7.150
	1.9	5.331	5.524	5.756	6.156
	2.0	3.238	3.473	3.728	4.145

Table 6.1 (Contd.)

Sample 2. Synthetic cis poly isoprene

	α	25°C.	40°C	55°C.	70°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T} \times 10^4$	1.1	7.142	6.720	6.149	6.004
	1.2	7.564	7.115	6.630	6.337
	1.3	7.905	7.426	6.947	6.605
	1.4	8.215	7.704	7.214	6.851
	1.5	8.496	7.947	7.443	7.073
	1.6	8.735	8.144	7.632	7.263
	1.7	8.918	8.280	7.767	7.409
	1.8	9.027	8.337	7.836	7.495
	1.9	9.045	8.301	7.825	7.510
	2.0	8.960	8.158	7.724	7.442
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	0.637	0.667	0.697	0.726
	1.2	1.154	1.208	1.262	1.314
	1.3	1.574	1.674	1.720	1.792
	1.4	1.913	2.002	2.091	2.178
	1.5	2.191	2.294	2.395	2.495
	1.6	2.427	2.540	2.652	2.763
	1.7	2.637	2.760	2.882	3.002
	1.8	2.841	2.975	3.106	3.235
	1.9	3.057	3.201	3.342	3.481
	2.0	3.303	3.460	3.612	3.761
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10	1.1	1.724	1.778	1.761	1.883
	1.2	3.362	3.464	3.509	3.652
	1.3	4.853	4.991	5.079	5.252
	1.4	6.207	6.367	6.485	6.695
	1.5	7.434	7.599	7.741	7.997
	1.6	8.546	8.695	8.862	9.172
	1.7	9.552	9.663	9.860	10.24
	1.8	10.46	1.051	10.75	11.20
	1.9	11.29	11.24	11.55	12.08
	2.0	12.04	1.187	12.26	12.90

Table 6.1 (Contd.)

Sample 3. Synthetic cis poly isoprene

	α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r}_o^2}{\partial T}$ x 10^4	1.1	-0.771	-0.654	-0.201	-0.017
	1.2	+2.600	+2.460	+2.627	+2.503
	1.3	4.617	4.333	4.273	4.042
	1.4	5.876	5.507	5.285	5.016
	1.5	6.356	5.956	5.652	5.390
	1.6	5.924	5.554	5.262	5.053
	1.7	4.415	4.151	3.989	3.887
	1.8	1.681	1.617	1.744	1.809
	1.9	-2.379	-2.123	-1.498	-1.196
	2.0	-7.783	-7.058	-5.662	-5.053
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	0.871	0.912	0.952	0.992
	1.2	1.446	1.514	1.580	1.647
	1.3	1.868	1.956	2.041	2.127
	1.4	2.200	2.303	2.404	2.505
	1.5	2.505	2.622	2.738	2.852
	1.6	2.845	2.978	3.110	3.240
	1.7	3.283	3.437	3.588	3.739
	1.8	3.882	4.064	4.243	4.420
	1.9	4.703	4.925	5.140	5.356
	2.0	5.811	6.085	6.350	6.618
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10	1.1	-0.196	-0.183	-0.062	-0.006
	1.2	+1.215	+1.264	+1.491	+1.547
	1.3	2.983	3.071	3.329	3.426
	1.4	4.674	4.799	5.045	5.209
	1.5	5.858	6.012	6.234	6.473
	1.6	6.103	6.270	6.490	6.795
	1.7	4.977	5.134	5.405	5.754
	1.8	2.048	2.168	2.575	2.925
	1.9	-3.115	-3.069	-2.408	-2.112
	2.0	-10.95	-11.01	-9.949	-9.781

Table 6.1 (Contd.)

Sample 4. Natural Rubber

	α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r}_o^2}{\partial T}$ x 10^4	1.1	3.337	3.501	3.205	3.062
	1.2	3.585	3.673	3.394	3.251
	1.3	4.002	4.003	3.727	3.570
	1.4	4.623	4.527	4.237	4.046
	1.5	5.480	5.277	4.952	4.709
	1.6	6.611	6.290	5.908	5.588
	1.7	8.051	7.604	7.139	6.720
	1.8	9.838	9.259	8.685	8.144
	1.9	12.01	11.29	10.59	9.902
	2.0	14.60	13.74	12.88	12.04
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	0.603	0.631	0.659	0.687
	1.2	1.129	1.180	1.233	1.285
	1.3	1.573	1.646	1.719	1.791
	1.4	1.935	2.025	2.115	2.204
	1.5	2.213	2.316	2.418	2.520
	1.6	2.404	2.515	2.627	2.737
	1.7	2.506	2.622	2.738	2.853
	1.8	2.517	2.634	2.750	2.866
	1.9	2.435	2.548	2.660	2.772
	2.0	2.258	2.362	2.466	2.570
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10	1.1	0.667	0.777	0.775	0.807
	1.2	1.351	1.534	1.545	1.614
	1.3	2.132	2.359	2.396	2.501
	1.4	3.094	3.345	3.415	3.554
	1.5	4.323	4.584	4.693	4.856
	1.6	5.901	6.170	6.317	6.494
	1.7	7.915	8.196	8.377	8.552
	1.8	10.45	10.75	10.96	11.11
	1.9	13.59	13.94	14.16	14.27
	2.0	17.41	17.84	18.06	18.09

Table 6.1 (Contd.)

Sample 5. Natural Rubber

α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T} \times 10^4$				
1.1	0.067	0.275	0.995	0.603
1.2	2.423	2.398	2.735	2.368
1.3	4.447	4.275	4.291	3.912
1.4	5.958	5.686	5.469	5.080
1.5	6.776	6.447	6.104	5.718
1.6	6.713	6.377	6.027	5.668
1.7	5.581	5.296	5.086	4.786
1.8	3.214	3.049	3.174	2.969
1.9	-0.504	-0.470	+0.252	0.180
2.0	-5.613	-5.292	-3.621	-3.524
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$				
1.1	0.762	0.798	0.832	0.868
1.2	1.307	1.368	1.427	1.489
1.3	1.697	1.776	1.854	1.933
1.4	1.992	2.085	2.176	2.269
1.5	2.253	2.358	2.461	2.565
1.6	2.540	2.657	2.775	2.892
1.7	2.912	3.048	3.182	3.316
1.8	3.431	3.592	3.748	3.907
1.9	4.157	4.353	4.540	4.734
2.0	5.150	5.394	5.624	5.865
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10				
1.1	0.015	0.069	0.281	0.183
1.2	1.018	1.111	1.408	1.317
1.3	2.595	2.746	3.038	2.996
1.4	4.304	4.516	4.761	4.789
1.5	5.705	5.964	6.165	6.262
1.6	6.355	6.631	6.840	6.982
1.7	5.813	6.060	6.375	6.517
1.8	3.637	3.791	4.358	4.432
1.9	-0.615	-0.632	+0.379	0.295
2.0	-7.384	-7.668	-5.973	-6.327

Table 6.1 (Contd.)

Sample 6. Natural Rubber

	α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T}$ x 10^4	1.1	3.788	3.576	3.551	3.406
	1.2	5.023	4.718	4.582	4.355
	1.3	6.131	5.747	5.582	5.214
	1.4	7.068	6.617	6.301	5.946
	1.5	7.773	7.274	6.896	6.501
	1.6	8.181	7.653	7.237	6.823
	1.7	8.217	7.687	7.260	6.852
	1.8	7.807	7.303	6.900	6.528
	1.9	6.878	6.438	6.098	5.797
	2.0	5.370	5.037	4.808	4.623
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	0.622	0.651	0.679	0.708
	1.2	1.110	1.162	1.213	1.264
	1.3	1.492	1.561	1.630	1.698
	1.4	1.792	1.876	1.958	2.041
	1.5	2.039	2.134	2.227	2.321
	1.6	2.256	2.362	2.465	2.569
	1.7	2.472	2.587	2.701	2.815
	1.8	2.712	2.839	2.964	3.088
	1.9	3.003	3.143	3.281	3.419
	2.0	3.370	3.527	3.683	3.837
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10	1.1	0.792	0.821	0.896	0.937
	1.2	1.955	2.015	2.147	2.221
	1.3	3.337	3.426	3.599	3.701
	1.4	4.786	4.903	5.105	5.232
	1.5	6.150	6.293	6.515	6.665
	1.6	7.279	7.444	7.679	7.854
	1.7	8.023	8.203	8.449	8.653
	1.8	8.228	8.417	8.675	8.914
	1.9	7.746	7.936	8.208	8.490
	2.0	6.424	6.605	6.900	7.235

Table 6.1 (Contd.)

Sample 7. Poly dimethyl siloxane + 1% vinyl side groups

	α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \overline{r_o^2}}{\partial T}$ x 10^4	1.1	1.966	2.221	2.031	2.237
	1.2	3.545	3.511	3.459	3.461
	1.3	4.804	4.627	4.529	4.418
	1.4	5.862	5.589	5.415	5.231
	1.5	6.705	6.363	6.116	5.882
	1.6	7.284	6.899	6.595	6.333
	1.7	7.543	7.139	6.805	6.535
	1.8	7.417	7.023	6.691	6.437
	1.9	6.840	6.487	6.198	5.988
	2.0	5.750	5.477	5.280	5.145
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$ x 10	1.1	1.198	1.251	1.305	1.357
	1.2	2.141	2.237	2.332	2.425
	1.3	2.885	3.105	3.142	3.268
	1.4	3.474	3.629	3.782	3.934
	1.5	3.950	4.127	4.301	4.473
	1.6	4.359	4.554	4.746	4.936
	1.7	4.744	4.956	5.165	5.371
	1.8	5.149	5.379	5.607	5.830
	1.9	5.618	5.869	6.118	6.361
	2.0	6.195	6.473	6.746	7.015
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10^2	1.1	0.746	0.935	0.932	1.148
	1.2	2.531	2.764	2.986	3.269
	1.3	4.823	5.108	5.484	5.840
	1.4	7.358	7.700	8.173	8.606
	1.5	9.869	10.27	10.80	11.31
	1.6	12.09	12.55	13.11	13.71
	1.7	13.76	14.27	14.85	15.53
	1.8	14.62	15.17	15.77	16.53
	1.9	14.39	14.96	15.62	16.45
	2.0	12.82	13.40	14.14	15.04

Table 6.1 (Contd.)

Sample 8. Poly dimethyl siloxane + 1% vinyl side groups

	α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T}$ x 10^4	1.1	0.239	0.069	0.409	0.990
	1.2	1.649	1.540	1.755	2.036
	1.3	3.629	3.419	3.455	3.524
	1.4	5.454	5.130	5.007	4.917
	1.5	6.876	6.458	6.215	6.016
	1.6	7.708	7.233	6.919	6.664
	1.7	7.774	7.291	6.967	6.716
	1.8	6.905	6.473	6.211	6.038
	1.9	4.941	4.637	4.529	4.523
	2.0	1.751	1.672	1.836	2.112
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$ x 10	1.1	1.392	1.457	1.518	1.577
	1.2	2.472	2.585	2.694	2.801
	1.3	3.236	3.383	3.525	3.665
	1.4	3.776	3.947	4.113	4.277
	1.5	4.187	4.375	4.559	4.741
	1.6	4.560	4.765	4.965	5.163
	1.7	4.989	5.213	5.433	5.649
	1.8	5.567	5.818	6.063	6.303
	1.9	6.387	6.676	6.958	7.233
	2.0	7.542	7.885	8.218	8.543
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10^2	1.1	0.100	0.031	0.207	0.554
	1.2	1.279	1.310	1.647	2.104
	1.3	3.926	4.056	4.508	5.042
	1.4	7.334	7.554	8.087	8.681
	1.5	10.80	11.09	11.68	12.33
	1.6	13.61	13.95	14.59	15.31
	1.7	15.05	15.42	16.10	16.92
	1.8	14.43	14.79	15.52	16.47
	1.9	11.03	11.34	12.15	13.29
	2.0	4.155	4.357	5.268	6.677

Table 6.1 (Contd.)

Sample 10. Poly dimethyl siloxane

	α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T}$ x 10^4	1.1	-2.393	-1.699	-1.231	-0.932
	1.2	-0.271	-0.133	+0.428	+0.615
	1.3	+1.891	+2.065	2.179	2.217
	1.4	3.930	3.907	3.856	3.752
	1.5	5.754	5.566	5.373	5.148
	1.6	7.275	6.954	6.647	6.326
	1.7	8.396	7.976	7.588	7.204
	1.8	9.009	8.529	8.098	7.687
	1.9	9.004	8.507	8.077	7.683
	2.0	8.268	7.806	7.428	7.103
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$ x 10	1.1	2.381	2.487	2.593	2.698
	1.2	4.196	4.383	4.569	4.753
	1.3	5.514	5.760	6.003	6.245
	1.4	6.440	6.726	7.011	7.293
	1.5	7.078	7.393	7.705	8.016
	1.6	7.535	7.870	8.202	8.532
	1.7	7.915	8.266	8.615	8.961
	1.8	8.322	8.692	9.059	9.422
	1.9	8.862	9.258	9.648	10.03
	2.0	9.641	10.07	10.50	10.92
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10^2	1.1	-1.586	-1.257	-1.007	-0.836
	1.2	-0.336	+0.183	+0.651	+1.025
	1.3	+3.295	3.982	4.623	5.143
	1.4	8.546	9.378	10.16	10.78
	1.5	14.66	15.61	16.49	17.20
	1.6	20.87	21.91	22.88	23.66
	1.7	26.43	27.52	28.56	29.43
	1.8	30.56	31.68	32.79	33.76
	1.9	32.52	33.62	34.80	35.93
	2.0	31.54	32.59	33.83	35.18

Table 6.1 (Contd.)

Sample 11. Poly dimethyl siloxane

$\frac{\partial \ln \bar{r_o^2}}{\partial T}$ x 10^4	α	25°C.	40°C.	55°C.	70°C.
	1.1	3.799	3.594	3.535	3.653
	1.2	5.147	4.910	4.745	4.681
	1.3	6.375	6.060	5.802	5.627
	1.4	7.425	7.033	6.701	6.443
	1.5	8.237	7.782	7.394	7.079
	1.6	8.741	8.245	7.824	7.476
	1.7	8.865	8.353	7.927	7.574
	1.8	8.533	8.035	7.636	7.311
	1.9	7.669	7.224	6.891	6.634
	2.0	6.211	5.864	5.644	5.500
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$ x 10	1.1	1.919	2.006	2.091	2.174
	1.2	3.426	3.580	3.731	3.880
	1.3	4.597	4.803	5.006	5.206
	1.4	5.515	5.762	6.006	6.245
	1.5	6.263	6.543	6.819	7.091
	1.6	6.922	7.231	7.536	7.837
	1.7	7.574	7.913	8.247	8.576
	1.8	8.303	8.675	9.041	9.401
	1.9	9.190	9.603	10.01	10.41
	2.0	10.32	10.78	11.24	11.68
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10^2	1.1	2.452	2.544	2.745	3.116
	1.2	6.211	6.504	6.881	7.425
	1.3	10.79	11.25	11.77	12.46
	1.4	15.68	16.28	16.93	17.73
	1.5	20.39	21.08	21.85	22.75
	1.6	24.40	25.17	26.04	27.04
	1.7	27.22	28.03	28.99	30.12
	1.8	28.33	29.17	30.23	31.49
	1.9	27.24	28.08	29.24	30.67
	2.0	23.45	24.25	25.54	27.18

Table 6.1 (Contd.)

Sample 17. Ethylene-Propylene rubber. 25-75°C. Marks on clamps

	α	25°C.	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r}_o^2}{\partial T}$ x 10^3	1.1	-1.183	-1.078	-0.856	-0.797
	1.2	-1.058	-0.941	-0.798	-0.712
	1.3	-0.699	-0.615	-0.518	-0.462
	1.4	-0.455	-0.396	-0.321	-0.287
	1.5	-0.459	-0.404	-0.326	-0.291
	1.6	-0.817	-0.735	-0.621	-0.544
	1.7	-1.621	-1.464	-1.267	-1.090
	1.8	-2.941	-2.637	-2.291	-1.920
	1.9	-4.810	-4.246	-3.666	-2.972
	2.0	-7.207	-6.229	-5.309	-4.147
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	1.533	1.606	1.677	1.749
	1.2	2.717	2.846	2.973	3.100
	1.3	3.411	3.573	3.733	3.893
	1.4	3.904	4.089	4.271	4.455
	1.5	4.483	4.695	4.905	5.115
	1.6	5.436	5.694	5.949	6.203
	1.7	7.051	7.388	7.719	8.047
	1.8	9.616	10.08	10.53	10.98
	1.9	13.42	14.07	14.70	15.32
	2.0	18.75	19.65	20.55	21.40
$\left(\frac{\partial U}{\partial l}\right)_{TV}$	1.1	-0.400	-0.406	-0.368	-0.376
	1.2	-0.652	-0.648	-0.617	-0.609
	1.3	-0.589	-0.577	-0.542	-0.533
	1.4	-0.466	-0.451	-0.407	-0.400
	1.5	-0.539	-0.528	-0.474	-0.464
	1.6	-1.064	-1.066	-1.006	-0.976
	1.7	-2.297	-2.323	-2.267	-2.190
	1.8	-4.493	-4.558	-4.520	-4.359
	1.9	-7.907	-8.028	-8.028	-7.734
	2.0	-12.80	-12.99	-13.05	-12.57

Table 6.1 (Contd.)

Sample 17. Ethylene Propylene Rubber. 25-75°C. Marks on rubber

	α	25°C	40°C.	55°C.	70°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T} \times 10^3$	1.1	-1.408	-1.193	-1.001	-0.949
	1.2	-0.955	-0.802	-0.701	-0.640
	1.3	-0.697	-0.586	-0.516	-0.460
	1.4	-0.618	-0.529	-0.463	-0.404
	1.5	-0.756	-0.664	-0.578	-0.502
	1.6	-1.161	-1.034	-0.899	-0.782
	1.7	-1.880	-1.672	-1.450	-1.259
	1.8	-2.949	-2.593	-2.230	-1.925
	1.9	-4.378	-3.778	-3.210	-2.740
	2.0	-6.142	-5.173	-4.330	-3.647
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	1.607	1.682	1.757	1.833
	1.2	2.635	2.759	2.883	3.008
	1.3	3.384	3.543	3.703	3.861
	1.4	4.041	4.232	4.423	4.612
	1.5	4.799	5.026	5.252	5.476
	1.6	5.846	6.124	6.399	6.672
	1.7	7.373	7.724	8.071	8.414
	1.8	9.570	10.03	10.48	10.92
	1.9	12.63	13.23	13.82	14.41
	2.0	16.73	17.53	18.32	19.10
$\left(\frac{\partial U}{\partial l}\right)_{TV}$	1.1	-0.475	-0.458	-0.434	-0.450
	1.2	-0.584	-0.554	-0.539	-0.542
	1.3	-0.582	-0.549	-0.536	-0.527
	1.4	-0.629	-0.601	-0.583	-0.562
	1.5	-0.883	-0.865	-0.838	-0.805
	1.6	-1.503	-1.498	-1.458	-1.411
	1.7	-2.648	-2.655	-2.602	-2.539
	1.8	-4.477	-4.493	-4.427	-4.344
	1.9	-7.149	-7.170	-7.091	-6.985
	2.0	-10.82	-10.84	-10.75	-10.62

Table 6.1 (Contd.)

Sample 17. Ethylene Propylene Rubber. 50-100°C. Marks on clamps

	α	55°C.	70°C.	85°C.	100°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T}$ x 10^3	1.1	-1.632	-1.408	-1.361	-1.128
	1.2	-0.964	-0.837	-0.783	-0.665
	1.3	-0.740	-0.647	-0.599	-0.507
	1.4	-0.701	-0.621	-0.571	-0.478
	1.5	-0.817	-0.731	-0.666	-0.562
	1.6	-1.094	-0.983	-0.885	-0.758
	1.7	-1.546	-1.384	-1.227	-1.070
	1.8	-2.177	-1.930	-1.682	-1.487
	1.9	-2.978	-2.605	-2.225	-1.991
	2.0	-3.922	-3.374	-2.821	-2.549
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	1.875	1.955	2.037	2.114
	1.2	2.943	3.068	3.195	3.318
	1.3	3.807	3.969	4.133	4.292
	1.4	4.600	4.797	4.995	5.187
	1.5	5.459	5.693	5.927	6.155
	1.6	6.516	6.796	7.075	7.347
	1.7	7.907	8.247	8.584	8.916
	1.8	9.766	10.19	10.60	11.01
	1.9	12.23	12.75	13.27	13.79
	2.0	15.43	16.09	16.74	17.40
$\left(\frac{\partial U}{\partial l}\right)_{TV}$	1.1	-0.654	-0.637	-0.668	-0.626
	1.2	-0.707	-0.685	-0.700	-0.661
	1.3	-0.744	-0.722	-0.730	-0.682
	1.4	-0.860	-0.842	-0.847	-0.786
	1.5	-1.154	-1.142	-1.142	-1.066
	1.6	-1.722	-1.715	-1.703	-1.620
	1.7	-2.661	-2.656	-2.621	-2.543
	1.8	-4.070	-4.059	-3.985	-3.931
	1.9	-6.044	-6.019	-5.885	-5.878
	2.0	-8.681	-8.632	-8.411	-8.481

Table 6.1 (Contd.)

Sample 17. Ethylene Propylene Rubber. 50-100°C. Marks on rubber

	α	55°C.	70°C.	85°C.	100°C.
$\frac{\partial \ln \overline{r_o^2}}{\partial T}$ x 10^3	1.1	-1.107	-1.045	-0.844	-0.767
	1.2	-1.313	-1.249	-1.051	-0.910
	1.3	-0.678	-0.633	-0.514	-0.462
	1.4	-0.243	-0.204	-0.136	-0.142
	1.5	-0.362	-0.301	-0.235	-0.230
	1.6	-1.280	-1.150	-1.016	-0.888
	1.7	-3.195	-2.922	-2.602	-2.122
	1.8	-6.231	-5.726	-5.007	-3.775
	1.9	-10.42	-9.579	-8.118	-5.594
	2.0	-15.65	-14.39	-11.71	-7.347
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.1	1.659	1.731	1.800	1.870
	1.2	3.184	3.323	3.456	3.590
	1.3	3.727	3.888	4.044	4.202
	1.4	4.022	4.193	4.361	4.534
	1.5	4.799	5.004	5.205	5.411
	1.6	6.793	7.085	7.374	7.660
	1.7	1.074	11.20	11.67	12.11
	1.8	17.36	18.13	18.88	19.58
	1.9	27.39	28.62	29.81	30.90
	2.0	41.58	43.44	45.25	46.89
$\left(\frac{\partial U}{\partial l}\right)_{TV}$	1.1	-0.442	-0.457	-0.418	-0.416
	1.2	-0.959	-0.997	-0.945	-0.910
	1.3	-0.679	-0.694	-0.629	-0.618
	1.4	-0.297	-0.275	-0.203	-0.228
	1.5	-0.509	-0.469	-0.404	-0.428
	1.6	-2.010	-2.004	-1.697	-1.906
	1.7	-5.494	-5.610	-5.627	-5.350
	1.8	-11.66	-12.01	-12.12	-11.45
	1.9	-21.19	-21.94	-22.18	-20.89
	2.0	-34.80	-36.13	-36.54	-34.36

Table 6.1 (Contd.)

