

THERMODYNAMICS OF CRYSTAL LATTICES AND THE TEMPERATURE  
DEPENDENCE OF THE ELASTIC CONSTANTS.

THESIS

SUBMITTED BY

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INTRODUCTION.

The investigations described in this paper form part of a programme started by Max Born in his paper "Thermodynamics of Crystals and Melting" (1). There, following a method of Stern (2), the free energy of a body-centred cubic crystal was calculated on the assumption that the forces between the atoms are central, and explicit expressions were obtained for the equation of state and the elastic constants  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  (Voigt's notation) as functions of temperature and pressure. But the difference  $c_{11} - c_{12}$  was negative which indicated that the body-centred cubic lattice is unstable under central forces. This led to a series of investigations of the stability of different lattice types under central forces (3). These showed that of the three cubic Bravais lattices only the face-centred one is stable, and so the thermodynamical calculations had to be repeated for this lattice. This task proved to be so laborious that simplified methods had to be adopted. M. Bradburn (4) derived the equation of state using an exact method as well as various approximations

and showed that the latter were sufficient for all practical purposes. The simplest of these methods consists in performing a statistical average at an early stage in the calculations instead of on the final formula as demanded by rigorous argument. The results of this process were encouraging and it now seemed possible to derive in the same way the simple expressions for the elastic constants. This is done in the present paper. The law of central force is assumed to be the sum of two terms of the form  $ar^{-n}$  one corresponding to attraction, the other to repulsion. The exponents  $m$  and  $n$  have been varied over a wide

range

$$\begin{array}{l} m = \left( \begin{array}{c} 4 \\ 8 \end{array} \right), \left( \begin{array}{c} 5 \\ 10 \end{array} \right), \left( \begin{array}{c} 6 \\ 12 \end{array} \right), \left( \begin{array}{c} 7 \\ 14 \end{array} \right), \left( \begin{array}{c} 6 \\ 14 \end{array} \right) \\ n = \left( \begin{array}{c} 4 \\ 8 \end{array} \right), \left( \begin{array}{c} 5 \\ 10 \end{array} \right), \left( \begin{array}{c} 6 \\ 12 \end{array} \right), \left( \begin{array}{c} 7 \\ 14 \end{array} \right), \left( \begin{array}{c} 6 \\ 14 \end{array} \right) \end{array}$$

in order to see how the elastic properties depend on the choice of exponents. The results are presented in the form of diagrams which are briefly discussed. A detailed discussion in relation to all the thermodynamical properties is outside the scope of this thesis and will be given later.

I take this opportunity of thanking Professor Born who suggested this problem, for his interest in my work and his kind advice on many occasions. I am also indebted to Dr. R. Fürth for his numerous helpful suggestions and his encouragement.

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### 1. The Free Energy of a Crystal Lattice.

The free energy  $A$  of an elastic solid is a function of the temperature  $T$  and of the six homogeneous strain components. All other thermodynamical properties may be obtained by differentiation e.g.

$$\text{the entropy} \quad S = - \frac{\partial A}{\partial t}$$

$$\text{the energy} \quad E = S + AT$$

and the generalised forces corresponding to any molar parameter  $f_r = - \frac{\partial A}{\partial a_r}$ . In the case of a crystal lattice in thermodynamical equilibrium these molar parameters are the strain components.

Let us consider the free energy of a cubic lattice of the Bravais type (simple, face-centred or body-centred) in which the cubic cells have sides of length  $a$ .

Then the lattice points of the undistorted cubic lattice are given by the vectors

$$r^0 = (l_1 a, l_2 a, l_3 a)$$

If we apply a homogeneous deformation the cubic cell

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of a side  $a$  is transformed into a parallelepiped described by the three lattice vectors  $\underline{a}_1, \underline{a}_2, \underline{a}_3$ . The lattice points are given by the vectors

$$r^l = l_1 \underline{a}_1 + l_2 \underline{a}_2 + l_3 \underline{a}_3$$

and the shape of the cell is defined by the scalar products of these vectors with one another i.e. by

$$(1.1) \quad g_{11}, g_{22}, g_{33}, g_{12}, g_{23} \text{ and } g_{31} \quad \text{where} \\ g_{\alpha\beta} = \underline{a}_\alpha \cdot \underline{a}_\beta$$

These six parameters are invariant with respect to rigid motion of the crystal, and as pointed out above, they play the part of molar parameters. The free energy

$A$  of the system is a function of these six quantities and the temperature; also, if we neglect surface effects it is clear that  $A$  is proportional to the number of particles  $N$  making up the lattice. Instead of the  $g_{\alpha\beta}$  it is convenient to introduce the six dimensionless strain components. The general definition of these for any lattice is given in paper IX of the series "The

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Stability of Crystal Lattices"; in this case (a cubic lattice) it reduces simply to the following:

$$\begin{aligned}(1.2) \quad e_{11} &= \frac{a_1^2 - a^2}{a^2} = \frac{g_{11} - g_{11}^0}{a^2} = \frac{\delta g_{11}}{a^2} \\ e_{22} &= \frac{a_2^2 - a^2}{a^2} = \frac{g_{22} - g_{22}^0}{a^2} = \frac{\delta g_{22}}{a^2} \\ e_{33} &= \frac{a_3^2 - a^2}{a^2} = \frac{g_{33} - g_{33}^0}{a^2} = \frac{\delta g_{33}}{a^2} \\ e_{12} &= \frac{a_1 \cdot a_2}{a^2} = \frac{g_{12} - g_{12}^0}{a^2} = \frac{\delta g_{12}}{a^2} \\ e_{23} &= \frac{a_2 \cdot a_3}{a^2} = \frac{g_{23} - g_{23}^0}{a^2} = \frac{\delta g_{23}}{a^2} \\ e_{31} &= \frac{a_3 \cdot a_1}{a^2} = \frac{g_{31} - g_{31}^0}{a^2} = \frac{\delta g_{31}}{a^2}\end{aligned}$$

where 
$$g_{\alpha\beta}^0 = \begin{cases} a^2, & \alpha = \beta \\ 0 & \alpha \neq \beta \end{cases}$$

The notation used here is Brillouin's; Voigt uses

$$\begin{aligned}(1.3) \quad 2x_x &= e_{11} & x_y &= e_{12} \\ 2y_y &= e_{22} & y_z &= e_{23} \\ 2z_z &= e_{33} & z_x &= e_{31}\end{aligned}$$

Then we may write

$$(1.4) \quad A = N f(a, T, e_{11}, e_{22}, e_{33}, e_{12}, e_{23}, e_{31})$$

The function  $f$  apparently depends on  $T$  and seven geometrical variables, but only six of the latter are

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independent for there exists a linear identity connecting the first derivatives of  $f$  viz:

$$a \frac{\partial f}{\partial a} = 2(e_{11}+1) \frac{\partial f}{\partial e_{11}} + \dots + 2e_{12} \frac{\partial f}{\partial e_{12}} + \dots +$$

By repeated differentiation we obtain identities

between higher derivatives. These are only used for

the case  $e_{11} = e_{22} = e_{33} = e_{12} = e_{23} = e_{31} = 0$  when we have

$$(1.5) \quad a \frac{\partial f}{\partial a} = 2 \left( \frac{\partial f}{\partial e_{11}} + \frac{\partial f}{\partial e_{22}} + \frac{\partial f}{\partial e_{33}} \right)$$

$$(1.6) \quad a^2 \frac{\partial^2 f}{\partial a^2} - a \frac{\partial f}{\partial a} = 4 \left( \frac{\partial^2 f}{\partial e_{11}^2} + \frac{\partial^2 f}{\partial e_{22}^2} + \frac{\partial^2 f}{\partial e_{33}^2} \right) \\ + 8 \left( \frac{\partial^2 f}{\partial e_{11} \partial e_{22}} + \frac{\partial^2 f}{\partial e_{22} \partial e_{33}} + \frac{\partial^2 f}{\partial e_{33} \partial e_{11}} \right)$$

If we expand  $f$  for a given value of  $a$  in a power

series of  $e_{11} \dots e_{12} \dots$ , the result for a cubic lattice

takes the form

$$(1.7) \quad f = f_0 + \frac{1}{2} f_1 (e_{11} + e_{22} + e_{33}) + \frac{1}{8} f_{11} (e_{11}^2 + e_{22}^2 + e_{33}^2) \\ + \frac{1}{4} f_{12} (e_{11} e_{22} + e_{22} e_{33} + e_{33} e_{11}) + \frac{1}{2} f_{44} (e_{12}^2 + e_{23}^2 + e_{31}^2)$$

in Brillouin's notation and

$$(1.8) \quad f = f_0 + f_1 (x_x + y_y + z_z) + \frac{1}{2} \left\{ f_{11} (x_x^2 + y_y^2 + z_z^2) \right. \\ \left. + 2f_{12} (x_x y_y + y_y z_z + z_z x_x) + f_{44} (x_y^2 + y_z^2 + z_x^2) \right\}$$

in Voigt's notation. Then if  $V$  is the volume con-

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taining  $N$  particles, the density of free energy is  $A/V$ .

Also, if  $\kappa$  is the number of cells of volume  $v = a^3$

corresponding to one particle,  $V = N\kappa a^3 = N\kappa v$ . The

value of  $\kappa$  varies with the type of lattice. As  $a$

is defined as the projection of the smallest distance

in the crystal on the side of the cube,  $\kappa$  has the

value 1 for the simple cubic lattice, 4 for the body-

centred lattice and 2 for the face-centred lattice.

The density of free energy  $A/V = f/\kappa a^3$  which, using

(1.7) and (1.8), can be written

$$(1.9) \quad \frac{A}{V} = \frac{f_0}{\kappa a^3} - p/2 (e_{11} + e_{22} + e_{33}) + 1/8 c_{11} (e_{11}^2 + e_{22}^2 + e_{33}^2) \\ + 1/4 c_{12} (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) + 1/8 c_{44} (e_{12}^2 + e_{23}^2 + e_{31}^2)$$

in Brillouin's notation or as

$$(1.10) \quad \frac{A}{V} = \frac{f_0}{\kappa a^3} - p(x_x + y_y + z_z) + 1/2 \{ c_{11} (x_x^2 + y_y^2 + z_z^2) \\ + 2c_{12} (x_x y_y + y_y z_z + z_z x_x) + c_{44} (x_y^2 + y_z^2 + z_x^2) \}$$

in Voigt's, where

$$(1.11) \quad -p = \frac{1}{\kappa a^3} f_1(a, T)$$

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$$(1.12) \quad c_{11} = \frac{1}{\kappa a^3} f''(a, T)$$

$$c_{12} = \frac{1}{\kappa a^3} f'_{12}(a, T)$$

$$c_{44} = \frac{1}{\kappa a^3} f_{44}(a, T)$$

(1.11) is the equation of state for the cubic crystal, giving  $a$  as a function of  $p$  and  $T$ , and so the thermal expansion for any pressure.  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  are the elastic constants in Voigt's notation for a given temperature and volume, which can be replaced with the help of (1.11) by the external hydrostatic pressure.

All the thermodynamical properties of the crystal can be expressed in terms of the functions  $f$ ,  $f_{12}$ ,  $f_{44}$  and their derivatives. Our problem lies in deriving explicit expressions for them.

Assuming that the thermic motion may be regarded as harmonic, the free energy  $A$  of a crystal lattice at high temperatures is given by the following expression:

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$$(1.13) \quad A = \underline{\phi} + 3NkT \log \frac{\hbar\bar{\omega}}{kT}$$

where  $\underline{\phi}$  is the potential energy of the non-vibrating but homogeneously deformed lattice and  $\bar{\omega}$  is a mean frequency per  $2\pi$  seconds.

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## 2. Lattice Dynamics.

The position of any lattice point in a homogeneously deformed lattice is given by the vector  $\underline{r}^l$  where

$$(2.1) \quad \underline{r}^l = l_1 \underline{a}_1 + l_2 \underline{a}_2 + l_3 \underline{a}_3$$

Consider a small displacement  $\underline{u}^l$  from this equilibrium position so that the position of the particle is now defined by the vector  $\underline{r}^l + \underline{u}^l$ . The distance between the particles  $l$  and  $l'$  will be:

$$(2.2) \quad r^{ll'} = |\underline{r}^{ll'}| = |\underline{r}^l - \underline{r}^{l'} + \underline{u}^l - \underline{u}^{l'}|$$

Assume that the potential energy between two such particles depends only on their distance apart and denote it by  $\phi^{ll'}$ . For the undeformed lattice

$$(2.3) \quad \phi^{ll'} = \phi(|\underline{r}^l - \underline{r}^{l'}|) = \phi(|\underline{r}^{l-l'}|)$$

We now introduce the notation

$$(2.4) \quad \phi^l = \phi(|\underline{l}|)$$

$$(2.5) \quad \phi_x^l = x^l D\phi^l$$

$$(2.6) \quad \phi_{xy}^l = \delta_{xy} D\phi^l + x^l y^l D^2\phi^l$$

$$\text{with } \delta_{xy} = \begin{cases} 1, & x=y \\ 0, & x \neq y \end{cases} \quad \text{and } D = \frac{1}{r} \frac{d}{dr}$$

For the deformed lattice we can expand  $\phi^{ll'}$  as a series in ascending powers of  $\underline{u}^{ll'}$  as follows:

$$(2.7) \quad \phi^{ll'} = \phi^{l-l'} + \sum_x \phi_x^{l-l'} u_x^{ll'} + \frac{1}{2} \sum_{xy} \phi_{xy}^{l-l'} u_x^{ll'} u_y^{ll'}$$

(2.5) and (2.6) have no meaning if  $l=0$  so we define

$\phi_x^0$  and  $\phi_{xy}^0$  by

$$(2.8) \quad \phi_x^0 = 0 \quad \text{and} \quad \sum_l \phi_{xy}^l = 0.$$

Summing (2.7) over all  $l$  and  $l'$  we get twice the

potential energy of the deformed lattice since the

potential between each pair of particles has been

counted twice. The potential energy  $\bar{\Phi}$  of the whole

lattice can be developed as a power series in  $\underline{u}^{ll'}$ :

$$\bar{\Phi} = \bar{\Phi}_0 + \bar{\Phi}_1 + \bar{\Phi}_2 + \dots \quad \text{where}$$

$$(2.9) \quad \bar{\Phi}_1 = \frac{1}{2} \sum_{ll'} \sum_x \phi_x^{l-l'} u_x^{ll'} \quad \text{and}$$

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$$(2.10) \quad \bar{\Phi}_2 = \frac{1}{4} \sum_{\ell\ell'} \sum_{xy} \phi_{xy}^{\ell-\ell'} u_x^{\ell\ell'} u_y^{\ell\ell'}$$

Since  $u^{\ell\ell'} = u^\ell - u^{\ell'}$  these expressions can be rewritten with the help of (2.8) as

$$\bar{\Phi}_1 = \sum_{\ell} \sum_x u_x^\ell \left[ \sum_{\ell'} \phi_x^{\ell-\ell'} \right]$$

and

$$\bar{\Phi}_2 = -\frac{1}{2} \sum_{\ell\ell'} \sum_{xy} \phi_{xy}^{\ell-\ell'} u_x^\ell u_y^{\ell'}$$

The force exerted by all the particles on one is

$$(2.11) \quad \underline{K}^\ell = - \frac{\partial \bar{\Phi}}{\partial u^\ell}$$

The equilibrium condition that  $\underline{K}^\ell = 0$  is satisfied

since  $\sum_{\ell'} \phi_x^{\ell-\ell'}$  vanishes.

The equation of motion of any particle of mass  $\mu$  is

$$(2.12) \quad \mu \ddot{u}_x^\ell = - \frac{\partial \bar{\Phi}_2}{\partial u_x^\ell} = \sum_{\ell'} \sum_y \phi_{xy}^{\ell-\ell'} u_y^{\ell'}$$

Assuming that the solution is of the form  $u^\ell = \underline{U}^\ell e^{-i\omega t}$

where  $\underline{U}^\ell = U e^{i(\ell \cdot r)}$ ,  $\omega$  is the frequency of one of the

independent normal modes of vibration, and  $(\ell \cdot r) = \ell_1 r_1 + \ell_2 r_2 + \ell_3 r_3$

If we restrict ourselves in our choice of wave vector

by the cyclic lattice condition (5) which postulates

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that the displacement is to be periodic in a volume having the same shape as the elementary cell and having

$N$  cells, the equations of motion become:

$$(2.13) \quad \mu \omega^2 u_x = \sum_y [x,y] u_y$$

$$\text{where} \quad [xy] = -\sum_l \phi_{xy}^l e^{-i(lx)}$$

Then it follows from (2.8) that

$$\begin{aligned} [xy] &= -\sum_l' \phi_{xy}^l e^{-i(lx)} - \phi_{xy}^0 \\ &= \sum_l' \phi_{xy}^l (1 - e^{-i(lx)}) \end{aligned}$$

where  $\sum_l'$  means that the term corresponding to  $l_1=l_2=l_3=0$  is omitted. If we assume that the thermic motion can be regarded as harmonic, the free energy of a crystal lattice at high temperatures is

$$A = \underline{\Phi} + kT \sum_{p=1}^{3N} \log \left( \frac{\hbar \omega_p}{kT} \right)$$

where  $\underline{\Phi}$  is the potential energy of the non-vibrating but homogeneously deformed lattice and  $\omega_p$  ( $p=1, 2, \dots, 3N$ )

are the proper frequencies per  $2\pi$  seconds. We can

$$\text{write} \quad A = \underline{\Phi} + 3NkT \log \frac{\hbar \bar{\omega}}{kT} \quad \text{where}$$

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$$3N \log \bar{\omega} = \sum_{p=1}^{3N} \log \omega_p = 1/2 \sum_{p=1}^{3N} \log \omega_p^2$$

The frequencies  $\omega_p$  consist of three branches  $\omega^{(1)}(\alpha), \omega^{(2)}(\alpha), \omega^{(3)}(\alpha)$  their squares being the latent roots of (2.13). Hence

$$\mu^3 (\omega^{(1)}(\alpha), \omega^{(2)}(\alpha), \omega^{(3)}(\alpha))^2 = \det. [xy]$$

where  $\det. [xy]$  denotes the determinant of the coefficients  $[xy]$ . Each root takes  $N$  values equally distributed in the  $d$  space, and so

$$\log \bar{\omega} = 1/6N \sum_{(N)} \log (\omega^{(1)}(\alpha), \omega^{(2)}(\alpha), \omega^{(3)}(\alpha))^2 = \frac{1}{6N} \sum_{(N)} \log \{ \mu^{-3} \det [xy] \} \text{ i.e.}$$

$$(2.14) \quad \log \bar{\omega} = \frac{1}{6} \log \langle \det. [xy] \rangle_{Av} - 1/2 \log \mu$$

where the average taken over  $\alpha, \alpha_1, \alpha_2, \alpha_3$ , the phases of the waves is defined by

$$f_{Av} = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} \int \int f(\alpha_1, \alpha_2, \alpha_3) d\alpha_1 d\alpha_2 d\alpha_3$$

Written in full the determinant of the coefficients

$[xy]$  is:

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$$(2.15) \quad \det[x y] = \begin{vmatrix} \sum_l' \phi_{xx}(1-e^{-i(l\omega)}) & \sum_l' \phi_{xy}(1-e^{-i(l\omega)}) & \sum_l' \phi_{xz}(1-e^{-i(l\omega)}) \\ \sum_l' \phi_{yx}(1-e^{-i(l\omega)}) & \sum_l' \phi_{yy}(1-e^{-i(l\omega)}) & \sum_l' \phi_{yz}(1-e^{-i(l\omega)}) \\ \sum_l' \phi_{zx}(1-e^{-i(l\omega)}) & \sum_l' \phi_{zy}(1-e^{-i(l\omega)}) & \sum_l' \phi_{zz}(1-e^{-i(l\omega)}) \end{vmatrix}$$

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### 3. The Potential Energy.

Assuming that the forces between the atoms are central, the potential energy of the homogeneously deformed lattice is given by the expression

$$(3.1) \quad \bar{\Phi} = \frac{1}{2} N \sum_l' \phi(r^l)$$

We wish to expand  $\bar{\Phi}$  in terms of the strain components.

The square of the distance of the lattice points of the deformed lattice from the origin is

$$(3.2) \quad (r^l)^2 = \sum_{\alpha\beta} g_{\alpha\beta} l_\alpha l_\beta$$

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using the notation of (1.1).

We denote by  $\rho^{ll}$  half of the change in this square over its value in the undeformed lattice and thus obtain:

$$(3.3) \quad (\underline{r}^l)^2 = (\underline{r}^{0l})^2 + 2\rho^{ll}.$$

Then in the notation of (1.2)

$$(3.4) \quad \rho^{ll} = \frac{1}{2} \sum_{\alpha\beta} \delta g_{\alpha\beta} l_\alpha l_\beta$$

$$= \frac{1}{2} a^2 \sum_{\alpha\beta} e_{\alpha\beta} l_\alpha l_\beta$$

$$= \frac{1}{2} a^2 \left\{ e_{11} l_1^2 + e_{22} l_2^2 + e_{33} l_3^2 + 2e_{12} l_1 l_2 + 2e_{23} l_2 l_3 + 2e_{31} l_3 l_1 \right\}$$

and (3.5)  $(\rho^{ll})^2 = \frac{1}{4} a^4 \sum_{\alpha\beta\gamma\delta} e_{\alpha\beta} e_{\gamma\delta} l_\alpha l_\beta l_\gamma l_\delta$

$$= \frac{1}{4} a^4 \left\{ (e_{11}^2 l_1^4 + e_{22}^2 l_2^4 + e_{33}^2 l_3^4) \right.$$

$$+ 4 \left[ e_{12} l_1 l_2 (e_{11} l_1^2 + e_{22} l_2^2) + e_{23} l_2 l_3 (e_{22} l_2^2 + e_{33} l_3^2) \right.$$

$$\left. + e_{31} l_3 l_1 (e_{33} l_3^2 + e_{11} l_1^2) \right]$$

$$+ 2(e_{11} e_{22} l_1^2 l_2^2 + e_{22} e_{33} l_2^2 l_3^2 + e_{33} e_{11} l_3^2 l_1^2)$$

$$+ 4(e_{12}^2 l_1^2 l_2^2 + e_{23}^2 l_2^2 l_3^2 + e_{31}^2 l_3^2 l_1^2)$$

$$+ 8(e_{12} e_{13} l_1^2 l_2 l_3 + e_{23} e_{21} l_2^2 l_1 l_3 + e_{31} e_{32} l_3^2 l_1 l_2)$$

$$\left. + 8(e_{11} e_{23} l_1^2 l_2 l_3 + e_{22} e_{13} l_2^2 l_1 l_3 + e_{33} e_{12} l_3^2 l_1 l_2) \right\}$$

Also, if  $\phi(\underline{r}^e)$  is an arbitrary function of  $\underline{r}$ , then:

$$(3.6) \quad \begin{aligned} \phi(\underline{r}^e) &= \phi(\underline{r}^{0e} + 2\rho^{ee})^{1/2} \\ &= \phi(\underline{r}^{0e}) + \rho^{ee} D\phi(\underline{r}^{0e}) + 1/2(\rho^{ee})^2 D^2\phi(\underline{r}^{0e}) \end{aligned}$$

or more briefly,  $\phi^e = \phi^{0e} + \rho^{ee} D\phi^{0e} + 1/2(\rho^{ee})^2 D^2\phi^{0e}$

where  $\phi^e = \phi(\underline{r}^e)$  and  $\phi^{0e} = \phi(\underline{r}^{0e})$

Using these expansions we can derive an expression for the potential energy of the deformed cubic lattice:

$$(3.7) \quad \begin{aligned} \underline{\Phi} &= 1/2 N \sum_l' \phi \{ (\underline{r}^{0e})^2 + 2\rho^{ee} \}^{1/2} \\ &= 1/2 N \sum_l' (\phi^{0e} + \rho^{ee} D\phi^{0e} + 1/2(\rho^{ee})^2 D^2\phi^{0e} + \dots) \end{aligned}$$

We introduce the notation  $S_n^{pqr} = a^{2(p+q+r)} \sum_l' (l_1)^{2p} (l_2)^{2q} (l_3)^{2r} D^n \phi^{0e}$

$$S_0^0 = \sum_l' \phi^{0e}$$

$S_n^{pqr}$  has some symmetry viz.

$$S_n^{pqr} = S_n^{p+q} = S_n^{q+r} = S_n^{r+p} = S_n^{r+q} = S_n^{p+r}$$

and  $S_n^{pqr} = 0$  if any of  $p, q, r$ , is odd.

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Using (3.4) and (3.5) in (3.7) we finally obtain the

result:

$$\begin{aligned} (3.8) \quad \bar{\Phi} &= 1/2 N \left\{ \delta_0^0 + 1/2 (e_{11} + e_{22} + e_{33}) \delta_1' + 1/8 \delta_2^2 (e_{11}^2 + e_{22}^2 + e_{33}^2) \right. \\ &\quad \left. + 1/4 (e_{11} e_{22} + 2e_{12}^2 + e_{22} e_{33} + 2e_{23}^2 + e_{33} e_{11} + 2e_{31}^2) \delta_2'' \right\} \\ &= N \left\{ A_0 + 1/2 A_1 (e_{11} + e_{22} + e_{33}) + 1/8 A_2 (e_{11}^2 + e_{22}^2 + e_{33}^2) \right. \\ &\quad \left. + 1/4 A_3 (e_{11} e_{22} + 2e_{12}^2 + e_{22} e_{33} + 2e_{23}^2 + e_{33} e_{11} + 2e_{31}^2) \right\} \end{aligned}$$

where  $A_0 = 1/2 \delta_0^0$                        $A_2 = 1/2 \delta_2^2$

$A_1 = 1/2 \delta_1'$                        $A_3 = 1/2 \delta_2''$

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#### 4. The Mean Frequency.

The mean frequency may be determined from determinant

(2.15) which must be expanded in the same way as we

expanded the static terms in the preceding paragraph.

This expansion presents some difficulty owing to the

types of lattice sums which occur. These lattice sums

all contain an exponential term  $e^{-\alpha(\mathbf{r}_i)}$  which prevents

any simplification due to symmetry. The problem was first attacked by M. Born in his paper "The Thermodynamics of Crystals and Melting" (1). In order to obtain a solution he assumed that only first and second neighbours were of any account in the static terms and only first neighbours in the vibrational terms. These assumptions enabled him to obtain a qualitative result but it was impossible to estimate its accuracy and some method of obtaining a quantitative result was sought for. An effort was made to evaluate the determinant (2.15) exactly but this proved to be so laborious that the attempt was abandoned as it was evident that the accuracy of the result would not be worth the work involved. Some form of simplification was required to enable a result to be reached more rapidly without too great a sacrifice in accuracy. A practical simplification was obtained by M. Bradburn<sup>(4)</sup> who found by numerical computation that for a lattice under volume stress without shearing the relation

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$$(4.1) \quad \langle \log \det. [xy] \rangle_{AV} = \log \det \{ [xy]_{AV} \}$$

where  $\det. \{ [xy]_{AV} \}$  denotes the determinant formed by averaging the coefficients of (2.15), was true to a very high degree of accuracy. On the assumption that the same formula can be applied to the crystal lattice under shearing stress, an expression for the mean frequency can be obtained. This is the method of simplification which is used in this paper.

-:-

### 5. Reduction of Det. $\{ [xy]_{AV} \}$

If we average the coefficients of determinant (2.15) over  $(d_1, d_2, d_3)$  we obtain a determinant of lattice sums not involving an exponential term viz.

$$(5.1) \quad \det. \{ [xy]_{AV} \} = \begin{vmatrix} \sum_l \phi_{xx}^l & \sum_l \phi_{xy}^l & \sum_l \phi_{xz}^l \\ \sum_l \phi_{yx}^l & \sum_l \phi_{yy}^l & \sum_l \phi_{yz}^l \\ \sum_l \phi_{zx}^l & \sum_l \phi_{zy}^l & \sum_l \phi_{zz}^l \end{vmatrix}$$

Recalling the definitions (2.6) we can expand the above determinant as follows:

$$\begin{aligned} \text{Det. } \{ [xy]_{\Lambda\nu} \} = & \sum_l \sum_{l'} \sum_{l''} \left\{ [D\phi^l + (x^l)^2 D^2\phi^l] [ (D\phi^{l'} + (y^{l'})^2 D^2\phi^{l'}) (D\phi^{l''} + (z^{l''})^2 D^2\phi^{l''}) \right. \\ & \left. - (y^{l'} z^{l''} D^2\phi^{l'}) (y^{l''} z^{l''} D^2\phi^{l''}) \right] \\ & + (x^l y^{l'} D^2\phi^l) [ (y^{l'} z^{l''} D^2\phi^{l'}) (x^{l''} z^{l''} D^2\phi^{l''}) \\ & \left. - (x^{l''} y^{l'} D^2\phi^{l'}) (D\phi^{l''} + (z^{l''})^2 D^2\phi^{l''}) \right] \\ & + (x^l z^{l''} D^2\phi^l) [ (x^{l'} y^{l'} D^2\phi^{l'}) (y^{l''} z^{l''} D^2\phi^{l''}) \\ & \left. - (x^{l''} z^{l''} D^2\phi^{l''}) (D\phi^{l'} + (y^{l'})^2 D^2\phi^{l'}) \right] \left. \right\} \end{aligned}$$

$$\text{Then det. } \{ [xy]_{\Lambda\nu} \} = \sum_l \sum_{l'} \sum_{l''} \{ l l' l'' \}$$

$$\begin{aligned} \text{where } \{ l l' l'' \} = & D\phi^l D\phi^{l'} D\phi^{l''} + (\pm^l)^2 D^2\phi^l D\phi^{l'} D\phi^{l''} \\ & + 1/2 (\pm^{l'} \times \pm^{l''})^2 D\phi^l D^2\phi^{l'} D^2\phi^{l''} \\ & + 1/6 (\pm^l \cdot \pm^{l'} \times \pm^{l''})^2 D^2\phi^l D^2\phi^{l'} D^2\phi^{l''} \end{aligned}$$

We now expand  $\{ l l' l'' \}$  by introducing (3.4), (3.5) and

(3.6). The full derivation of the first two terms is

shown here. The method of derivation of the remaining

two terms is merely indicated since the calculation is

heavy. Terms above the second order in  $\rho^{ll}$  are neglected.

First Term.

$$\sum_l \sum_{l'} \sum_{l''} D\phi^l D\phi^{l'} D\phi^{l''} = \left[ \sum_l (D\phi^{ol} + \rho^{ll} D^2\phi^{ol} + 1/2(\rho^{ll})^2 D^3\phi^{ol} + \dots) \right]^3$$

using (3.6).

(21)

$$\text{i.e. } \sum_{\ell} \sum_{\ell'} \sum_{\ell''} \mathcal{D}\phi^{\ell} \mathcal{D}\phi^{\ell'} \mathcal{D}\phi^{\ell''}$$

$$= \left[ \sum_{\ell} \mathcal{D}\phi^{\ell} \right]^3 + 3 \sum_{\ell} (\rho^{\ell\ell} \mathcal{D}^2 \phi^{\ell}) \left[ \sum_{\ell'} \mathcal{D}\phi^{\ell'} \right]^2$$

$$+ 3/2 \sum_{\ell} (\rho^{\ell\ell})^2 \mathcal{D}^3 \phi^{\ell} \left( \sum_{\ell'} \mathcal{D}\phi^{\ell'} \right)^2 + 3 \left( \sum_{\ell} \rho^{\ell\ell} \mathcal{D}^2 \phi^{\ell} \right) \sum_{\ell'} \mathcal{D}\phi^{\ell'}$$

Substituting for  $\rho^{\ell\ell}$  and  $(\rho^{\ell\ell})^2$  by means of (3.4) and (3.5)

we have

$$\sum_{\ell} \sum_{\ell'} \sum_{\ell''} \mathcal{D}\phi^{\ell} \mathcal{D}\phi^{\ell'} \mathcal{D}\phi^{\ell''} = \left( \sum_{\ell} \mathcal{D}\phi^{\ell} \right)^3$$

$$+ 3/2 a^2 \left[ \sum_{\ell} (e_{11} l_1^2 + e_{22} l_2^2 + e_{33} l_3^2) \mathcal{D}^2 \phi^{\ell} \right] \left[ \sum_{\ell'} \mathcal{D}\phi^{\ell'} \right]^2$$

$$+ 3/4 a^4 \left[ \sum_{\ell} (e_{11} l_1^4 + e_{22} l_2^4 + e_{33} l_3^4 + 2e_{12} l_1 l_2 + 2e_{23} l_2 l_3 + 2e_{31} l_3 l_1) \mathcal{D}^2 \phi^{\ell} \right] \left[ \sum_{\ell'} \mathcal{D}\phi^{\ell'} \right]^2$$

$$+ 3/8 a^4 \left[ \sum_{\ell} (e_{11}^2 l_1^4 + e_{22}^2 l_2^4 + e_{33}^2 l_3^4 + 2(e_{11} e_{22} + 2e_{12}^2) l_1 l_2 + \dots) \mathcal{D}^3 \phi^{\ell} \right] \left[ \sum_{\ell'} \mathcal{D}\phi^{\ell'} \right]^2$$

and other terms involving odd powers of  $l_1$ ,  $l_2$  or  $l_3$

which vanish on summation.

$$\sum_{\ell} \sum_{\ell'} \sum_{\ell''} \mathcal{D}\phi^{\ell} \mathcal{D}\phi^{\ell'} \mathcal{D}\phi^{\ell''} = (\delta_1^0)^3 + 3/2 (e_{11} + e_{22} + e_{33}) \delta_2^1 (\delta_1^0)^2$$

$$+ (e_{11}^2 + e_{22}^2 + e_{33}^2) \left\{ 3/4 (\delta_2^1)^2 \delta_1^0 + 3/8 \delta_3^2 (\delta_1^0)^2 \right\}$$

$$+ (e_{11} e_{22} + e_{22} e_{33} + e_{33} e_{11}) \left\{ 3/2 (\delta_2^1)^2 \delta_1^0 + 3/4 \delta_3^2 (\delta_1^0)^2 \right\}$$

$$+ (e_{12}^2 + e_{23}^2 + e_{31}^2) \left\{ 3/2 \delta_3^2 (\delta_1^0)^2 \right\}.$$

Second Term.

$$\begin{aligned}
& \bar{\Sigma}'_{l} \bar{\Sigma}'_{l'} \bar{\Sigma}'_{l''} (\pm^l)^2 \mathcal{D}^2 \phi^l \mathcal{D} \phi^{l'} \mathcal{D} \phi^{l''} \\
&= \bar{\Sigma}'_l \left\{ [(\pm^l)^2 + 2\rho^{ll}] [\mathcal{D}^2 \phi^l + \rho^{ll} \mathcal{D}^3 \phi^l + 1/2(\rho^{ll})^2 \mathcal{D}^4 \phi^l + \dots] \right\} \\
&\times \left\{ \bar{\Sigma}'_{l'} [\mathcal{D} \phi^{l'} + \rho^{l'l'} \mathcal{D}^2 \phi^{l'} + \frac{1}{2}(\rho^{l'l'})^2 \mathcal{D}^3 \phi^{l'} + \dots] \right\}^2 \\
&= \bar{\Sigma}'_l \bar{\Sigma}'_{l'} \bar{\Sigma}'_{l''} \left\{ (\pm^l)^2 + 2\rho^{ll} \right\} \left\{ \mathcal{D}^2 \phi^l \mathcal{D} \phi^{l'} \mathcal{D} \phi^{l''} + \rho^{ll} \mathcal{D}^3 \phi^l \mathcal{D} \phi^{l'} \mathcal{D} \phi^{l''} \right. \\
&\quad + 2\rho^{ll'} \mathcal{D}^2 \phi^{l'} \mathcal{D}^2 \phi^l \mathcal{D} \phi^{l''} + 2\rho^{ll'} \mathcal{D}^2 \phi^{l'} \rho^{ll} \mathcal{D}^3 \phi^l \mathcal{D} \phi^{l''} \\
&\quad + (\rho^{ll} \mathcal{D}^2 \phi^l)^2 \mathcal{D}^2 \phi^{l'} + 1/2 (\rho^{ll})^2 \mathcal{D}^4 \phi^l \mathcal{D} \phi^{l'} \mathcal{D} \phi^{l''} \\
&\quad \left. + (\rho^{l'l'})^2 \mathcal{D}^3 \phi^{l'} \mathcal{D}^2 \phi^l \mathcal{D} \phi^{l''} \right\}
\end{aligned}$$

Substituting for  $\rho^{ll}$  and  $(\rho^{ll})^2$  as before we have:

$$\begin{aligned}
& \bar{\Sigma}'_l \bar{\Sigma}'_{l'} \bar{\Sigma}'_{l''} (\pm^l)^2 \mathcal{D}^2 \phi^l \mathcal{D} \phi^{l'} \mathcal{D} \phi^{l''} = 3 (\delta_1^0)^2 \delta_2^1 \\
&\quad + (e_{11} + e_{22} + e_{33}) \left\{ (\delta_1^0)^2 \delta_2^1 + 1/2 (\delta_1^0) (\delta_3^2 + 2\delta_3^1) + 3\delta_1^0 (\delta_2^1)^2 \right\} \\
&+ (e_{44} + e_{22} + e_{33}) \left\{ 1/8 (\delta_1^0)^2 (\delta_4^3 + 2\delta_4^2) + 1/2 \delta_1^0 \delta_2^1 (\delta_3^2 + 2\delta_3^1) + 3/4 (\delta_2^1)^3 \right. \\
&\quad \left. + \delta_1^0 (\delta_2^1)^2 + 1/2 \delta_3^2 (\delta_1^0)^2 + 3/4 \delta_1^0 \delta_2^1 \delta_3^2 \right\} \\
&+ (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) \left\{ 1/4 (\delta_1^0)^2 [2\delta_4^2 + \delta_4^1 + 4\delta_3^1] + \delta_1^0 [3/2 \delta_3^1 \delta_2^1 + 2(\delta_2^1)^2 \right. \\
&\quad \left. + \delta_2^1 (\delta_3^2 + 2\delta_3^1)] + 3/2 (\delta_2^1)^3 \right\} \\
&+ (e_{12} + e_{23} + e_{31}) \left\{ 1/2 (\delta_1^0)^2 (2\delta_4^2 + \delta_4^1) + 2\delta_3^1 (\delta_1^0)^2 + 3\delta_1^0 \delta_2^1 \delta_3^1 \right\}
\end{aligned}$$

Third Term.

$$\begin{aligned}
\frac{1}{2} (\underline{t}^{e'} \times \underline{t}^{e''})^2 &= \frac{1}{2} \left\{ (\underline{t}^{e'})^2 (\underline{t}^{e''})^2 - (\underline{t}^{e'} \cdot \underline{t}^{e''})^2 \right\} \\
&= \frac{1}{2} \left\{ [(\underline{t}^{oe'})^2 + 2\rho \dot{e}e'] [\underline{t}^{oe''} + 2\rho \dot{e}e''] - [\underline{t}^{oe'} \underline{t}^{oe''} + 2\rho \dot{e}e'']^2 \right\} \\
&= \frac{1}{2} \left\{ (\underline{t}^{oe'} \times \underline{t}^{oe''})^2 + 2\rho \dot{e}e' (\underline{t}^{oe''})^2 \right. \\
&\quad \left. + 2\rho \dot{e}e'' (\underline{t}^{oe'})^2 + 4\rho \dot{e}e' \rho \dot{e}e'' \right. \\
&\quad \left. - 4\rho \dot{e}e'' \underline{t}^{oe'} \underline{t}^{oe''} - 4(\rho \dot{e}e' e'')^2 \right\}
\end{aligned}$$

$$\therefore \sum_{\underline{e}}^{-1} \sum_{\underline{e}'}^{-1} \sum_{\underline{e}''}^{-1} \frac{1}{2} (\underline{t}^{e'} \times \underline{t}^{e''})^2 \mathcal{D} \phi^e \mathcal{D}^2 \phi^{e'} \mathcal{D}^2 \phi^{e''}$$

$$\begin{aligned}
&= 3 \delta_1^0 (\delta_2')^2 + (e_{11} + e_{22} + e_{33}) \left\{ \delta_1^0 \delta_2' (\delta_3^2 + 2\delta_3'') + 2(\delta_2')^2 \delta_3^0 + 3/2 (\delta_2')^3 \right\} \\
&+ (e_{11}^2 + e_{22}^2 + e_{33}^2) \left\{ (\delta_2')^3 + 1/2 \delta_2' (\delta_1^0 + \delta_2') (\delta_3^2 + 2\delta_3'') + 1/4 \delta_1^0 \delta_2' (\delta_4^3 + 2\delta_4'') \right. \\
&\quad \left. + 1/4 \delta_1^0 \delta_3'' (2\delta_3^2 + \delta_3'') + 3/8 \delta_3^2 (\delta_2')^2 + 1/2 \delta_1^0 \delta_3^2 \delta_2' \right\} \\
&+ (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) \left\{ 2(\delta_2')^3 + \delta_2' (\delta_1^0 + \delta_2') (\delta_3^2 + 2\delta_3'') + 1/2 \delta_1^0 \delta_2' (2\delta_4^3 + \delta_4'') \right. \\
&\quad \left. + 1/4 \delta_1^0 [(\delta_3^2)^2 + 3(\delta_3'')^2 + 2\delta_3^2 \delta_3''] + 3/4 \delta_3'' (\delta_2')^2 \right. \\
&\quad \left. + \delta_1^0 (\delta_2')^2 + \delta_1^0 \delta_2' \delta_3'' \right\}.
\end{aligned}$$

$$\begin{aligned}
&(e_{12}^2 + e_{23}^2 + e_{31}^2) \left\{ \delta_1^0 \delta_2' (2\delta_4^3 + \delta_4'') + 3/2 \delta_3'' (\delta_2')^2 + 2\delta_3'' \delta_1^0 \delta_2' \right. \\
&\quad \left. - \delta_1^0 (\delta_3'')^2 - \delta_1^0 (\delta_2')^2 \right\}
\end{aligned}$$

Fourth Term.

$$\begin{array}{c}
 (+l. +l' +l'')^2 = \left| \begin{array}{ccc}
 (+l)^2 + 2\rho ll & +l^0 +l^{l'} + 2\rho ll' & +l^0 +l^{l''} + 2\rho ll'' \\
 +l^0 +l^{l'} + 2\rho ll' & (+l')^2 + 2\rho l'l' & +l^0 +l^{l''} + 2\rho l'l'' \\
 +l^0 +l^{l''} + 2\rho ll'' & +l^0 +l^{l'} + 2\rho l'l' & (+l'')^2 + 2\rho l''l''
 \end{array} \right|^2
 \end{array}$$

$$\therefore \sum_l \sum_{l'} \sum_{l''} \frac{1}{6} (+l. +l' +l'')^2 D^2 \phi^l D^2 \phi^{l'} D^2 \phi^{l''}$$

$$= (\delta_2^1)^3 + (e_{11} + e_{22} + e_{33}) \left\{ \frac{1}{2} (\delta_2^1)^2 (\delta_3^2 + 2\delta_3'') + (\delta_2^1)^3 \right\}$$

$$\begin{aligned}
 & + (e_{11}^2 + e_{22}^2 + e_{33}^2) \left\{ \frac{1}{8} (\delta_2^1)^2 (\delta_4^3 + 2\delta_4^{2'}) + \frac{1}{4} \delta_2^1 \delta_3'' (2\delta_3^2 + \delta_3'') \right. \\
 & \quad \left. + \frac{1}{2} (\delta_2^1)^2 (\delta_3^2 + 2\delta_3'') \right\}
 \end{aligned}$$

$$\begin{aligned}
 & + (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) \left\{ \frac{1}{4} (\delta_2^1)^2 (2\delta_4^{2'} + \delta_4''') + \frac{1}{4} \delta_2^1 [(\delta_3^2)^2 + 2\delta_3^2 \delta_3'' + 3(\delta_3'')^2] \right. \\
 & \quad \left. + (\delta_2^1)^3 + (\delta_2^1)^2 (\delta_3^2 + 2\delta_3'') \right\}
 \end{aligned}$$

$$\begin{aligned}
 & + (e_{12}^2 + e_{23}^2 + e_{31}^2) \left\{ \frac{1}{2} (\delta_2^1)^2 (2\delta_4^{2'} + \delta_4''') - (\delta_2^1)^3 - \delta_2^1 (\delta_3'')^2 \right\}
 \end{aligned}$$

Summing these four terms we obtain an expression for

$$\det. \left\{ [xy]_{Av} \right\}$$

(25)

$$\begin{aligned}
\det. \{ [xy]_{Av} \} &= (\delta_1^0 + \delta_2^1)^3 \\
&+ (e_{11} + e_{22} + e_{33}) (\delta_1^0 + \delta_2^1)^2 \left\{ \frac{1}{2} (\delta_3^2 + 2\delta_3'' + 5\delta_2^1) \right\} \\
&+ (e_{11}^2 + e_{22}^2 + e_{33}^2) (\delta_1^0 + \delta_2^1) \left\{ \frac{1}{8} (\delta_1^0 + \delta_2^1) (\delta_3^2 + 2\delta_3'' + 3\delta_2^1) + \delta_2^1 (\delta_3^2 + 2\delta_3'') \right. \\
&\quad \left. + \frac{1}{4} \delta_3'' (2\delta_3^2 + \delta_3'') + \frac{7}{4} (\delta_2^1)^2 + \frac{1}{2} \delta_1^0 \delta_3^2 \right\} \\
&+ (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) (\delta_1^0 + \delta_2^1) \left\{ \frac{1}{4} (\delta_1^0 + \delta_2^1) (2\delta_3^2 + \delta_3'' + 3\delta_2^1) + \delta_1^0 \delta_3'' \right. \\
&\quad \left. + \frac{9}{2} (\delta_2^1)^2 + \frac{1}{4} [(\delta_3^2)^2 + 2\delta_3'' \delta_3^2 + 3(\delta_3'')^2] + 2\delta_2^1 (\delta_3^2 + 2\delta_3'') \right\} \\
&+ (e_{12}^2 + e_{23}^2 + e_{31}^2) (\delta_1^0 + \delta_2^1) \left\{ \frac{1}{2} (\delta_1^0 + \delta_2^1) (2\delta_3^2 + \delta_3'' + 3\delta_2^1) + 2\delta_1^0 \delta_3'' - (\delta_2^1)^2 - (\delta_3'')^2 \right\}
\end{aligned}$$

$$\begin{aligned}
\text{Hence } \log \det. \{ [xy]_{Av} \} &= \log \beta_0^3 + \log \left\{ 1 + \frac{\beta_1}{\beta_0} (e_{11} + e_{22} + e_{33}) \right. \\
&\quad \left. + \frac{\beta_2}{\beta_0^2} (e_{11}^2 + e_{22}^2 + e_{33}^2) \right. \\
&\quad \left. + \frac{\beta_3}{\beta_0^2} (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) \right. \\
&\quad \left. + \frac{\beta_4}{\beta_0^2} (e_{12}^2 + e_{23}^2 + e_{31}^2) \right\}
\end{aligned}$$

$$\begin{aligned}
\text{i.e. } \log \det. \{ [xy]_{Av} \} &= B_0 + B_1 (e_{11} + e_{22} + e_{33}) \\
&\quad + \frac{1}{4} B_2 (e_{11}^2 + e_{22}^2 + e_{33}^2) \\
&\quad + \frac{1}{2} B_3 (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) \\
&\quad + B_4 (e_{12}^2 + e_{23}^2 + e_{31}^2)
\end{aligned}$$

where the coefficients have the following values:

$$(5.2) \quad \beta_0 = (\delta_1^0 + \delta_2^1)$$

$$\beta_1 = \frac{1}{2} (\delta_3^2 + 2\delta_4^3 + 5\delta_2^1)$$

$$\begin{aligned} \beta_2 = & \frac{1}{8} (\delta_1^0 + \delta_2^1) (\delta_4^3 + 2\delta_4^4 + 3\delta_3^2) + \delta_2^1 (\delta_3^2 + 2\delta_3^3) \\ & + \frac{1}{4} [7(\delta_2^1)^2 + 2\delta_3^2 \delta_3^3 + (\delta_3^3)^2 + 2\delta_3^2 \delta_1^0] \end{aligned}$$

$$\begin{aligned} \beta_3 = & \frac{1}{4} (\delta_1^0 + \delta_2^1) (2\delta_4^4 + \delta_4^5 + 3\delta_3^3) + 2\delta_2^1 (\delta_3^2 + 2\delta_3^3) \\ & + \frac{1}{4} [(\delta_3^2)^2 + 2\delta_3^2 \delta_1^0 + 3(\delta_3^3)^2] + \delta_1^0 \delta_3^3 + \frac{9}{2} (\delta_2^1)^2 \end{aligned}$$

$$\beta_4 = \frac{1}{2} (\delta_1^0 + \delta_2^1) (2\delta_4^5 + \delta_4^6 + 3\delta_3^4) + 2\delta_1^0 \delta_3^3 - (\delta_3^3)^2 - (\delta_2^1)^2$$

$$B_0 = \log \beta_0^3 \qquad B_2 = (4\beta_2 - 2\beta_1^2) / \beta_0^2$$

$$B_1 = \beta_1 / \beta_0 \qquad B_3 = (2\beta_3 - 2\beta_1^2) / \beta_0^2$$

$$B_4 = \beta_4 / \beta_0^2$$

Thus from (2.14)

$$\begin{aligned} (5.3) \quad \log \bar{\omega} = & \frac{1}{6} \left\{ B_0 + B_1 (e_{11} + e_{22} + e_{33}) + \frac{1}{4} B_2 (e_{11}^2 + e_{22}^2 + e_{33}^2) \right. \\ & \left. + \frac{1}{2} B_3 (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) + B_4 (e_{12}^2 + e_{23}^2 + e_{31}^2) \right\} \\ & - \frac{1}{2} \log \mu \end{aligned}$$

We now substitute (3.8) and (4.3) in (1.13) and obtain the following expression for  $A$  :

(27)

$$\begin{aligned}
 (5.4) \quad A = N \left\{ A_0 + 1/2 A_1 (e_{11} + e_{22} + e_{33}) + 1/8 A_2 (e_{11}^2 + e_{22}^2 + e_{33}^2) \right. \\
 + 1/4 A_3 (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11} + 2e_{12}^2 + 2e_{23}^2 + 2e_{31}^2) \\
 + 3kT \log \frac{h}{kT} + \frac{kT}{2} \left[ B_0 + B_1 (e_{11} + e_{22} + e_{33}) \right. \\
 + 1/4 B_2 (e_{11}^2 + e_{22}^2 + e_{33}^2) + 1/2 B_3 (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) \\
 \left. + B_4 (e_{12}^2 + e_{23}^2 + e_{31}^2) \right] - \frac{3kT}{2} \log \mu \left. \right\}
 \end{aligned}$$

and (5.5)

$$\begin{aligned}
 \frac{A}{V} = \frac{1}{ka^3} \left\{ \text{const} - 3kT \log T + (A_0 + \frac{kT}{2} B_0) \right. \\
 + 1/2 (A_1 + kTB_1) (e_{11} + e_{22} + e_{33}) \\
 + 1/8 (A_2 + kTB_2) (e_{11}^2 + e_{22}^2 + e_{33}^2) \\
 + 1/4 (A_3 + kTB_3) (e_{11}e_{22} + e_{22}e_{33} + e_{33}e_{11}) \\
 \left. + 1/2 (A_4 + kTB_4) (e_{12}^2 + e_{23}^2 + e_{31}^2) \right\}
 \end{aligned}$$

Comparing (5.5) with (1.9) and using results (1.11)

and (1.12) we have:

$$\begin{aligned}
 (5.6) \quad -p &= \frac{1}{ka^3} (A_1 + kTB_1) \\
 e_{11} &= \frac{1}{ka^3} (A_2 + kTB_2) \\
 e_{12} &= \frac{1}{ka^3} (A_3 + kTB_3) \\
 e_{11} &= \frac{1}{ka^3} (A_4 + kTB_4)
 \end{aligned}$$

6. Calculation for a Particular Law of Force.

We now take a particular law of force. We choose the law of force used in all the papers in the series on

"The Stability of Crystal Lattices" viz:

$$\phi^{ol} = \frac{umn}{n-m} \left[ -\frac{1}{m} \left( \frac{r_0}{r^{ol}} \right)^m + \frac{1}{n} \left( \frac{r_0}{r^{ol}} \right)^n \right]$$

where the first term denotes the attractive and the second the repulsive effect of the potential.  $u$  is the dissociation energy of a molecule formed of two particles,  $r_0$  is the equilibrium distance (since

$$\left( \frac{\partial \phi^{ol}}{\partial r^{ol}} \right)_{r^{ol}=r_0} = 0 \text{ ) and } r^{ol} = a(l_1^2 + l_2^2 + l_3^2)^{1/2} = al \text{ as before; } u$$

can also be expressed as a quantity having the dimensions of temperature viz  $u = k\theta$  where  $\theta$  can be chosen as the unit of temperature.