Sample 18. Poly buta diene rubber

	α	40°C.	55°C.	70°C.	85°C.	100°C.
$\frac{\partial \ln \bar{r_o^2}}{\partial T}$ x 10^4	1.02	-14.02	-13.41	-13.93	-9.313	-8.439
	1.04	-7.626	-7.007	-7.032	-4.852	-4.466
	1.06	-4.935	-4.482	-4.464	-3.038	-2.719
	1.08	-3.070	-2.794	-2.811	-1.786	-1.482
	1.10	-1.446	-1.336	-1.414	-0.663	-0.386
	1.12	+0.139	+0.100	-0.049	+0.485	+0.702
	1.14	1.782	1.610	+1.388	1.733	1.846
	1.16	3.540	3.253	2.954	3.127	3.093
	1.18	5.455	5.069	4.694	4.701	4.476
	1.20	7.565	7.093	6.640	6.487	6.032
$-T\left(\frac{\partial S}{\partial l}\right)_{TV}$	1.02	0.791	0.827	0.864	0.896	0.931
	1.04	1.352	1.413	1.474	1.531	1.590
	1.06	1.875	1.960	2.045	2.124	2.206
	1.08	2.353	2.459	2.565	2.665	2.768
	1.10	2.774	2.899	3.024	3.143	3.264
	1.12	3.131	3.271	3.412	3.547	3.683
	1.14	3.412	3.566	3.719	3.866	4.014
	1.16	3.609	3.772	3.933	4.089	4.246
	1.18	3.713	3.879	4.045	4.205	4.367
	1.20	3.714	3.879	4.044	4.204	4.368
$\left(\frac{\partial U}{\partial l}\right)_{TV}$ x 10	1.02	-2.413	-2.528	-2.796	-2.241	-2.229
	1.04	-2.606	-2.641	-2.866	-2.266	-2.272
	1.06	-2.510	-2.513	-2.716	-2.084	-2.032
	1.08	-2.063	-2.065	-2.257	-1.603	-1.450
	1.10	-1.282	-1.218	-1.400	-0.729	-0.463
	1.12	+0.137	+0.108	-0.057	+0.627	+0.990
	1.14	2.016	1.990	+1.859	2.558	2.970
	1.16	4.500	4.508	4.438	5.157	5.539
	1.18	7.649	7.741	7.766	8.514	8.758
	1.20	11.53	11.77	11.95	12.72	12.69

Table 6.2

Values of $(\partial U/\partial l)_{TV}$ averaged over all values of α

	$(\partial U/\partial l)_{TV}$ x 10 Kg.cm.$^{-2}$					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	3.866	4.037	4.148	4.439		
2	7.547	7.619	7.786	8.107		
3	3.954	4.078	4.359	4.589		
Mean	5.122	5.245	5.431	5.712		
4	6.683	6.950	7.070	7.185		
5	3.680	3.861	3.734	3.753		
6	5.472	5.606	5.817	5.990		
Mean	5.278	5.472	5.540	5.642		
7	0.930	0.971	1.019	1.074		
8	0.817	0.839	0.898	0.974		
Mean	0.874	0.905	0.959	1.024		
10	2.105	1.961	2.053	2.135		
11	1.862	1.924	2.002	2.100		
Mean	1.984	1.943	2.028	2.118		
17C	-31.20	-31.58	-31.28	-30.21		
17R	-29.75	-29.68	-29.26	-28.78		
17C			-27.30	-27.11	-26.69	-26.27
Mean	-30.48	-30.63	-29.26	-28.70	-26.69	-26.27
18		1.504	1.515	1.391	2.006	2.250

Table 6.3

Values of $\partial \ln \bar{r_o^2} / \partial T$ averaged over all values of α

$\partial \ln \bar{r_o^2} / \partial T \times 10^4$

Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	3.893	3.747	3.511	3.511		
2	8.401	7.813	7.313	6.999		
3	3.873	3.616	3.579	3.460		
Mean	5.374	5.059	4.801	4.623		
4	7.214	6.917	6.472	6.103		
5	4.792	4.225	3.792	3.476		
6	6.624	6.205	5.914	5.605		
Mean	6.210	5.782	5.393	5.061		
7	5.772	5.334	5.312	5.170		
8	4.693	4.392	4.330	4.354		
Mean	5.233	4.863	4.821	4.762		
10	6.715	6.447	5.630	5.303		
11	7.100	6.700	6.410	6.198		
Mean	6.908	6.574	6.020	5.751		
17C	-21.25	-18.75	-15.97	-13.22		
17R	-20.94	-18.02	-15.38	-13.31		
17C			-16.57	-14.52	-12.82	-11.20
Mean	-21.10	-18.39	-15.97	-13.68	-12.82	-11.20
18		-1.261	-1.191	-1.403	-0.312	-0.134

2. Stress-Strain Equations

(a) Kinetic theory

The simple kinetic theory may be expressed, for one dimensional elongation, in the form:

$$f = C(\alpha - \alpha^{-2}) \qquad (6.1)$$

where C is constant for a given rubber sample at a fixed temperature. This equation predicts a linear relationship between f and the quantity $(\alpha - \alpha^{-2})$. The typical graphs shown in Figure 6.4 indicate that in this work, as in all previous work, equation 6.1 is obeyed only over a very small range of values of α. As has been stated in Chapter 3 of this thesis the reason for the departure from this equation is not fully understood. The shape of the curves obtained suggests that a quadratic equation of the form:

$$f = a + b\phi + c\phi^2 \qquad (6.2)$$

where a, b and c are constants and $\phi = (\alpha - \alpha^{-2})$, should give a better representation of the data. From the definitions of ϕ and of α it is clear that the retractive force f must be zero when $\alpha = 1$, i.e. $\phi = 0$. Thus equation 6.2 may be rewritten:

$$f = b\phi + c\phi^2 \qquad (6.2a)$$

and this predicts a linear relationship between f/ϕ and ϕ. Typical examples, shown in Figure 6.5, indicate that over the range of extension ratios used, equation 6.2a gives a fairly good representation of the stress strain behaviour.

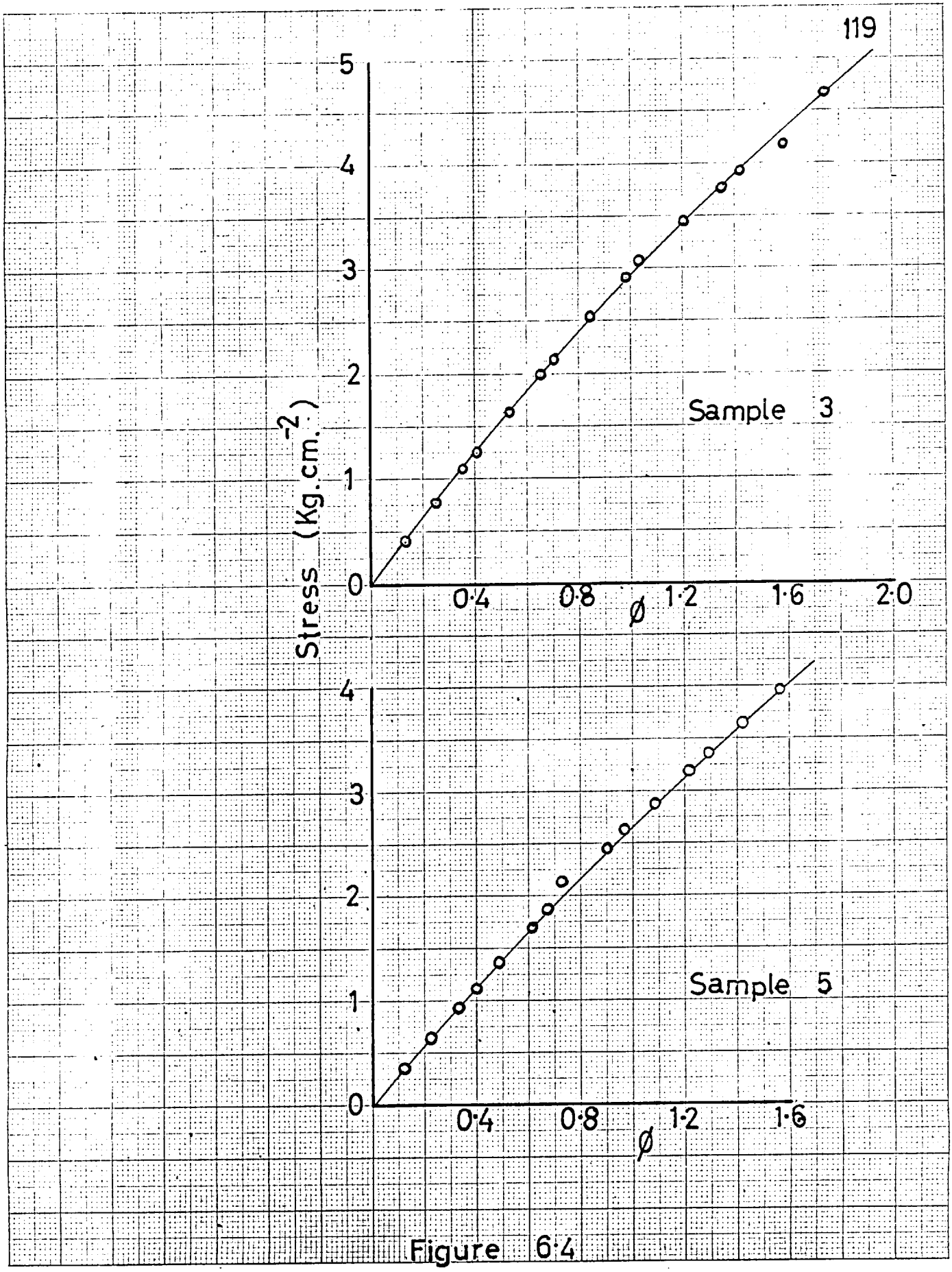
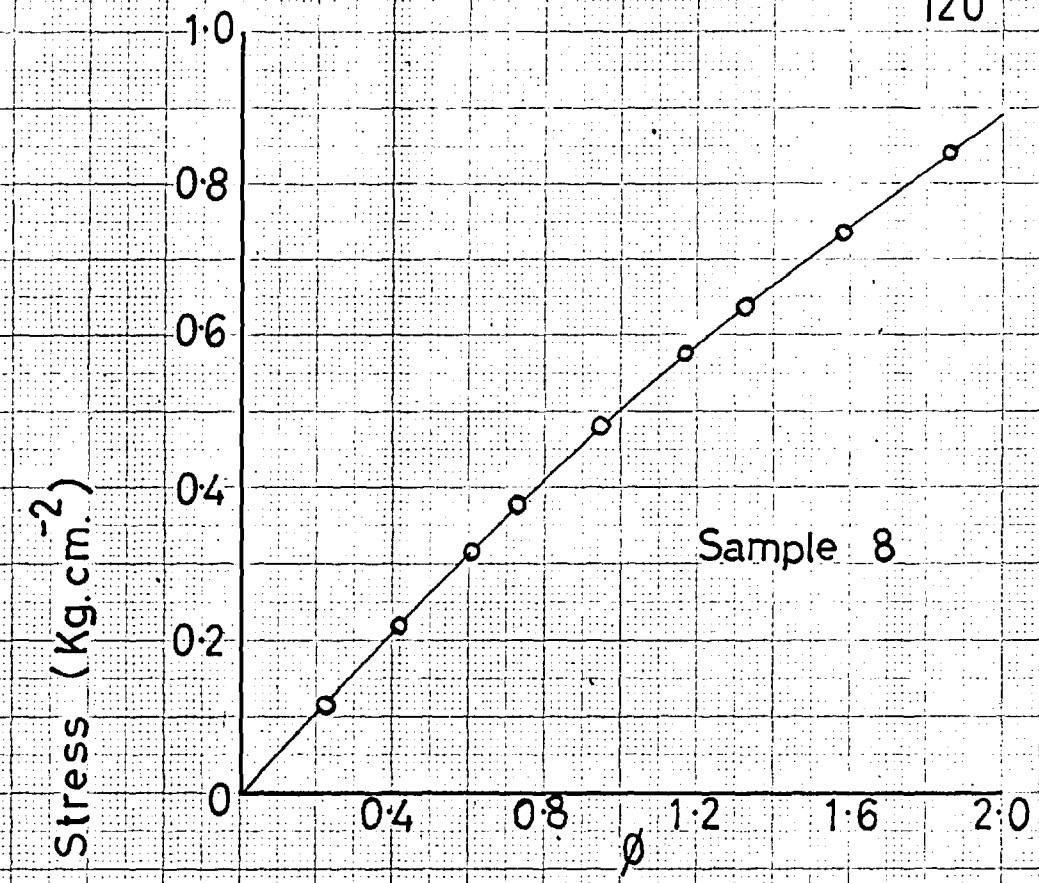

Stress (Kg.cm.$^{-2}$)
0
1
2
3
4
5
0·4
0·8
1·2
1·6
2·0
ø
Sample 3
0
1
2
3
4
0·4
0·8
1·2
1·6
ø
Sample 5

Figure 6·4



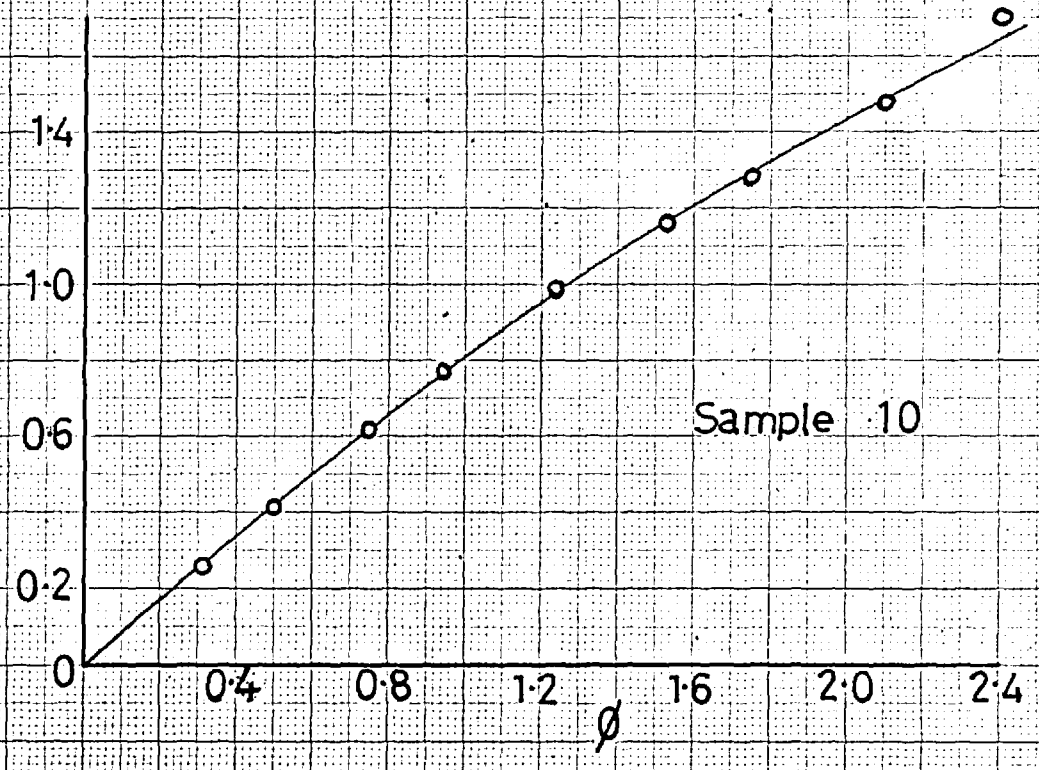


Figure 6·4 (cont.)

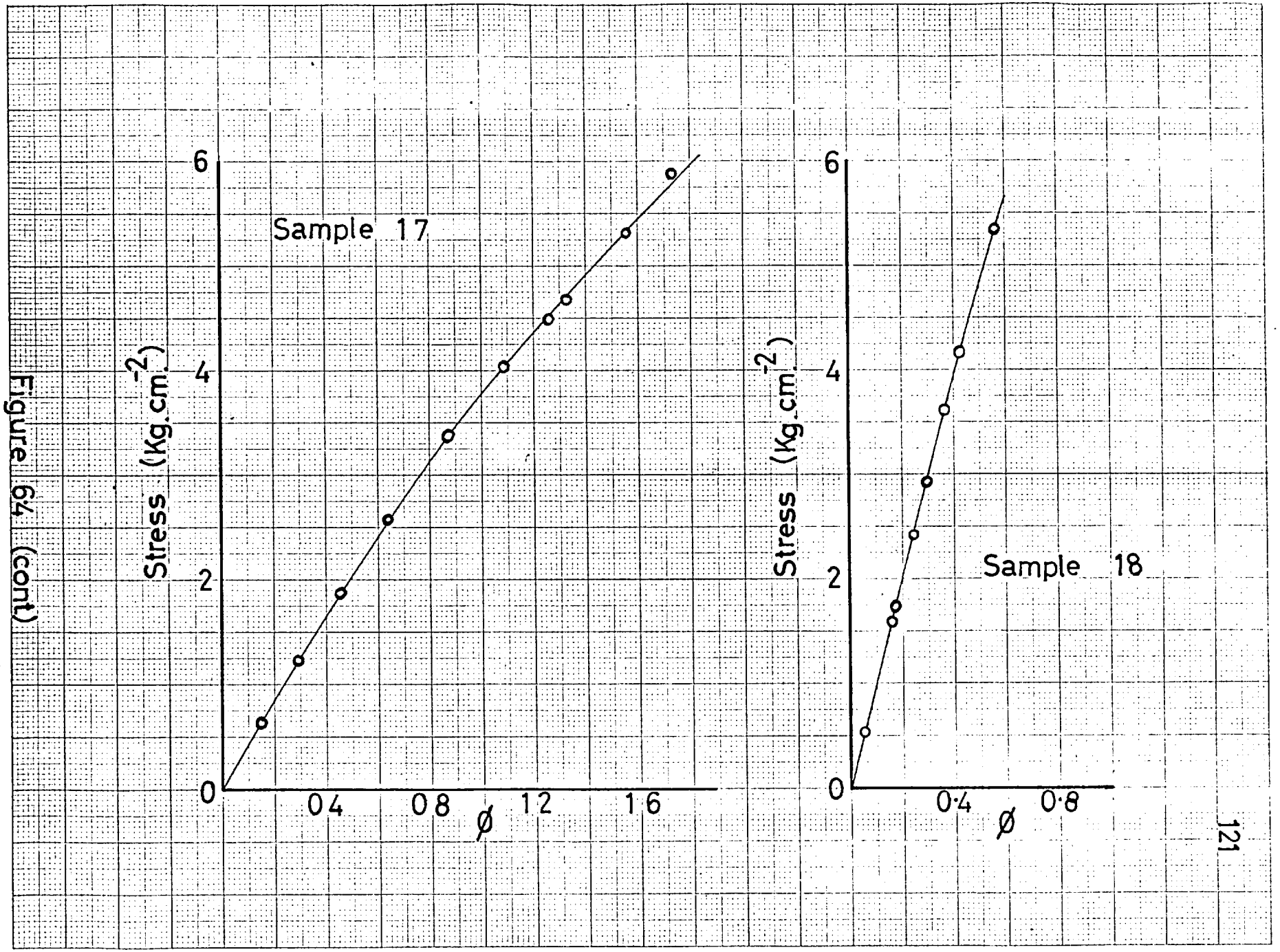


Figure 64 (cont)

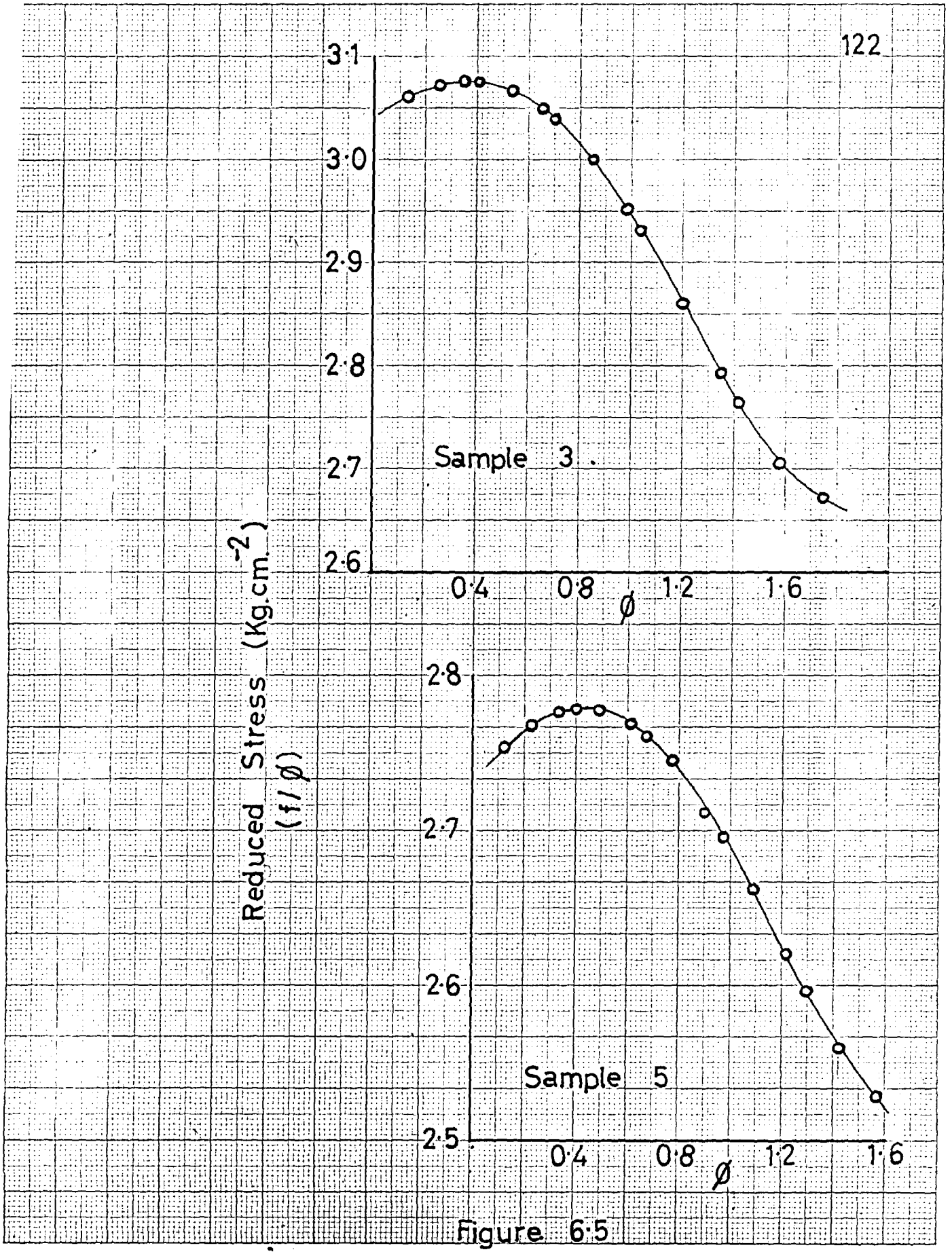

3·1
3·0
2·9
2·8
2·7
2·6
Sample 3
0·4
0·8
1·2
1·6
ϕ
Reduced Stress (f/ϕ) (Kg.cm.-2)
2·8
2·7
2·6
2·5
Sample 5
0·4
0·8
1·2
1·6
ϕ

Figure 6·5

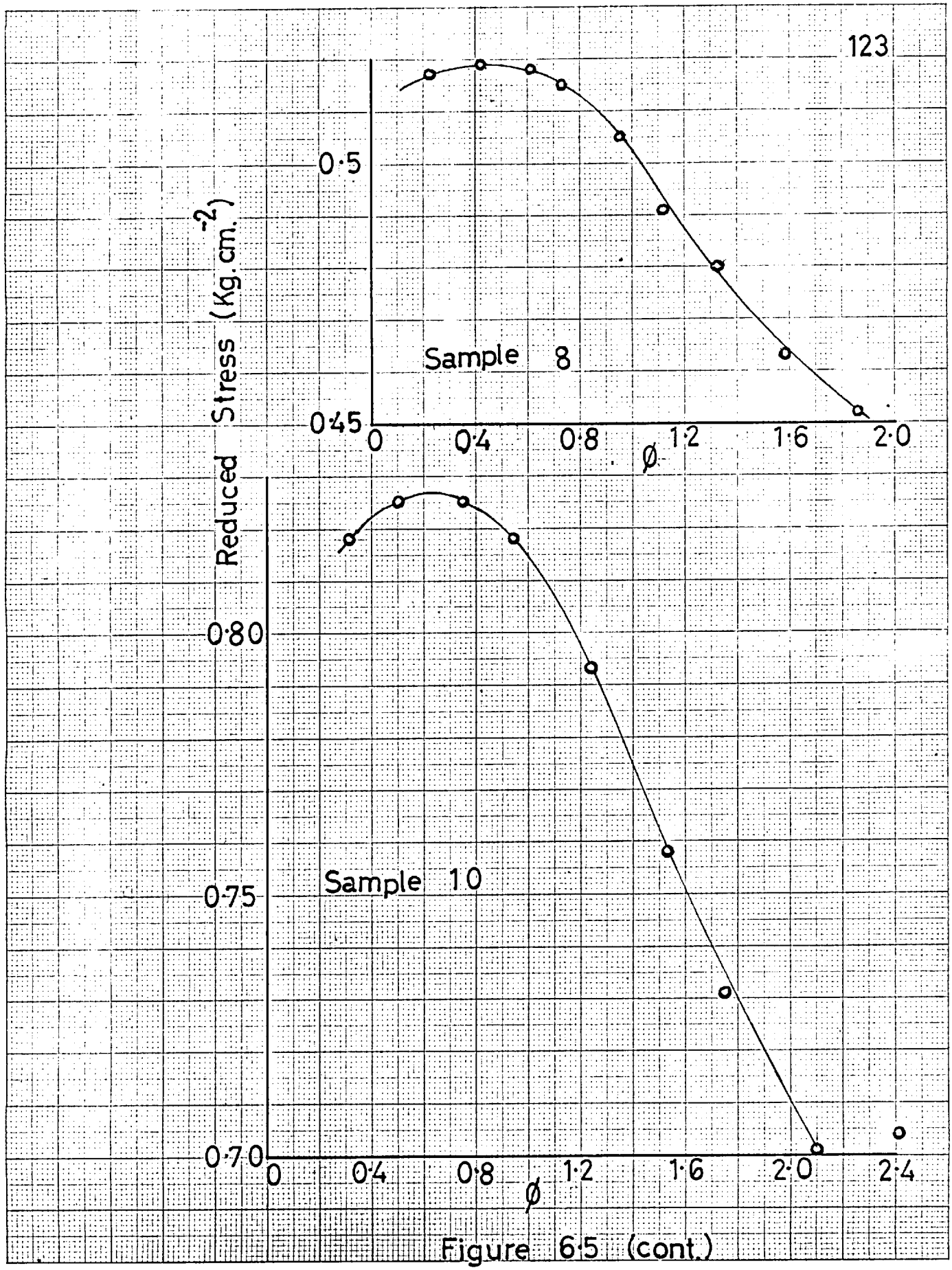


Figure 6·5 (cont.)