Successive differentiation gives the following:

$$D\phi^{ol} = \frac{umn}{r_0^2(n-m)} \left[ \left( \frac{r_0}{r^{ol}} \right)^{m+2} - \left( \frac{r_0}{r^{ol}} \right)^{n+2} \right]$$

$$D^2\phi^{ol} = \frac{umn}{r_0^4(n-m)} \left[ -(m+2) \left( \frac{r_0}{r^{ol}} \right)^{m+4} + (n+2) \left( \frac{r_0}{r^{ol}} \right)^{n+4} \right]$$

$$D^3\phi^{ol} = \frac{umn}{r_0^6(n-m)} \left[ +(m+2)(m+4) \left( \frac{r_0}{r^{ol}} \right)^{m+6} - (n+2)(n+4) \left( \frac{r_0}{r^{ol}} \right)^{n+6} \right]$$

(29)

$$D^4 \phi^{ol} = \frac{umr}{r_0^3(n-m)} \left[ -(m+2)(m+4)(m+6) \left(\frac{r_0}{r_0 l}\right)^{m+8} + (n+2)(n+4)(n+6) \left(\frac{r_0}{r_0 l}\right)^{n+8} \right]$$

Substituting these values in (3.8) we find

$$\begin{aligned} \Phi = & \frac{1}{2} N \frac{umr}{n-m} \left\{ -\frac{1}{m} \left(\frac{r_0}{a}\right)^m S_m^0 + \frac{1}{n} \left(\frac{r_0}{a}\right)^n S_n^0 \right\} \\ & + \frac{1}{2}(e_{11} + e_{22} + e_{33}) \left[ \left(\frac{r_0}{a}\right)^m S_{m+2}^1 - \left(\frac{r_0}{a}\right)^n S_{n+2}^1 \right] \\ & + \frac{1}{8}(e_{11}^2 + e_{22}^2 + e_{33}^2) \left[ -(m+2) \left(\frac{r_0}{a}\right)^m S_{m+4}^2 + (n+2) \left(\frac{r_0}{a}\right)^n S_{n+4}^2 \right] \\ & + \frac{1}{4}(e_{11}e_{22} + 2e_{12}^2 + \dots) \left[ -(m+2) \left(\frac{r_0}{a}\right)^m S_{m+4}^{21} + n+2 \left(\frac{r_0}{a}\right)^n S_{n+4}^2 \right] \end{aligned}$$

where 
$$S_n^{k_1, k_2, k_3} = \int_l^{-1} \frac{l_1^{2k_1} l_2^{2k_2} l_3^{2k_3}}{(l_1^2 + l_2^2 + l_3^2)^{n/2}}$$

We note that the  $S$ 's are not all independent of one another for

$$(6.1) \quad 3 S_{n+2}^1 = S_n^0$$

$$(6.2) \quad 3 S_{n+4}^2 + 6 S_{n+4}^{21} = S_n^0$$

$$(6.3) \quad 3 S_{n+6}^3 + 18 S_{n+6}^{21} + 6 S_{n+6}^{111} = S_n^0$$

$$(6.4) \quad 3 S_{n+6}^3 + 6 S_{n+6}^{21} = S_{n+4}^2$$

$$(6.5) \quad 6 S_{n+6}^{21} + 3 S_{n+6}^{111} = S_{n+4}^{21}$$

We introduce instead of  $r_0$  the quantity  $a_0$  defined as

the value of  $a$  which satisfies the equilibrium condition. The equilibrium condition requires that

$$\left(\frac{t_0}{a}\right)^m S'_{m+2} - \left(\frac{t_0}{a}\right)^n S'_{n+2} = 0$$

$$\therefore a_0 \text{ is given by } \left(\frac{t_0}{a_0}\right)^{n-m} = \frac{S'_{m+2}}{S'_{n+2}} = \gamma \text{ say}$$

$$\text{Then since } S'_{m+2} = \frac{1}{3} S_m^{\circ}, \quad \gamma = S_m^{\circ} / S_n^{\circ}$$

$$\text{and since } t_0^{n-m} = \gamma a_0^{n-m}, \quad t_0 = \gamma^{\frac{1}{n-m}} a_0$$

Using these results it is possible to express the  $S_i$  in terms of the  $S_j^{\circ}$ . For example:

$$\begin{aligned} S_0^{pqr} &= a^{2(p+q+r)} \int_l l_1^{2p} l_2^{2q} l_3^{2r} \phi^{ol} \\ &= \frac{umr}{n-m} a^{2(p+q+r)} \int_l l_1^{2p} l_2^{2q} l_3^{2r} \left[ -\frac{1}{m} \left(\frac{a_0}{al}\right)^m \gamma^{\frac{m}{n-m}} + \frac{1}{n} \left(\frac{a_0}{al}\right)^n \gamma^{\frac{n}{n-m}} \right] \\ &= \frac{umr}{n-m} a^{2(p+q+r)} \left(\frac{a_0}{a}\right)^m \gamma^{\frac{m}{n-m}} \left[ -\frac{1}{m} S_m^{pqr} + \frac{1}{n} \gamma \left(\frac{a_0}{a}\right)^{n-m} S_n^{pqr} \right] \end{aligned}$$

and similarly for  $S_n^{pqr}$

The values of the  $S_i$  in terms of the  $S_j^{\circ}$  are given below

in Table I.

Table I.

1.  $\delta_0^0 = C \left(\frac{a_0}{a}\right)^m \left[ -\frac{1}{m} S_m^0 + \gamma \left(\frac{a_0}{a}\right)^{n-m} \frac{1}{n} S_n^0 \right]$
2.  $\delta_1^1 = C \left(\frac{a_0}{a}\right)^m \left[ S_{m+2}^1 - \gamma \left(\frac{a_0}{a}\right)^{n-m} S_{n+2}^1 \right]$
3.  $\delta_2^2 = C \left(\frac{a_0}{a}\right)^m \left[ -(m+2) S_{m+4}^2 + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2) S_{n+4}^2 \right]$
4.  $\delta_2'' = C \left(\frac{a_0}{a}\right)^m \left[ -(m+2) S_{m+4}'' + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2) S_{n+4}'' \right]$
5.  $\delta_1^0 = C \left(\frac{a_0}{a}\right)^{m+2} \left[ S_{m+2}^0 - \gamma \left(\frac{a_0}{a}\right)^{n-m} S_{n+2}^0 \right]$
6.  $\delta_2^1 = C \left(\frac{a_0}{a}\right)^{m+2} \left[ -(m+2) S_{m+4}^1 + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2) S_{n+4}^1 \right]$
7.  $\delta_3^2 = C \left(\frac{a_0}{a}\right)^{m+2} \left[ (m+2)(m+4) S_{m+6}^2 - \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n+4) S_{n+6}^2 \right]$
8.  $\delta_3'' = C \left(\frac{a_0}{a}\right)^{m+2} \left[ (m+2)(m+4) S_{m+6}'' - \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n+4) S_{n+6}'' \right]$
9.  $\delta_4^3 = C \left(\frac{a_0}{a}\right)^{m+2} \left[ (m+2)(m+4)(m+6) S_{m+8}^3 + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n+4)(n+6) S_{n+8}^3 \right]$
10.  $\delta_4^{21} = C \left(\frac{a_0}{a}\right)^{m+2} \left[ -(m+2)(m+4)(m+6) S_{m+8}^{21} + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n+4)(n+6) S_{n+8}^{21} \right]$
11.  $\delta_4''' = C \left(\frac{a_0}{a}\right)^{m+2} \left[ -(m+2)(m+4)(m+6) S_{m+8}''' + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n+4)(n+6) S_{n+8}''' \right]$
12.  $\delta_3^2 + 2\delta_3'' + 5\delta_2^1 = \frac{C}{3a_0^2} \left(\frac{a_0}{a}\right)^{m+2} \left[ (m+2)(m-1) S_{m+2}^0 - \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n-1) S_{n+2}^0 \right]$
13.  $\delta_3^2 + 2\delta_3'' = \frac{C}{3a_0^2} \left(\frac{a_0}{a}\right)^{m+2} \left[ (m+2)(m+4) S_{m+2}^0 - \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n+4) S_{n+2}^0 \right]$
14.  $\delta_4^3 + 2\delta_4^{21} = \frac{C}{3a_0^2} \left(\frac{a_0}{a}\right)^{m+2} \left[ (m+2)(m+4)(m+6) S_{m+6}^2 + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n+4)(n+6) S_{n+6}^2 \right]$
15.  $2\delta_4^{21} + \delta_4''' = \frac{C}{3a_0^2} \left(\frac{a_0}{a}\right)^{m+2} \left[ -(m+2)(m+4)(m+6) S_{m+6}'' + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n+4)(n+6) S_{n+6}'' \right]$
16.  $\delta_1^0 + \delta_2^1 = \frac{C}{3a_0^2} \left(\frac{a_0}{a}\right)^{m+2} \left[ (1-m) S_{m+2}^0 - \gamma \left(\frac{a_0}{a}\right)^{n-m} (1-n) S_{n+2}^0 \right]$

where  $C = \frac{umh}{n-m} \gamma^{\frac{m}{n-m}}$ .

A method of evaluating the  $S_i$ 's and the numerical results for various values of  $m$  and  $n$  is given in paper IV of "The Stability of Crystal Lattices". Some of these numerical results as well as a few not given in the above publication are given in Table II, (p.39), Thus for given values of  $m$  and  $n$  the  $S_i$ 's and therefore the  $S_i$ 's can be calculated. Hence the values of the  $A_i$ 's and the  $B_i$ 's are determined.

These calculations can be checked by means of (1.5) and (1.6).

$$(1.5) \quad a \frac{\partial f}{\partial a} = 2 \left[ \frac{\partial f}{\partial e_{11}} + \frac{\partial f}{\partial e_{22}} + \frac{\partial f}{\partial e_{33}} \right] \quad \text{which holds}$$

only for  $e_{11} = e_{22} = e_{33} = e_{12} = e_{23} = e_{31} = 0$  becomes on using (1.7) in

the case  $e_{11} = \dots = e_{31} = 0$

$$(6.6) \quad a \frac{\partial f_0}{\partial a} = 3f_0$$

Now our expression for  $f_0$  is

$$f_0 = A_0 + \frac{1}{2} kT B_0 - 3kT \log T + \text{const.}$$

$$\therefore \frac{\partial f_0}{\partial a} = \frac{\partial}{\partial a} \left( A_0 + \frac{1}{2} kT B_0 \right) = \frac{\partial}{\partial a} \left( \frac{1}{2} S_0^0 + \frac{1}{2} kT \log (S_1^0 + S_2^0) \right)$$

$$\text{But } S_0^0 = C \left( \frac{a_0}{a} \right)^m \left[ -\frac{1}{m} S_m^0 + \gamma \left( \frac{a_0}{a} \right)^{n-m} S_n^0 \right]$$

(33)

$$\text{and } (\delta_1^0 + \delta_2^1) = \frac{C}{3(a_0)^2} \left( \frac{a_0}{a} \right)^{m+2} \left[ (1-m) S_{m+2}^0 - \gamma \left( \frac{a_0}{a} \right)^{n-m} (1-n) S_{n+2}^0 \right]$$

$$\therefore a \frac{\partial f_0}{\partial a} = \frac{C}{2} \left( \frac{a_0}{a} \right)^m \left[ S_m^0 - \gamma \left( \frac{a_0}{a} \right)^{n-m} S_n^0 \right]$$

$$+ \frac{1}{2} kT \times \frac{3}{\delta_1^0 + \delta_2^1} \times \frac{C}{3a_0^2} \left( \frac{a_0}{a} \right)^{m+2} \left[ (m+2)(m-1) S_{m+2}^0 - \gamma \left( \frac{a_0}{a} \right)^{n-m} (n+2)(n-1) S_{n+2}^0 \right]$$

$$= \frac{3}{2} \delta_1^1 + \frac{\frac{1}{2} kT}{\delta_1^0 + \delta_2^1} \times 3 (\delta_3^2 + 2 \delta_3'' + 5 \delta_2^1)$$

(see Table I, no. 12)

$$= 3 \left\{ A_1 + kT B_1 \right\} = 3 f_1$$

We have indeed

$$a \frac{\partial f_0}{\partial a} = 3 f_1$$

Applying (1.6) to (1.7) we have another equation to

**check these results:**

$$(6.7) \quad a^2 \frac{\partial^2 f_0}{\partial a^2} = 3(f_1 + f_{11} + 2f_{12})$$

which can also be written in the form

$$(6.8) \quad a \frac{\partial f_1}{\partial a} = 2f_1 + f_{11} + 2f_{12}$$

In our case

$$f_1 = A_1 + kT B_1$$

$$= \frac{1}{2} \delta_1^1 + kT \left\{ \frac{\delta_3^2 + 2 \delta_3'' + 5 \delta_2^1}{2 (\delta_1^0 + \delta_2^1)} \right\}$$

(34)

$$\text{Now } \delta_1' = C \left(\frac{a_0}{a}\right)^m \left[ S_{m+2}' - \gamma \left(\frac{a_0}{a}\right)^{n-m} S_{n+2}' \right]$$

$$\begin{aligned} \therefore a \frac{\partial}{\partial a} \left( \frac{1}{2} \delta_1' \right) &= \frac{C}{2} \left(\frac{a_0}{a}\right)^m \left[ -m S_{m+2}' + \gamma \left(\frac{a_0}{a}\right)^{n-m} n S_{n+2}' \right] \\ &= \delta_1' + \frac{1}{2} \delta_2^2 + \delta_2'' \end{aligned}$$

$$\text{i.e. } a \frac{\partial}{\partial a} (A_1) = 2A_1 + A_2 + 2A_3$$

Using Table I nos. 12 and 16,

$$\delta_3^2 + 2\delta_3'' + 5\delta_2' = \frac{C}{3a_0^2} \left(\frac{a_0}{a}\right)^{m+2} \left[ (m+2)(m-1) S_{m+2}^0 - \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n-1) S_{n+2}^0 \right]$$

$$\delta_1^0 + \delta_2' = \frac{C}{3(a_0^2)} \left(\frac{a_0}{a}\right)^{m+2} \left[ (1-m) S_{m+2}^0 + \gamma \left(\frac{a_0}{a}\right)^{n-m} (1-n) S_{n+2}^0 \right]$$

$$\begin{aligned} \therefore a \frac{\partial}{\partial a} (B_1) &= \frac{1}{2} \cdot \frac{C}{3a_0^2} \left(\frac{a_0}{a}\right)^{m+2} \left[ \frac{-(m+2)^2(m-1) S_{m+2}^0 + \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)^2(n-1) S_{n+2}^0}{\delta_1^0 + \delta_2'} \right] \\ (6.9) \quad &- \frac{1}{2} \left[ \frac{C}{3a_0^2} \left(\frac{a_0}{a}\right)^{m+2} \right]^2 \left[ \frac{(m+2)(m-1) S_{m+2}^0 - \gamma \left(\frac{a_0}{a}\right)^{n-m} (n+2)(n-1) S_{n+2}^0}{(\delta_1^0 + \delta_2')} \right]^2 \end{aligned}$$

-:-

We wish to show that  $a \frac{\partial}{\partial a} (B_1) = 2B_1 + B_2 + 2B_3$ To do this we evaluate  $2B_1 + B_2 + 2B_3$  in terms of  $\delta$ 's

From (5.2)

$$2B_1 + B_2 + 2B_3 = \frac{\delta_3^2 + 2\delta_3'' + 5\delta_2'}{\delta_1^0 + \delta_2'} + \frac{4\beta_2 + 4\beta_3 - 6\beta_1^2}{(\delta_1^0 + \delta_2')^2}$$

(35)

$$\begin{aligned}
2B_1 + B_2 + 2B_3 &= \frac{(\delta_3^2 + 2\delta_3'' + 5\delta_2') + \frac{1}{2}(\delta_4^3 + 2\delta_4^{2'}) + \frac{3}{2}(\delta_3^2 + 2\delta_3'') + 2(2\delta_4^{2'} + \delta_4''')}{(\delta_1^0 + \delta_2')} \\
&+ \frac{(\delta_3^2 + 2\delta_3'')(2\delta_1^0 - 3\delta_2' + \frac{1}{2}\delta_3^2 - \delta_3'') - \frac{25}{2}(\delta_2')^2}{(\delta_1^0 + \delta_2')^2} \\
&= \frac{\frac{1}{2}(\delta_4^3 + 2\delta_4^{2'}) + (2\delta_4^{2'} + \delta_4''') + 5\delta_2' + \frac{9}{2}(\delta_3^2 + 2\delta_3'')}{(\delta_1^0 + \delta_2')} \\
&- \frac{(\delta_3^2 + 2\delta_3'')( \frac{1}{2}\delta_3^2 + \delta_3'' + 5\delta_2' ) + \frac{25}{2}(\delta_2')^2}{(\delta_1^0 + \delta_2')^2}
\end{aligned}$$

Using Table I nos. 13, 14, 15,

$$\begin{aligned}
2B_1 + B_2 + 2B_3 &= \frac{1}{\delta_1^0 + \delta_2'} \times \frac{c}{6a_0^2} \left( \frac{a_0}{a} \right)^{m+2} \left[ -(m+2)^2(m-1) S_{m+2}^0 + \gamma \left( \frac{a_0}{a} \right)^{n-m} (n+2)^2(n-1) S_{m+2}^0 \right] \\
&- \frac{1}{(\delta_1^0 + \delta_2')^2} \left[ \frac{c}{3a_0^2} \left( \frac{a_0}{a} \right)^{m+2} \right]^2 \left\{ 25 \left[ -(m+2) S_{m+2}^0 + \gamma \left( \frac{a_0}{a} \right)^{n-m} (n+2) S_{m+2}^0 \right]^2 \right. \\
&\left. + \left[ (m+2)(m+4) S_{m+2}^0 - \gamma \left( \frac{a_0}{a} \right)^{n-m} (n+2)(n+4) S_{m+2}^0 \right] \left[ (m+2)(m+6) S_{m+2}^0 - \gamma \left( \frac{a_0}{a} \right)^{n-m} (n+2)(n+6) S_{m+2}^0 \right] \right\}
\end{aligned}$$

(36)

$$\begin{aligned} \therefore 2B_1 + B_2 + 2B_3 &= \frac{C}{6a_0^2} \frac{\left(\frac{a_0}{a}\right)^{m+2}}{\delta_1^0 + \delta_2^1} \left[ -(m+2)^2(m-1)S_{m+2}^0 + \gamma(m+2)^2(n-1)\left(\frac{a_0}{a}\right)^{n-m} S_{m+2}^0 \right] \\ &\quad - \frac{1}{2} \left[ \frac{C}{3a_0^2} \frac{\left(\frac{a_0}{a}\right)^{m+2}}{\delta_1^0 + \delta_2^1} \right]^2 \left[ (m+2)(m-1)S_{m+2}^0 - \gamma\left(\frac{a_0}{a}\right)^{n-m}(n+2)(n-1)S_{m+2}^0 \right]^2 \\ &= a \frac{\partial}{\partial a} (B_1) \text{ as shown in (6.9)} \end{aligned}$$

$$\begin{aligned} \therefore a \frac{\partial}{\partial a} (A_1 + kTB_1) &= 2(A_1 + kTB_1) + (A_2 + kTB_2) \\ &\quad + 2(A_3 + kTB_3) \\ \text{i.e. } a \frac{\partial}{\partial a} (f_1) &= 2f_1 + f_{11} + 2f_{12}. \end{aligned}$$

Thus we have shown that equations (6.6) and (6.8)

which should be valid for any function  $f$  are actually true in our particular case.

:-

### 7. Special Values of $m$ and $n$ .

As a special simplification we take special values of

$m$  and  $n$ . Before doing so, it is convenient to write

equations (5.6) in a slightly different form. We

introduce a quantity which has the dimensions of a

(37)

pressure viz.

$$p_0 = \frac{R\theta}{V_0}$$

where  $R = kN$  is the gas constant and  $V_0 = N\kappa a_0^3$

$$\text{Then } V/V_0 = \frac{N\kappa a^3}{N\kappa a_0^3} = \left(\frac{a}{a_0}\right)^3$$

We introduce the volume  $v$  of the cell to replace the lattice constant  $a$  and  $v_0$  to replace  $a_0$ , according to the relation

$$v/v_0 = \left(\frac{a}{a_0}\right)^3$$

Finally the change in volume is expressed with the help of a parameter  $\xi$  given by

$$\left(\frac{v_0}{v}\right)^{n-m} = (1 + \xi)$$

If we divide equations (5.6) by  $u = k\theta$  we have

$$\frac{-\kappa a^3}{k\theta} p = \frac{A_1}{u} + B_1 T/\theta$$

$$\frac{\kappa a^3}{k\theta} c_{11} = \frac{A_2}{u} + B_2 T/\theta$$

$$\frac{\kappa a^3}{k\theta} c_{12} = \frac{A_3}{u} + B_3 T/\theta$$

$$\frac{\kappa a^3}{k\theta} c_{14} = \frac{A_4}{u} + B_4 T/\theta$$

$$\text{But } \frac{\kappa a^3}{k\theta} = \frac{N\kappa a^3}{R\theta} = \frac{N\kappa a_0^3}{R\theta} \left(\frac{a}{a_0}\right)^3 = \frac{V_0}{p_0 V_0} (1 + \xi)^{-3/n-m}$$

$$\text{i.e. } \frac{\kappa a^3}{k\theta} = \frac{1}{\rho_0} (1 + \xi)^{-3/n-m}$$

Thus the final set of equations may be written:

$$(7.1) \quad -\rho/\rho_0 = (1 + \xi)^{3/n-m} (A_1/\mu + B_1 T/\theta)$$

$$(7.2) \quad c_1/\rho_0 = (1 + \xi)^{3/n-m} (A_2/\mu + B_2 T/\theta)$$

$$(7.3) \quad c_{12}/\rho_0 = (1 + \xi)^{3/n-m} (A_3/\mu + B_3 T/\theta)$$

$$(7.4) \quad c_{44}/\rho_0 = (1 + \xi)^{3/n-m} (A_4/\mu + B_4 T/\theta)$$

The particular values of  $m$  and  $n$  that we choose are:

$$(I) \quad m = 4, \quad n = 8.$$

$$(II) \quad m = 5, \quad n = 10.$$

$$(III) \quad m = 6, \quad n = 12.$$

$$(IV) \quad m = 6, \quad n = 14.$$

$$(V) \quad m = 7, \quad n = 14.$$

The calculations are carried out for the case of the

face-centred cubic lattice and tables are given

showing the values of the  $\xi$ 's the  $A$ 's and the  $B$ 's for the

above values of the exponents extending over the range

$\xi = 0.15 \dots 0.4$ . We use  $\left[ \delta_{\frac{pq}{n}}^{pqr} \right]$  in the tables to denote

$$\delta_{\frac{pq}{n}}^{pqr} \div C \left( \frac{a_0}{a} \right)^m \quad \text{or} \quad \delta_{\frac{pq}{n}}^{pqr} \div \frac{C}{a^2} \left( \frac{a_0}{a} \right)^{m+2} \quad \text{as the case may be.}$$

Table II.

$m$	$S_m^0$	$S_{m+2}^1$	$S_{m+4}^2$	$S_{m+4}''$	$S_{m+6}^3$	$S_{m+6}^{2'}$	$S_{m+6}'''$
4	6.3346	2.1115	1.1979	0.4568	0.4431	0.2125	0.03176
5	2.9995	0.9998	0.5460	0.2269	0.3275	0.1094	0.008157
6	1.8067	0.6022	0.3204	0.1409	0.1821	0.06906	0.002708
7	1.1808	0.3936	0.2056	0.0940	0.1126	0.04650	0.000996
8	0.80012	0.2667	0.1375	0.06458	0.07349	0.03208	0.000395
9	0.55210	0.1840	0.09407	0.04498	0.04923	0.02242	0.000151
10	0.38473	0.1282	0.06512	0.03156	0.03363	0.01575	0.0000597
11	0.26960	0.08987	0.04543	0.02222	0.02324	0.011098	0.0000239
12	0.18956	0.06319	0.03185	0.01567	0.01618	0.007832	0.00000970
13	0.13355	0.04452	0.02238	0.01107	0.01132	0.005533	0.00000396
14	0.09421	0.031403	0.01576	0.007820	0.007944	0.003909	0.00000159
16	0.04698	0.01566	0.007846	0.003908	0.003939	0.001954	0.000000265

Table III.

EXONENTS CONSTANTS	$\left\{ \begin{matrix} m=4 \\ n=8 \end{matrix} \right\}$	$\left\{ \begin{matrix} m=5 \\ n=10 \end{matrix} \right\}$	$\left\{ \begin{matrix} m=6 \\ n=12 \end{matrix} \right\}$	$\left\{ \begin{matrix} m=6 \\ n=14 \end{matrix} \right\}$	$\left\{ \begin{matrix} m=7 \\ n=14 \end{matrix} \right\}$
$\gamma = S_m^0/S_m$	7.91706	7.79638	9.5310	19.1774	12.5337
$\gamma \frac{m}{n-m}$	7.91706	7.79638	9.5310	9.1642	12.5337
$C/u$	63.3365	77.9638	114.3722	96.2236	175.4718

Table IV (1) :  $m = 4, n = 8.$ 

$\xi$	$[\delta_1']$	$[\delta_2'']$	$[\delta_2''']$	$[\delta_1^{\circ}]$	$[\delta_2']$
.15	-0.3167	5.3351	3.1389	-1.6961	8.059
.1	-0.2111	4.7906	2.8833	-1.5438	7.5515
.05	-0.1056	4.2462	2.6276	-1.3915	7.044
0	0	3.7017	2.372	-1.2392	6.5365
-.05	0.1056	3.1572	2.1164	-1.0869	6.0290
-.1	0.2111	2.6128	1.8607	-0.9346	5.5215
-.15	0.3167	2.0683	1.6051	-0.7823	5.014
-.2	0.4223	1.5239	1.3494	-0.6300	4.5066
-.25	0.5279	0.9794	1.0938	-0.4777	3.9991
-.3	0.6334	0.435	.8382	-0.3254	3.4916
-.35	0.7390	-0.1095	.5825	-0.1731	2.9841
-.4	0.8446	-0.6539	.3269	-0.02084	2.4766

$\xi$	$[\delta_3'']$	$[\delta_3''']$	$[\delta_4''']$	$[\delta_4^{2'}]$	$[\delta_4''']$
.15	-55.768	-27.7178	426.9884	207.7594	-0.3867
.1	-52.6746	-26.2187	404.6233	197.2851	-0.4264
.05	-49.5813	-24.7195	382.2583	186.8109	-0.4661
0	-46.4879	-23.2203	359.8932	176.3366	-0.5058
-.05	-43.3945	-21.7211	337.5281	165.8623	-0.5455
-.1	-40.3012	-20.222	315.1631	155.3881	-0.5852
-.15	-37.2078	-18.7228	292.7980	144.9138	-0.6249
-.2	-34.1145	-17.2236	270.433	134.4395	-0.6646
-.25	-31.0211	-15.7244	248.0679	123.9653	-0.7043
-.3	-27.9278	-14.2253	225.7028	113.491	-0.7440
-.35	-24.8344	-12.7261	203.3378	103.0167	-0.7837
-.4	-21.7411	-11.2269	180.9727	92.5424	-0.8234

Table IV (2).  $m=5, n=10$ .

$\xi$	$[\delta_1']$	$[\delta_2'']$	$[\delta_2''']$	$[\delta_1^{\circ}]$	$[\delta_2']$
0.15	-0.1499	3.1843	1.8072	-0.5188	4.0434
0.1	-0.09995	2.8796	1.6596	-0.4449	3.7478
0.05	-0.04997	2.5750	1.5119	-0.3710	3.4522
0	0	2.2704	1.3643	-0.2971	3.1566
-0.05	0.04997	1.9658	1.2167	-0.2232	2.8610
-0.1	0.09995	1.6612	1.0690	-0.1493	2.5654
-0.15	0.1499	1.3565	0.9214	-0.07542	2.2698
-0.2	0.1999	1.0519	0.7738	-0.00152	1.9742
-0.25	0.2499	0.7473	0.6262	0.07238	1.6787
-0.3	0.2998	0.4427	0.4785	0.1463	1.3831
-0.35	0.3498	0.1381	0.3309	0.2202	1.0875
-0.4	0.3998	-0.1666.	0.1833	0.2941.	0.7919

$\xi$	$[\delta_3^2]$	$[\delta_3''']$	$[\delta_4^3]$	$[\delta_4^{2'}]$	$[\delta_4^{1''}]$
0.15	-35.0216	-17.6811	311.9089	156.528	-0.4565
0.1	-32.9358	-16.6548	294.955	148.3214	-0.4666
0.05	-30.8499	-15.6286	278.0011	140.1147	-0.4768
0	-28.7641	-14.6024	261.0471	131.9081	-0.487
-0.05	-26.6783	-13.5762	244.0932	123.7015	-0.4971
-0.1	-24.5924	-12.55	227.1392	115.4948	-0.5073
-0.15	-22.5066	-11.5237	210.1853	107.2882	-0.5174
-0.2	-20.4207	-10.4975	193.2313	99.0816	-0.5276
-0.25	-18.3349	-9.4713	176.2774	90.875	-0.5378
-0.3	-16.2490	-8.4451	159.3234	82.6683	-0.5479
-0.35	-14.1632	-7.4189	142.3695	74.4617	-0.5581
-0.4	-12.0773	-6.3926.	125.4155	66.2551	-0.5683

Table IV (8),  $m=6, n=12$ .

$\xi$	$[s_1']$	$[s_2']$	$[s_3']$	$[s_4']$	$[s_5']$
0.15	-0.09034	2.3242	1.2773	-0.2325	2.6851
0.1	-0.06023	2.1117	1.1728	-0.1876	2.4756
0.05	-0.03011	1.8992	1.0683	-0.1427	2.2661
0	0	1.6867	0.9637	-0.09780	2.0566
-0.05	0.03011	1.4742	0.8592	-0.05290	1.8471
-0.1	0.06023	1.2617	0.7546	-0.00800	1.6376
-0.15	0.09034	1.0492	0.6501	0.03689	1.4281
-0.2	0.1205	0.8367	0.5455	0.08179	1.2186
-0.25	0.1506	0.6242	0.4410	0.1267	1.0091
-0.3	0.1807	0.4117	0.3364	0.1716	0.7995
-0.35	0.2108	0.1992	0.2319	0.2165	0.5900
-0.4	0.2409	-0.01326	0.1273	0.2614	0.3805

$\xi$	$[s_6']$	$[s_7']$	$[s_8']$	$[s_9']$	$[s_{10}']$
0.15	-27.6979	-14.0337	280.5374	141.9683	-0.3090
0.1	-26.0152	-13.1989	265.2727	134.4568	-0.3121
0.05	-24.3326	-12.3641	250.0008	126.9452	-0.3151
0	-22.6499	-11.5293	234.4433	119.4337	-0.3182
-0.05	-20.9672	-10.6945	219.4786	111.9222	-0.3212
-0.1	-19.2846	-9.8597	204.2139	104.4107	-0.3243
-0.15	-17.6019	-9.02495	188.9493	96.8991	-0.3273
-0.2	-15.9193	-8.1902	173.6846	89.3876	-0.3304
-0.25	-14.2366	-7.3554	158.4200	81.8761	-0.3334
-0.3	-12.5540	-6.5206	143.1552	74.3646	-0.3365
-0.35	-10.8713	-5.6858	127.8905	66.8530	-0.3395
-0.4	-9.1887	-4.8510	112.6258	59.3415	-0.3426

Table IV (a)  $m=6, n=14$ .

$\xi$	$[s_1']$	$[s_2']$	$[s_3']$	$[s_4']$	$[s_5']$
0.15	-0.09033	2.9988	1.6321	-0.2360	3.3923
0.1	-0.06022	2.7570	1.5122	-0.1909	3.1520
0.05	-0.03011	2.5151	1.3922	-0.1459	2.9118
0	0	2.2733	1.2722	-0.1009	2.6715
-0.05	0.03011	2.0315	1.1522	-0.05580	2.4312
-0.1	0.06022	1.7896	1.0323	-0.01075	2.1910
-0.15	0.09033	1.5478	0.9123	+0.03430	1.9507
-0.2	0.1204	1.3060	0.7923	0.07934	1.7105
-0.25	0.1505	1.0642	0.6723	0.1244	1.4702
-0.3	0.1807	0.8223	0.5524	0.1694	1.2299
-0.35	0.2108	0.5805	0.4324	0.2145	0.9897
-0.4	0.2409	0.3387	0.3124	0.2595	0.7494

$\xi$	$[s_2'']$	$[s_3'']$	$[s_4'']$	$[s_5'']$	$[s_6'']$
0.15	-38.8276	-19.6518	429.7309	217.3686	-0.3486
0.1	-36.6610	-18.5427	407.9795	206.5788	-0.3470
0.05	-34.4945	-17.4937	386.2282	195.7890	-0.3485
0	-32.3279	-16.4146	364.4768	184.9992	-0.3500
-0.05	-30.1613	-15.3356	342.7254	174.2094	-0.3514
-0.1	-27.9948	-14.2565	320.9741	163.4196	-0.3529
-0.15	-25.8282	-13.1775	299.2227	152.6298	-0.3544
-0.2	-23.6617	-12.0984	277.4714	141.8400	-0.3559
-0.25	-21.4951	-11.0194	255.7200	131.0502	-0.3573
-0.3	-19.3286	-9.9403	233.9686	120.2604	-0.3587
-0.35	-17.1620	-8.8613	212.2173	109.4706	-0.3602
-0.4	-14.9955	-7.7822	190.4659	98.6808	-0.3617

Table IV (5),  $m=7$ ,  $n=14$ .

$\xi$	$[\delta_1']$	$[\delta_2']$	$[\delta_2'']$	$[\delta_1''']$	$[\delta_2''']$
.15	-0.05904	1.7849	0.9576	-0.1251	1.9557
.1	-0.03936	1.6268	0.8791	-0.09565	1.7987
.05	-0.01968	1.4688	0.8007	-0.06620	1.6416
0	0	1.3107	0.7223	-0.03676	1.4846
-.05	0.01968	1.1527	0.6439	-0.007317	1.3276
-.1	0.03936	0.9946	0.5655	0.02213	1.1705
-.15	0.05904	0.8365	0.4871	0.05157	1.0135
-.2	0.07872	0.6785	0.4086	0.08101	0.8565
-.25	0.09840	0.5204	0.3302	0.1046	0.6995
-.3	0.11808	0.3624	0.2518	0.1399	0.5424
-.35	0.13776	0.2043	0.1734	0.1693	0.3854
-.4	0.15744	0.04626	0.09498	0.1988	0.2284

$\xi$	$[\delta_3^2]$	$[\delta_3'']$	$[\delta_4^3]$	$[\delta_4^{21}]$	$[\delta_4''']$
.15	-23.2554	-11.7676	263.6148	133.3414	-0.1724
.1	-21.8394	-11.0624	249.3985	126.2894	-0.1733
.05	-20.4234	-10.3571	235.1823	119.2374	-0.1743
0	-19.0074	-9.6519	220.9660	112.1854	-0.1752
-.05	-17.5914	-8.9467	206.7498	105.1334	-0.1762
-.1	-16.1754	-8.2414	192.5335	98.0814	-0.1771
-.15	-14.7594	-7.5362	178.3173	91.0294	-0.1781
-.2	-13.3433	-6.8309	164.1010	83.9774	-0.1791
-.25	-11.9273	-6.1257	149.8848	76.9254	-0.1800
-.3	-10.5113	-5.4204	135.6685	69.8734	-0.1810
-.35	-9.0953	-4.7152	121.4523	62.8214	-0.1819
-.4	-7.6793	-4.0094	107.2360	55.7694	-0.1829

Table V (1)  $m = 4, n = 8.$ 

$\xi$	$[\beta_0]$	$[\beta_1]$	$[\beta_2]$	$[\beta_3]$	$[\beta_4]$	$A_1/\mu$
0.15	6.3629	-35.4544	766.7471	1201.5945	316.9676	-11.5345
0.1	6.0077	-33.6773	690.5789	1083.1736	284.1852	-7.3554
0.05	5.6525	-31.9001	618.3835	970.8786	253.1634	-3.5105
0	5.2973	-30.1230	550.1611	864.7163	223.9019	0
-0.05	4.9421	-28.3459	485.9117	764.6848	196.4010	3.1762
-0.1	4.5869	-26.5687	425.6353	670.7479	170.5895	6.0180
-0.15	4.2317	-24.7916	369.3315	583.0131	146.6806	8.5285
-0.2	3.8765	-23.0144	317.0010	501.3734	124.4609	10.6987
-0.25	3.5214	-21.2373	268.6432	425.8904	104.0019	12.5375
-0.3	3.1662	-19.4602	224.2583	356.4849	85.3031	14.0420
-0.35	2.8110	-17.6830	183.8466	293.2369	68.3653	15.2122
-0.4	2.4558	-15.9059	147.4075	236.1160	53.1887	16.0480

$\xi$	$A_2/\mu$	$A_3/\mu$	$B_1$	$B_2$	$B_3$	$B_4$
0.15	194.2949	114.3147	-5.5721	13.6579	-2.7378	7.8290
0.1	166.8812	100.4392	-5.6057	13.6871	-2.8252	7.8739
0.05	141.1917	87.3733	-5.6436	13.7179	-2.9258	7.9236
0	117.2263	75.1171	-5.6865	13.7504	-3.0418	7.9790
-0.05	94.9852	63.6703	-5.7356	13.7842	-3.1774	8.0412
-0.1	74.4683	53.6703	-5.7923	13.8189	-3.3412	8.1079
-0.15	55.6754	43.2056	-5.8585	13.8534	-3.5302	8.1910
-0.2	38.6069	34.1875	-5.9368	13.8862	-3.7652	8.2822
-0.25	23.2625	25.9790	-6.0310	13.9136	-4.0536	8.3873
-0.3	9.6423	18.5800	-6.1463	13.9256	-4.4316	8.5094
-0.35	-2.2537	11.9908	-6.2907	13.9223	-4.9252	8.6521
-0.4	-12.4255	6.2110	-6.4769	13.8680	-5.5982	8.8193

Table V (2)  $m = 5, n = 10$ .

$\xi$	$\beta_0$	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$	$A_1/\mu$
0.15	3.5246	-25.0835	369.9260	592.9778	146.7908	-6.7210
0.1	3.3029	-23.7533	330.7033	530.8709	129.9945	-4.2859
0.05	3.0812	-22.4231	293.6637	472.1839	114.1789	-2.0455
0	2.8595	-21.0930	258.8072	416.9169	99.3442	0
-0.05	2.6378	-19.7628	226.1337	365.0697	85.4902	1.8507
-0.1	2.4161	-18.4326	195.6434	316.6425	72.6171	3.5066
-0.15	2.1944	-17.1024	167.3361	271.6351	60.7247	4.9677
-0.2	1.9727	-15.7723	141.3516	230.0475	49.8132	6.2340
-0.25	1.7510	-14.4421	117.2709	191.8802	39.8824	7.3054
-0.3	1.5293	-13.1119	95.5130	157.1327	30.9324	8.1821
-0.35	1.3076	-11.7818	75.6117	125.1525	22.9633	8.8639
-0.4	1.0859	-10.4536	58.2395	97.8973	15.9749	9.3509

$\xi$	$A_2/\mu$	$A_3/\mu$	$B_1$	$B_2$	$B_3$	$B_4$
0.15	142.7478	81.0149	-7.1167	17.8178	-5.8283	11.8163
0.1	123.4792	71.1621	-7.1917	17.8178	-6.1138	11.9162
0.05	105.3981	61.8848	-7.2774	17.8077	-6.4490	12.0267
0	88.5045	53.1830	-7.3765	17.7826	-6.8476	12.1496
-0.05	72.7984	45.0567	-7.4921	17.7735	-7.3290	12.2866
-0.1	58.2797	37.5059	-7.6291	17.6531	-7.9207	12.4396
-0.15	44.9484	30.5306	-7.7936	17.5179	-8.6632	12.6104
-0.2	32.8046	24.1307	-7.9952	17.4418	-9.6193	12.8001
-0.25	21.8484	18.3064	-8.2478	16.9384	-10.8896	13.0076
-0.3	12.0796	13.0575	-8.5737	16.3351	-12.6447	13.2255
-0.35	3.4982	8.3842	-9.0100	14.5190	-15.9749	13.4295
-0.4	-3.8957	4.2863	-9.6245	12.2833	-19.2303	13.5465

Table V (3)  $m = 6, n = 12.$ 

$\xi$	$[\beta_0]$	$[\beta_1]$	$[\beta_2]$	$[\beta_3]$	$[\beta_4]$	$A_1/\mu$
0.15	2.4527	-21.1698	257.2695	418.1806	98.5621	-5.9411
0.1	2.2880	-20.0145	229.1067	373.0492	86.5980	-3.7885
0.05	2.1234	-18.8651	202.5609	330.5353	75.3650	-1.8081
0	1.9588	-17.7128	177.6313	290.5492	64.8604	0
-0.05	1.7942	-16.5604	154.3182	253.1197	55.0865	1.6359
-0.1	1.6296	-15.4081	132.6214	218.2471	46.0424	3.0997
-0.15	1.4650	-14.2557	112.5406	185.9313	37.7268	4.3912
-0.2	1.3004	-13.1034	94.0764	156.1724	30.1419	5.5105
-0.25	1.1357	-11.9512	77.2282	128.9701	23.2859	6.4577
-0.3	0.9711	-10.7988	61.9965	104.3255	17.1602	7.2326
-0.35	0.8065	-9.6464	48.3814	82.2378	11.7639	7.8353
-0.4	0.6419	-8.4941	36.3821	62.7065	7.0970	8.2658

$\xi$	$A_2/\mu$	$A_3/\mu$	$B_1$	$B_2$	$B_3$	$B_4$
0.15	152.8478	24.0029	-8.6314	22.0692	-9.9675	16.3847
0.1	132.8350	73.7739	-8.7488	21.9722	-10.5523	16.5419
0.05	114.0380	64.1434	-8.8843	21.8366	-11.2474	16.7147
0	96.4556	55.1102	-9.0427	21.6421	-12.0900	16.9044
-0.05	80.0890	46.6753	-9.2300	21.3659	-13.1260	17.1123
-0.1	64.9369	38.8378	-9.4553	20.9624	-14.4321	17.3383
-0.15	51.0006	31.5987	-9.7311	20.3686	-16.1163	17.5792
-0.2	38.2789	24.9569	-10.0768	19.4613	-18.3649	17.8258
-0.25	26.7729	18.9134	-10.5229	18.0250	-21.4921	18.0527
-0.3	16.4816	13.4674	-11.1199	15.6488	-26.0608	18.1961
-0.35	7.4059	8.6196	-11.9606	11.4078	-33.2528	18.0855
-0.4	-0.4550	4.3692	-13.2329	2.9871	-45.8347	17.2249

Table V.(4).  $m = 6, n = 14$ .

$\xi$	$[\beta_0]$	$[\beta_1]$	$[\beta_2]$	$[\beta_3]$	$[\beta_4]$	$A_1/\mu$
0.15	3.1563	-30.5844	532.8530	870.6386	204.0697	-4.8262
0.1	2.9611	-29.0232	478.1587	782.4830	180.9003	-3.1120
0.05	2.7659	-27.4615	426.4043	697.0084	159.0657	-1.5026
0	2.5707	-25.8998	377.5886	620.2272	138.5604	0
-0.05	2.3755	-24.3381	331.7117	546.1222	119.3867	1.3940
-0.1	2.1802	-22.7764	288.7741	476.6998	101.5438	2.6772
-0.15	1.9850	-21.2148	248.7703	411.9590	85.0323	3.9472
-0.2	1.7898	-19.6531	211.7157	351.9000	69.8519	4.9017
-0.25	1.5946	-18.0914	177.5949	296.5259	56.0028	5.8376
-0.3	1.3994	-16.5297	146.4132	245.3326	43.4847	6.6518
-0.35	1.2042	-14.9681	118.1703	199.8210	32.2981	7.3409
-0.4	1.0090	-13.4064	92.8667	158.4932	22.4426	7.9011

$\xi$	$A_2/\mu$	$A_3/\mu$	$B_1$	$B_2$	$B_3$	$B_4$
0.15	160.2188	84.2006	-9.6900	26.1592	-13.0030	20.4845
0.1	142.4694	78.1423	-9.8016	25.9968	-13.6550	20.6320
0.05	125.5143	69.4747	-9.9287	25.7972	-14.4118	20.7928
0	109.3709	61.2069	-10.0752	25.5368	-15.3058	20.9677
-0.05	94.0479	53.3426	-10.2457	25.1936	-16.3824	21.1575
-0.1	79.5595	45.8893	-10.4268	24.7332	-17.6986	21.3621
-0.15	65.9214	38.8539	-10.6874	24.0960	-19.3428	21.5799
-0.2	53.1495	32.2443	-10.9805	23.2172	-21.4418	21.8051
-0.25	41.2614	26.0688	-11.3454	21.9372	-24.2044	22.0242
-0.3	30.2768	20.3368	-11.8120	20.0112	-28.4936	22.2051
-0.35	20.2173	15.0588	-12.4300	16.9616	-33.4078	22.2735
-0.4	11.1076	10.2463	-13.2871	11.7920	-41.7212	22.0447

Table V. (5).  $m=7, n=14$ .

$\xi$	$[\beta_0]$	$[\beta_1]$	$[\beta_2]$	$[\beta_3]$	$[\beta_4]$	$A_1/\mu$
0.15	1.8306	-18.5061	193.4480	317.3718	72.2664	-5.9569
0.1	1.7030	-17.4855	171.9350	282.6181	63.1734	-3.7986
0.05	1.5754	-16.4648	151.5927	249.8639	54.6470	-1.8130
0	1.4478	-15.4441	132.5530	219.1068	46.6844	0
-0.05	1.3203	-14.4234	114.7720	190.3523	39.2944	1.6403
-0.1	1.1927	-13.4027	98.2495	163.5976	32.4732	3.1080
-0.15	1.0651	-12.3821	82.9858	138.8433	26.2204	4.4029
-0.2	0.9375	-11.3614	68.9806	116.0889	20.5365	5.5253
-0.25	0.8099	-10.3407	56.2342	95.3331	15.4176	6.4749
-0.3	0.6823	-9.3200	44.7463	76.5809	10.8746	7.2519
-0.35	0.5547	-8.2994	34.5171	59.8271	6.8966	7.8562
-0.4	0.4271	-7.2787	25.5436	45.0687	3.4918	8.2879

$\xi$	$A_2/\mu$	$A_3/\mu$	$B_1$	$B_2$	$B_3$	$B_4$
0.15	180.0868	96.6132	-10.1093	26.5101	-4.9832	21.5650
0.1	157.0026	84.8444	-10.2672	26.2935	-15.9457	21.7821
0.05	135.3061	73.7645	-10.4510	25.8636	-17.1033	22.0175
0	114.9954	63.3716	-10.6670	25.3653	-18.5221	22.2706
-0.05	96.0724	53.6677	-10.9247	24.6795	-20.2893	22.5433
-0.1	78.5351	44.6508	-11.2376	23.7128	-22.5471	22.8289
-0.15	62.3854	36.3228	-11.6255	22.3129	-25.5155	23.1139
-0.2	47.6216	28.6819	-12.1189	20.2074	-29.5652	23.3664
-0.25	34.2453	21.7298	-12.7678	16.8856	-35.3600	23.5042
-0.3	22.2550	15.4650	-13.6594	11.2958	-44.1717	23.3581
-0.35	11.6256	9.8887	-14.9611	1.0062	-58.8326	22.4111
-0.4	2.4352	4.9999	-17.0403	-20.7402	-86.7139	19.1386

Table VI.