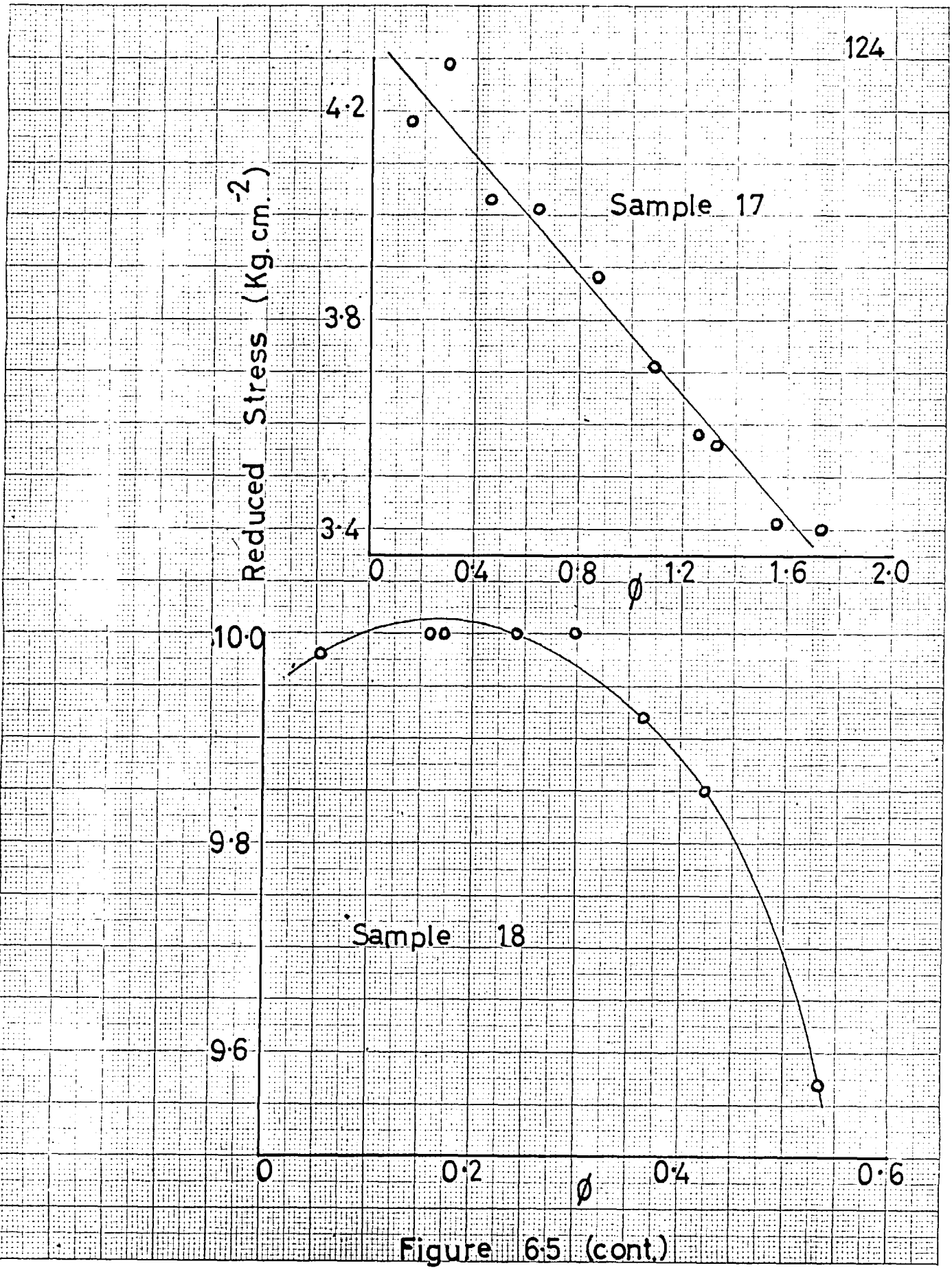


Figure 6·5 (cont.)

Though this equation is purely empirical its form suggests that it may be regarded as equation 6.1 modified by the addition of a correction term. Thus the constant b of equation 6.2a being the initial slope of the curve should correspond to the kinetic theory constant C of equation 6.1. Values of the constants band c of equation 6.2a, subsequently designated C_o and C' are listed in Tables 6.4 and 6.5 respectively. As would be expected if C_o corresponds to the kinetic theory constant C the values of C_o show a linear increase with increasing temperature. Values of C_o/C, where C is calculated from swelling measurements, are shown in Table 6.0 and are approximately constant for both natural rubber and synthetic cis poly isoprene, indicating that C_o, like C, depends on the degree of crosslinking.

Table 6.0

Values of C_o/C where $C = \frac{\nu RT}{M_c}$

Samples	25°C.	40°C.	55°C.	70°C.
1, 2, 3	1.20	1.21	1.21	1.18
4, 5, 6	1.13	1.12	1.10	1.09
7, 8	0.25	0.25	0.24	0.24
10, 11	0.31	0.31	0.30	0.31

The values for the two types of poly dimethyl siloxane show a rather wider divergence but the divergence is much less than that of the corresponding values of C_o. This may possibly be due to the differences in the two rubbers as discussed in the thermodynamics section.

This suggestion is supported by the observation of Tobolsky, Carlson and Indictor (75) that the magnitude of C_o/C, which they designate a 'front factor', decreases with increasing size of side chain in a series of crosslinked poly acrylates. Similarly in this work the values of C_o/C for the siloxane containing some vinyl side groups (samples 7 and 8) are lower than those for the pure dimethyl siloxanes. However, as for the thermodynamic quantities, these conclusions are not reliable due to possible differences in the action of the crosslinking agents used.

The values of C' appear to be about 10% of the corresponding values of C_o for the poly isoprenes and poly dimethyl siloxanes and only slightly higher about 12-13% for the ethylene propylene rubbers. This sort of ratio seems to be a satisfactory indication of the deviation of the stress strain data from the kinetic theory. In the case of poly buta diene C' is about 20% of C_o and this rather high value is probably due to the rubber having a very low maximum elongation so that the kinetic theory cannot be expected to be valid.

If C' is regarded as a measure of the deviation from the kinetic theory it is significant that the values increase with increasing temperature. If, as Flory and Ciferri (19) suggest, deviations are due to failure to attain equilibrium, it might be expected that the deviation, and hence the value of C', would decrease with increasing temperature. Hence this suggestion by Flory and Ciferri is not wholly satisfactory at least in this respect.

Table 6.4

Values of C_o obtained from original data

Sample	Value of C_c (b of eqn. 6.2a)					
	25°C.	40°C.	55°C.	70°C.	80°C.	100°C.
1	3.00	3.12	3.23	3.33		
2	3.13	3.38	3.46	3.58		
3	3.37	3.47	3.58	3.69		
4	3.11	3.24	3.45	3.58		
5	3.03	3.16	3.25	3.35		
6	2.92	3.03	3.17	3.26		
7	0.55	0.56	0.58	0.59		
8	0.57	0.58	0.61	0.62		
10	0.87	0.91	0.96	0.99		
11	0.85	0.88	0.91	0.95		
17C	4.26	4.53	4.75	4.93		
17R	4.17	4.37	4.57	4.87		
17C			4.74	4.92	5.18	5.45
18		10.72	11.03	11.39	11.78	9.51

Table 6.5

Values of -C' obtained from the original data

	Value of -C' (c of eqn. 6.2a)					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	0.294	0.315	0.331	0.349		
2	0.328	0.403	0.444	0.468		
3	0.394	0.394	0.410	0.405		
4	0.390	0.437	0.505	0.537		
5	0.304	0.330	0.336	0.346		
6	0.324	0.344	0.375	0.389		
7	0.060	0.062	0.065	0.068		
8	0.062	0.063	0.069	0.070		
10	0.073	0.085	0.095	0.102		
11	0.063	0.070	0.074	0.081		
17C	0.533	0.563	0.575	0.553		
17R	0.487	0.472	0.455	0.502		
17C			0.605	0.581	0.609	0.648
18		1.828	1.828	1.953	2.136	2.990

The fact that the retractive force f must be zero when $\alpha = 1$ suggested that it might be profitable to alter the value of l_o and thus of all the α's in small steps to find the value of l_o which gives the lowest value of f_o when $\alpha = 1$. Values of this correction factor δ have already been listed in Table 5.7, column 1, and the resulting values of f_o are compared in Table 5.6 column 2, with the original values of f_o given in column 1 of this table. In all cases the change in l_o was very small only once being greater than 1% and in most cases being less than 0.5%. However, this change did produce a large decrease in the value of f_o and hence these new values are considered to be more accurate than the old uncorrected values. Tables 6.6 and 6.7 give the values of C_o and C' respectively for these corrected values of α. Comparison with Tables 6.4 and 6.5 shows that there has been very little, less than 1%, change in the values of C_o and C' hence all comments on the original values apply equally well to the values obtained after adjusting l_o.

The typical graphs of f/ϕ vs. ϕ, shown in Figure 6.6, for these adjusted values of l_o show that the relationship is more nearly linear than was the relationship of the unadjusted values of l_o as illustrated in Figure 6.5. The complete values of α, α^{-1}, ϕ, f and f/ϕ for the original values of l_o are listed in Appendix 2.

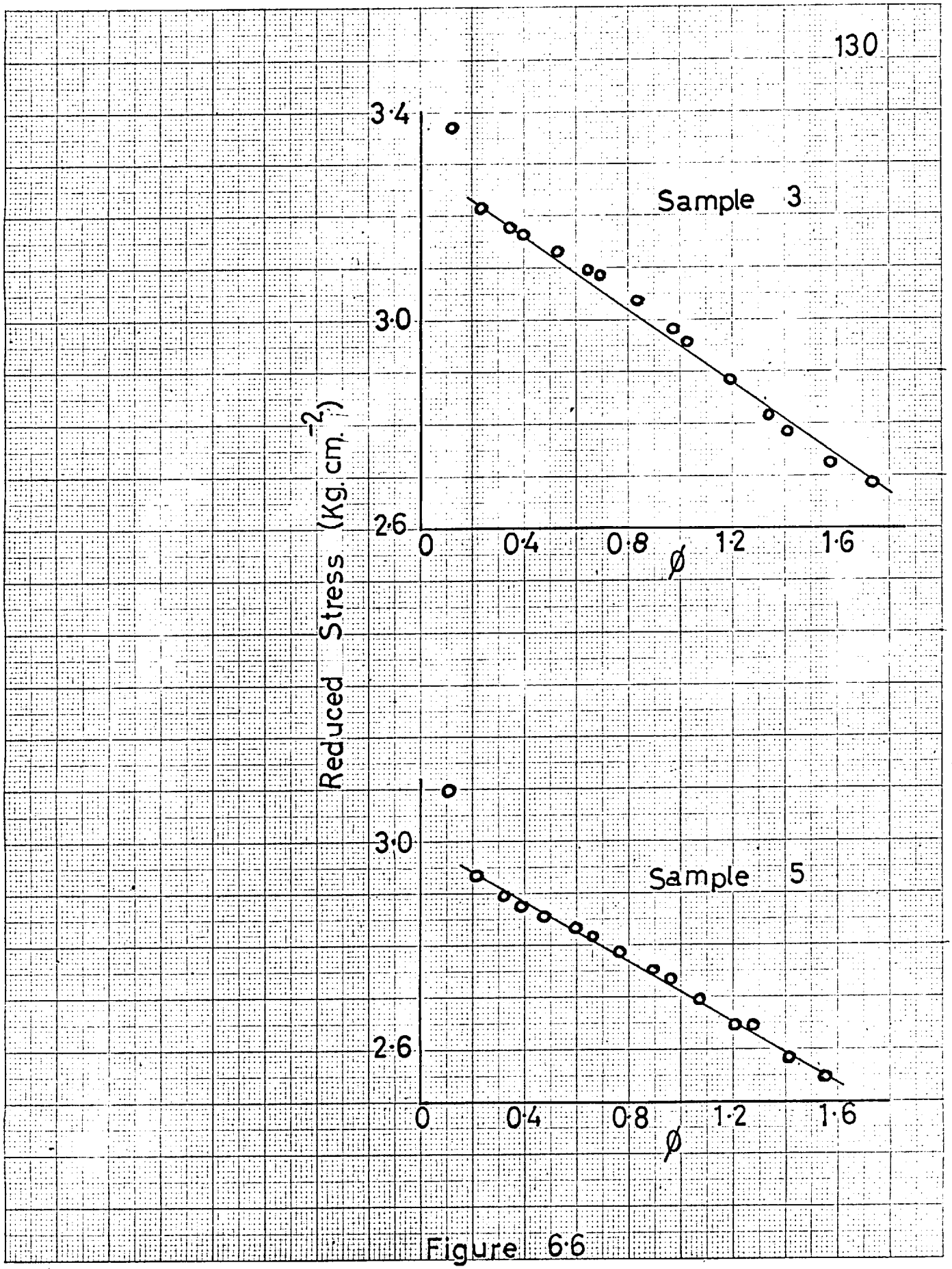

Sample 3
3·4
3·0
2·6
0
0·4
0·8
1·2
1·6
ϕ
Reduced Stress (Kg. cm.$^{-2}$)
Sample 5
3·0
2·6
0
0·4
0·8
1·2
1·6
ϕ

Figure 6·6

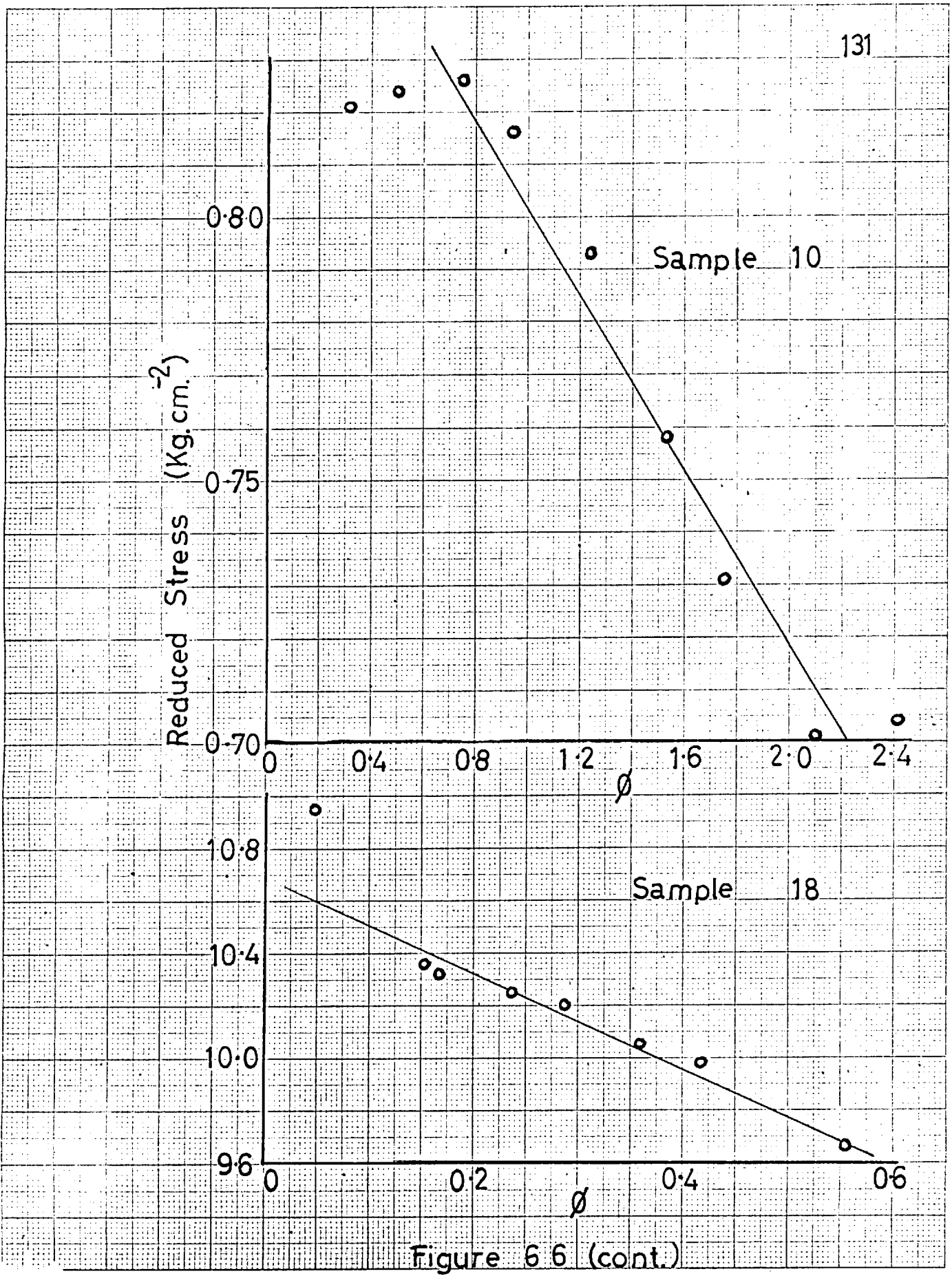


Figure 6 6 (cont.)

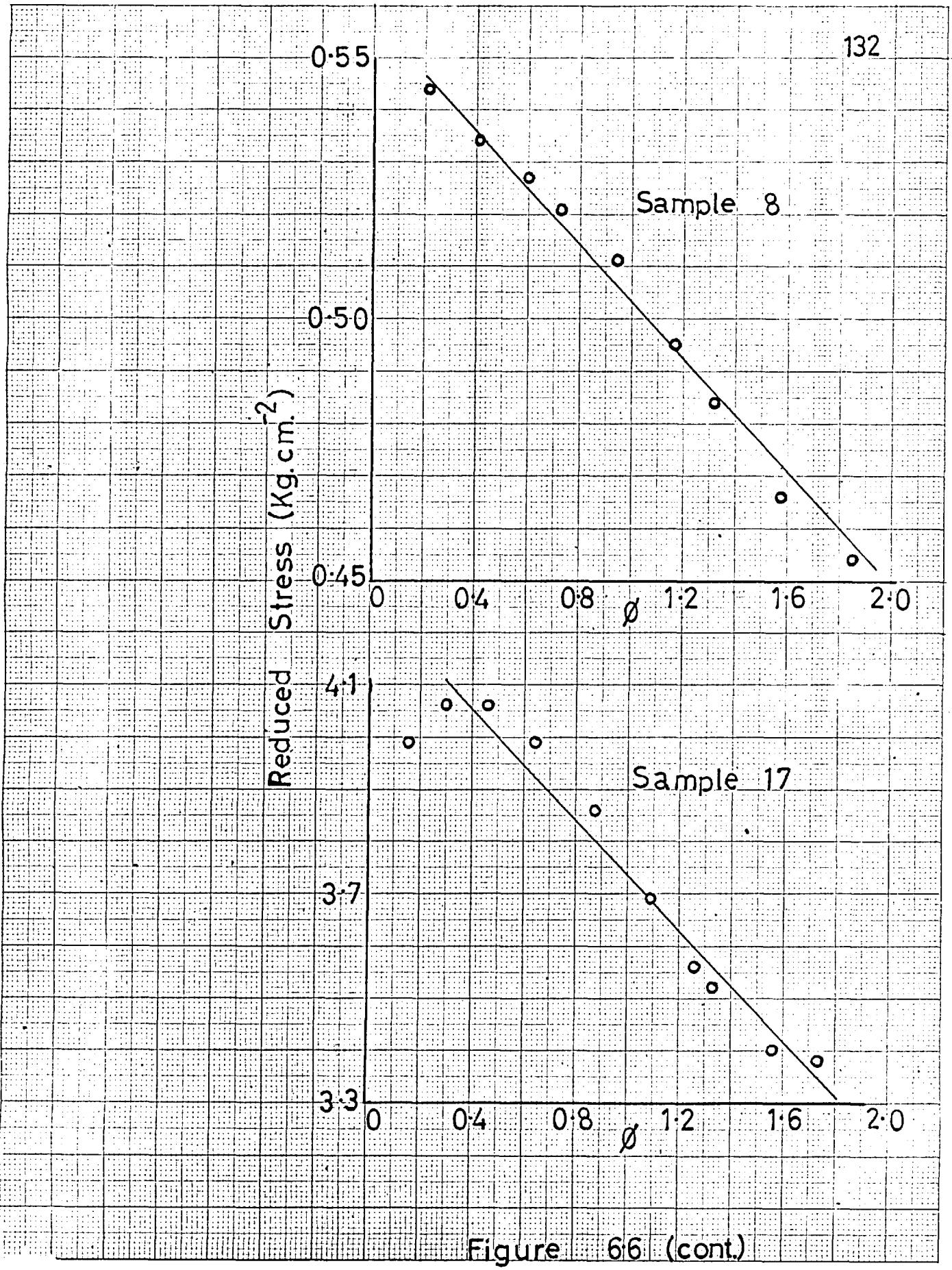


Figure 66 (cont.)

Table 6.6

Values of C_o obtained from values of α adjusted to give the minimum value of $|f_o|$

	Value of C_o					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	2.98	3.10	3.21	3.32		
2	3.12	3.30	3.44	3.56		
3	3.35	3.45	3.57	3.67		
4	3.01	3.14	3.25	3.36		
5	3.01	3.14	3.23	3.33		
6	2.86	2.96	3.08	3.17		
7	0.54	0.55	0.57	0.59		
8	0.57	0.58	0.61	0.62		
10	0.87	0.91	0.96	0.99		
11	0.85	0.88	0.91	0.95		
17C	4.27	4.53	4.77	4.96		
17R	4.33	4.39	4.59	4.90		
17C			4.72	4.91	5.18	5.45
18		10.68	11.01	11.39	11.80	9.50

Table 6.7

Values of -C' obtained from values of α adjusted to give the minimum value of $|f_o|$

	Value of -C'					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	0.288	0.309	0.326	0.345		
2	0.327	0.401	0.439	0.464		
3	0.390	0.390	0.407	0.402		
4	0.383	0.414	0.434	0.458		
5	0.299	0.323	0.330	0.341		
6	0.304	0.320	0.340	0.350		
7	0.058	0.061	0.064	0.067		
8	0.062	0.063	0.068	0.070		
10	0.073	0.085	0.095	0.102		
11	0.063	0.069	0.074	0.081		
17C	0.536	0.563	0.581	0.560		
17R	0.491	0.477	0.460	0.510		
17C			0.601	0.576	0.609	0.646
18		1.815	1.821	1.953	2.144	2.991

(b) Mooney-Rivlin Phenomenological Equation

The Mooney Rivlin equation may be expressed, for the case of one dimensional extension, by the equation:

$$f/\phi = C_1 + C_2\alpha^{-1} \qquad (6.3)$$

where ϕ is the quantity $(\alpha - \alpha^{-2})$. This equation suggests there should be a linear relationship between f/ϕ and α^{-1}. Typical examples of such graphs are shown in Figure 6.7 and complete lists of values of C_1 and C_2 obtained are given in Tables 6.8 and 6.9. The values of C_1 increase with increasing temperature, thus supporting the suggestion that the first term of the phenomenological equation is related to the only term in the kinetic theory equation. Moreover, the agreement between different samples of the same polymer is quite good. Examination of the graphs however shows that the relationship between f/ϕ and α^{-1} is by no means linear and this doubtless accounts for the marked divergences between values of C_2 obtained from different samples of the same rubber. In fact because of this non-linear relationship these values of C_1 and C_2 are of little or no value though it may be remarked in passing that the values of C_2 tend to increase with increasing temperature, which does not support the suggestion of Flory and Ciferri (18) that the existence of this C_2 term is due to failure to achieve equilibrium.