$\xi$	$(1+\xi)^{3/n-m}$ for $m=4, n=8$	$(1+\xi)^{3/n-m}$ for $m=5, n=10$	$(1+\xi)^{3/n-m}$ for $m=6, n=12$	$(1+\xi)^{3/n-m}$ for $m=6, n=14$	$(1+\xi)^{3/n-m}$ for $m=7, n=14$
0.15	1.1105	1.0875	1.0724	1.0538	1.0617
0.1	1.0741	1.0589	1.0488	1.0364	1.0417
0.05	1.0373	1.0297	1.0241	1.0185	1.0211
0	1	1	1	1	1
-0.05	0.96626	0.96969	0.97468	0.98095	0.97826
-0.1	0.92402	0.93874	0.94868	0.96126	0.95585
-0.15	0.88525	0.90709	0.92195	0.94088	0.93272
-0.2	0.84590	0.87469	0.89443	0.91973	0.90880
-0.25	0.80593	0.84147	0.86603	0.89774	0.88401
-0.3	0.76529	0.80734	0.83666	0.87481	0.85825
-0.35	0.72391	0.77223	0.80623	0.85083	0.83142
-0.4	0.68173	0.73602	0.77459	0.82567	0.80340

-:-

With the help of the above tables we can easily compute the quantities (7.1), (7.2), (7.3) and (7.4) as functions of  $p$  and  $T$ . Since (7.1) is linear in  $p/p_0$  and  $T/T_0$ , we can draw a system of straight lines giving  $p/p_0$  against  $T/T_0$  for constant  $\xi$ , one line to each value of  $\xi$ . From these lines the curves of  $\xi$  against  $T/T_0$  for constant  $p/p_0$  are found, and finally the isobars and isotherms giving  $v/v_0 = (1+\xi)^{-3/n-m}$  as a function

(51)

of  $T/\theta$  for constant  $p/p_0$  and  $\tau/p_0$  as a function of  $p/p_0$  for constant  $T/\theta$  respectively. Similarly, by drawing a set of lines for each of the equations (7.2), (7.3) and (7.4), the graphs of the elasticity constants  $e_{11}, c_{12}$  and  $c_{44}$  as functions of  $T/\theta$  for constant  $p/p_0$  can be drawn. The resulting graphs are all shown below.

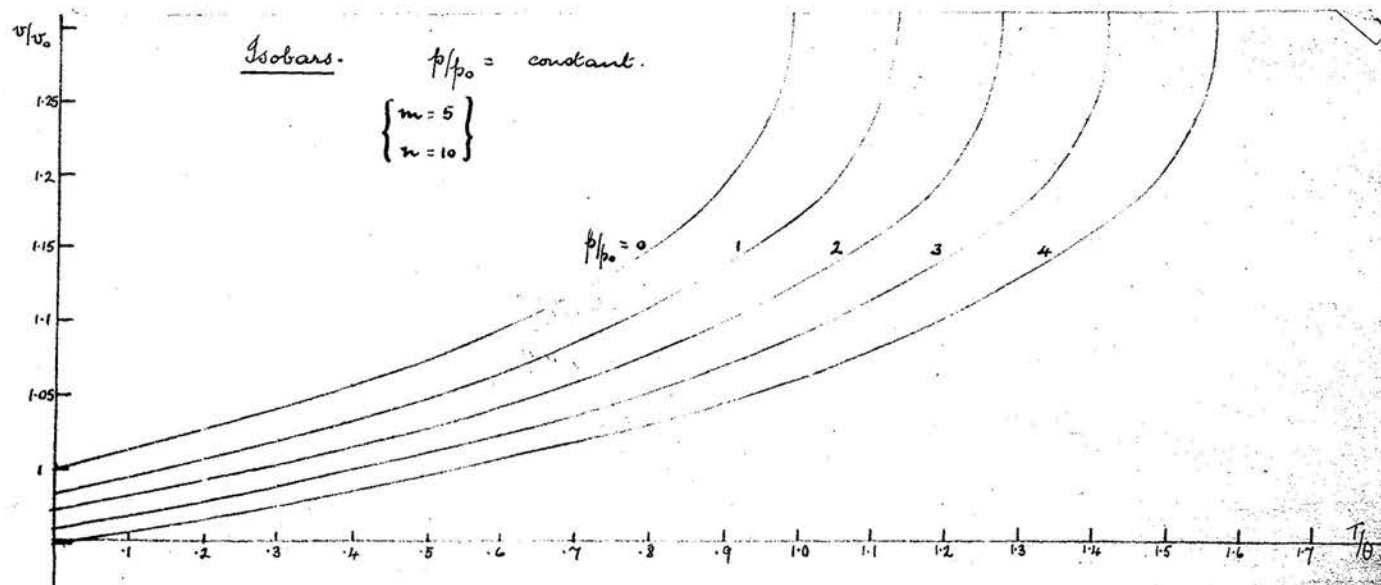
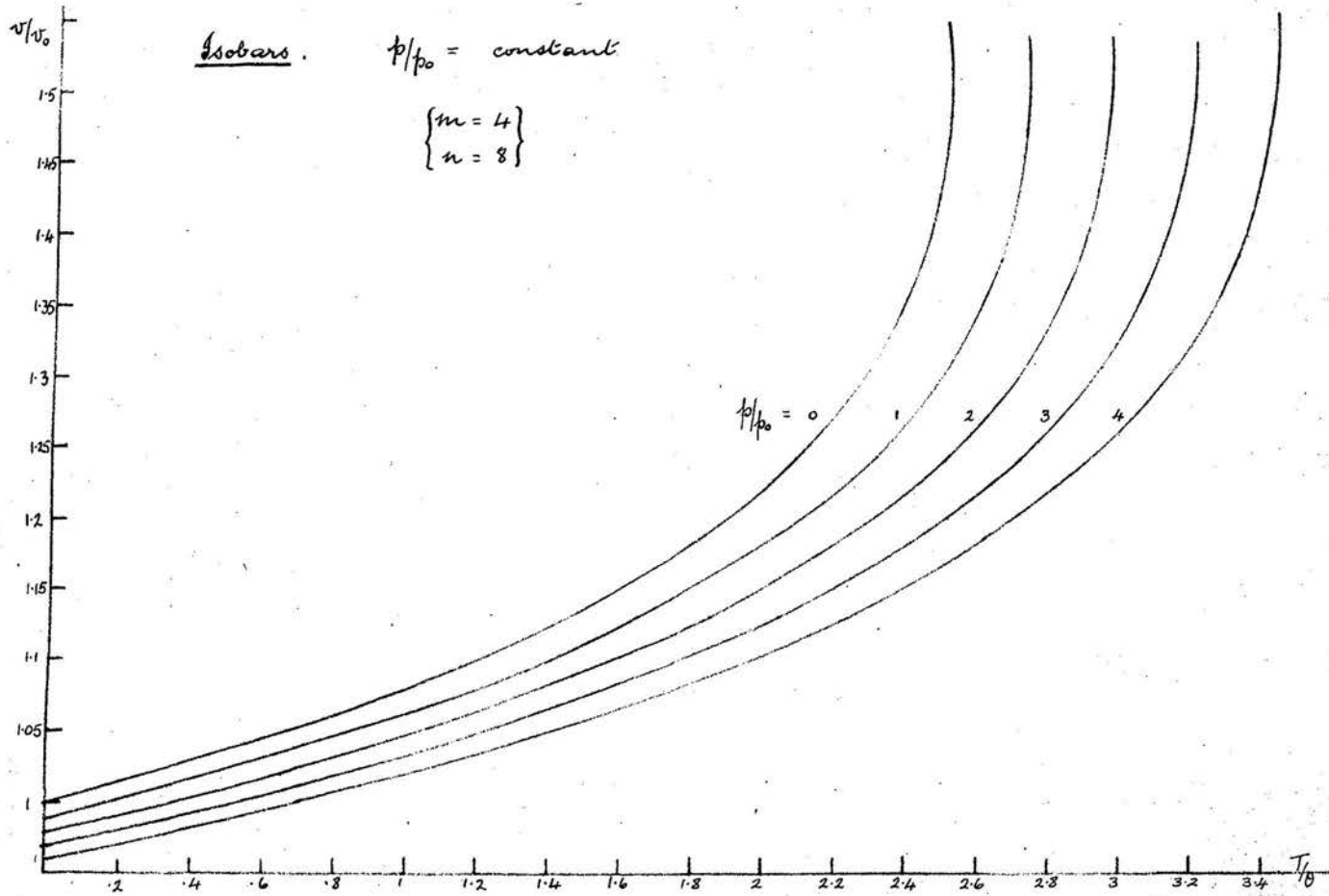
We have drawn five sets of diagrams corresponding to the five different pairs of exponents already mentioned.

The curves are all clearly marked, and the diagram of straight lines represents the relation between  $T_m/\theta$  and  $p/p_0$  where  $T_m/\theta$  is the value of  $T/\theta$  corresponding to complete instability. On all the curves this value of  $T/\theta$  occurs where the gradient of the tangent becomes infinite. The diagram is drawn for values of  $T_m/\theta$  given by the isobars, but the values of  $T_m/\theta$  taken from the curves of the elastic constants are practically the same, so it is necessary to draw only one diagram.

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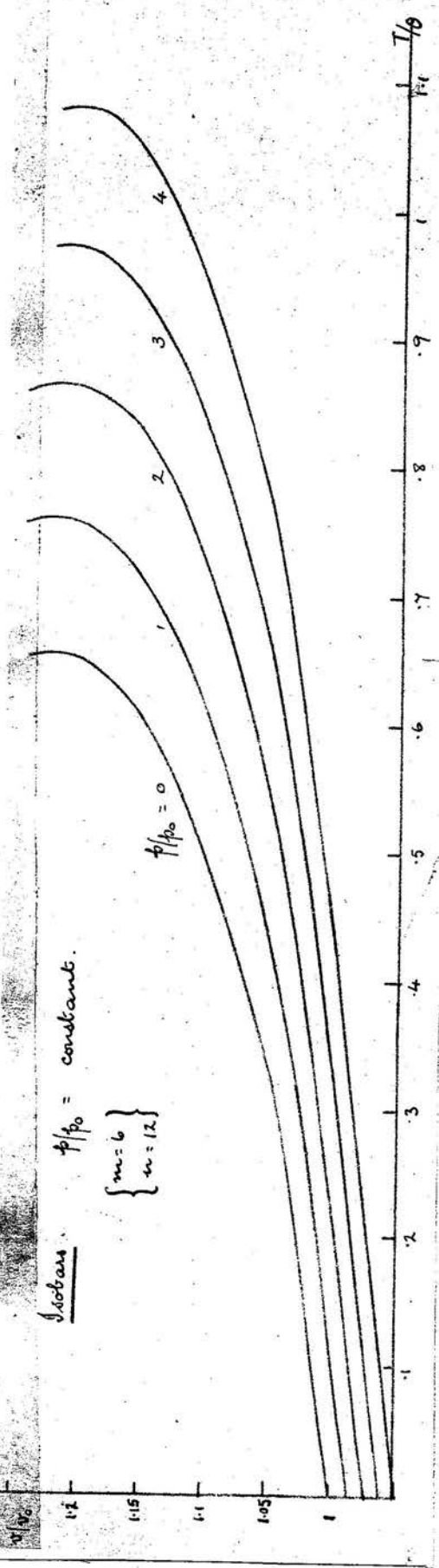
DIAGRAMS OF RESULTS.



Isobars.  $p/p_0 = \text{constant.}$

$$\begin{cases} m=6 \\ n=12 \end{cases}$$

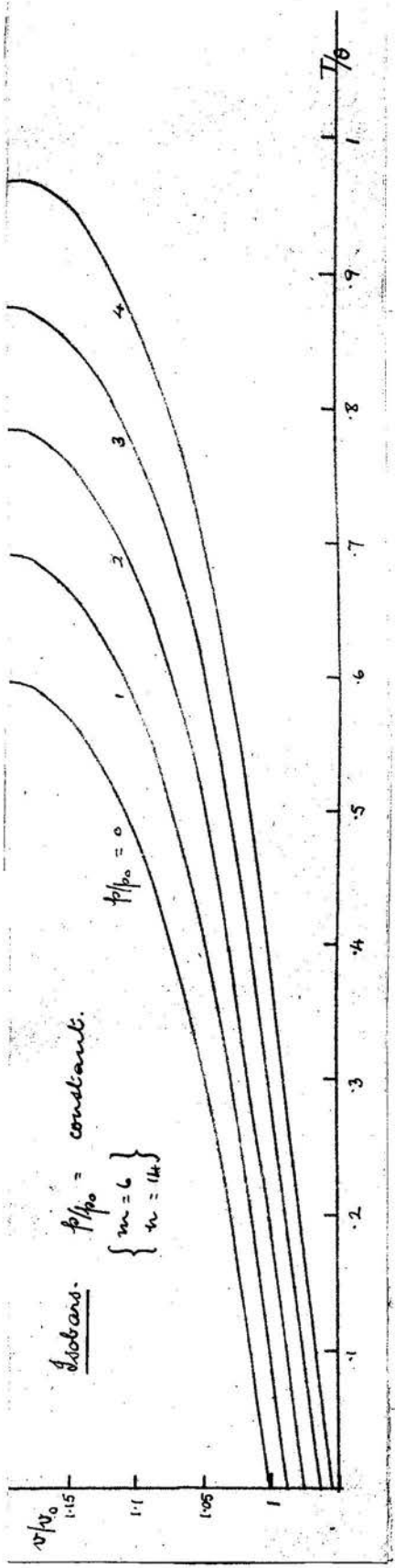
$$p/p_0 = 0$$



Isobars.  $p/p_0 = \text{constant.}$

$$\begin{cases} m=6 \\ n=144 \end{cases}$$

$$p/p_0 = 0$$

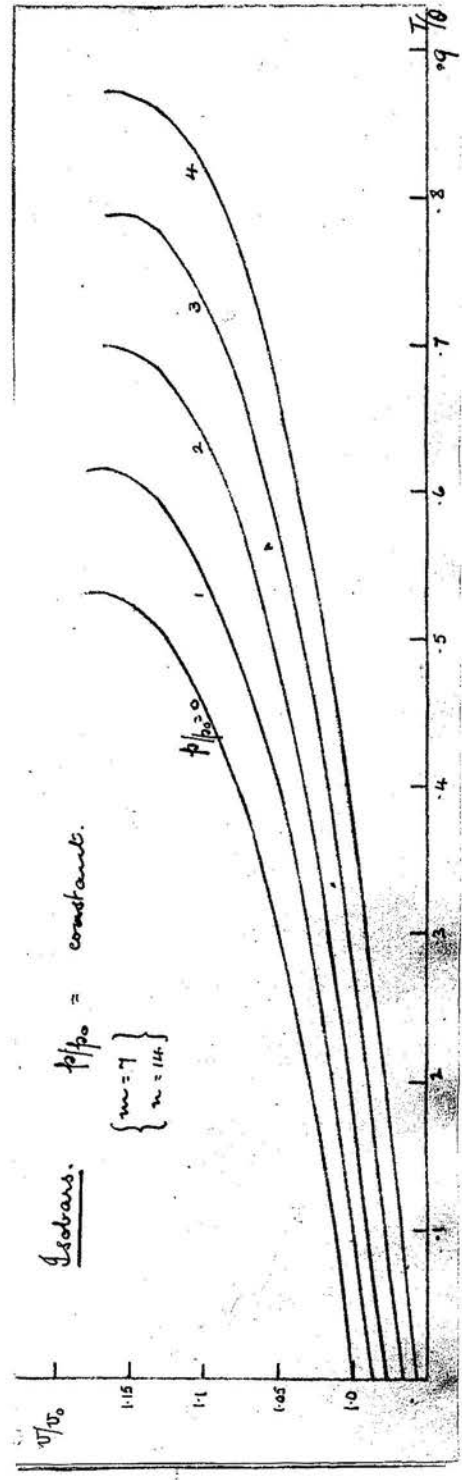


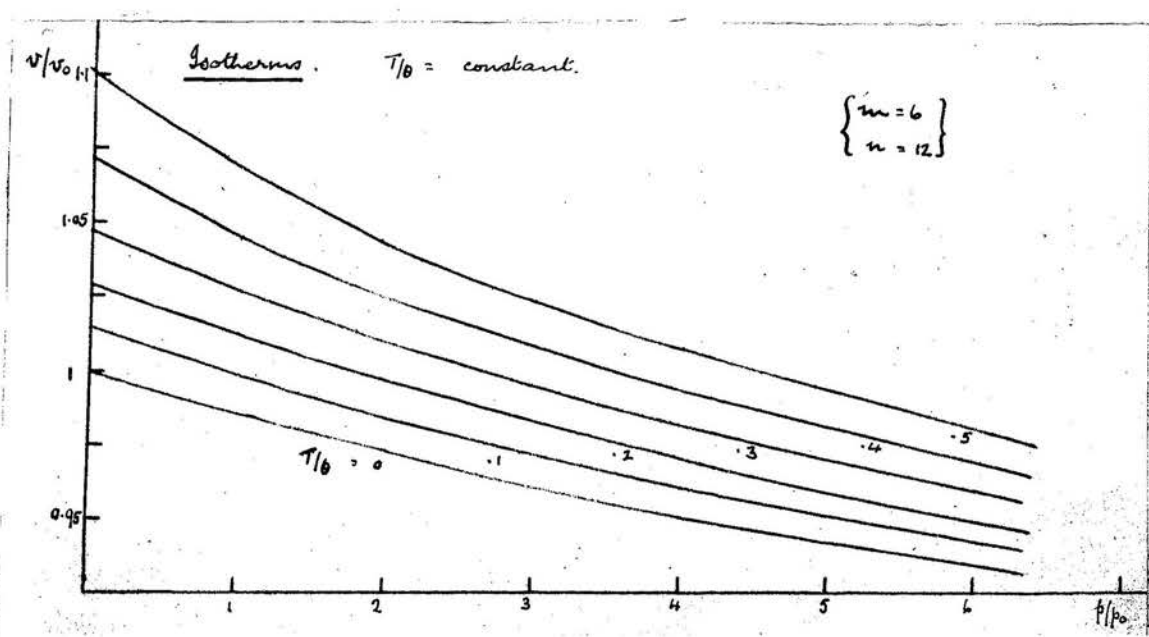
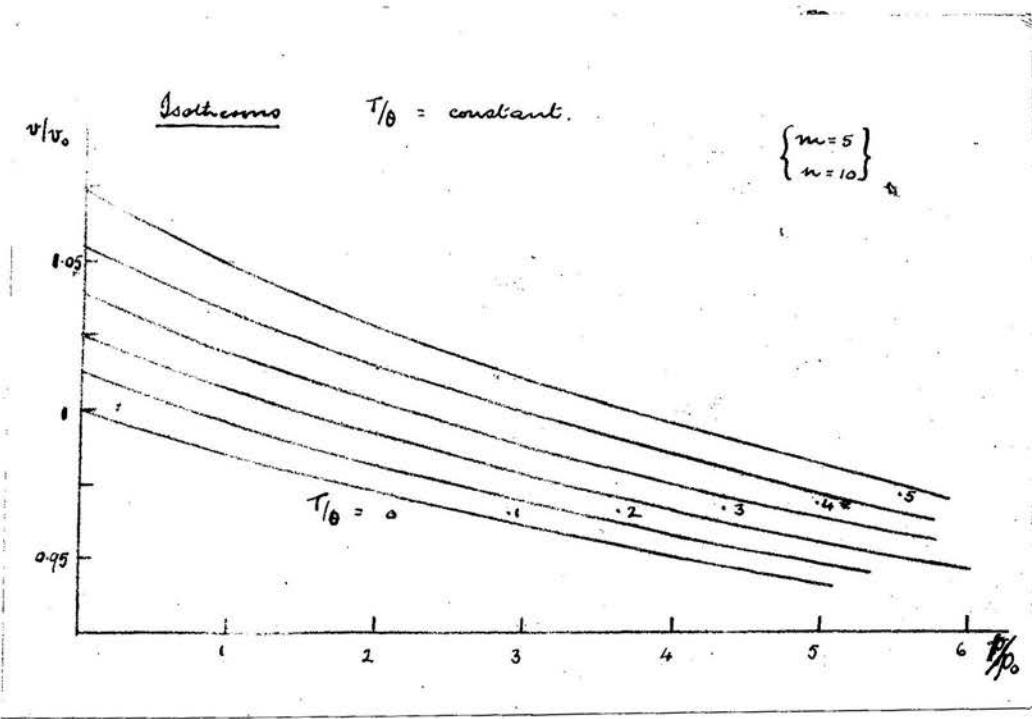
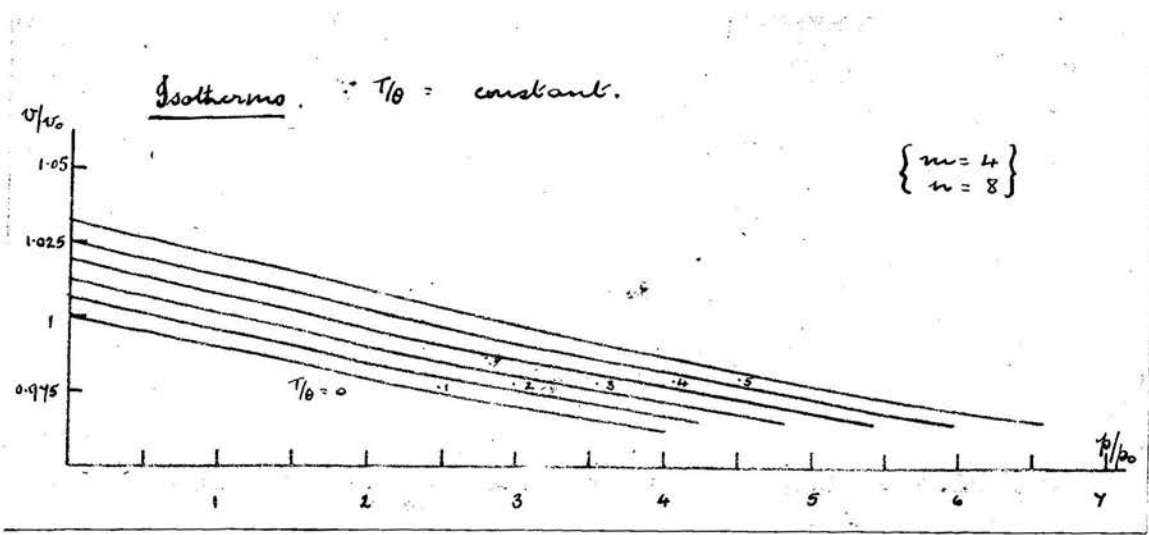
Isobars.

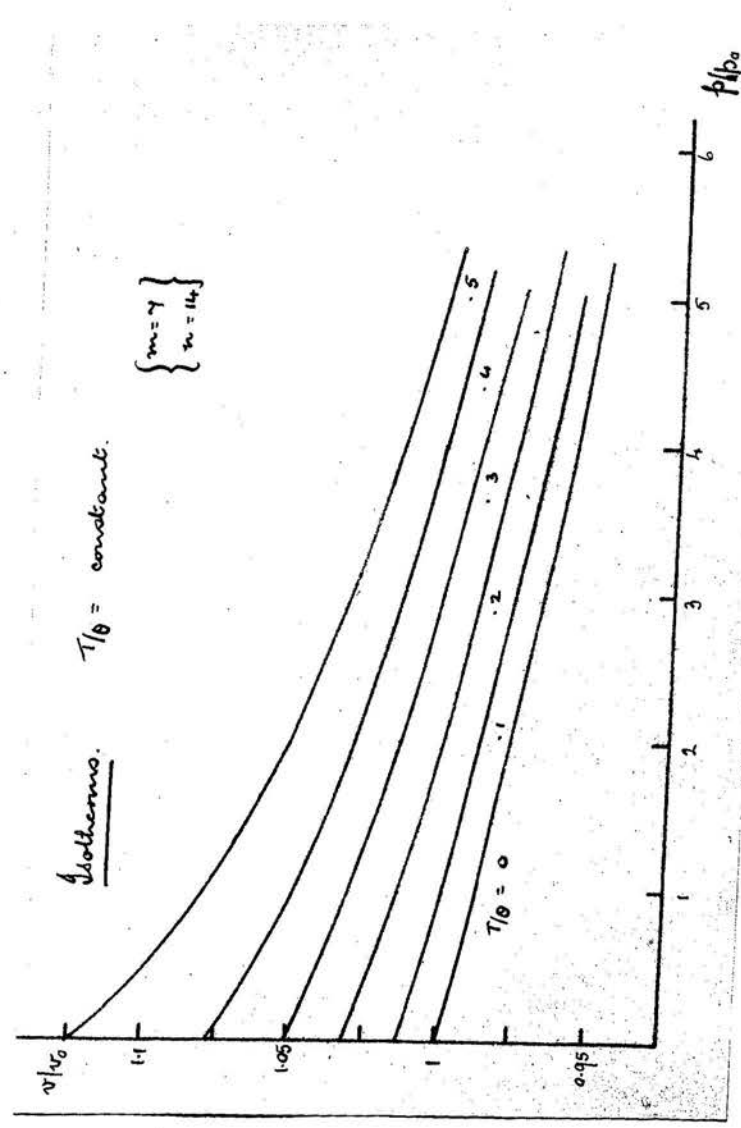
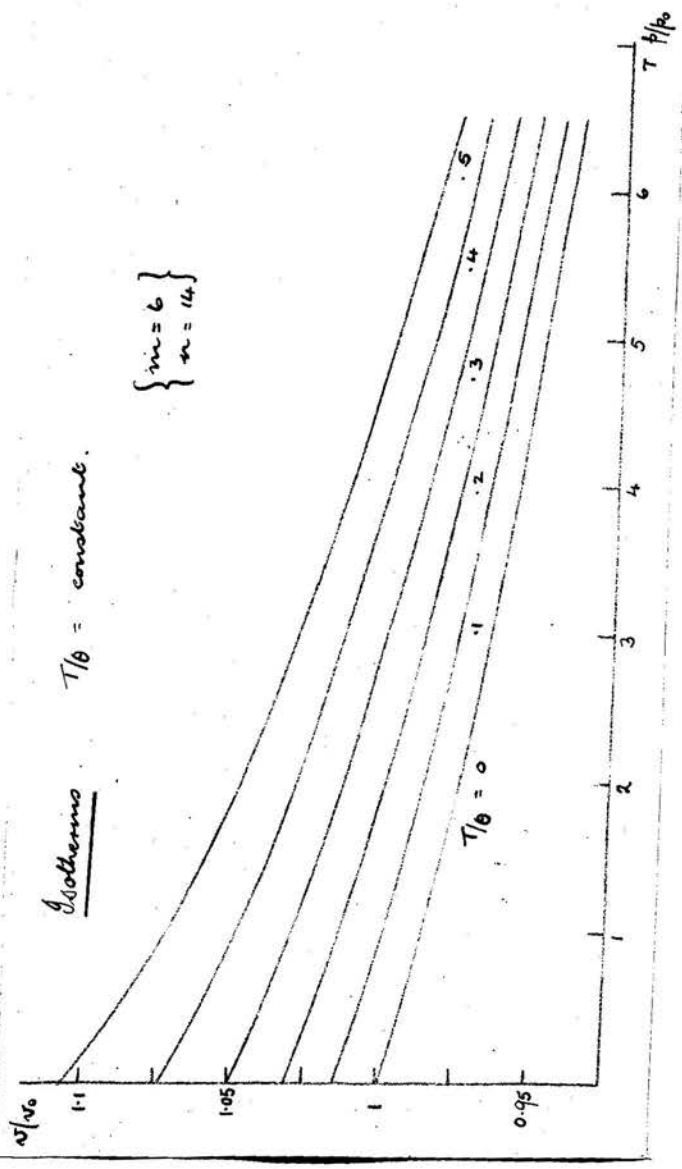
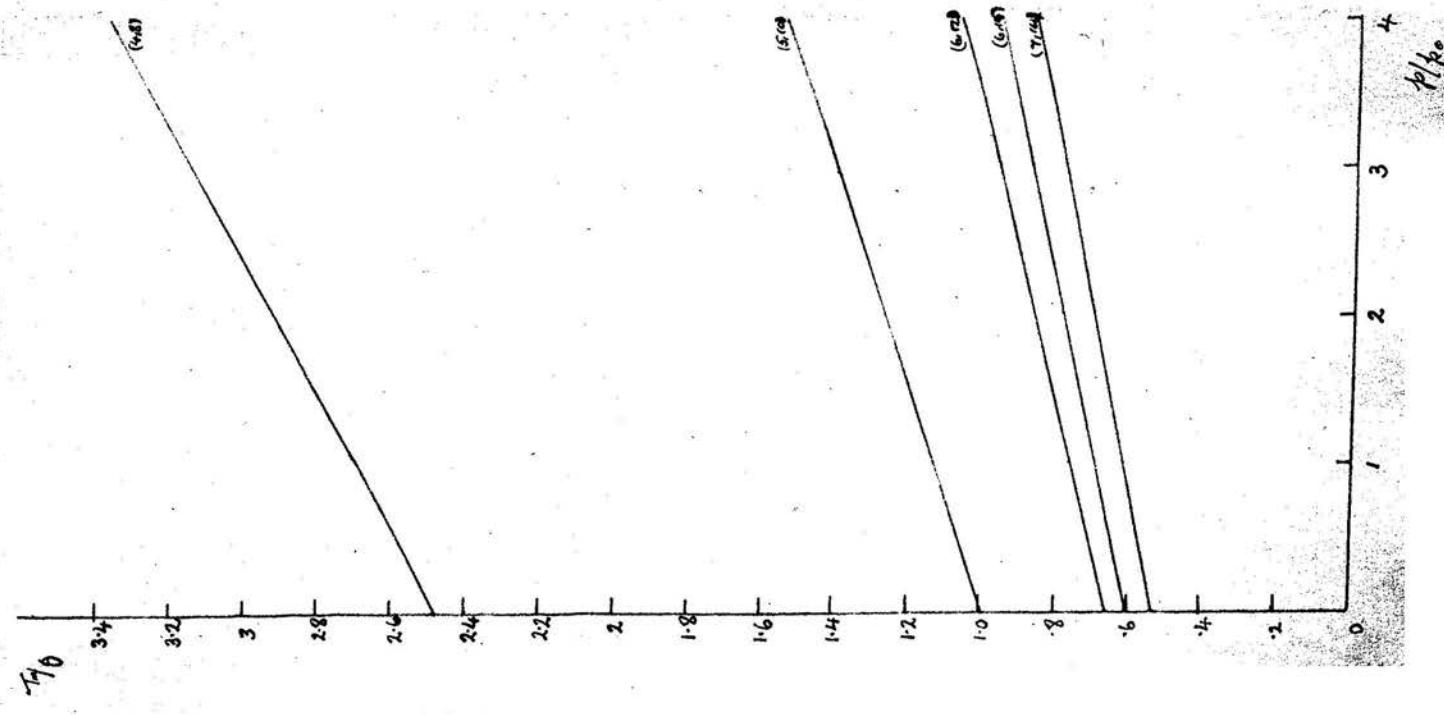
$p/p_0 = \text{constant.}$

$$\begin{cases} m=7 \\ n=144 \end{cases}$$

$$p/p_0 = 0$$



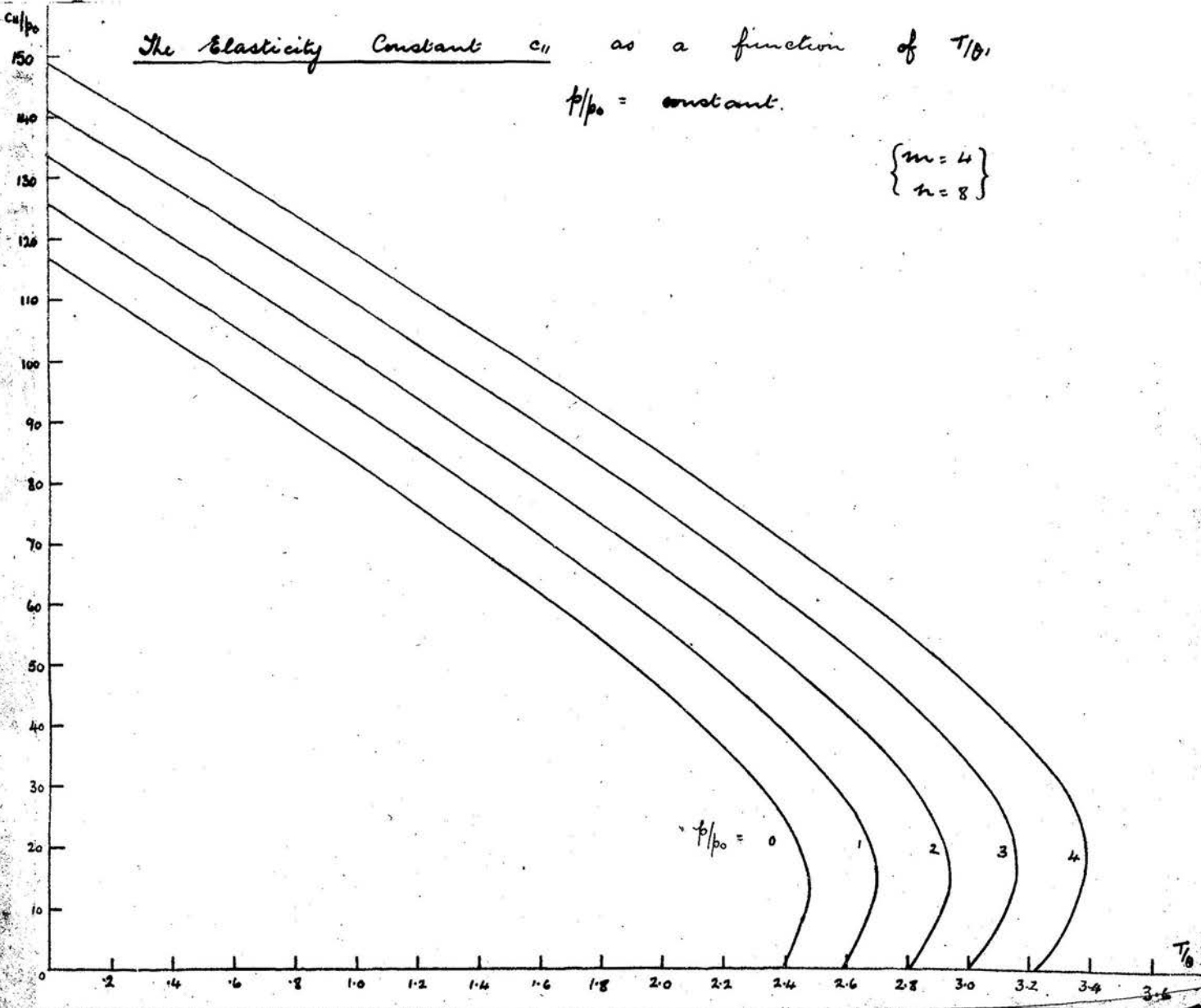




The Elasticity Constant  $c_{11}$  as a function of  $T/\theta$

$p/p_0 = \text{constant}$

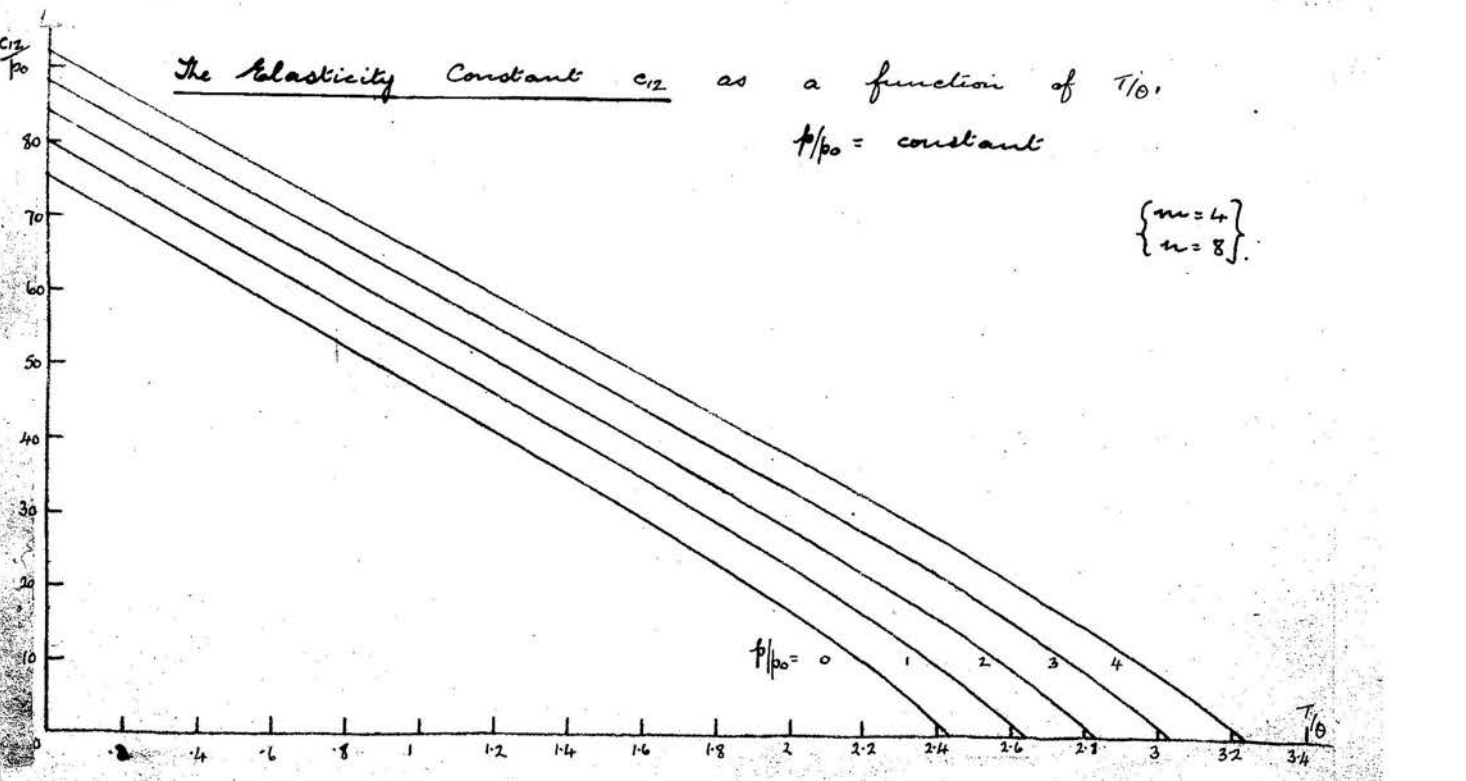
$\begin{cases} m=4 \\ n=8 \end{cases}$

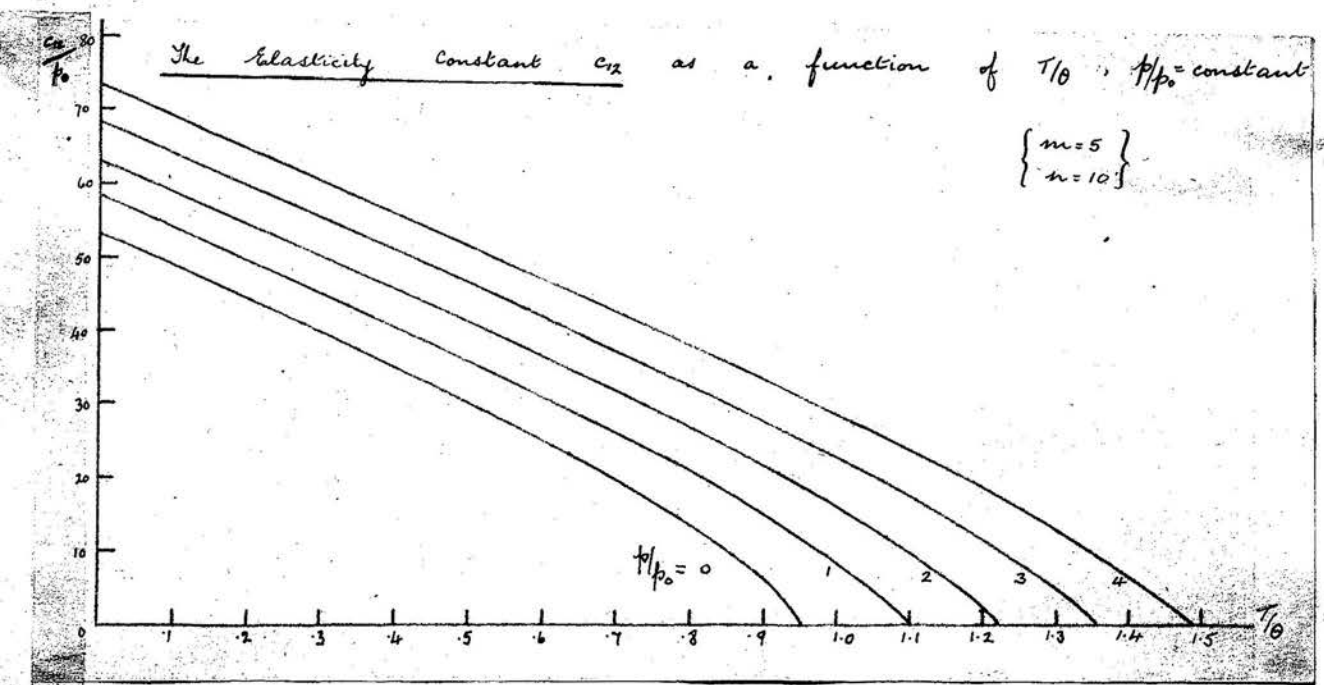
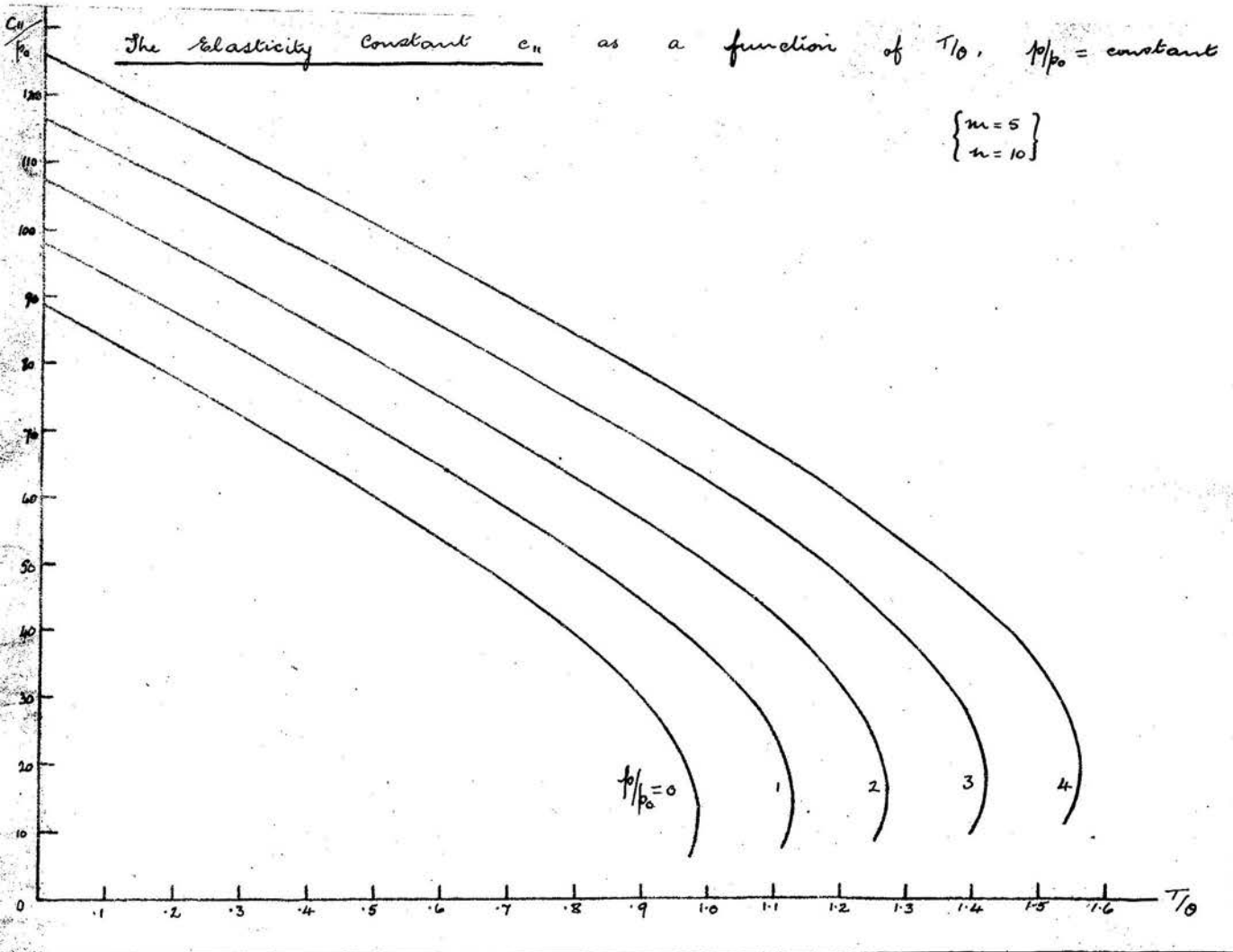


The Elasticity Constant  $c_{12}$  as a function of  $T/\theta$

$p/p_0 = \text{constant}$

$\begin{cases} m=4 \\ n=8 \end{cases}$

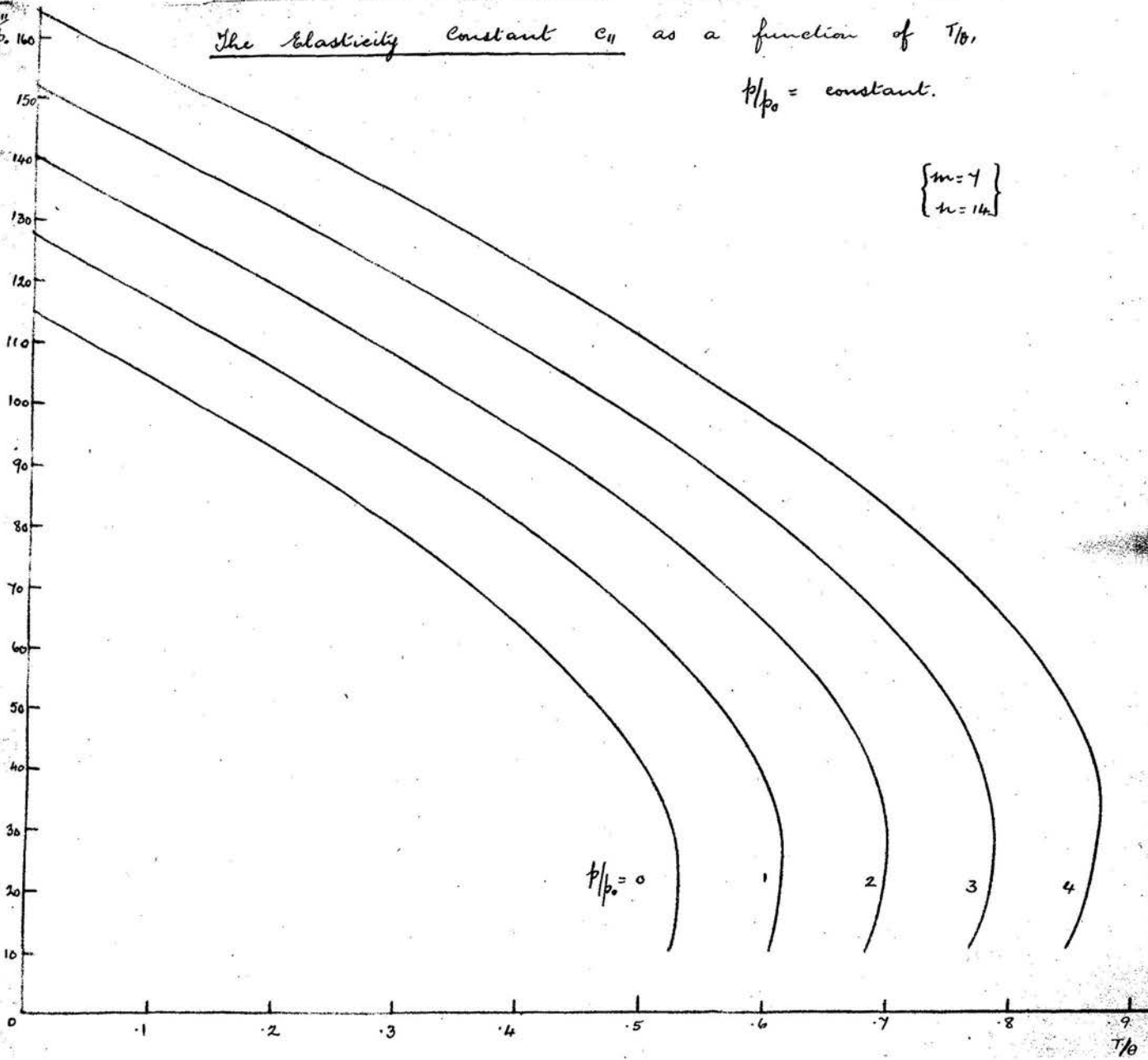




The elasticity constant  $c_{11}$  as a function of  $T/\theta$ .

$p/p_0 = \text{constant}$ .