Mooney-Rivlin graphs were drawn for the values of α which had been adjusted to give the minimum values of f_o. Typical

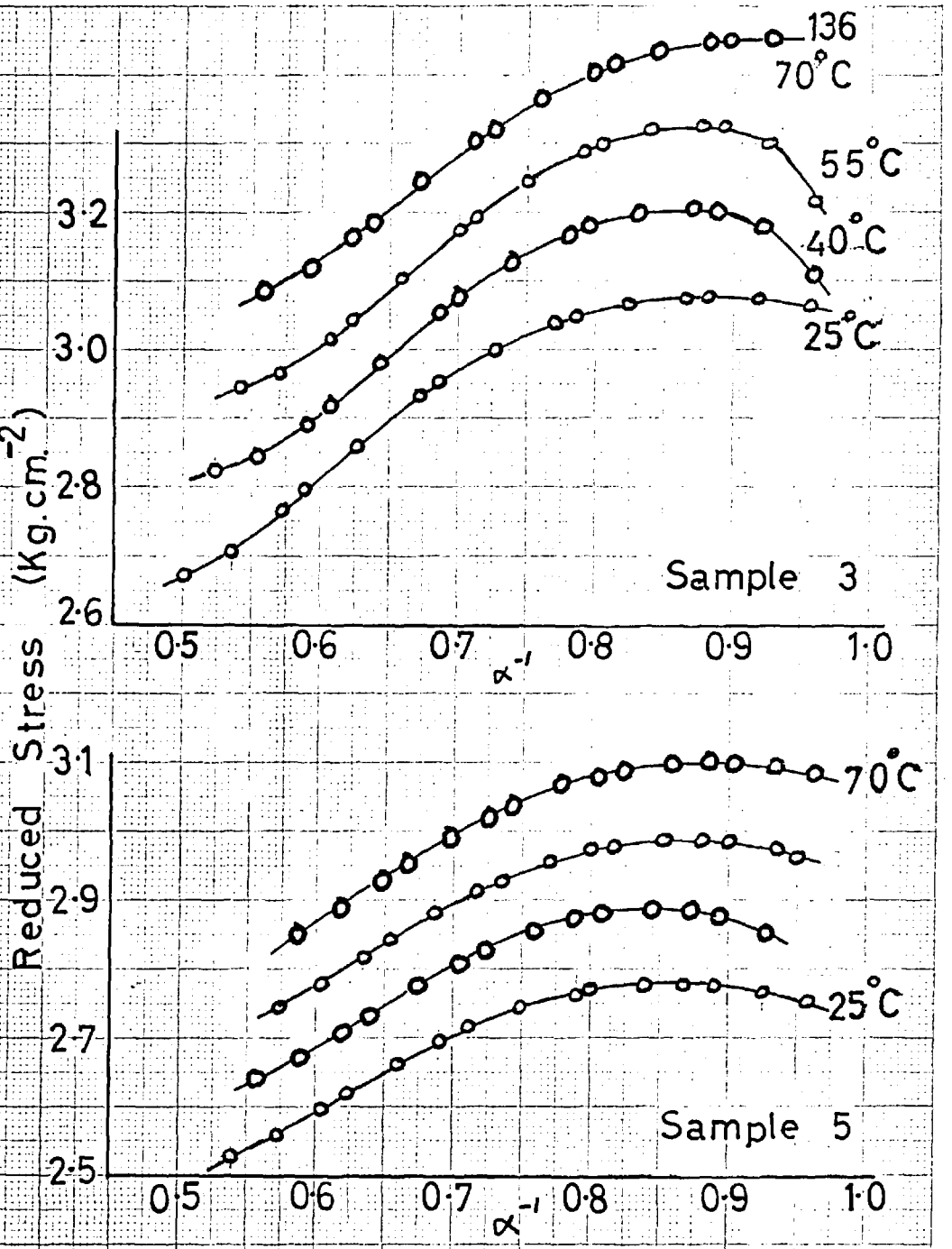


Figure 6·7

Typical Mooney Rivlin Graphs

original values of l_o

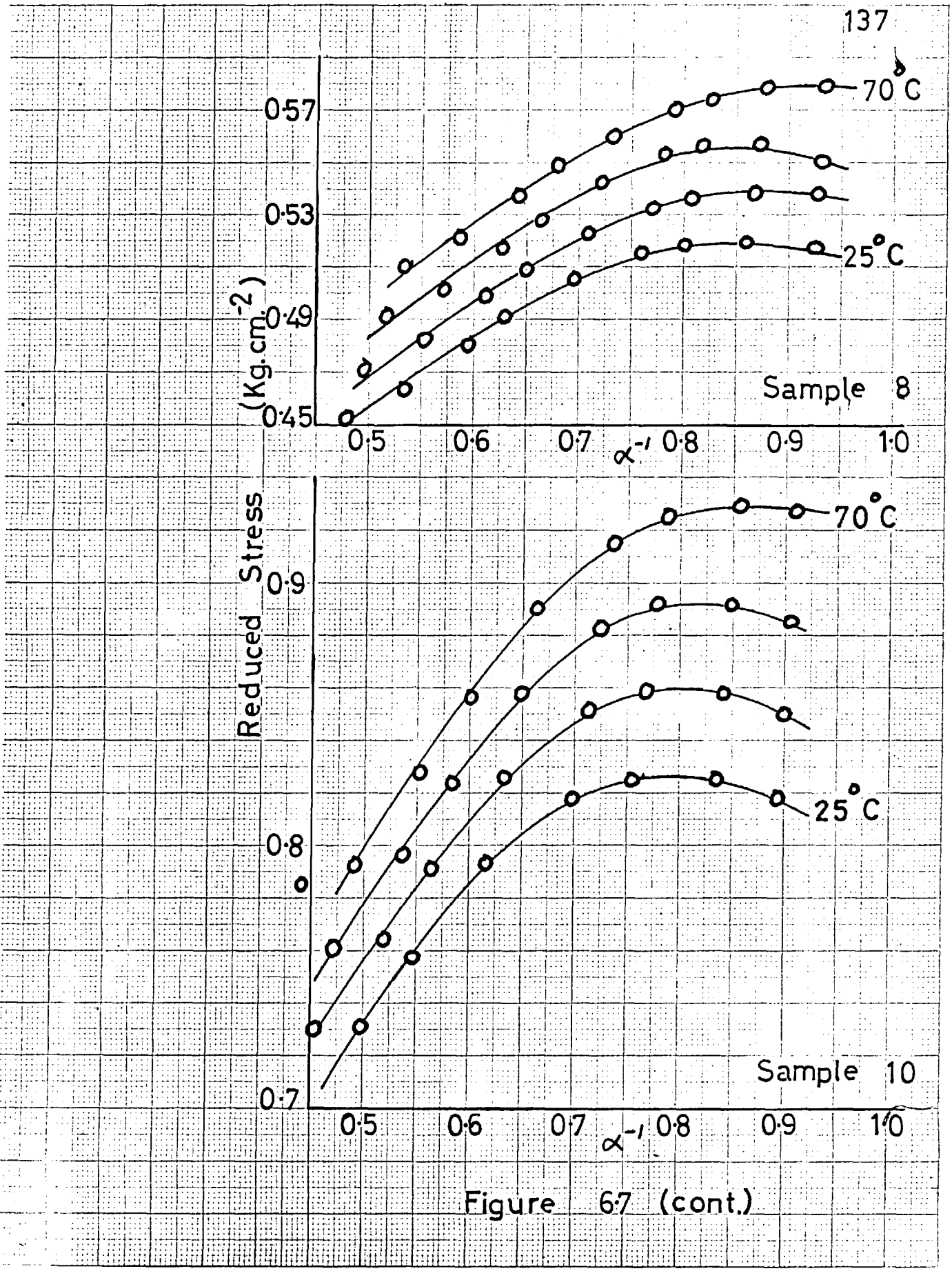


Figure 6·7 (cont.)

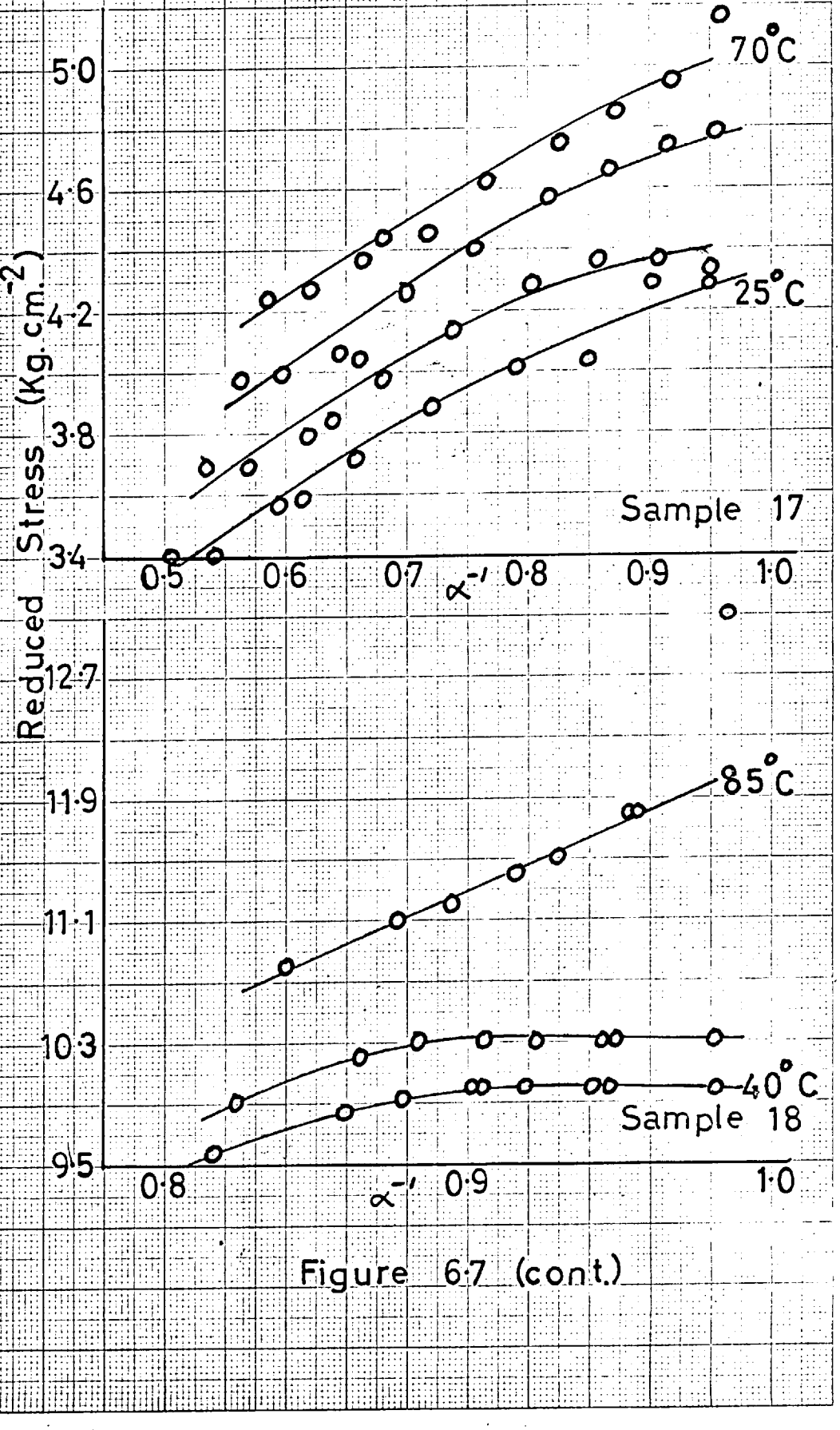


Figure 6·7 (cont.)

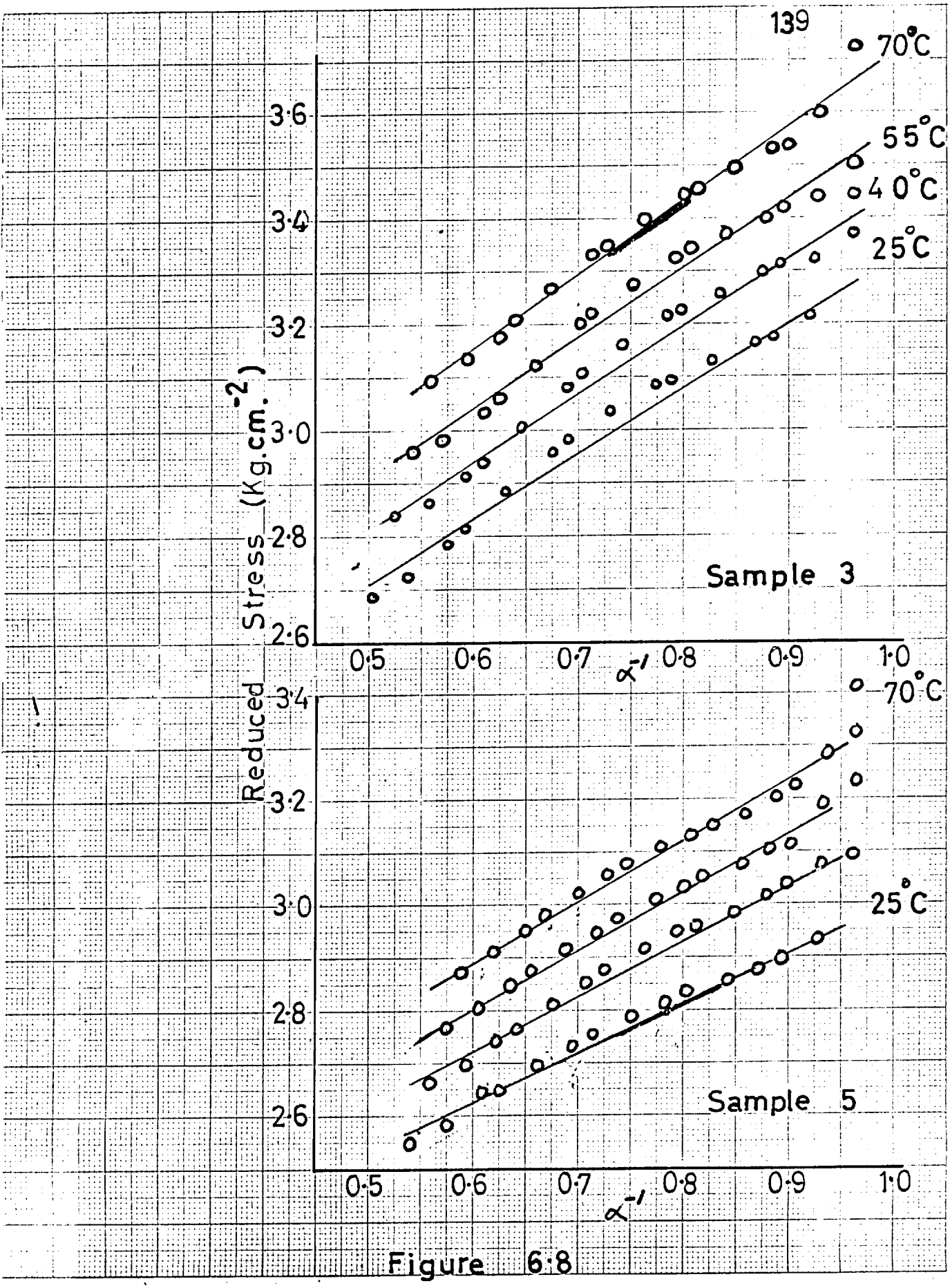

70°C
55°C
40°C
25°C
Sample 3
Reduced Stress (Kg.cm.$^{-2}$)
3·6
3·4
3·2
3·0
2·8
2·6
0·5
0·6
0·7
0·8
0·9
1·0
α^{-1}
70°C
25°C
Sample 5

Figure 6·8

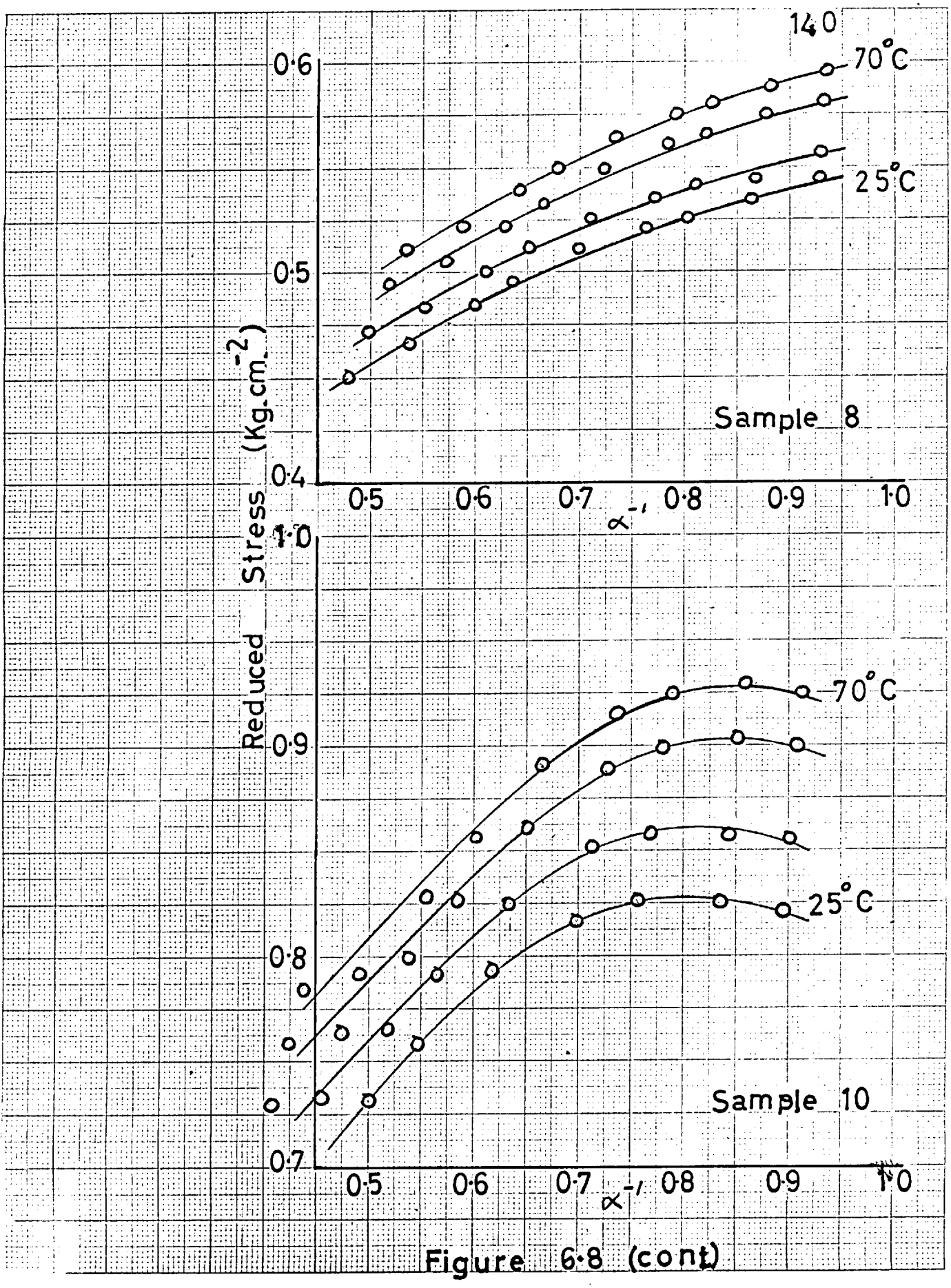


Figure 6·8 (cont)

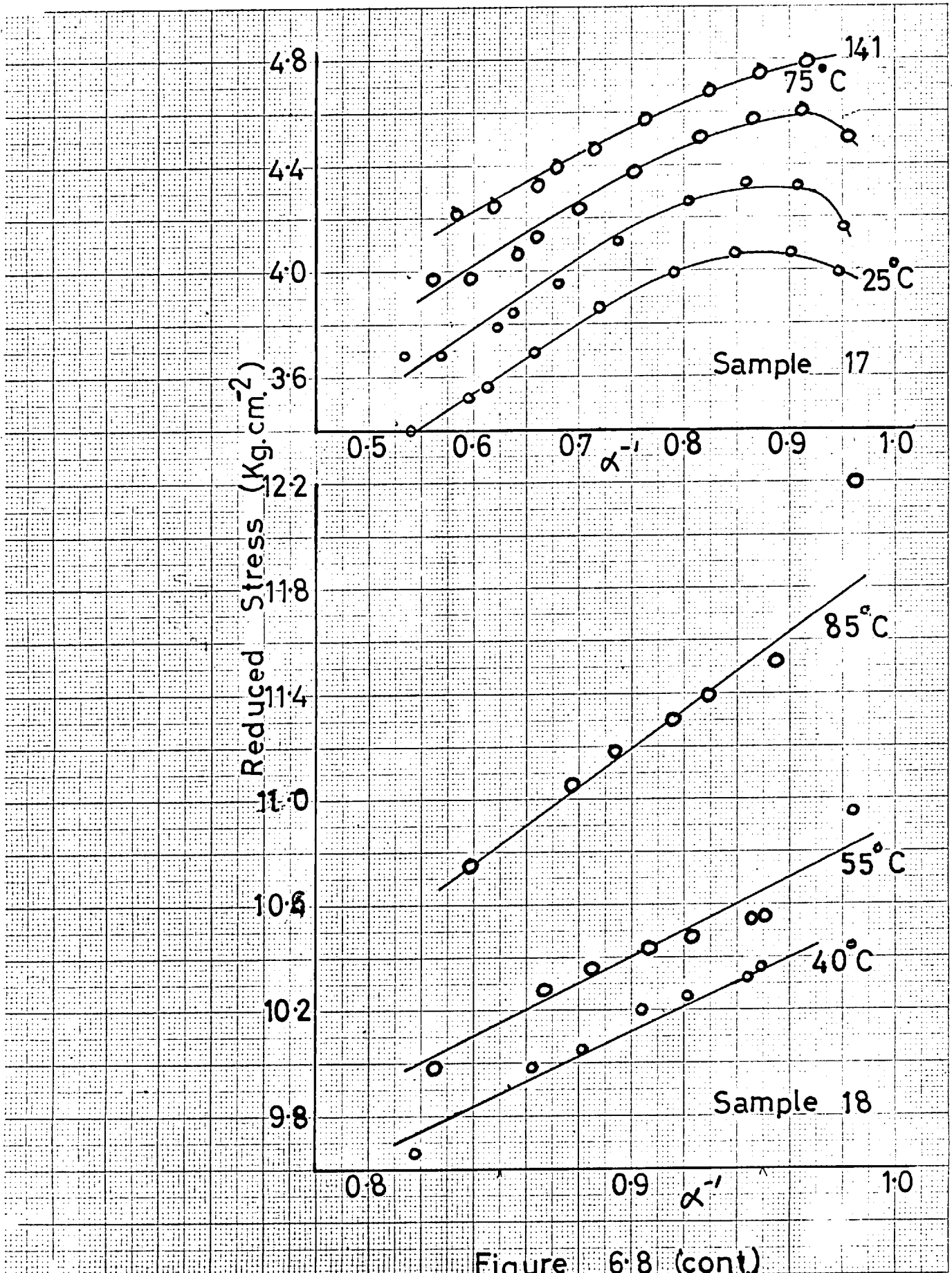


Figure 6·8 (cont.)

examples of these graphs are given in Figure 6.8 and complete lists of values of C_1 and C_2 obtained are given in Tables 6.10 and 6.11. Examination of these typical graphs shows that the relationship between f/ϕ and α^{-1} is still not linear but the graphs are more uniform than those obtained with the unadjusted data. Similarly there is rather better agreement between values of C_2 obtained from different samples of the same rubber though this agreement is still far from satisfactory. The most surprising effect of the small alterations of l_o involved in this adjustment is the large changes in the values of C_2 for the poly isoprenes, ethylene propylene rubber and poly buta diene so that the ratio of C_1/C_2 is much nearer to unity. Results published by previous workers usually have this ratio between one and two. Some of these published results are given in Table 6.12.

The failure to obtain a linear relationship between f/ϕ and α^{-1}, together with the fact that the values of ϕ close to zero were very sensitive to changes in l_o as shown in Figure 5.3, suggested that it would be profitable to alter l_o again in a series of small steps and determine what change in l_o is required to give a linear Mooney-Rivlin graph. This procedure was carried out twice, the first time all values of α were used and the second time only those values greater than or equal to 1.095 were included. The values of the correction factors γ are given in columns 2 and 3 of Table 5.7 and the values of f_o obtained by applying equation 6.2a to the resulting values of α are given in columns 3 and 4 of Table 5.6.