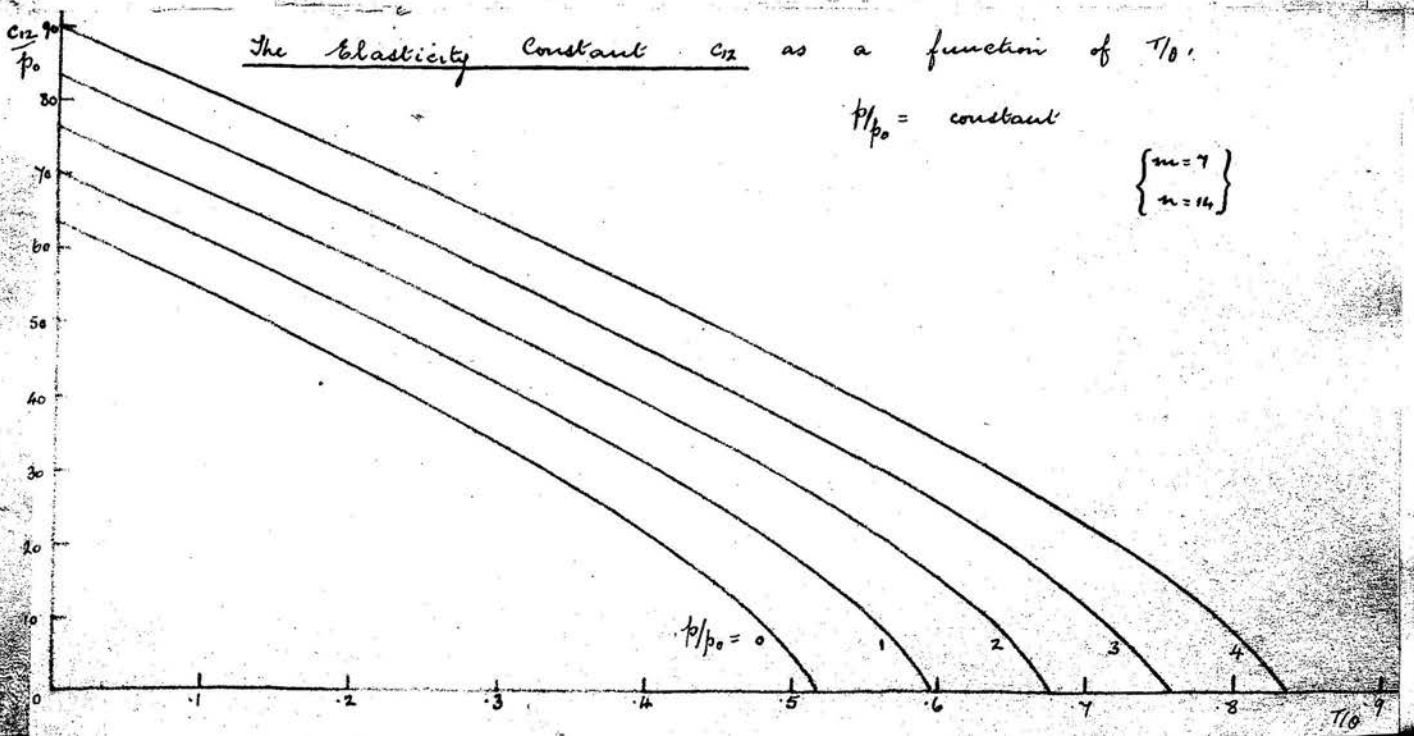
$\left\{ \begin{array}{l} m=7 \\ n=14 \end{array} \right\}$

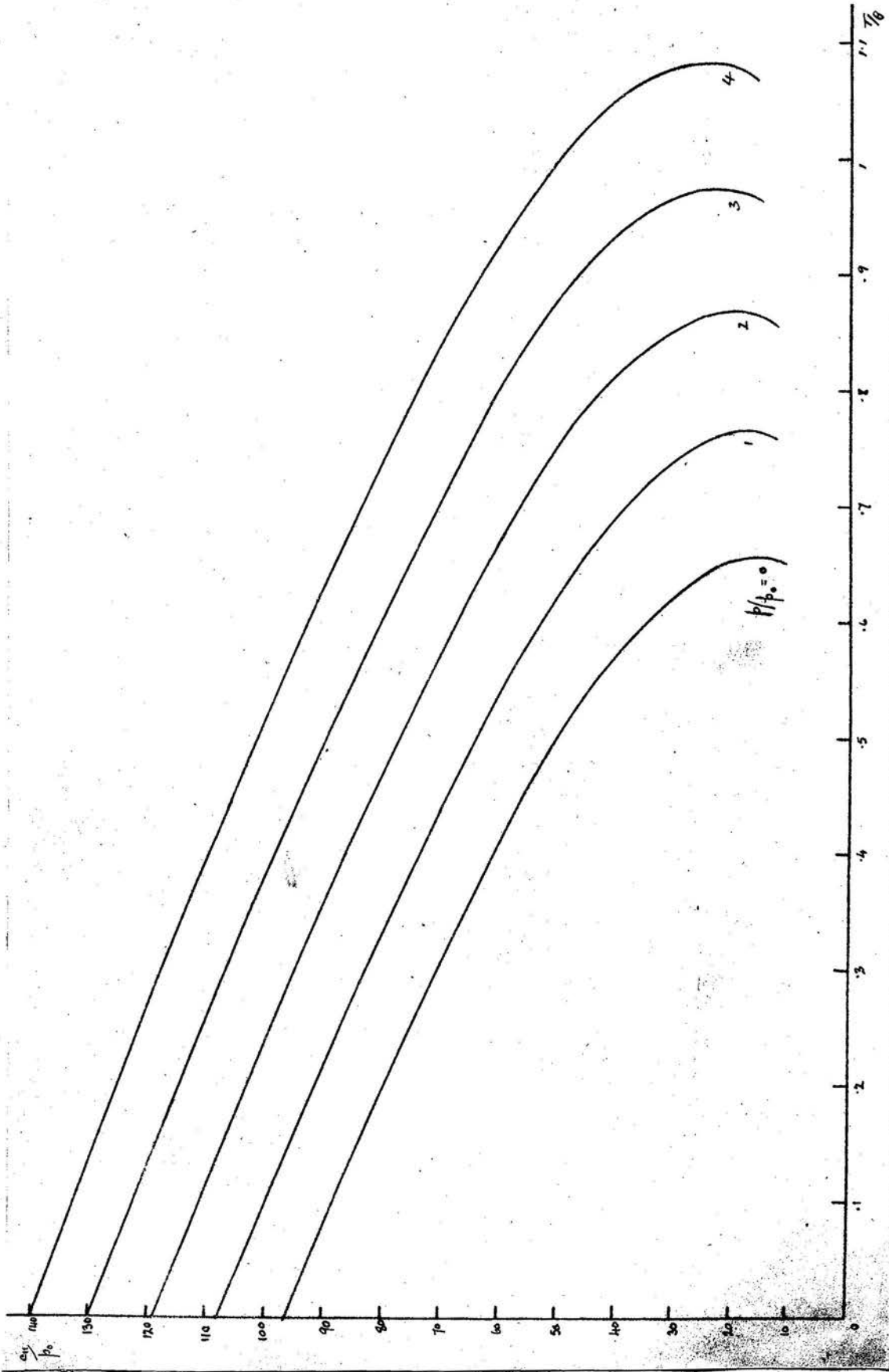


The elasticity constant  $c_{12}$  as a function of  $T/\theta$ .

$p/p_0 = \text{constant}$

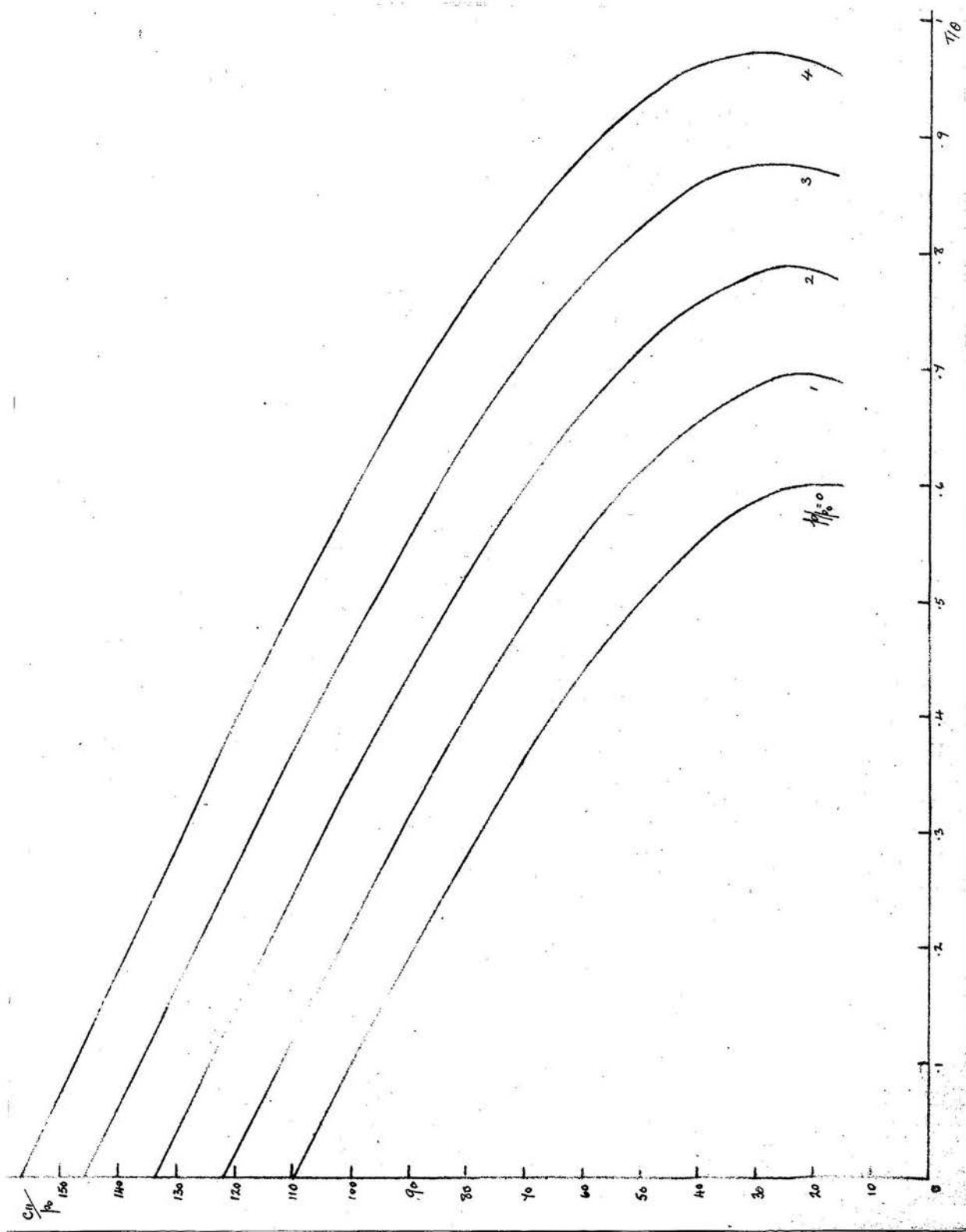
$\left\{ \begin{array}{l} m=7 \\ n=14 \end{array} \right\}$





The Elasticity Constant  $c_{11}$  as a function of  $T/T_0$ ,  $p/p_0 = \text{constant}$

$$\begin{cases} m=6 \\ n=12 \end{cases}$$

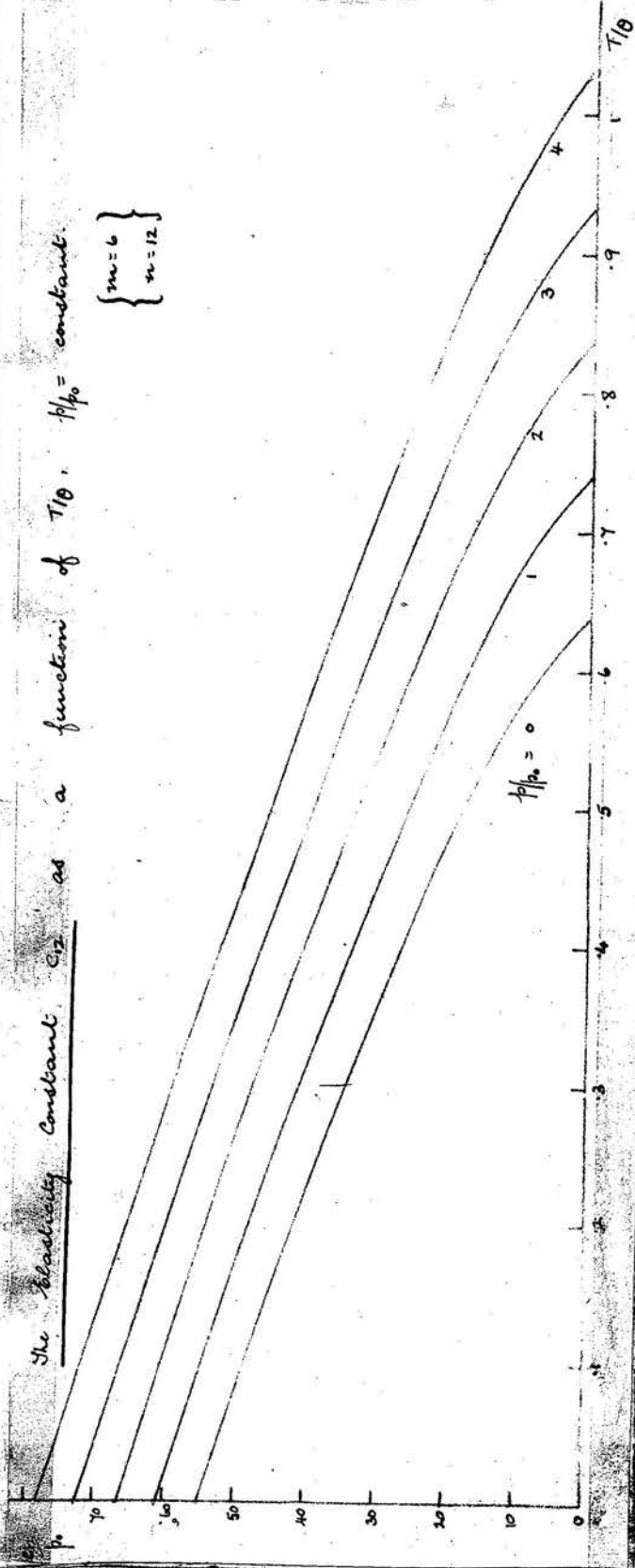


The Elasticity Constant  $c_{11}$  as a function of  $T_{10}$ ,  $p_1/p_0 = \text{constant}$

$$\begin{cases} n = 6 \\ n = 14 \end{cases}$$

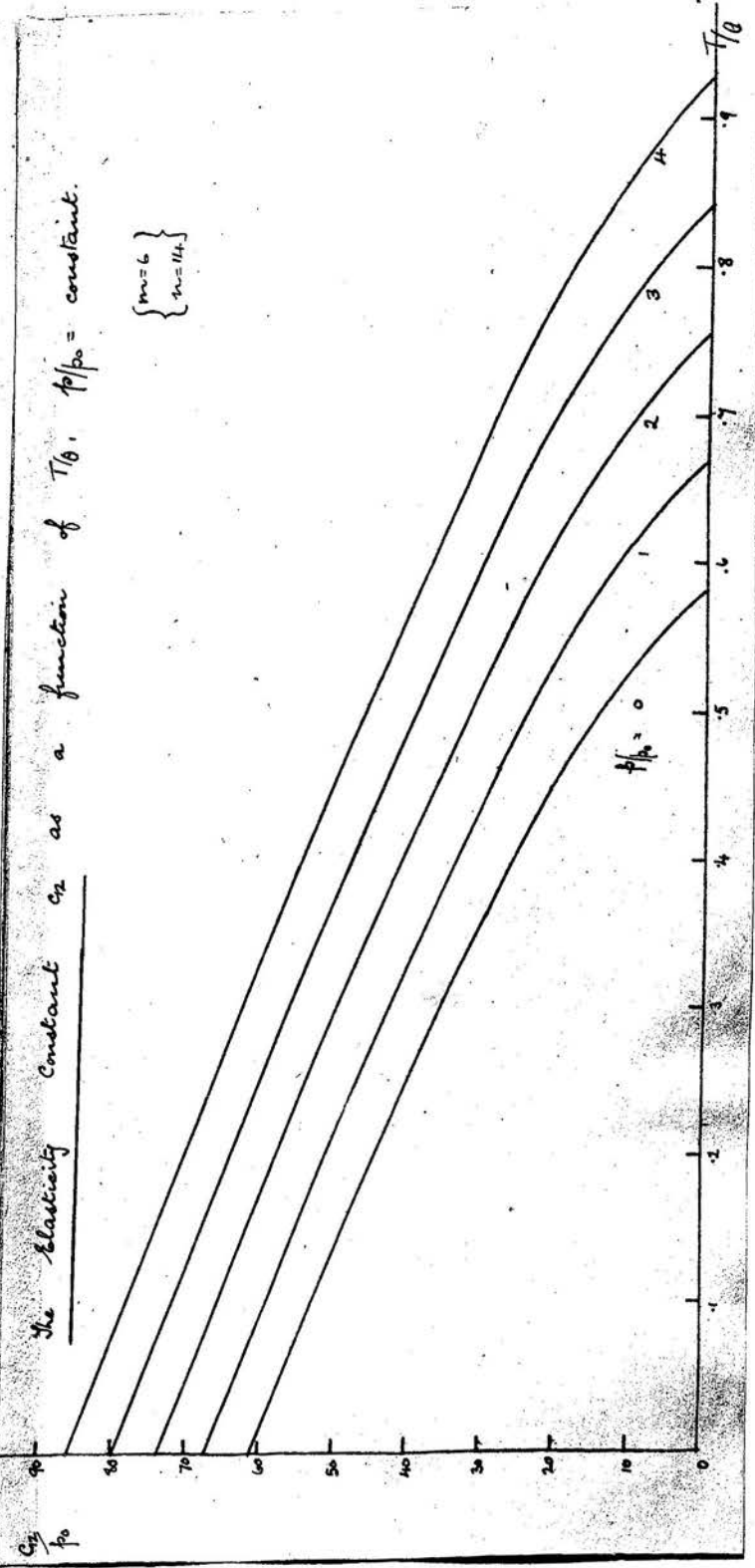
The Elasticity Constant  $e_2$  as a function of  $T/\theta$ ,  $p/p_0 = \text{constant}$ .

$$\begin{cases} m=6 \\ n=12 \end{cases}$$

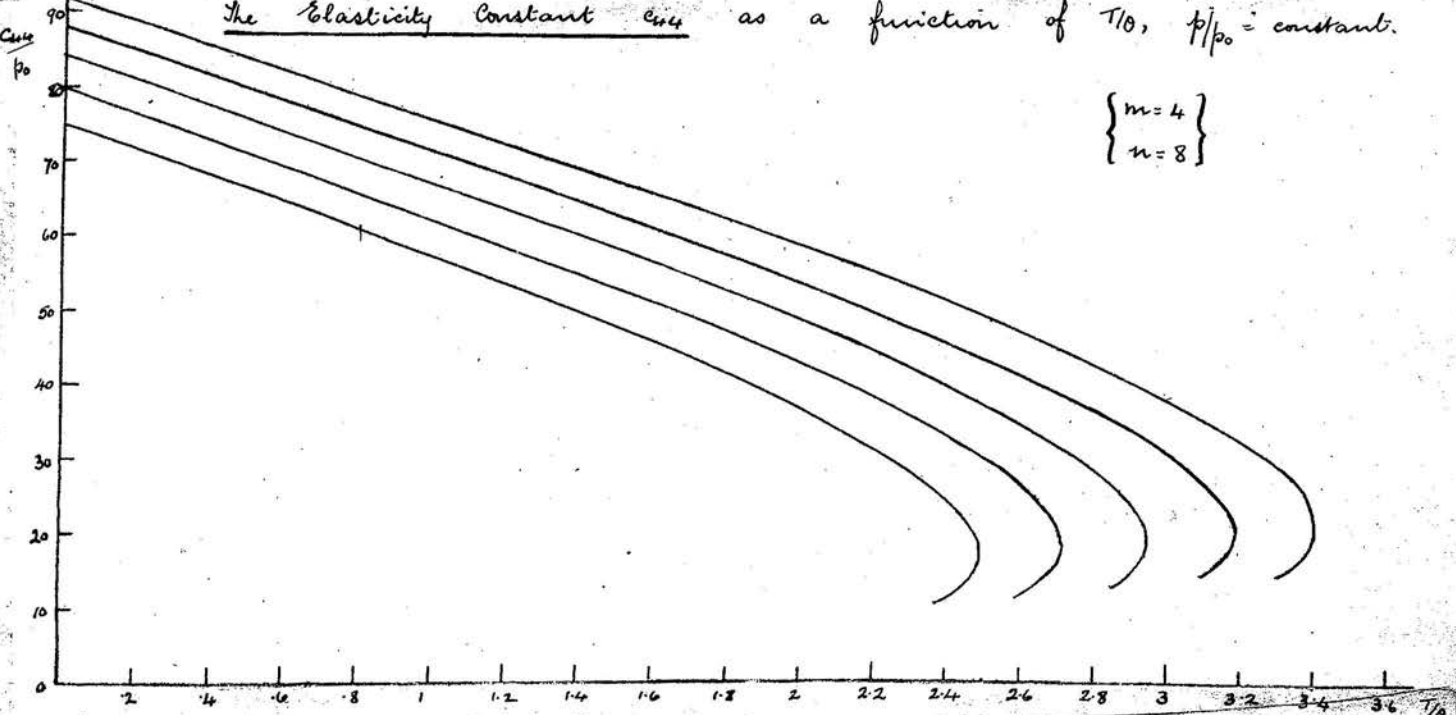


The Elasticity Constant  $e_2$  as a function of  $T/\theta$ ,  $p/p_0 = \text{constant}$ .

$$\begin{cases} m=6 \\ n=14 \end{cases}$$

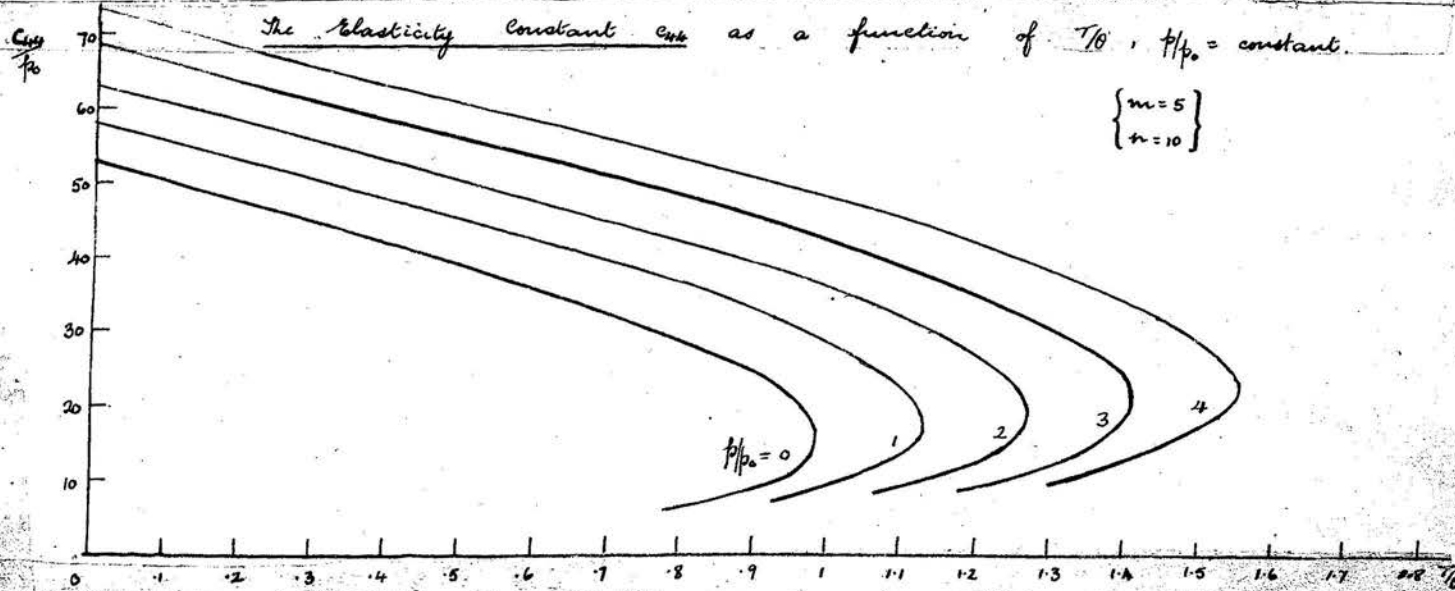


The Elasticity Constant  $c_{112}$  as a function of  $T/\theta$ ,  $p/p_0 = \text{constant}$ .