Table 6.8

Values of C_1 for original values of l_o

	Value of C_1					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	2.17	2.26	2.31	2.35		
2	2.12	2.14	2.20	2.28		
3	2.25	2.41	2.50	2.56		
4	2.16	2.24	2.29	2.40		
5	2.26	2.42	2.46	2.51		
6	1.97	2.05	2.07	2.16		
7	0.377	0.388	0.399	0.409		
8	0.384	0.396	0.414	0.418		
10	0.602	0.618	0.634	0.643		
11	0.636	0.657	0.681	0.699		
17C	0.374	0.341	0.297	0.237		
17R	0.339	0.290	0.273	0.260		
17C			0.353	0.286	0.262	0.269
18		7.976	8.152	5.547	0.380	-8.54

Table 6.9

Values of C_2 for original values of l_o

	Value of C_2					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	0.658	0.663	0.757	0.841		
2	0.938	0.052	1.108	1.145		
3	0.948	0.888	0.911	0.998		
4	0.429	0.468	0.531	0.508		
5	0.589	0.507	0.586	0.660		
6	0.747	0.752	0.873	0.879		
7	0.119	0.127	0.134	0.144		
8	0.159	0.167	0.165	0.184		
10	0.273	0.292	0.312	0.342		
11	0.199	0.206	0.209	0.222		
17C	3.272	3.552	3.847	4.125		
17R	3.285	3.593	3.875	4.155		
17C			3.699	3.994	4.285	4.545
18		2.151	2.336	5.797	12.18	22.42

Table 6.10

Values of C_1 for values of l_o adjusted to give minimum value of $|f_o|$

	Values of C_1					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	1.947	2.005	2.071	2.123		
2	2.02	1.97	1.93	1.96		
3	2.02	2.14	2.26	2.31		
4	1.63	1.67	1.71	1.76		
5	1.98	2.08	2.08	2.15		
6	1.77	1.81	1.89	1.93		
7	0.33	0.34	0.35	0.36		
8	0.36	0.37	0.38	0.39		
10	0.60	0.61	0.62	0.64		
11	0.63	0.64	0.66	0.67		
17C	2.56	2.83	2.99	3.20		
17R	2.61	2.76	2.87	3.49		
17C			2.74	3.02	3.25	3.59
18		3.57	5.83	5.55	3.90	-4.31

Table 6.11

Values of C_2 for values of l_o adjusted to the minimum value of $|f_o|$

	Values of C_2					
Sample	25°C.	40 C.	55°C.	70°C.	85°C.	100°C.
1	1.076	1.136	1.174	1.234		
2	1.127	1.346	1.555	1.656		
3	1.346	1.336	1.310	1.413		
4	1.444	1.522	1.604	1.647		
5	1.065	1.062	1.199	1.219		
6	1.122	1.196	1.207	1.286		
7	0.220	0.225	0.230	0.238		
8	0.214	0.221	0.232	0.230		
10	0.286	0.307	0.335	0.354		
11	0.220	0.249	0.262	0.272		
17C	1.676	1.630	1.738	1.746		
17R	1.570	1.732	1.916	1.331		
17C			2.022	1.914	1.933	1.789
18		7.359	5.072	5.797	8.113	17.58

Table 6.12

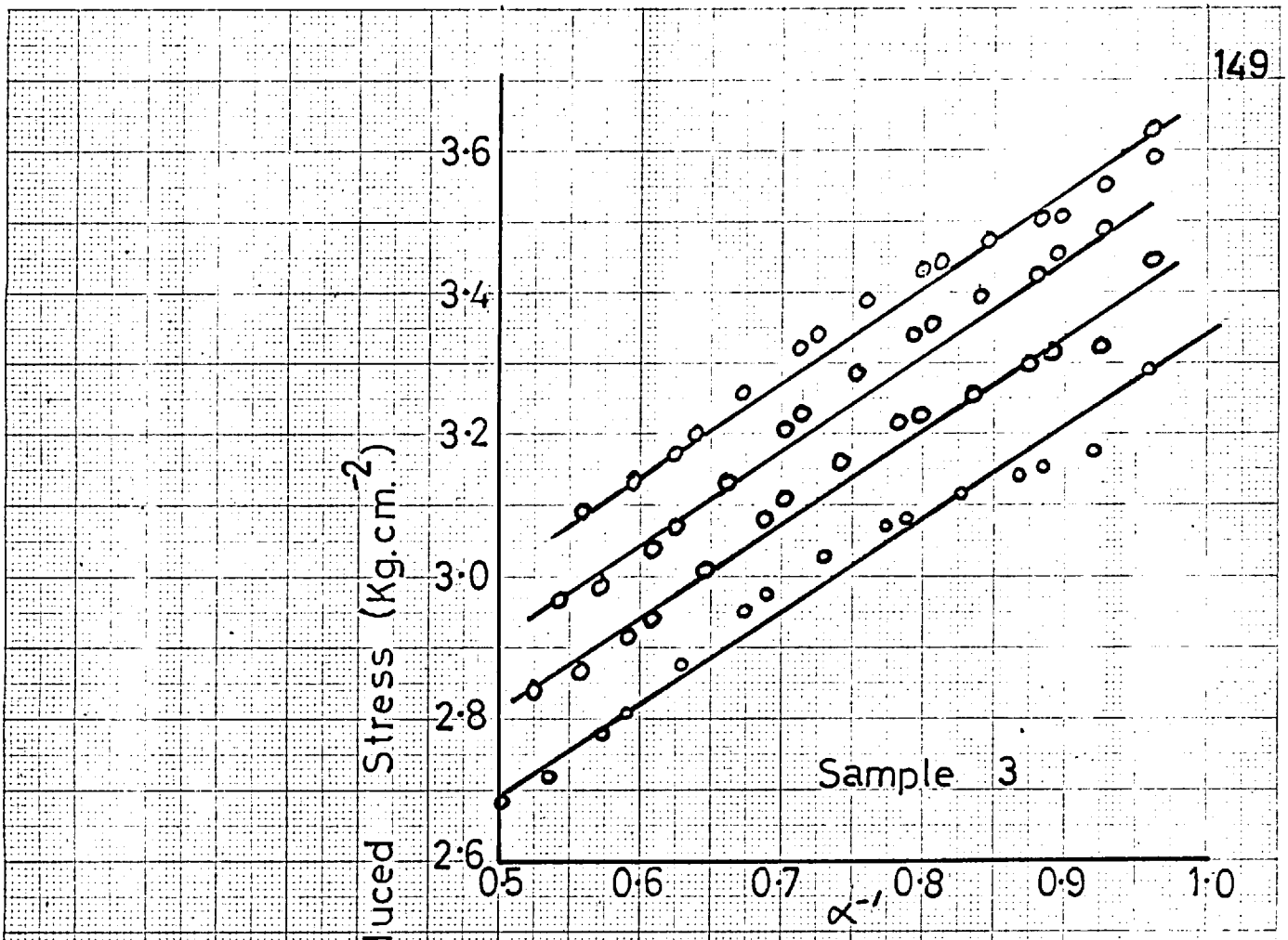
Values of C_1 and C_2 obtained in previous work

Material	Temp.	C_1	C_2	Ref.
Natural rubber	25°C	1.73	1.05	28
(S cured)	25°C.	1.17	1.00	28
Natural rubber (Peroxide cured)	25°C.	.	0.75	28
75/25 Butadiene-Styrene	25°C.	1.88	1.00	28
Viton	45°C.	3.324	2.86	66
Natural rubber (γ radiation)	34°C.	0.90	1.42	18
Natural rubber (S cured)	34°C.	2.00	2.00	18
Polydimethyl siloxane 1.65% Benzoyl Perox.	30°C.	0.70	0.62	18
Butyl rubber	49°C.	1.24	1.50	18
Poly methyl methacrylate	145°C	1.00	4.80	18
Poly ethyl acrylate	49°C.	1.54	0.72	18

Examination of Tables 5.6 and 5.7 shows that whilst the differences in the values of γ for the three sets of corrections are not very large, the differences in the corresponding values of $|f_d|$ are very marked and the values of $|f_d|$ obtained from the values of l_o required to give a linear Mooney-Rivlin graph are nowhere near zero. This is considered to indicate that the Mooney-Rivlin equation is obeyed only when spurious values of l_o are used so reducing still further the limited value of this equation. However the graphs obtained as shown by the typical examples displayed in Figures 6.9 and 6.10 are reasonably linear and the complete sets of values of C_1 and C_2 obtained in this way are given in Tables 6.13 to 6.16 inclusive.

However, consideration of Tables 6.13 to 6.16 shows that whilst good linear Mooney-Rivlin graphs may be obtained for individual sets of data by use of this procedure, the correlation between different samples of the same polymer is far from satisfactory and the variation with temperature of values of C_1 and C_2 for any one sample is much more haphazard than for the values of C_1 and C_2 shown in Tables 6.8 to 6.11. The negative values of C_1 obtained for some samples when only values of $\alpha > 1.095$ were used are associated with very high values of C_2 and are due to the very steep slopes obtained as a result of the large correction needed to give the linear relationship.

Thus although values of C_1 and C_2 have been obtained by four methods none can be considered satisfactory and one is led to the conclusion that the Mooney-Rivlin equation is an adequate representation


3·6
3·4
3·2
3·0
2·8
2·6
Reduced Stress (Kg.cm.$^{-2}$)
Sample 3
0·5
0·6
0·7
0·8
0·9
1·0
α^{-1}

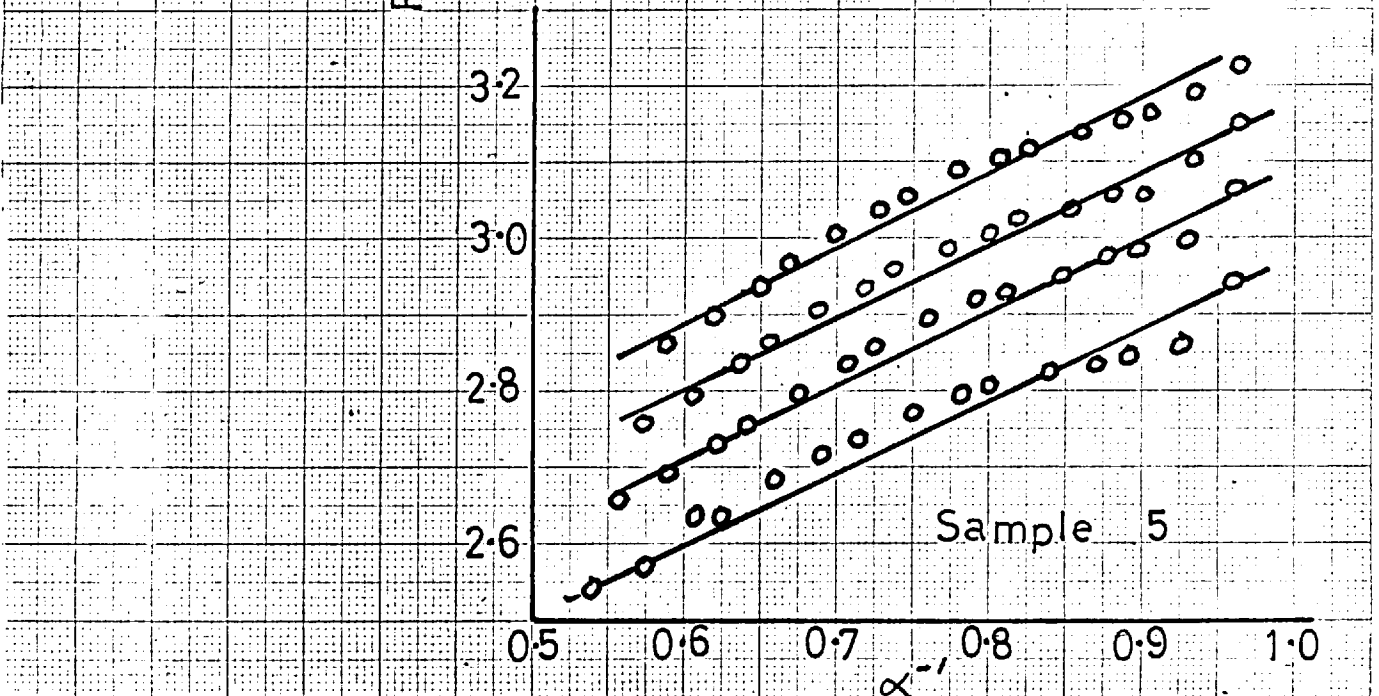

3·2
3·0
2·8
2·6
Sample 5
0·5
0·6
0·7
0·8
0·9
1·0
α^{-1}

Figure 6·9

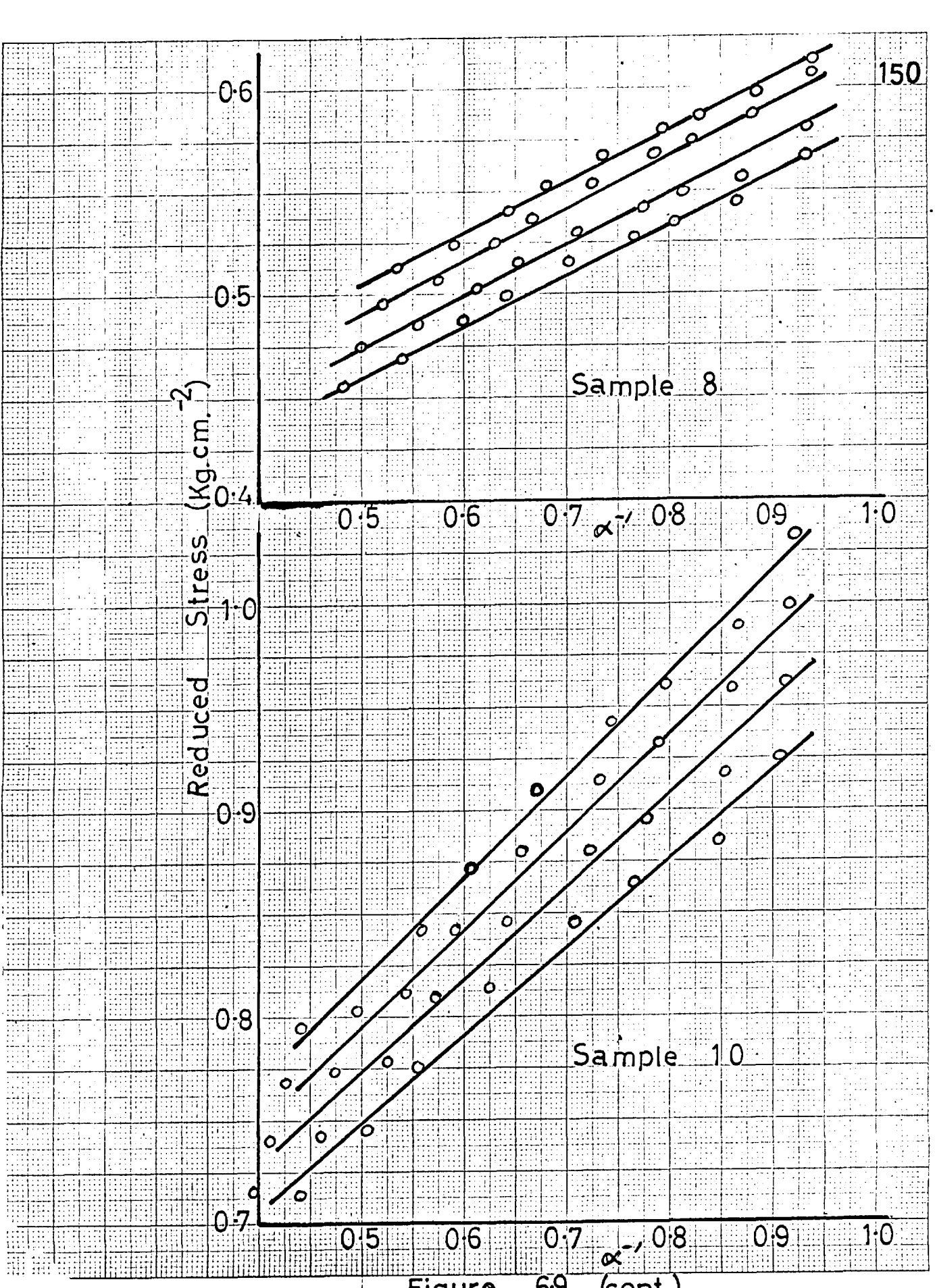


Figure 6·9 (cont.)

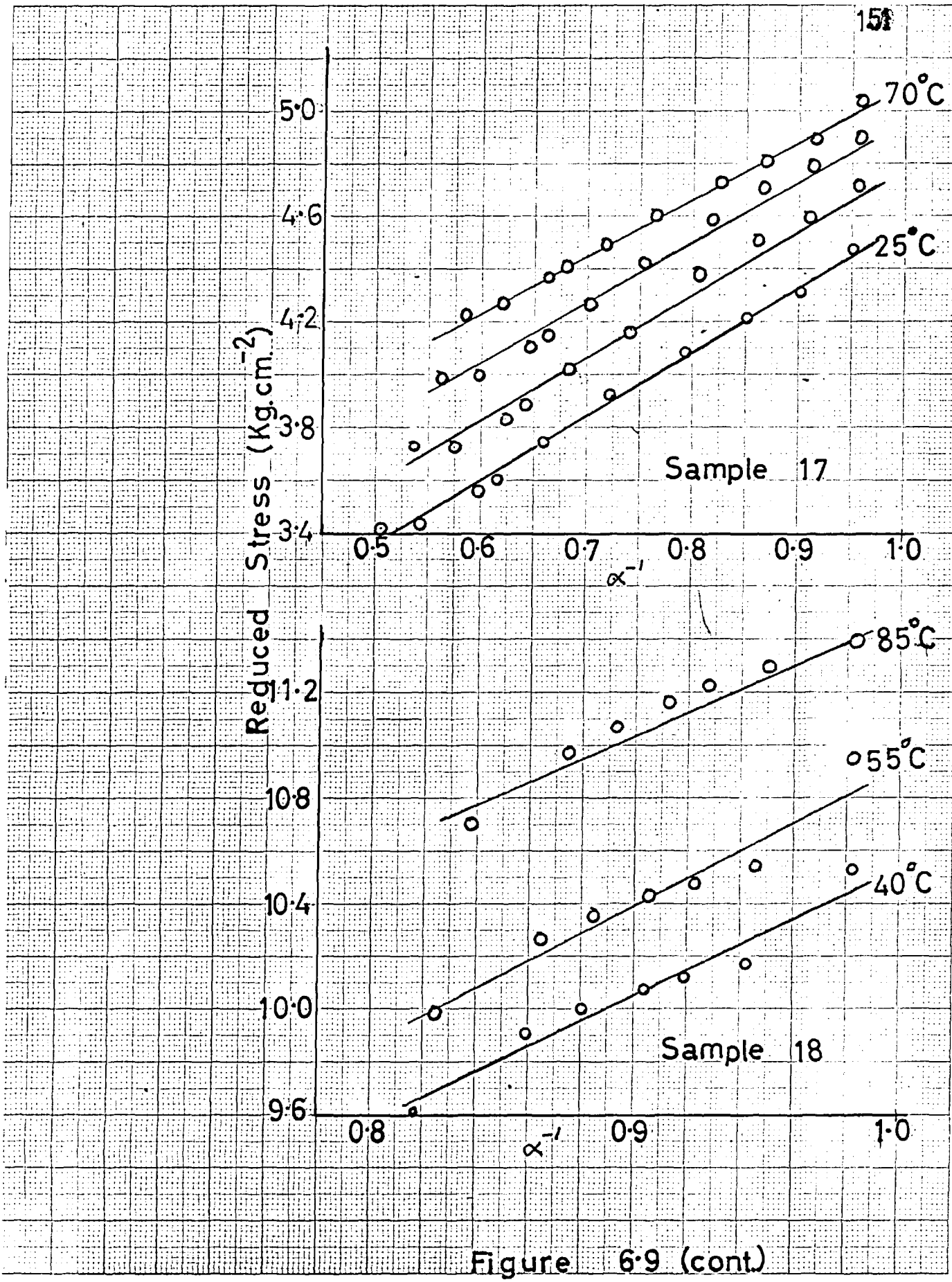


Figure 6·9 (cont.)

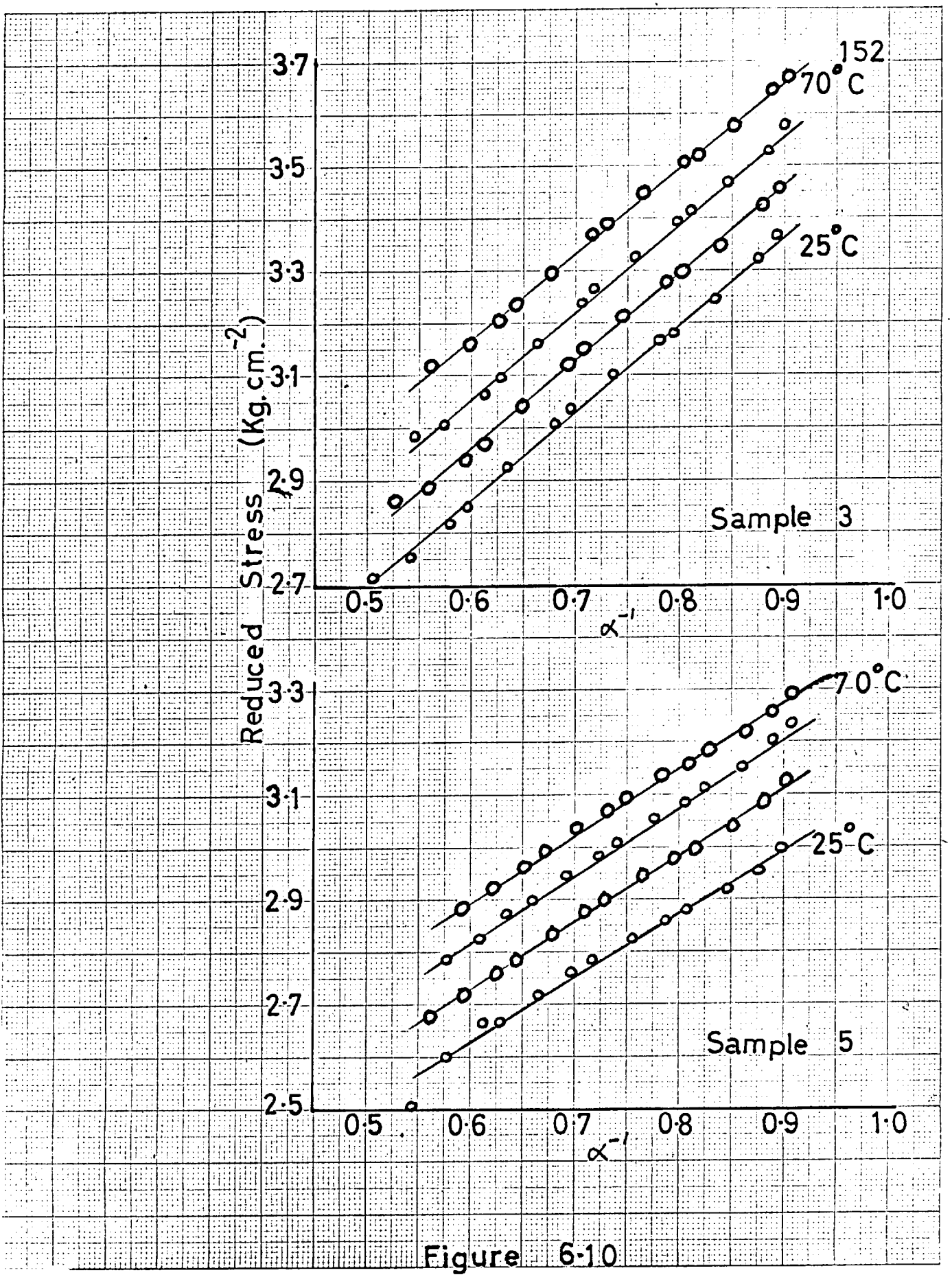

Reduced Stress (Kg.cm.$^{-2}$)
3·7
3·5
3·3
3·1
2·9
2·7
0·5
0·6
0·7
0·8
0·9
1·0
α^{-1}
152
70°C
25°C
Sample 3
3·3
3·1
2·9
2·7
2·5
70°C
25°C
Sample 5

Figure 6-10

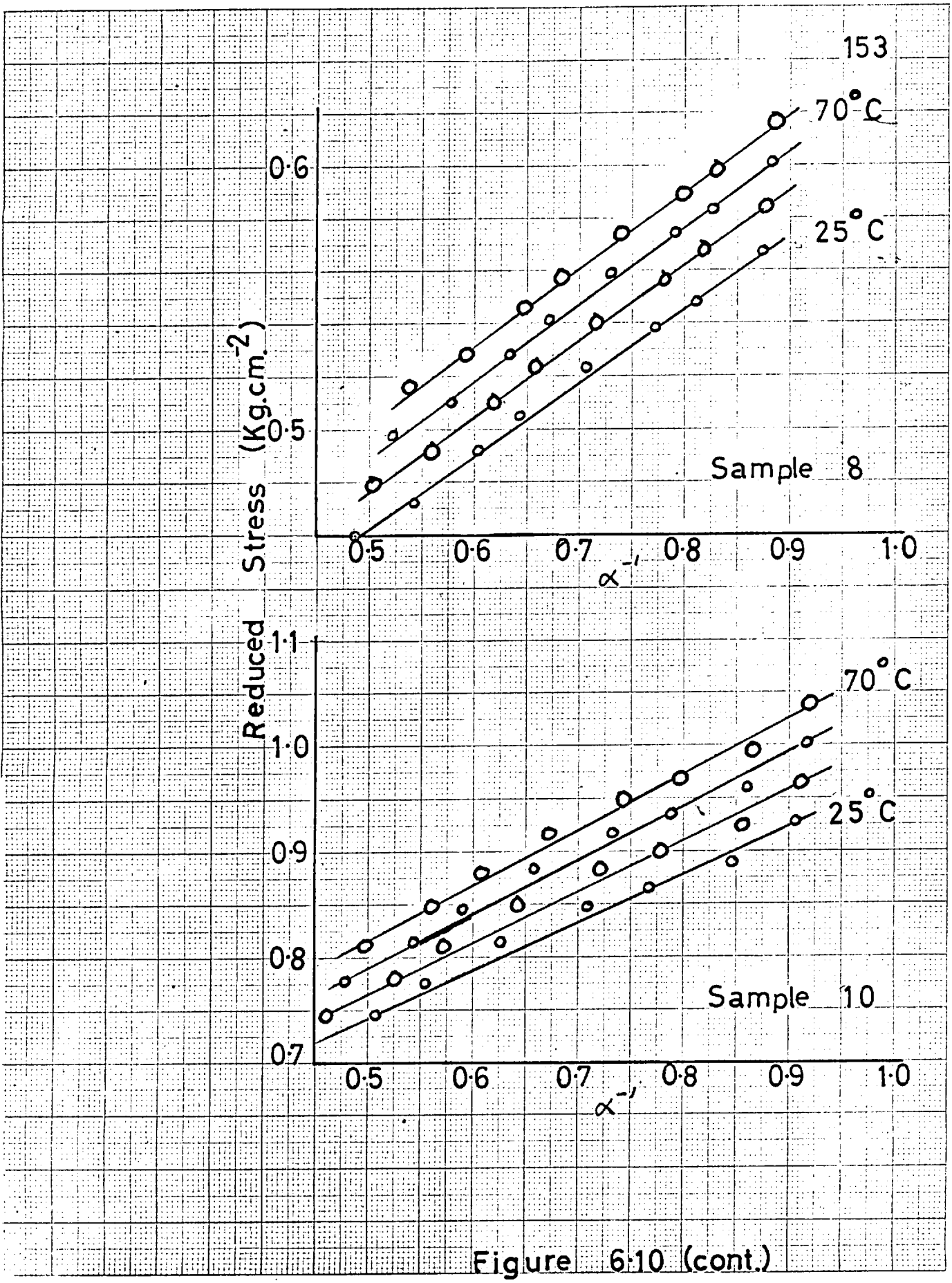


Figure 6·10 (cont.)

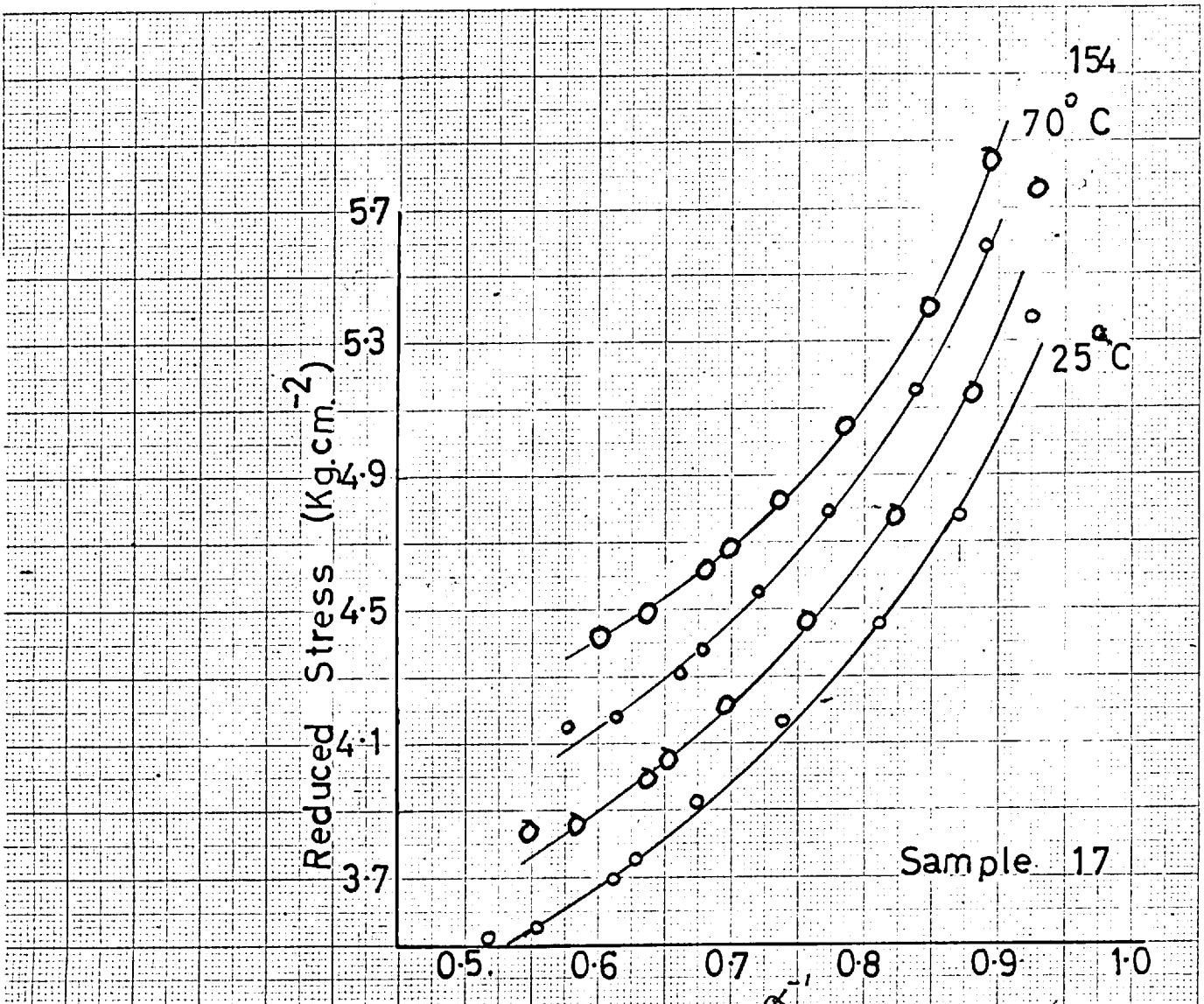


Figure 6·10 (cont.)

of stress-strain behaviour only over a very limited range of extension ratios. This coupled with the phenomenological nature of this equation would suggest that its use is limited to engineering applications where the strain is in the particular range where the equation may be said to be valid.

Table 6.13

Values of C_1 for values of l_o adjusted to give best linear Mooney-Rivlin graph. All values of α used.

	Values of C_1					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	1.998	2.051	2.125	2.185		
2	1.963	1.969	2.007	2.049		
3	2.082	2.140	2.178	2.396		
4	1.812	1.883	1.990	2.085		
5	2.110	2.154	2.252	2.348		
6	1.851	1.909	2.002	2.056		
7	0.332	0.343	0.361	0.366		
8	0.343	0.358	0.360	0.382		
10	0.539	0.548	0.555	0.565		
11	0.578	0.601	0.622	0.636		
17C	2.140	2.286	2.547	2.937		
17R	2.254	2.476	2.506	2.618		
17C			2.527	2.896	3.102	3.036
18		5.900	5.830	5.547	7.002	8.429

Table 6.14

Values of C_2 for values of l_o adjusted to give best linear Mooney-Rivlin graphs. All values of α used.

	Values of C_2					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	1.001	1.052	1.080	1.127		
2	1.219	1.346	1.433	1.518		
3	1.244	1.336	1.441	1.268		
4	1.109	1.142	1.107	1.095		
5	0.849	0.940	0.925	0.918		
6	0.975	1.027	1.021	1.073		
7	0.210	0.214	0.205	0.223		
8	0.238	0.235	0.262	0.247		
10	0.422	0.448	0.481	0.503		
11	0.325	0.323	0.329	0.347		
17C	2.425	2.546	2.463	2.157		
17R	2.193	2.198	2.503	2.685		
17C			2.362	2.106	2.163	2.607
18		4.613	5.072	5.797	4.516	2.857

Table 6.15

Values of C_1 for values of J_o adjusted to give best linear Mooney-Rivlin graphs. $\alpha \geq 1.095$ only.

	Values of C_1					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	1.893	1.928	1.948	1.981		
2	1.845	1.781	1.806	1.901		
3	1.853	1.965	2.036	2.186		
4	1.812	1.883	1.827	1.895		
5	1.929	1.962	2.018	2.154		
6	1.726	1.802	1.787	1.854		
7	0.307	0.319	0.331	0.334		
8	0.325	0.335	0.347	0.360		
10	0.539	0.548	0.555	0.565		
11	0.579	0.578	0.599	0.617		
17C	0.209	0.119	-0.164	-0.203		
17R	0.199	0.154	0.043	0.006		
17C			0.112	0.058	-0.198	-0.203
18		7.101	7.161	5.000	-0.181	-8.009

Table 6.16

Values of C_2 for values of l_o adjusted to give best linear Mooney-Rivlin graphs. $\alpha \geq 1.095$ only.

	Values of C_2					
Sample	25°C.	40°C.	55°C.	70°C.	85°C.	100°C.
1	1.200	1.296	1.427	1.515		
2	1.453	1.697	1.803	1.785		
3	1.682	1.659	1.700	1.637		
4	1.109	1.142	1.424	1.452		
5	1.181	1.270	1.330	1.242		
6	1.231	1.243	1.441	1.463		
7	0.268	0.266	0.268	0.287		
8	0.278	0.284	0.287	0.287		
10	0.422	0.448	0.481	0.503		
11	0.325	0.380	0.382	0.389		
17C	5.524	5.948	6.621	6.906		
17R	5.872	6.179	6.708	7.045		
17C			5.594	5.945	6.620	6.908
18		3.032	3.335	6.346	12.762	21.867

(c) Krigbaum and Kaneko Cubic Lattice Model

As discussed in Chapter 2, part 6b, Krigbaum and Kaneko (43) derived an equation for the retractive force f in a strained elastomer which may be represented by:

$$f = \nu kT \frac{V^{\frac{1}{3}}}{V_o^{\frac{2}{3}}} (\alpha - \alpha^{-2}) Q \qquad (6.4)$$

where $Q = 1 + \frac{9}{10N}\left(\frac{V}{V_o}\right)^{\frac{2}{3}}(3e^{2K} - e^{-2K})(\alpha^2 + \frac{4}{3\alpha}) +$

$$\frac{81}{56N^2}\left(\frac{V}{V_o}\right)^{4/3}(15e^{4K} - 10 + 3e^{-4K})(\alpha^4 + \frac{8\alpha}{5} + \frac{8}{5\alpha}) + \ldots.$$

Equation 6.4 may be regarded as equivalent to the kinetic theory equation modified by the factor Q which contains the contribution due to internal energy changes with deformation. In the expression for Q, the quantities N, $\frac{V}{V_o}$ and K are not readily obtainable for a particular polymer. Thus the university computer was programmed to evaluate Q for a range of suitable values of these parameters. Two values of $\frac{V}{V_o}$, 1 and 1.01, were used in turn and Table 6.17 shows that this large change in $\frac{V}{V_o}$ has relatively little effect on the values of Q.

Subsequent calculations therefore used a value of unity for the parameter $\frac{V}{V_o}$. Six values of N of 40, 70, 100, 150, 300 and 450 were then used in turn and values of K from -1.0 in steps of 0.1 to + 1.0 were used with each value of N.

Figure 6.11 shows the variation in Q with K at α = 2 for

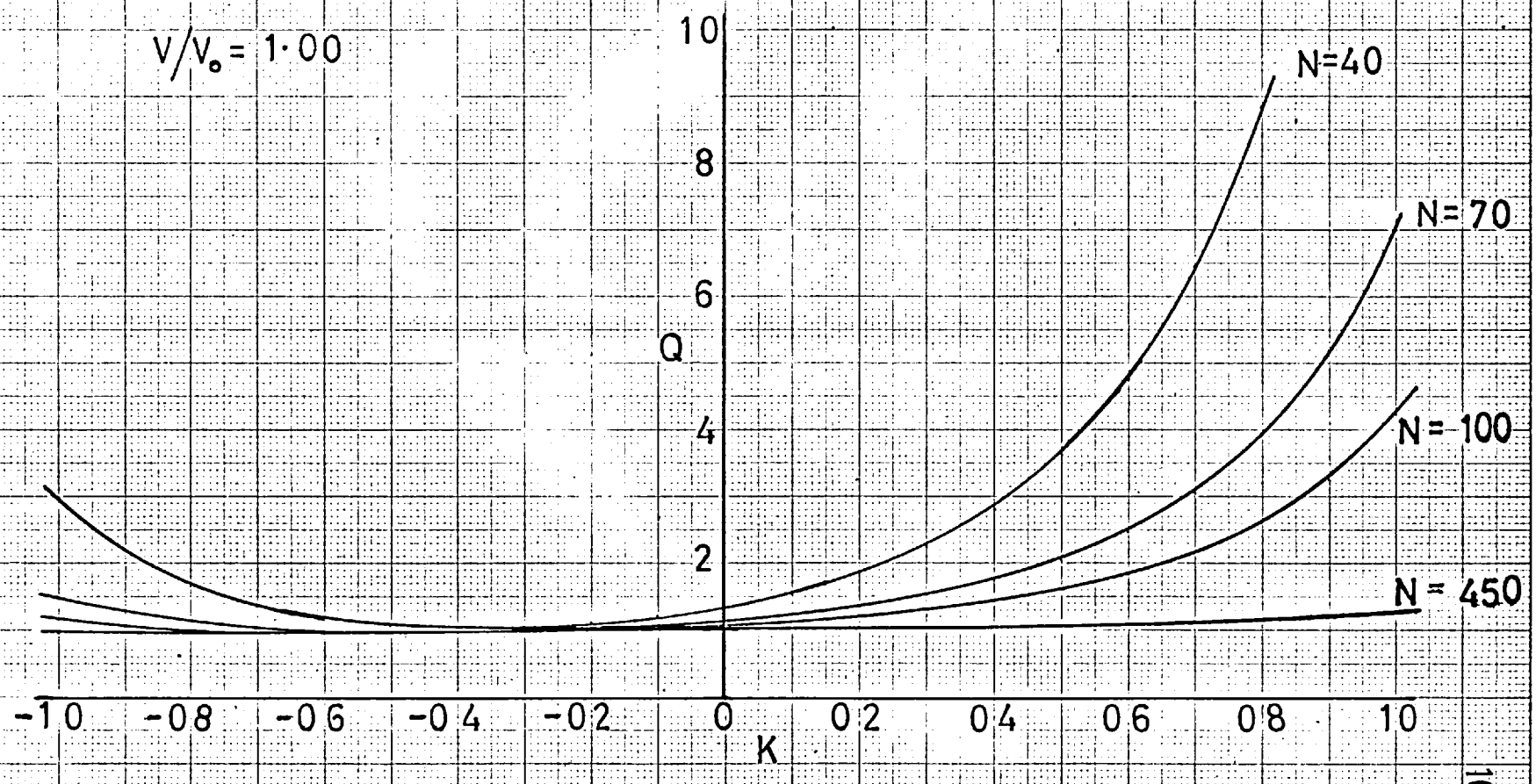


Figure 6·11

Variation of the Krigbaum & Kaneko factor 'Q' with K and N

each value of N. Consideration of the deviations observed from the kinetic theory indicate that at α = 2 the value of Q must be less than unity. Figure 6.11 shows that this occurs only when K is large and negative. According to Krigbaum and Kaneko the value of K for poly isoprenes should be about -0.1 whereas Figure 6.11 shows that on this cubic lattice model the value needs to be -0.7 in order to give Q a value less than unity. The values of C' obtained in this work were about 10% of C_o which suggests that at α = 2 the value of Q should be about 0.8. Values as low as this are never realised in this cubic lattice model which therefore fails both to give a sufficiently large correction and to give the correction at a reasonable value of K. However the value assumed for N appears to make little or no difference to the values of Q in the most interesting range, i.e. Q $\simeq$ 1.0, so at least this model does not demand any knowledge of the size of the network chains.

A further objection to this model is that the value of K required to give Q less than unity is always negative. For most polymers the extended configurations are more stable and thus for such polymers K should be positive. The fact that all polymers show the same sort of deviation from the kinetic theory whilst the contribution to the retractive force made by the variation in internal energy may be positive or negative supports Flory's view that these deviations are not due to internal energy effects.

Table 6.17

Values of Krigbaum and Kaneko parameter Q for two values of $\frac{V}{V_o}$ at K = 1.0, 0 and -1.0 and N = 100

	Values of Q when $\frac{V}{V_o}$ = 1.0		
	K = 1.0	K = 0	K = -1.0
1.1	2.012	1.049	0.949
1.2	2.103	1.052	0.953
1.3	2.227	1.056	0.960
1.4	2.385	1.060	0.971
1.5	2.579	1.066	0.985
1.6	2.812	1.072	1.004
1.7	3.089	1.080	1.028
1.8	3.412	1.088	1.059
1.9	3.788	1.097	1.097
2.0	4.219	1.107	1.143

	Values of Q when $\frac{V}{V_o}$ = 1.01		
	K = 1.0	K = 0	K = -1.0
1.1	2.028	1.049	0.950
1.2	2.120	1.052	0.954
1.3	2.246	1.056	0.961
1.4	2.407	1.061	0.972
1.5	2.604	1.067	0.987
1.6	2.842	1.073	1.006
1.7	3.124	1.081	1.031
1.8	3.453	1.089	1.063
1.9	3.835	1.098	1.102
2.0	4.274	1.108	1.149

Summary of Conclusions

(a) Thermodynamic

Values of the entropy and internal energy components of the elastic force and values of the quantity $\partial \ln \bar{r}_o^2 / \partial T$ have been evaluated by means of an analysis which assumes the validity of the Kinetic Theory. Although the results are conventional, uncertainty in the applicability of this theory means that little information may be derived from them. The results do however maintain the generally accepted picture that the retractive force is mainly but not entirely due to entropy changes and have not indicated any polymers other than poly isoprenes and poly dimethyl siloxanes to have positive values of $\partial \ln \bar{r}_o^2 / \partial T$.

(2) Theories of Elasticity

An attempt has been made to evaluate the two main theories on the basis of the experimental results obtained. Whilst the Kinetic theory must be regarded as an oversimplification and the shape of the stress strain curves indicates that any successful relationship will need more than one material parameter, the only current alternative is not satisfactory as it fails both to fit the observed stress-strain data and to suggest any mechanism for elastic recovery. An empirical quadratic equation has been suggested which gives a reasonable representation of the observed data but like the phenomenological theory does not suggest any mechanism for elastic recovery.

A third theory has been evaluated by calculation and found to be quantitatively inadequate though use of a more sophisticated model may improve this.

It is thus clear that whilst the basis of rubbery elasticity is fairly well understood, an exact understanding of the details of the mechanism is not yet in sight.

APPENDIX 1

Programme 1

THERMODYNAMICS CALCULATION PROGRAMME

```
ROUTINE 1

A=0
B=0
C=0
D=0
E=0
F=0
G=0
H=0
U=0
V=0
I=0(1)K
A'=XI
B'=YI
A=A+A'
B=B+B'
C'=A'A'
D'=C'A'
E'=D'A'
F'=E'A'
G'=F'A'
H'=A'B'
U'=H'A'
V'=U'A'
C=C+C'
D=D+D'
E=E+E'
F=F+F'
G=G+G'
H=H+H'
U=U+U'
V=V+V'
REPEAT
π=K+1
A'=πFF-2FCD-πEG+EDD+GCC
B'=πEF-CDE-ADF-πDG+DDD+ACG
C'=πVF-BDF-CDV-πGU+BCG+DDU
D'=πEE-EDA-ECC-πFD+FCA+DDC
E'=πED-EAC-DDA-πFC+CCD+FAA
F'=πEU-EBC-UDA-πFH+FBA+HDC
G'=B'D'-A'E'
H'=C'D'-A'F'
H'=H'/G'
U'=B'F'-C'E'
U'=U'/G'
G'=πE-DA
V'=πH-AB-πCH'+AAH'-πDU'+ACU'
V'=V'/G'
G'=B-DV'-CU'-AH'
G'=G'/π
D=0
I=0(1)K
B=XIXI
C=BXI
ZI=YI-G'-XIH'-BU'-CV'
D=ZIZI+D
REPEAT
D=D/π
D=ØSQRT (D)
RETURN
**  **

CHAPTER  0

VARIABLES 1

1)READ (I')
CAPTION
SAMPLE
PRINT (I') 3,0
READ (Y)
READ (X)
READ (N)
READ (T)
READ (Q)
NEWLINE
NEWLINE

M=0
2)READ (WM)
M=M+1
JUMP  2
0)JUMP 3, T'=3
JUMP 101, T'≠6
M=M-1
P=0
*CAPTION
SD L,T
NEWLINE
```

```
R=0
J=0(1)M
K=0
4)READ (XK)
READ (YK)
K=K+1
JUMP  4

3)K=K-1
JUMPDOWN (R1)
P=0
D=1/D
I=0(1)K
C=ZID
C=ØMOD (C)
JUMP 5,  C )2.5
XP=XI
YP=YI
P=P+1
5)REPEAT
K=P-1
JUMPDOWN (R1)
PRINT (D) 0,3
PRINT (K) 1,2
JUMP 6,  D )0.03
AR=G'
BR=H'
CR=U'
DR=V'
WR=WJ
R=R+1
JUMP 8
6)PUNCH (3)
8)NEWLINE
REPEAT
JUMP 7, 6)/ R
M=R-1
K=M
NEWLINE
P=0
A=T
W=1/Y
J=0(1)N
B=AA
C=AB
I=0(1)K
EP=0.001WWI
FP=AI+ABI+BCI+CDI
P=P+1

REPEAT
A=A+Q
REPEAT
ACROSS 1/1
7)ACROSS 2/2
101)END

CLOSE

**********

CHAPTER  1

A→14
B→14
C→14
D→14
E→89
F→89
G→14
H→14
U→29
V→14
W→14
X→14
Y→14
Z→14
π→14

1)R=P-1
P=0
CAPTION
  SD L,F   Lo
NEWLINE
J=0(1)N
I=0(1)K
XI=FP
YI=EP
P=P+1
REPEAT
JUMPDOWN (R1)
PRINT (D) 0,3
A=2.0
A'=0
2)A'=-A'
3)A=A-0.03A'
B=AA
C=AB
A'=G'+AH'+BU'+CV'
JUMP 3, A' ) 0.0005
A'=-A'
```

```
JUMP 2, A'> 0.0005
GJ=A
PRINT (A) 1,3
NEWLINE
REPEAT
NEWLINE
A=GN=Go
B=NQGo
A=A/B
CAPTION
  X
PRINT (A) 0,3
NEWLINE
NEWLINE
B=X-0.00003
C=X+0.00013
JUMP 4, B > A
JUMP 4, A > C
CAPTION
  SD  A,F
NEWLINE
P=0
J=0(1)N
A=1/GJ
I=0(1)K
FP=FPA
XI=FP
YI=EP
P=P+1
REPEAT
JUMPDOWN (R1)
PRINT (D) 0,3
NEWLINE
AJ=G'
BJ=H'
CJ=U'
DJ=V'
REPEAT
P=0
J=0(1)N
I=0(1)K
A=FPFP
B=AFP
EP=AJ+BJFP+CJA+DJB
P=P+1
REPEAT
REPEAT
ACROSS 1/2
4)ACROSS 2/2
CLOSE
```

```
CHAPTER  2

VARIABLES  1

2)NEWLINE
CAPTION
SAMPLE
PRINT (I') 3,0
CAPTION
LOAD OF GARBAGE NO GO
NEW LINE
JUMP 3
1)NEWLINE
CAPTION
DF/DT
NEWLINE
4)D=NQ
D=1/D
I=1(1)10
A=1+0.1I
B=AA
C=AB
HI=Ao+ABo+BCo+CDo
GI=AN+ABN+BCN+CDN
GI=GI-HI
GI=GID
PRINT (GI) 0,3
NEWLINE
REPEAT
NEWLINE
CAPTION
  DF/DT.1    RMSDT    TDS/DL  DE/DL
NEWLINE
A=T+273.16
J=0(1)N
W=0
V=0
B=1/A
I=1(1)10
C=1+0.1I
D=CC
E=CD
HI=AJ+CBJ+DCJ+EDJ
XI=B-GI/HI+X
YI=XI-B
YI=-YIHI
PRINT (YI) 0,3
PRINT (XI) 0,3
YI=-AYI
PRINT (YI) 0,3
```

```
YI=AXIHI
PRINT (YI) 0,3
NEWLINE
W=XI+W
V=YI+V
REPEAT
W=0.1W
V=0.1V
PRINT (W) 0,3
PRINT (V) 0,3
NEWLINE
A=A+Q
NEWLINE
REPEAT
3)I=0(1)9
PUNCH (13)
REPEAT
I=0(1)30
PUNCH (0)
REPEAT
ACROSS 1/*0
CLOSE
```

Programme 2

STRESS-STRAIN CALCULATIONS PROGRAMME

```
ROUTINE  1

A=O
B=O
C=O
D=O
E=O
F=O
G=O
H=O
U=O
V=O
I=O(1)K
A'=XI
B'=YI
A=A+A'
B=B+B'
C'=A'A'
D'=C'A'
E'=D'A'
F'=E'A'
G'=F'A'
H'=B'A'
U'=H'A'
V'=U'A'
C=C+C'
D=D+D'
E=E+E'
F=F+F'
G=G+G'
H=H+H'
U=U+U'
V=V+V'
REPEAT
π=K=1
A'=πFF2FCD-πEG+EDD+GCC
B'=πEF-CDE-ADF-πDG+DDD+ACG
C'=πVF-BDF-CDV-πGU+BCG+DDU
D'=πEE-EDA-ECC-πFD+FCA+DDC
E'=πED-EAC-DDA-πFC+CCD+FAA
F'=πEU-EBC-UDA-πFH+FBA+HDC
G'=B'D'-A'E'
H'=C'D'-A'F'
H'=H'/G'
U'=B'F'-C'E'
U'=U'/G'
G'=πE-DA
V'=πH-AB-πCH'+AAH'-πDU'+ACU'
V'=V'/G'
G'=B-DV'-CU'-AH'
G'=G'/π
D=O
I=O(1)K
B=XIXI
C=BXI
ZI=YI-G'-XIH'-BU'-CV'
D=ZIZI+D
REPEAT
D=D/π
D=ØSQRT (D)
RETURN
**  **

ROUTINE  2

A=O
B=O
C=O
D=O
L=O(1)K
A=A+XL
B=B+YL
C=C+XLXL
D=D+XLYL
REPEAT
π=K+1
E=AB-πD
F=AD-BC
G=AA-πC
G=1/G
E=EG
F=FG
D=O
L=O(1)K
ZL=F+EXL
ZL=YL-ZL
D=D+ZLZL
REPEAT
D=D/π
D=ØSQRT (D)
RETURN

**  **
```

```
ROUTINE 3

A=0
B=0
C=0
D=0
E=0
F=0
G=0
I=0(1)K
A'=XI
B'=YI
C'=A'A'
D'=C'A'
E'=D'A'
F'=A'B'
G'=F'A'
A=A+B'
B=B+A'
C=C+C'
D=D+D'
E=E+E'
F=F+F'
G=G+G'
REPEAT
π=K+1
A'=EB-CD
B'=DB-CC
C'=FC-GB
D'=πD-CB
E'=πC-BB
F'=AB-πF
U=B'F'-C'E'
V'=A'E'-B'D'
W=D'C'-F'A'
X=U/V'
Y=W/V'
Z=A-YB-XC
Z=Z/π
A=X
B=Y
C=Z
D=0
I=0(1)K
E=XIXI
ZI=C+BXI+*AE
ZI=YI-ZI
D=D+ZIZI
REPEAT
D=D/π
D=ØSQRT (D)
RETURN
**  **
```

```
CHAPTER 0

VARIABLES  1

1)READ (I')
CAPTION
SAMPLE
PRINT (I') 3,0
READ (Y)
READ (X)
READ (N)
READ (T)
READ (Q)
NEWLINE
NEWLINE

M=0
2)READ (WM)
M=M+1
JUMP 2
0) JUMP 3, T'=3
JUMP 101, T'≠6
M=M-1
P=0
CAPTION
  SD L,T
NEWLINE
R=0
J=0(1)M
K=0
4)READ (XK)
READ (YK)
K=K+1
JUMP 4

3)K=K-1
JUMPDOWN(R1)
P=0
D=1/D
I=0(1)K
C=ZID
C=ØMOD (C)
JUMP 5, C > 2.5
XP=XI
YP=YI
P=P+1
5)REPEAT
K=P-1
JUMPDOWN (R1)
PRINT (D) 0,3
JUMP 6, D>0.03
AR=G'
```

```
BR=H'
CR=U'
DR=V'
WR=WJ
R=R+1
JUMP 8
6)PUNCH (3)
8)NEWLINE
REPEAT
JUMP 7, 6 ⟩ R
M=R-1
K=M
NEWLINE
P=0
A=T
J=0(1)N
W=1/Y
B=AA
C=AB
I=0(1)K
EP=0.001WWI
FP=AI+ABI+BCI+CDI
P=P+1
REPEAT
Y=Y+2QXY
A=A+Q
REPEAT
ACROSS 1/1
7)ACROSS 2/2
101)END

CLOSE

CHAPTER 1

A→14
B→14
C→14
D→14
E→89
F→89
G→14
H→14
U→29
V→14
W→14
X→14
Y→14
Z→14
π→14

1)P=0
CAPTION
  SD  L,F   Lo
NEWLINE
J=0(1)N
I=0(1)K
XI=FP
YI=EP
P=P+1
REPEAT
JUMPDOWN (R1)
PRINT (D) 0,3
A=2.0
A'=0
2)A'=-A'
3)A=A-0.03A'
B=AA
C=AB
A'=G'+AH'+BU'+CY'
JUMP 3, A' ⟩ 0.0005
A'=-A'
JUMP 2, A' ⟩ 0.0005
GJ=A
PRINT (A) 1,3
NEWLINE
REPEAT
NEWLINE
A=GN-Go
B=NQGo
A=A/B
CAPTION
 X
PRINT (A) 0,3
NEWLINE
NEWLINE
B=X-0.00003
C=X+0.00013
JUMP 4, B ⟩ A
JUMP 4, A ⟩ C
CAPTION
  SD  A,F
NEWLINE
P=0
J=0(1)N
A=1/GJ
I=0(1)K
FP=FPA
XI=FP
YI=EP
P=P+1
```

```
REPEAT
JUMPDOWN (R1)
PRINT (D) 0,3
NEWLINE
AJ=G'
BJ=H'
CJ=U'
DJ=V'
REPEAT
P=0
J=0(1)N
I=0(1)K
A=FPFP
B=AFP
EP=AJ+BJFP+CJA+DJB
P=P+1
REPEAT
REPEAT
ACROSS 1/2
4)ACROSS 2/6
CLOSE

CHAPTER  2

VARIABLES  1

1)A=1.005
I=0(1)29
AI=A
A=A-0.001
REPEAT
J=0(1)N
L=0(1)29
I=0(1)K
P=I+KJ+J
ZI=ALFP
YI=EP
XI=1/ZI
XI=ZI-XIXI
REPEAT

JUMPDOWN (R3)

CL=ØMOD (C)
REPEAT
I=1(1)29
C=Co-CI
JUMP 2,  0)C
Co=CI
S=I
2)REPEAT
PRINT (AS) 1,3
NEWLINE
CAPTION
  1/A      X      F
A=AS

R=0(1)1
L=0(1)K
P=L+KJ+J
XL=AFP
ZL=1/XL
XL=XL-ZLZL
πL=ZL
YL=EP
NEWLINE
PRINT (ZL) 1,3
PRINT (XL) 1,3
PRINT (YL) 1,3
JUMP 3, R=0
VL=YL/XL
PRINT (VL) 1,3
3)REPEAT
NEWLINE
CAPTION
   Co    C'    D    Fo    C1    C2    D
NEWLINE

JUMPDOWN (R3)

PRINT (B) 1,3
PRINT (A) 1,3
PRINT (D) 1,3
PRINT (C) 0,3
DONW 1/7
NEWLINE
A=1
REPEAT
NEWLINE
REPEAT
ACROSS 1/4
CLOSE

CHAPTER  4

VARIABLES  1

1)CAPTION
ALL  A
NEWLINE
NEWLINE
J=0(1)N
```

```
I=0(1)K
P=I+JK+J
CI=FP
DI=EP
REPEAT
I=0(1)29
L=0(1)K
ZL=CLAI
XL=1/ZL
ZL=ZL-XLXL
YL=DL/ZL
REPEAT
JUMPDOWN (R2)
UI=D
REPEAT
I=0(1)29
C=Uo-UI
JUMP 2, 0>C
Uo=UI
S=I
2)REPEAT
A=AS
PRINT (A) 1,3
NEWLINE
CAPTION
1/A     Ø     F/Ø
L=0(1)K
ZL=ACL
XL=1/ZL
ZL=ZL-XLXL
πL=ZL
YL=DL/ZL
NEWLINE
PRINT (XL) 1,3
PRINT (ZL) 1,3
PRINT (YL) 1,3
REPEAT
NEWLINE
CAPTION
  C1    C2    D    Fo    Co    C'    D
NEWLINE
JUMPDOWN (R2)

PRINT (F) 1,3
PRINT (E) 1,3
PRINT (D) 1,3
***DOWN 3/7
7)NEWLINE
NEWLINE
REPEAT
ACROSS 1/5
CLOSE
```

```
CHAPTER  5

VARIABLES  1

1)K'=K
CAPTION
A >/ 1.095
NEWLINE
NEWLINE
J=0(1)N
K=0
I=0(1)K'
P=I+JK'+J
JUMP 3, 1.095 >/ FP
CK=FP
DK=EP
K=K+1
3)REPEAT
K=K-1
I=0(1)29
L=0(1)K
ZL=CLAI
XL=1/ZL
ZL=ZL-XLXL
YL=DL/ZL
REPEAT
JUMPDOWN (R2)
UI=D
REPEAT
I=0(1)29
C=Uo-UI
JUMP 2,  0>C
Uo=UI
S=I
2)REPEAT
A=AS
PRINT (A) 1,3
NEWLINE
CAPTION
   1/A      X      F/X
R=0(1)I
L=0(1)K
ZL=ACL
XL=1/ZL
ZL=ZL-XLXL
πL=ZL
YL=DL/ZL
JUMP 4, R > 0
NEWLINE
PRINT (XL) 1,3
PRINT (ZL) 1,3
PRINT (YL) 1,3
```

```
4)REPEAT
NEWLINE
JUMP 5, R>0
CAPTION
  CI   C2   D   Fo   Co   C'   D
NEWLINE
5)JUMPDOWN (R2)

PRINT (F) 1,3
PRINT (E) 1,3
PRINT (D) 1,3
DOWN 3/7
7)NEWLINE
A=1
S=0
REPEAT
NEWLINE
REPEAT
K=K'
CCROSS 1/6
CLOSE

CHAPTER 6

VARIABLES 1

2)NEWLINE
CAPTION
SAMPLE
PRINT (I') 3,0
CAPTION
LOAD OF GARBAGE  NO GO
NEWLINE
JUMP 3
1)I=0(1)20
PUNCH(0)
REPEAT

PRINT (I') 2,0
P=0
I=0(1)N
PRINT (T) 2,0
NEWLINE
T=T+Q
J=0(1)K
PRINT (FP) 1,3
PRINT (EP) 1,3
NEWLINE
P=P+1
REPEAT
NEWLINE
REPEAT
I=0(1)20
PUNCH (0)
REPEAT
3)I=0(1)8
PUNCH(*13)
REPEAT
I=0(1)30
PUNCH (0)
REPEAT
ACROSS 1/0
CLOSE

CHAPTER 7

VARIABLES 1

1)I=0(1)K
YI=YI/XI
XI=πI
REPEAT
JUMPDOWN (R2)
PRINT (F) 1,3
PRINT (E) 1,3
PRINT (D) 1,3
UP
3)I=0(1)K
YI=DI
XI=πI
REPEAT
JUMPDOWN (R3)
PRINT (C) 0,3
PRINT (B) 1,3
PRINT (A) 1,3
PRINT (D) 1,3
UP
CLOSE
```

Programme 3

KRIGBAUM CUBIC LATTICE MODEL PROGRAMME

```
CHAPTER 0

1)I=0(1)9
PUNCH (13)
REPEAT
I=0(1)24
PUNCH (0)
REPEAT

READ (B)
READ (M)
READ (N)
READ (N')
READ (R)
READ (Z)
5)READ (V)
READ (J)

CAPTION
REDUCED VOLUME
NEWLINE
ACROSS 1/1

JUMP 5
0)CAPTION
RUBBISH
PUNCH (T')
END
ØEXP
CLOSE


CHAPTER 1

C → *239
D → 239

1)I=0(1)M
JUMP 6, I=0
JUMP 7, J=0
6)V'=VV
V'=ØLOG(V')
V'=0.333V'
V'=ØEXP(V')
Z'=V'
Q'=2
R'=1
S'=3
JUMP 4, I≠M
Q'=3
4)JUMPDOWN (R804/1)
7)B'=1/B
A'=BB
CI=A'+1.333B'
DI=A'A'+1.6B+1.6B'B'
CI=0.9CIV'
DI=1.4464DIV'V'
JUMP 8, J=0
V=V+0.00001J
8)B=B+0.1
REPEAT

L=0(1)R
Z'=0.5Z
CAPTION
K =
Q'=2
R'=1
S'=1
JUMPDOWN (R804/1)
JUMP 5, 0 > Z
E=ØEXP(Z)
F=1/E
JUMP 2
5)E=-Z
F=ØEXP(E)
E=1/F
2)D=15EE+3FF-10
D'=3E-F
E=5-3FF
I=0(1)M
π=N
G=CID'
H=DID
U=2FCI
V=4DIE
J=0(1)2
W=1/π
A=1+GW+HWW
B=UW+V WW
B=B/A
B=1-B
B=-BZ
Q'=5
R'=2
S'=3
Z'=A
JUMPDOWN (R804/1)
Z'=B
Q'=1
JUMP 3, J≠2
Q'=2
JUMP 3, I≠M
Q'=3
3)JUMPDOWN (R804/1)
π=π+N'
REPEAT
REPEAT
Z=Z-0.2
REPEAT
ACROSS 1/0
ØEXP
Ø  LOG
CLOSE
```

APPENDIX 2

Primary data. Values of α unadjusted

Sample 1

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.055	0.948	0.157	0.424	2.697
	1.101	0.909	0.275	0.747	2.715
	1.154	0.867	0.403	1.100	2.729
	1.183	0.845	0.469	1.281	2.734
	1.239	0.807	0.587	1.606	2.735
	1.316	0.769	0.739	2.013	2.725
	1.354	0.739	0.808	2.194	2.716
	1.429	0.700	0.939	2.528	2.691
	1.532	0.653	1.107	2.929	2.647
	1.581	0.633	1.180	3.097	2.625
	1.686	0.593	1.334	3.432	2.572
	1.816	0.551	1.513	3.799	2.510
	1.879	0.532	1.595	3.963	2.484
	2.013	0.497	1.767	4.314	2.442
	2.155	0.464	1.940	4.703	2.424
40	1.053	0.949	0.152	0.422	2.777
	1.095	0.914	0.260	0.733	2.817
	1.146	0.873	0.384	1.090	2.839
	1.173	0.852	0.447	1.272	2.845
	1.226	0.816	0.560	1.594	2.846
	1.298	0.770	0.705	1.999	2.835
	1.333	0.750	0.770	2.177	2.826
	1.403	0.713	0.895	2.506	2.800
	1.500	0.667	1.055	2.906	2.754
	1.544	0.648	1.125	3.071	2.731
	1.640	0.610	1.268	3.398	2.680
	1.760	0.568	1.437	3.762	2.618
	1.818	0.550	1.515	3.929	2.592
	1.941	0.515	1.675	4.273	2.550
	2.075	0.482	1.843	4.665	2.531

Primary data. Values of α unadjusted

Sample 1

Temp. °C	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
55	1.050	0.953	0.142	0.417	2.941
	1.089	0.919	0.245	0.724	2.953
	1.138	0.879	0.366	1.083	2.962
	1.164	0.859	0.425	1.260	2.963
	1.213	0.824	0.534	1.581	2.960
	1.282	0.780	0.674	1.984	2.945
	1.315	0.761	0.703	2.143	2.934
	1.379	0.725	0.853	2.482	2.908
	1.469	0.681	1.005	2.878	2.863
	1.509	0.663	1.070	3.039	2.841
	1.598	0.626	1.207	3.368	2.790
	1.709	0.585	1.366	3.731	2.731
	1.762	0.567	1.440	3.896	2.705
	1.876	0.553	1.592	4.236	2.662
	2.002	0.500	1.752	4.621	2.638
70	1.046	0.956	0.132	0.406	3.074
	1.085	0.922	0.234	0.723	3.083
	1.130	0.885	0.346	1.068	3.087
	1.155	0.866	0.405	1.250	3.086
	1.202	0.832	0.511	1.572	3.080
	1.267	0.789	0.644	1.970	3.061
	1.297	0.771	0.703	2.143	3.049
	1.358	0.736	0.816	2.464	3.020
	1.440	0.694	0.959	2.850	2.973
	1.478	0.677	1.021	3.011	2.950
	1.562	0.640	1.152	3.338	2.899
	1.662	0.602	1.300	3.692	2.840
	1.713	0.584	1.372	3.861	2.814
	1.819	0.550	1.516	4.201	2.770
	1.936	0.517	1.669	4.582	2.745

Primary data. Values of α unadjusted

Sample 2

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.046	0.956	0.133	0.391	2.935
	1.092	0.916	0.253	0.744	2.944
	1.131	0.884	0.350	1.029	2.945
	1.160	0.862	0.416	1.224	2.942
	1.220	0.820	0.548	1.604	2.928
	1.269	0.788	0.647	1.884	2.910
	1.310	0.764	0.727	2.102	2.891
	1.386	0.722	0.865	2.464	2.849
	1.468	0.685	0.992	2.779	2.802
	1.509	0.663	1.070	2.964	2.771
	1.614	0.619	1.231	3.326	2.703
	1.709	0.585	1.367	3.620	2.648
	1.768	0.566	1.448	3.794	2.620
	1.896	0.528	1.618	4.171	2.578
	2.001	0.500	1.751	4.502	2.571
40	1.044	0.958	0.126	0.386	3.062
	1.088	0.919	0.243	0.743	3.063
	1.124	0.889	0.333	1.021	3.061
	1.151	0.869	0.397	1.213	3.057
	1.208	0.828	0.523	1.592	3.043
	1.254	0.797	0.618	1.870	3.025
	1.292	0.774	0.693	2.083	3.006
	1.364	0.733	0.827	2.450	2.964
	1.433	0.698	0.946	2.761	2.918
	1.478	0.677	1.020	2.944	2.887
	1.576	0.635	1.173	3.304	2.816
	1.644	0.601	1.302	3.590	2.756
	1.719	0.582	1.381	3.759	2.723
	1.859	0.540	1.560	4.149	2.659
	1.956	0.511	1.695	4.465	2.634

Primary data. Values of α unadjusted

Sample 2

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
55	1.042	0.960	0.120	0.383	3.188
	1.084	0.923	0.233	0.740	3.178
	1.118	0.894	0.319	1.011	3.173
	1.144	0.874	0.380	1.205	3.168
	1.197	0.835	0.500	1.576	3.153
	1.240	0.806	0.591	1.851	3.135
	1.280	0.781	0.669	2.085	3.115
	1.343	0.744	0.789	2.429	3.077
	1.408	0.710	0.903	2.738	3.033
	1.448	0.691	0.971	2.917	3.003
	1.540	0.649	1.118	3.281	2.934
	1.620	0.617	1.240	3.564	2.875
	1.672	0.598	1.314	3.731	2.840
	1.799	0.556	1.489	4.122	2.768
	1.899	0.527	1.622	4.431	2.731
70	1.040	0.962	0.115	0.377	3.290
	1.080	0.926	0.223	0.734	3.296
	1.112	0.899	0.305	1.003	3.294
	1.137	0.880	0.363	1.194	3.289
	1.188	0.842	0.480	1.569	3.273
	1.229	0.814	0.566	1.842	3.254
	1.264	0.791	0.638	2.062	3.239
	1.325	0.755	0.755	2.412	3.195
	1.385	0.722	0.864	2.722	3.149
	1.423	0.703	0.929	2.897	3.120
	1.508	0.663	1.068	3.258	3.051
	1.582	0.632	1.182	3.538	2.992
	1.630	0.613	1.254	3.707	2.957
	1.741	0.575	1.410	4.073	2.888
	1.844	0.542	1.550	4.409	2.845

Primary data. Values of α unadjusted

Sample 3

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.043	0.956	0.133	0.406	3.061
	1.089	0.918	0.248	0.762	3.072
	1.132	0.883	0.354	1.090	3.076
	1.153	0.866	0.405	1.248	3.075
	1.213	0.824	0.534	1.637	3.067
	1.271	0.786	0.655	1.997	3.049
	1.297	0.771	0.703	2.137	3.039
	1.375	0.727	0.847	2.540	3.000
	1.456	0.687	0.983	2.901	2.952
	1.489	0.672	1.036	3.037	2.931
	1.595	0.627	1.202	3.436	2.859
	1.699	0.589	1.350	3.770	2.793
	1.749	0.572	1.420	3.923	2.764
	1.869	0.535	1.584	4.285	2.705
	1.999	0.501	1.746	4.664	2.672
40	1.042	0.958	0.128	0.396	3.104
	1.085	0.921	0.237	0.754	3.179
	1.127	0.888	0.338	1.081	3.200
	1.147	0.872	0.387	1.241	3.203
	1.201	0.832	0.511	1.634	3.197
	1.259	0.795	0.625	1.987	3.178
	1.280	0.781	0.669	2.120	3.167
	1.353	0.739	0.808	2.524	3.124
	1.429	0.700	0.938	2.883	3.072
	1.478	0.687	0.985	3.007	3.052
	1.555	0.643	1.141	3.402	2.980
	1.648	0.607	1.281	3.737	2.917
	1.694	0.590	1.347	3.894	2.890
	1.808	0.554	1.497	4.255	2.842
	1.913	0.523	1.640	4.629	2.822

Primary data. Values of α unadjusted

Sample 3

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
55	1.042	0.959	0.122	0.393	3.216
	1.081	0.925	0.226	0.746	3.300
	1.119	0.893	0.324	1.077	3.323
	1.140	0.877	0.370	1.231	3.327
	1.192	0.839	0.488	1.621	3.320
	1.243	0.804	0.597	1.970	3.299
	1.264	0.791	0.640	2.103	3.288
	1.332	0.750	0.772	2.503	3.244
	1.404	0.712	0.899	2.869	3.191
	1.429	0.700	0.939	2.979	3.173
	1.520	0.658	1.088	3.374	3.102
	1.607	0.623	1.217	3.704	3.042
	1.649	0.607	1.280	3.860	3.015
	1.753	0.570	1.430	4.241	2.965
	1.849	0.541	1.556	4.584	2.946
70	1.040	0.962	0.115	0.398	3.450
	1.078	0.928	0.215	0.743	3.453
	1.113	0.897	0.310	1.069	3.450
	1.132	0.883	0.354	1.221	3.447
	1.181	0.846	0.466	1.601	3.433
	1.230	0.813	0.570	1.964	3.412
	1.251	0.799	0.612	2.083	3.402
	1.315	0.760	0.737	2.479	3.364
	1.380	0.725	0.855	2.838	3.319
	1.403	0.712	0.897	2.963	3.302
	1.489	0.672	1.037	3.360	3.241
	1.570	0.638	1.160	3.695	3.186
	1.605	0.623	1.219	3.853	3.161
	1.685	0.593	1.333	4.157	3.118
	1.792	0.558	1.481	4.563	3.082

Primary data. Values of α unadjusted

Sample 4

Temp. °C.	α	α^{-1}	ϕ	f kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.103	0.907	0.281	0.694	2.468
	1.151	0.869	0.397	0.989	2.494
	1.175	0.851	0.450	1.126	2.504
	1.232	0.811	0.574	1.447	2.522
	1.297	0.771	0.703	1.782	2.533
	1.322	0.756	0.750	1.901	2.535
	1.401	0.714	0.890	2.259	2.532
	1.489	0.671	1.039	2.613	2.516
	1.522	0.657	1.090	2.732	2.507
	1.622	0.617	1.242	3.070	2.473
	1.731	0.578	1.397	3.388	2.426
	1.778	0.562	1.462	3.513	2.403
	1.904	0.525	1.628	3.806	2.338
	2.095	0.477	1.867	4.181	2.240
40	1.099	0.910	0.270	0.686	2.544
	1.144	0.874	0.380	0.981	2.580
	1.267	0.857	0.433	1.124	2.593
	1.221	0.819	0.549	1.437	2.615
	1.282	0.780	0.674	1.771	2.629
	1.305	0.766	0.719	1.891	2.632
	1.379	0.725	0.853	2.244	2.631
	1.459	0.685	0.989	2.589	2.618
	1.488	0.672	1.037	2.707	2.610
	1.584	0.631	1.185	3.053	2.577
	1.683	0.594	1.330	3.367	2.532
	1.727	0.579	1.391	3.491	2.509
	1.842	0.543	1.548	3.783	2.444
	2.019	0.495	1.774	4.150	2.339

Primary data. Values of α unadjusted

Sample 4

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
55	1.094	0.914	0.259	0.677	2.617
	1.137	0.879	0.364	0.970	2.663
	1.160	0.862	0.416	1.115	2.680
	1.211	0.826	0.529	1.432	2.707
	1.268	0.789	0.646	1.760	2.723
	1.291	0.775	0.691	1.883	2.727
	1.360	0.736	0.818	2.233	2.728
	1.433	0.698	0.947	2.571	2.716
	1.462	0.684	0.994	2.692	2.709
	1.549	0.646	1.131	3.030	2.678
	1.639	0.610	1.261	3.337	2.635
	1.680	0.595	1.326	3.465	2.613
	1.787	0.560	1.474	3.757	2.549
	1.951	0.513	1.688	4.124	2.443
70	1.090	0.918	0.247	0.677	2.736
	1.130	0.885	0.348	0.961	2.763
	1.153	0.868	0.400	1.111	2.776
	1.201	0.833	0.508	1.420	2.797
	1.256	0.796	0.622	1.749	2.812
	1.277	0.783	0.663	1.868	2.816
	1.341	0.746	0.785	2.214	2.819
	1.411	0.709	0.909	2.554	2.811
	1.437	0.696	0.952	2.672	2.806
	1.517	0.659	1.082	3.007	2.780
	1.600	0.625	1.209	3.314	2.741
	1.639	0.610	1.267	3.446	2.719
	1.738	0.575	1.407	3.737	2.656
	1.890	0.529	1.610	4.092	2.546

Primary data. Values of α unadjusted

Sample 5

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.044	0.958	0.126	0.347	2.753
	1.082	0.925	0.227	0.627	2.767
	1.124	0.890	0.332	0.923	2.776
	1.152	0.868	0.398	1.106	2.778
	1.192	0.839	0.488	1.356	2.777
	1.250	0.800	0.611	1.691	2.769
	1.282	0.790	0.674	1.861	2.761
	1.336	0.749	0.776	2.128	2.744
	1.407	0.711	0.902	2.448	2.715
	1.448	0.690	0.972	2.620	2.696
	1.518	0.659	1.085	2.888	2.662
	1.605	0.623	1.217	3.188	2.620
	1.658	0.603	1.295	3.360	2.596
	1.748	0.572	1.421	3.637	2.559
	1.856	0.539	1.566	3.959	2.528
40	1.043	0.959	0.124	0.344	2.782
	1.078	0.928	0.217	0.617	2.848
	1.118	0.894	0.318	0.916	2.876
	1.144	0.874	0.381	1.097	2.883
	1.183	0.845	0.468	1.351	2.886
	1.237	0.809	0.583	1.678	2.880
	1.267	0.789	0.644	1.851	2.872
	1.317	0.759	0.741	2.116	2.855
	1.384	0.723	0.862	2.436	2.826
	1.421	0.704	0.925	2.598	2.807
	1.468	0.673	1.033	2.864	2.773
	1.565	0.639	1.157	3.159	2.731
	1.614	0.619	1.231	3.332	2.707
	1.698	0.589	1.351	3.608	2.670
	1.799	0.556	1.490	3.934	2.640

Primary data. Values of α unadjusted

Sample 5

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
55	1.041	0.961	0.177	0.345	2.948
	1.074	0.931	0.207	0.616	2.972
	1.113	0.899	0.305	0.909	2.984
	1.137	0.880	0.364	1.086	2.987
	1.174	0.852	0.448	1.338	2.986
	1.225	0.816	0.559	1.666	2.978
	1.254	0.798	0.618	1.836	2.971
	1.300	0.769	0.709	2.094	2.955
	1.363	0.734	0.825	2.415	2.928
	1.398	0.716	0.886	2.578	2.911
	1.458	0.686	0.988	2.845	2.880
	1.530	0.653	1.103	3.135	2.841
	1.577	0.634	1.176	3.311	2.817
	1.656	0.604	1.291	3.587	2.779
	1.748	0.572	1.421	3.898	2.744
70	1.039	0.963	0.112	0.345	3.085
	1.070	0.935	0.197	0.609	3.094
	1.107	0.903	0.291	0.903	3.099
	1.130	0.885	0.347	1.076	3.100
	1.165	0.859	0.428	1.325	3.097
	1.214	0.824	0.536	1.654	3.087
	1.242	0.805	0.593	1.826	3.078
	1.284	0.779	0.678	2.076	3.069
	1.344	0.744	0.790	2.397	3.035
	1.377	0.726	0.849	2.563	3.018
	1.432	0.698	0.945	2.823	2.987
	1.498	0.667	1.053	3.106	2.950
	1.544	0.648	1.124	3.288	2.924
	1.617	0.618	1.235	3.564	2.886
	1.702	0.587	1.357	3.867	2.849

Primary data. Values of α unadjusted

Sample 6

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.054	0.949	0.153	0.390	2.546
	1.101	0.908	0.277	0.710	2.565
	1.153	0.867	0.401	1.035	2.579
	1.174	0.851	0.449	1.160	2.582
	1.240	0.806	0.590	1.524	2.584
	1.309	0.764	0.726	1.871	2.576
	1.339	0.747	0.782	2.009	2.570
	1.428	0.700	0.938	2.386	2.543
	1.524	0.656	1.093	2.737	2.504
	1.562	0.640	1.152	2.864	2.486
	1.678	0.596	2.323	3.215	2.430
	1.809	0.553	1.503	3.557	2.367
	1.856	0.539	1.565	3.672	2.346
	1.997	0.501	1.747	4.006	2.294
	2.155	0.464	1.940	4.388	2.262
40	1.050	0.953	0.143	0.382	2.680
	1.097	0.912	0.265	0.711	2.681
	1.146	0.873	0.384	1.032	2.687
	1.166	0.858	0.430	1.157	2.688
	1.228	0.814	0.565	1.520	2.688
	1.293	0.773	0.695	1.863	2.680
	1.321	0.757	0.748	2.001	2.674
	1.403	0.713	0.895	2.371	2.648
	1.492	0.670	1.043	2.724	2.612
	1.526	0.655	1.096	2.845	2.596
	1.633	0.612	1.258	3.199	2.542
	1.754	0.570	1.429	3.546	2.481
	1.797	0.557	1.487	3.660	2.461
	1.928	0.519	1.658	3.991	2.407
	2.076	0.482	1.845	4.366	2.367

Primary data. Values of α unadjusted

Sample 6

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
55	1.048	0.954	0.137	0.376	2.738
	1.092	0.916	0.254	0.705	2.777
	1.139	0.878	0.368	1.030	2.794
	1.157	0.864	0.411	1.149	2.798
	1.217	0.822	0.541	1.516	2.801
	1.279	0.782	0.667	1.863	2.792
	1.304	0.767	0.715	1.993	2.786
	1.381	0.724	0.857	2.364	2.760
	1.463	0.684	0.995	2.709	2.722
	1.495	0.669	1.048	2.836	2.706
	1.594	0.627	1.200	3.183	2.652
	1.705	0.587	1.360	3.526	2.592
	1.745	0.573	1.417	3.642	2.571
	1.866	0.536	1.578	3.973	2.517
	2.005	0.499	1.756	4.351	2.477
70	1.045	0.957	0.129	0.371	2.883
	1.088	0.919	0.243	0.704	2.900
	1.132	0.883	0.353	1.025	2.909
	1.150	0.870	0.394	1.147	2.911
	1.207	0.829	0.520	1.513	2.909
	1.265	0.791	0.639	1.853	2.899
	1.288	0.776	0.686	1.983	2.892
	1.361	0.735	0.821	2.353	2.865
	1.437	0.696	0.953	2.696	2.829
	1.468	0.681	1.004	2.823	2.813
	1.559	0.642	1.147	3.168	2.762
	1.661	0.602	1.298	3.511	2.704
	1.699	0.589	1.353	3.630	2.683
	1.810	0.552	1.505	3.958	2.630
	1.940	0.516	1.674	4.329	2.587

Primary data. Values of α unadjusted

Sample 7

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.091	0.917	0.251	0.118	0.469
	1.177	0.849	0.456	0.216	0.474
	1.281	0.781	0.671	0.319	0.476
	1.334	0.750	0.772	0.367	0.475
	1.481	0.675	1.025	0.481	0.469
	1.657	0.604	1.292	0.590	0.456
	1.733	0.577	1.401	0.630	0.449
	1.957	0.511	1.696	0.731	0.431
	2.225	0.449	2.023	0.842	0.416
40	1.085	0.921	0.237	0.116	0.489
	1.116	0.857	0.432	0.213	0.493
	1.265	0.791	0.639	0.316	0.494
	1.314	0.761	0.735	0.362	0.493
	1.451	0.689	0.975	0.474	0.486
	1.611	0.621	1.226	0.581	0.474
	1.682	0.595	1.329	0.621	0.467
	1.886	0.530	1.605	0.721	0.449
	2.133	0.469	1.913	0.830	0.434
55	1.080	0.927	0.224	0.114	0.511
	1.157	0.864	0.411	0.210	0.511
	1.249	0.800	0.609	0.311	0.511
	1.296	0.772	0.700	0.357	0.510
	1.423	0.703	0.929	0.468	0.504
	1.570	0.637	1.164	0.573	0.492
	1.634	0.612	1.260	0.612	0.486
	1.822	0.549	1.520	0.712	0.468
	2.048	0.488	1.810	0.818	0.452
70	1.075	0.930	0.210	0.111	0.529
	1.148	0.871	0.390	0.207	0.532
	1.235	0.810	0.580	0.308	0.531
	1.279	0.782	0.668	0.354	0.530
	1.397	0.716	0.885	0.462	0.522
	1.534	0.652	1.109	0.565	0.509
	1.592	0.628	1.198	0.603	0.503
	1.765	0.567	1.443	0.701	0.486
	1.973	0.507	1.716	0.808	0.471

Primary data. Values of χ unadjusted

Sample 8

Temp. °C.	χ	χ^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.080	0.926	0.223	0.115	0.517
	1.161	0.861	0.420	0.218	0.519
	1.249	0.801	0.608	0.315	0.518
	1.313	0.762	0.732	0.377	0.515
	1.436	0.696	0.951	0.481	0.505
	1.577	0.634	1.175	0.577	0.491
	1.680	0.595	1.325	0.637	0.480
	1.870	0.535	1.584	0.733	0.463
	2.090	0.478	1.862	0.841	0.452
40	1.076	0.929	0.213	0.115	0.538
	1.152	0.868	0.398	0.214	0.538
	1.235	0.809	0.580	0.311	0.536
	1.296	0.771	0.701	0.373	0.532
	1.411	0.709	0.908	0.475	0.523
	1.539	0.650	1.117	0.569	0.509
	1.637	0.611	1.264	0.630	0.499
	1.809	0.553	1.503	0.724	0.482
	2.012	0.497	1.765	0.831	0.471
55	1.073	0.932	0.203	0.112	0.550
	1.144	0.874	0.380	0.212	0.557
	1.223	0.818	0.554	0.308	0.556
	1.279	0.782	0.668	0.369	0.553
	1.386	0.721	0.866	0.470	0.542
	1.505	0.664	1.064	0.562	0.528
	1.595	0.627	1.202	0.622	0.517
	1.752	0.571	1.427	0.715	0.501
	1.939	0.516	1.673	0.821	0.491
70	1.069	0.936	0.194	0.112	0.579
	1.136	0.880	0.362	0.209	0.578
	1.211	0.826	0.529	0.304	0.574
	1.264	0.791	0.637	0.364	0.570
	1.364	0.733	0.827	0.463	0.560
	1.474	0.678	1.015	0.555	0.549
	1.558	0.642	1.146	0.615	0.537
	1.703	0.587	1.358	0.707	0.521
	1.874	0.534	1.589	0.810	0.510

Primary data. Values of α unadjusted

Sample 10

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.117	0.895	0.316	0.259	0.818
	1.197	0.836	0.499	0.411	0.825
	1.321	0.757	0.749	0.618	0.825
	1.432	0.699	0.944	0.771	0.818
	1.620	0.617	1.239	0.983	0.793
	1.829	0.547	1.530	1.160	0.758
	2.000	0.500	1.750	1.280	0.731
	2.292	0.436	2.101	1.474	0.701
	2.564	0.390	2.412	1.698	0.704
40	1.110	0.901	0.299	0.255	0.850
	1.186	0.843	0.475	0.407	0.858
	1.302	0.768	0.715	0.611	0.859
	1.403	0.713	0.896	0.762	0.851
	1.578	0.634	1.176	0.971	0.826
	1.769	0.565	1.450	1.147	0.791
	1.926	0.519	1.657	1.265	0.764
	2.201	0.454	1.995	1.457	0.730
	2.465	0.406	2.301	1.677	0.729
55	1.104	0.906	0.284	0.250	0.885
	1.176	0.850	0.453	0.404	0.892
	1.284	0.779	0.677	0.604	0.892
	1.379	0.725	0.854	0.754	0.883
	1.540	0.649	1.118	0.959	0.858
	1.713	0.584	1.373	1.131	0.824
	1.861	0.537	1.572	1.252	0.796
	2.115	0.473	1.891	1.439	0.761
	2.369	0.422	2.191	1.657	0.756
70	1.097	0.912	0.266	0.246	0.927
	1.166	0.858	0.430	0.400	0.929
	1.268	0.789	0.645	0.597	0.925
	1.358	0.737	0.815	0.746	0.915
	1.505	0.664	1.064	0.947	0.890
	1.665	0.601	1.304	1.116	0.856
	1.803	0.555	1.496	1.238	0.828
	2.037	0.491	1.795	1.422	0.792
	2.279	0.439	2.086	1.637	0.785

Primary data. Values of χ unadjusted

Sample 11

Temp. °C.	χ	χ^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.099	0.910	0.272	0.216	0.792
	1.196	0.836	0.497	0.398	0.800
	1.327	0.754	0.757	0.606	0.800
	1.371	0.729	0.841	0.671	0.798
	1.565	0.639	1.156	0.900	0.779
	1.761	0.568	1.437	1.081	0.752
	1.855	0.539	1.563	1.156	0.740
	2.135	0.469	1.915	1.368	0.714
	2.355	0.425	2.175	1.555	0.715
40	1.093	0.914	0.260	0.213	0.821
	1.187	0.843	0.475	0.393	0.829
	1.311	0.763	0.727	0.602	0.828
	1.349	0.741	0.801	0.661	0.826
	1.530	0.654	1.102	0.890	0.808
	1.710	0.585	1.367	1.069	0.782
	1.795	0.557	1.484	1.143	0.770
	2.055	0.486	1.822	1.354	0.743
	2.273	0.440	2.077	1.538	0.741
55	1.089	0.918	0.247	0.210	0.848
	1.178	0.850	0.455	0.390	0.857
	1.295	0.722	0.698	0.598	0.856
	1.330	0.752	0.766	0.654	0.854
	1.500	0.667	1.053	0.880	0.836
	1.663	0.601	1.303	1.058	0.812
	1.741	0.574	1.413	1.131	0.800
	1.989	0.503	1.733	1.339	0.773
	2.185	0.457	1.981	1.522	0.768
70	1.084	0.922	0.234	0.207	0.882
	1.169	0.856	0.436	0.387	0.887
	1.279	0.782	0.669	0.592	0.885
	1.313	0.762	0.733	0.647	0.882
	1.471	0.680	1.008	0.871	0.864
	1.624	0.616	1.244	1.046	0.841
	1.692	0.590	1.348	1.119	0.830
	1.922	0.520	1.652	1.325	0.802
	2.115	0.473	1.892	1.505	0.796

Primary data. Values of α unadjusted

Sample 17C

Temp. °C	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.053	0.949	0.152	0.631	4.18
	1.108	0.902	0.294	1.216	4.29
	1.176	0.850	0.454	1.863	4.03
	1.263	0.791	0.638	2.561	4.01
	1.388	0.721	0.869	3.369	3.88
	1.519	0.659	1.085	4.030	3.71
	1.631	0.613	1.255	4.492	3.58
	1.678	0.596	1.323	4.671	3.56
	1.848	0.541	1.555	5.307	3.41
	1.983	0.504	1.729	5.875	3.40
40	1.050	0.952	0.143	0.609	4.26
	1.102	0.907	0.279	1.218	4.36
	1.164	0.859	0.425	1.853	4.36
	1.245	0.803	0.600	2.567	4.28
	1.356	0.737	0.812	3.356	4.13
	1.470	0.680	1.007	3.997	3.97
	1.568	0.638	1.162	4.462	3.84
	1.610	0.621	1.224	4.646	3.79
	1.754	0.570	1.430	5.277	3.69
	1.871	0.535	1.585	5.847	3.69
55	1.044	0.957	0.128	0.612	4.78
	1.092	0.916	0.254	1.204	4.74
	1.152	0.868	0.398	1.857	4.66
	1.223	0.818	0.554	2.533	4.57
	1.424	0.702	0.930	3.963	4.26
	1.510	0.662	1.072	4.438	4.14
	1.550	0.645	1.134	4.641	4.16
	1.671	0.598	1.313	5.246	3.99
	1.777	0.563	1.461	5.812	3.97
70	1.042	0.959	0.122	0.629	5.16
	1.087	0.920	0.241	1.191	4.95
	1.145	0.873	0.383	1.853	4.85
	1.209	0.827	0.524	2.488	4.75
	1.305	0.766	0.718	3.314	4.62
	1.392	0.719	0.875	3.939	4.50
	1.467	0.682	1.002	4.416	4.40
	1.506	0.664	1.064	4.646	4.36
	1.610	0.621	1.225	5.233	4.27
	1.706	0.586	1.362	5.762	4.24

Primary data. Values of α unadjusted

Sample 17R

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
25	1.054	0.949	0.154	0.644	4.24
	1.106	0.904	0.290	1.196	4.13
	1.178	0.849	0.458	1.866	4.07
	1.264	0.791	0.639	2.552	3.99
	1.396	0.716	0.883	3.390	3.84
	1.524	0.656	1.094	4.026	3.68
	1.638	0.611	1.265	4.491	3.55
	1.684	0.594	1.332	4.666	3.56
	1.992	0.502	1.740	5.874	3.41
40	1.048	0.954	0.138	0.632	4.58
	1.099	0.910	0.270	1.204	4.47
	1.162	0.860	0.422	1.847	4.38
	1.243	0.804	0.597	2.550	4.27
	1.359	0.736	0.817	3.361	4.11
	1.474	0.679	1.013	4.009	3.95
	1.568	0.638	1.161	4.462	3.84
	1.608	0.622	1.221	4.643	3.80
	1.867	0.536	1.580	5.843	3.70
55	1.043	0.958	0.125	0.615	4.92
	1.090	0.918	0.248	1.191	4.81
	1.152	0.868	0.398	1.867	4.69
	1.222	0.819	0.552	2.523	4.58
	1.331	0.751	0.766	3.360	4.39
	1.433	0.698	0.947	3.994	4.22
	1.512	0.661	1.074	4.420	4.12
	1.549	0.646	1.132	4.611	4.14
	1.771	0.565	1.452	5.818	4.01
70	1.042	0.960	0.120	0.591	4.92
	1.085	0.922	0.235	1.175	5.00
	1.146	0.873	0.384	1.896	4.94
	1.206	0.829	o.519	2.509	4.84
	1.309	0.764	0.724	3.360	4.64
	1.395	0.717	0.881	3.950	4.48
	1.406	0.682	1.001	4.380	4.38
	1.503	0.665	1.061	4.594	4.33
	1.700	0.588	1.354	5.793	4.28

Primary data. Values of α unadjusted

Sample 17C

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
55	1.048	0.954	1.138	0.607	4.40
	1.143	0.875	0.377	1.674	4.44
	1.190	0.841	0.483	2.129	4.41
	1.225	0.816	0.559	2.447	4.42
	1.295	0.772	0.698	3.010	4.31
	1.361	0.735	0.820	3.474	4.23
	1.438	0.695	0.955	3.953	4.14
	1.534	0.652	1.109	4.465	4.02
	1.705	0.586	1.361	5.265	3.87
	1.839	0.544	1.543	5.887	3.87
70	1.047	0.955	0.134	0.618	4.61
	1.136	0.881	0.360	1.662	4.62
	1.178	0.849	0.458	2.105	4.60
	1.213	0.824	0.534	2.441	4.57
	1.276	0.784	0.661	2.984	4.51
	1.335	0.749	0.773	3.442	4.45
	1.405	0.712	0.899	3.932	4.37
	1.490	0.671	1.039	4.449	4.28
	1.640	0.610	1.269	5.259	4.14
	1.754	0.570	1.428	5.840	4.08
85	1.041	0.960	0.119	0.601	5.05
	1.125	0.889	0.334	1.660	4.97
	1.165	0.858	0.428	2.111	4.93
	1.195	0.837	0.494	2.417	4.90
	1.255	0.797	0.620	2.987	4.82
	1.305	0.766	0.719	3.418	4.76
	1.366	0.732	0.830	3.884	4.67
	1.447	0.691	0.969	4.434	4.58
	1.579	0.633	1.178	5.238	4.60
	1.677	0.596	1.321	5.805	4.39
100	1.041	0.961	0.117	0.587	5.02
	1.119	0.893	0.321	1.670	5.20
	1.157	0.865	0.409	2.116	5.18
	1.180	0.848	0.461	2.371	5.14
	1.241	0.806	0.592	2.994	5.05
	1.283	0.780	0.675	3.371	4.98
	1.347	0.742	0.796	3.898	4.89
	1.415	0.707	0.916	4.397	4.80
	1.533	0.652	1.108	5.192	4.69
	1.621	0.617	1.240	5.786	4.67

Primary data. Values of α unadjusted

Sample 18

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
40	1.018	0.982	0.054	0.538	9.98
	1.056	0.947	0.159	1.586	10.00
	1.061	0.942	0.173	1.729	10.00
	1.088	0.919	0.242	2.424	10.00
	1.108	0.903	0.293	2.925	10.00
	1.110	0.901	0.298	2.978	10.00
	1.137	0.879	0.364	3.614	9.92
	1.163	0.860	0.423	4.165	9.85
	1.164	0.859	0.427	4.206	9.85
	1.225	0.816	0.559	5.349	9.57
55	1.018	0.982	0.053	0.546	1.03
	1.053	0.949	0.152	1.570	1.03
	1.058	0.945	0.165	1.707	1.03
	1.084	0.923	0.233	2.410	1.03
	1.103	0.907	0.281	2.905	1.03
	1.105	0.905	0.286	2.957	1.03
	1.132	0.884	0.351	3.605	1.03
	1.155	0.866	0.406	4.140	1.02
	1.157	0.864	0.411	4.188	1.02
	1.214	0.824	0.535	5.312	0.99

Primary data. Values of α unadjusted

Sample 18

Temp. °C.	α	α^{-1}	ϕ	f Kg.cm.$^{-2}$	f/ϕ Kg.cm.$^{-2}$
70	1.016	0.984	0.048	0.547	1.14
	1.050	0.953	0.142	1.555	1.09
	1.054	0.949	0.154	1.686	1.09
	1.080	0.926	0.222	2.418	1.09
	1.097	0.911	0.266	2.883	1.08
	1.099	0.910	0.271	2.935	1.08
	1.125	0.889	0.334	3.585	1.07
	1.147	0.872	0.387	4.114	1.06
	1.149	0.870	0.391	4.161	1.06
	1.202	0.832	0.510	5.280	1.04
85	1.014	0.986	0.042	0.549	1.31
	1.046	0.956	0.131	1.543	1.18
	1.050	0.953	0.142	1.668	1.18
	1.075	0.930	0.210	2.423	1.15
	1.091	0.917	0.251	2.861	1.14
	1.093	0.915	0.256	2.915	1.14
	1.117	0.895	0.317	3.564	1.12
	1.138	0.878	0.367	4.087	1.11
	1.140	0.877	0.371	4.126	1.11
	1.191	0.840	0.486	5.256	1.08
100	1.015	0.985	0.044	0.698	1.59
	1.044	0.950	0.127	1.564	1.23
	1.048	0.954	0.138	1.670	1.21
	1.072	0.933	0.202	2.349	1.16
	1.087	0.920	0.242	2.769	1.14
	1.090	0.918	0.247	2.827	1.14
	1.113	0.898	0.306	3.475	1.14
	1.133	0.883	0.353	4.007	1.13
	1.134	0.882	0.356	4.033	1.13
	1.183	0.845	0.469	5.426	1.16

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