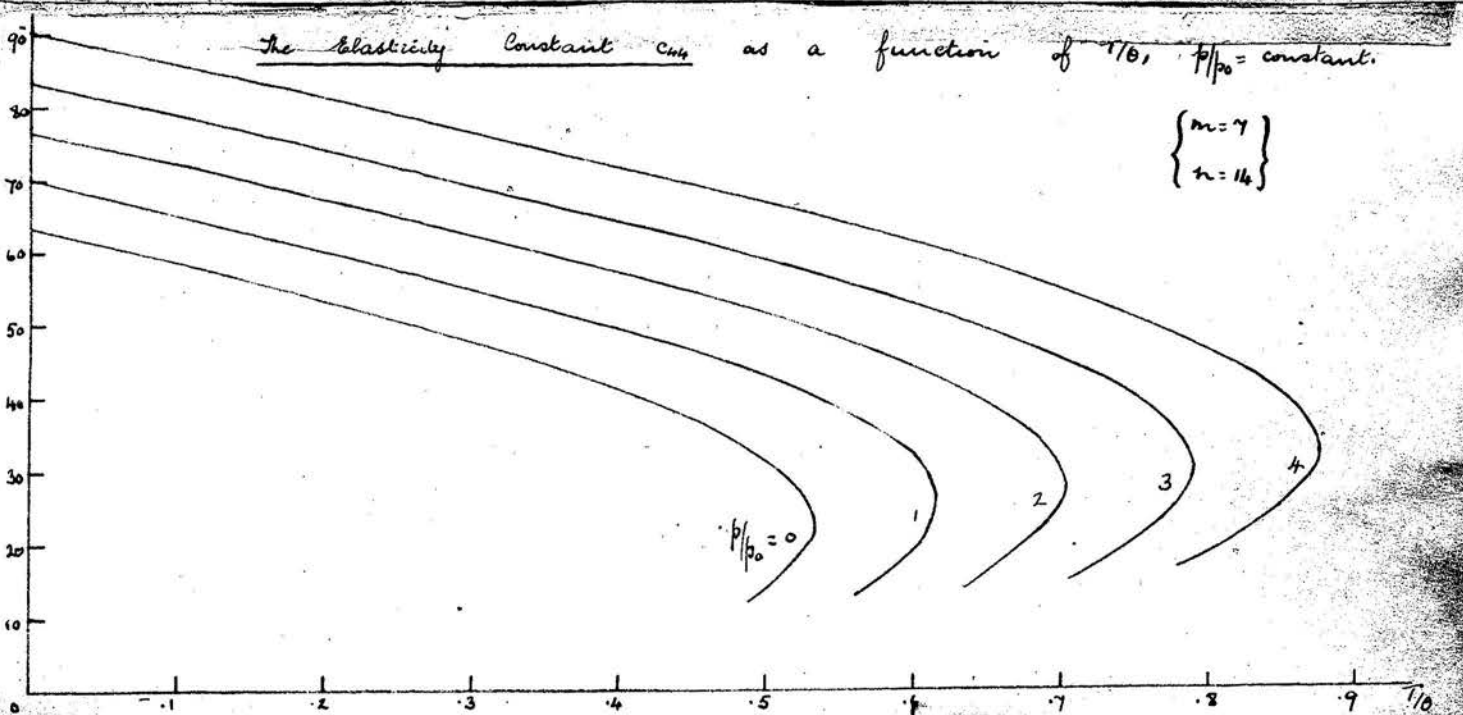
$$\begin{cases} m=4 \\ n=8 \end{cases}$$

The Elasticity Constant  $c_{112}$  as a function of  $T/\theta$ ,  $p/p_0 = \text{constant}$ .



$$\begin{cases} m=5 \\ n=10 \end{cases}$$

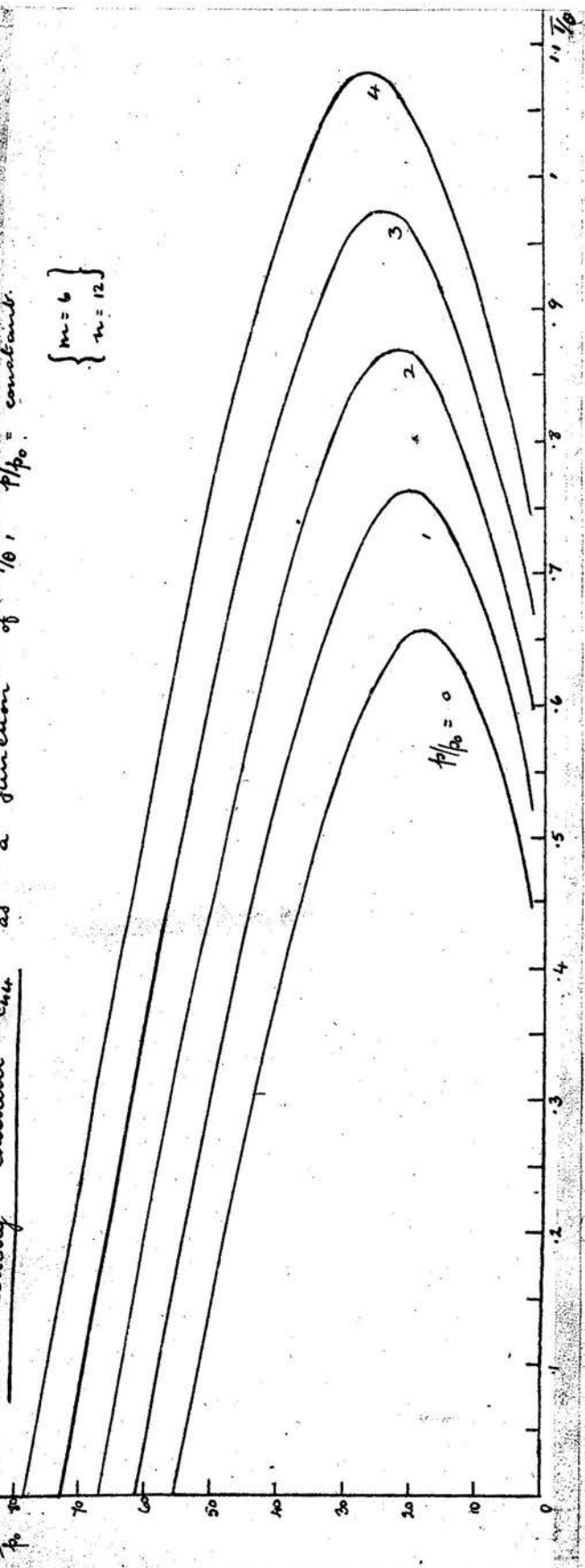
The Elasticity Constant  $c_{112}$  as a function of  $T/\theta$ ,  $p/p_0 = \text{constant}$ .



$$\begin{cases} m=7 \\ n=14 \end{cases}$$

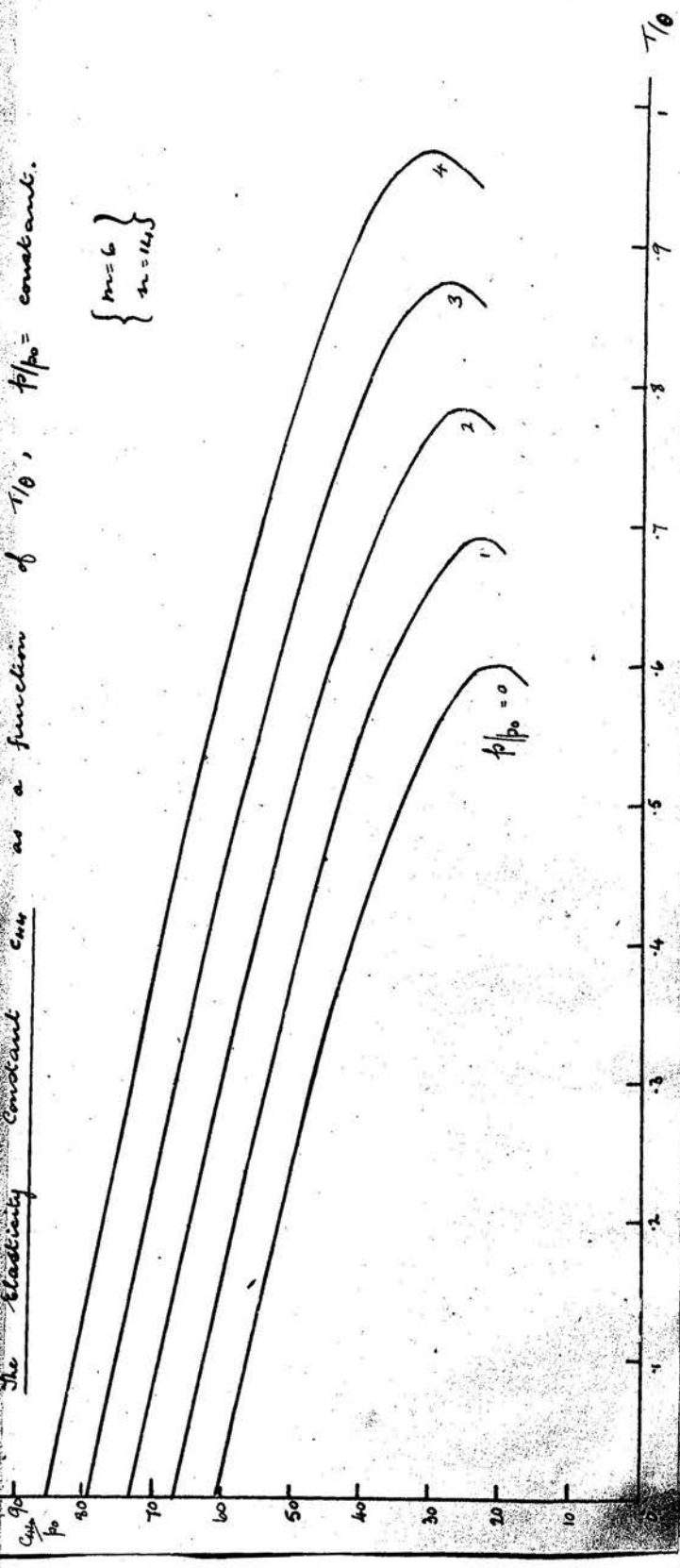
The elasticity constant  $c_{nr}$  as a function of  $T/\theta$ ,  $f/p_0 = \text{constant}$ .

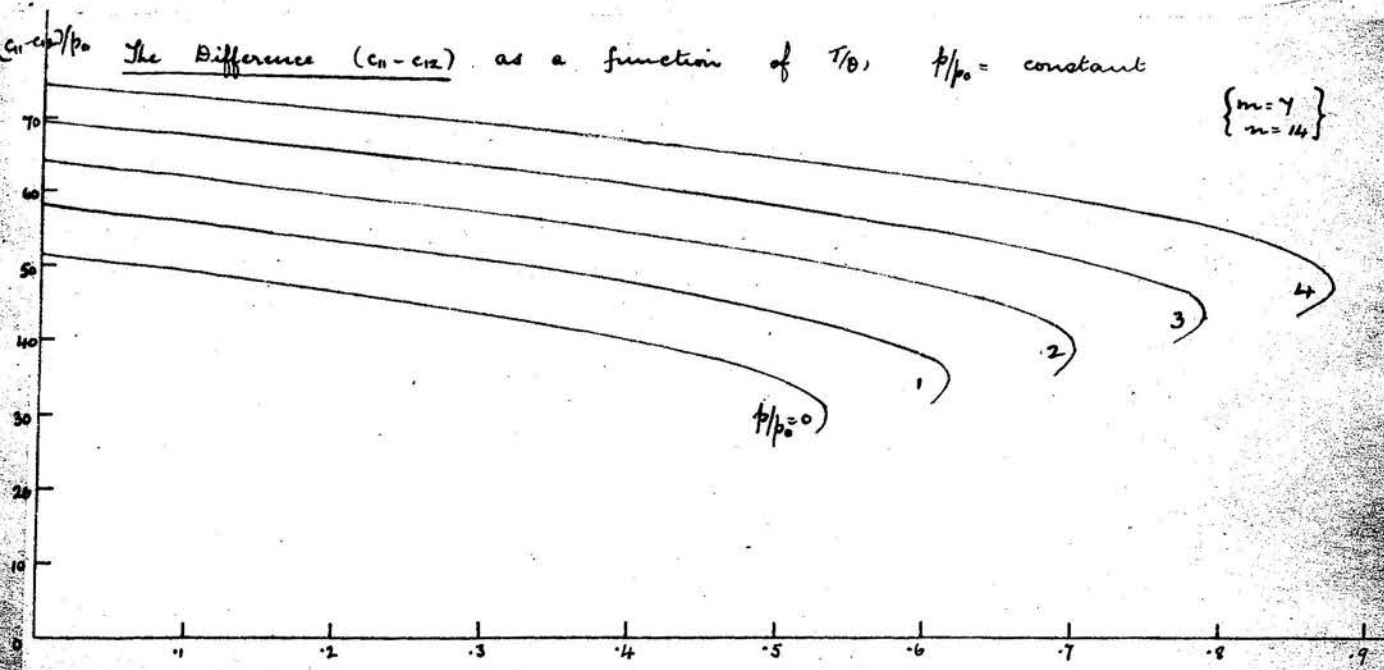
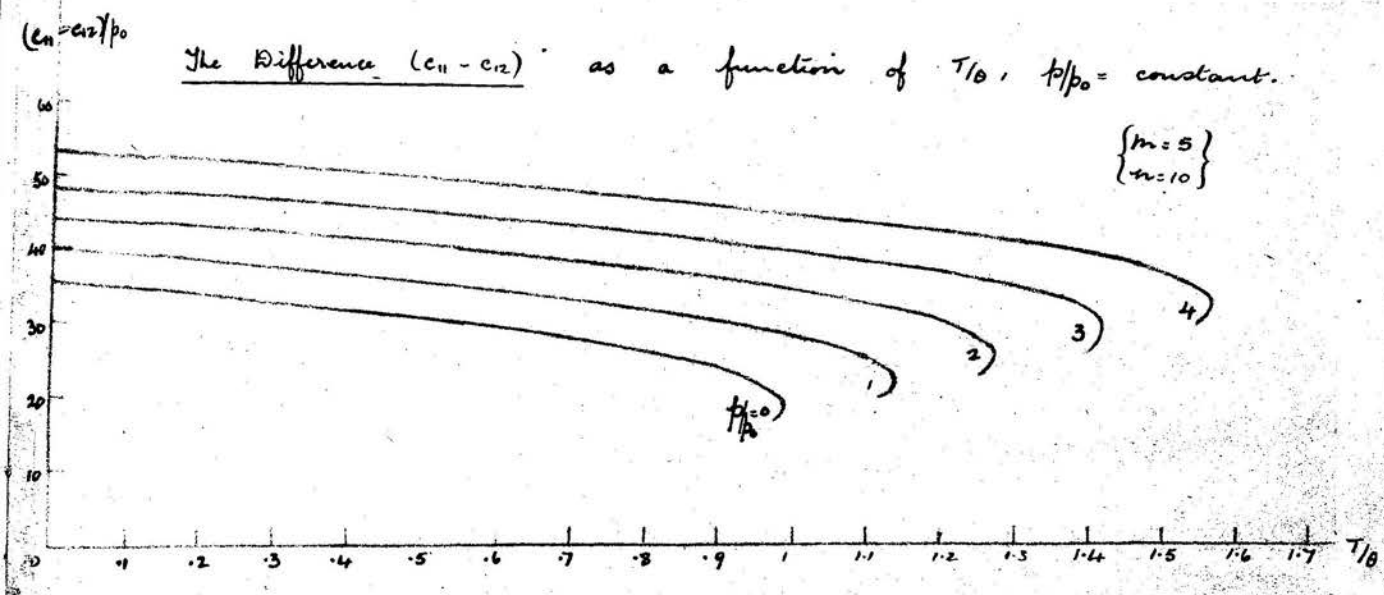
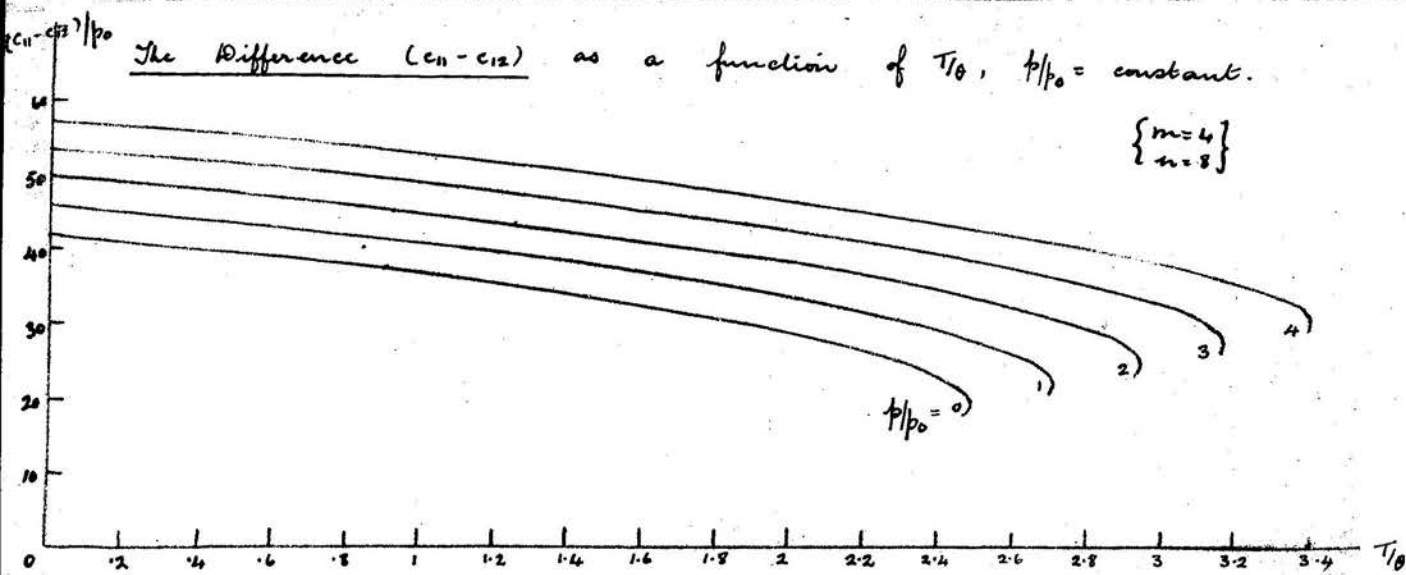
$$\begin{cases} m=6 \\ n=12 \end{cases}$$



The elasticity constant  $c_{nr}$  as a function of  $T/\theta$ ,  $f/p_0 = \text{constant}$ .

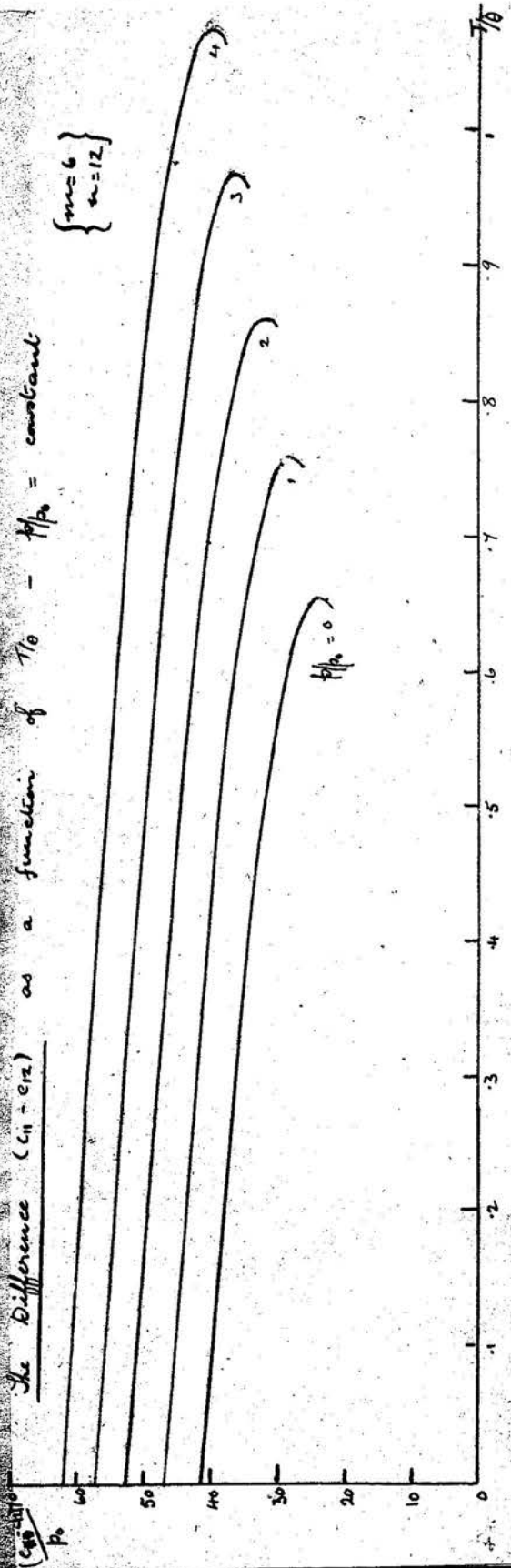
$$\begin{cases} m=6 \\ n=14 \end{cases}$$





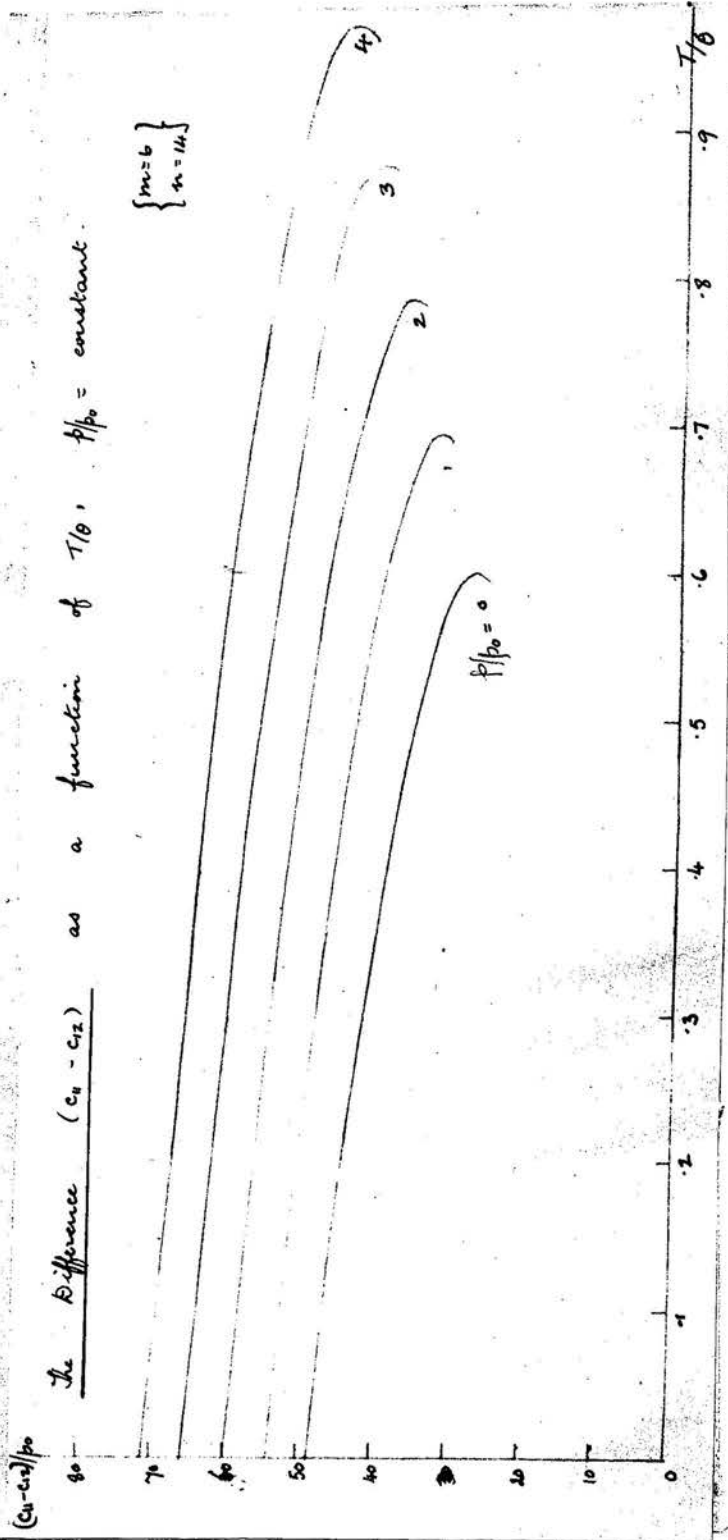
The Difference  $(c_{11} - c_{12})$  as a function of  $T/\theta$  -  $f/p_0 = \text{constant}$

$$\begin{cases} m=6 \\ n=12 \end{cases}$$



The Difference  $(c_{11} - c_{12})$  as a function of  $T/\theta$ ,  $f/p_0 = \text{constant}$ .

$$\begin{cases} m=6 \\ n=14 \end{cases}$$



### 8. Discussion of the Curves.

The curves all present the same general features.

The isobars show that  $\nu/\nu_0$  increases with  $T/\theta$ , at first linearly but later at a greater rate than  $T/\theta$  until the increase becomes infinite; the isotherms show that  $\nu/\nu_0$  decreases as  $p/p_0$  increases, at first at a greater rate than  $p/p_0$  but later at a decreasing rate until finally  $\nu/\nu_0$  decreases linearly with  $p/p_0$ . The other graphs showing the temperature dependence of the elastic constants for various hydrostatic pressures are all of the same type. All the elastic constants decrease linearly with  $T/\theta$  at first, but turn downwards eventually and reach the  $T/\theta$  axis at steep angles with the exception of the  $c_{12}$  curves which turn over after the  $T/\theta$  axis has been reached.

The graphs are in qualitative agreement with those shown in Born's "Thermodynamics of Crystals and Melting"(1) where the corresponding graphs are obtained

for the body-centred cubic lattice. Nevertheless there are some points of difference which cannot be passed over without comment. We note that the isobars though essentially the same in character for both types of lattice differ widely in the values of  $T_m/\theta$ . The graphs are drawn on almost identical scales, (Born's  $v_0$  is slightly larger than ours since his represents the equilibrium volume if first neighbours alone are taken into account, while ours is the actual equilibrium volume) but the difference in scales is not sufficient to account for the wide divergence in  $T_m/\theta$ . M. Bradburn has investigated this point (4) and found that the difference is due to the approximations made by Born who assumes in his paper that first and second neighbours alone act in the static potential and first neighbours only in the vibrational term. The difference in the curves depends mainly on the number of neighbours considered in the static potential. First neigh-

bours only is a good approximation in the thermic term but the static potential must be accurately determined.

We notice that our graphs show  $c_{11} > c_{12}$  whereas Born's give  $c_{12} > c_{11}$ . This difference is due to the difference in lattice type. The body-centred cubic lattice is an unstable configuration while the face-centred cubic lattice is stable. Therefore (Stability of Crystal Lattices I, (3.1),)  $c_{11} > c_{12}$  for the face-centred cubic lattice and  $c_{12} > c_{11}$  for the body-centred cubic lattice. As can be seen from (7.3) and (7.4) the curves of  $c_{12}$  and  $c_{44}$  coincide at  $T/\theta$ , but the marked similarity between them shown in Born's paper is not evident in our case. This may be due to the difference in the type of lattice or to the different approximations used in the two papers especially in the thermic term; for the relation  $c_{12} = c_{44}$  is true for a stable crystal in static equilibrium but in the case of a lattice in thermodynamical equilibrium the thermic term destroys the

equality.

In four out of the five different sets of exponents, we have chosen  $n=2m$  since Lennard-Jones found this assumption successful in the theory of the virial coefficient of gases (6) where he used  $m = 6$ . It is hoped that by comparing the above theoretical results with experimental ones it will be possible to determine which, if any, of the five sets of exponents is the most accurate.

$$(7.1) \quad p/p_0 = (1 + \xi)^{3/n-m} (A_1 + B_1 T/\theta)$$

which is the reduced equation of state contains three constants  $v_0$ ,  $p_0$  and  $\theta$  having the dimensions of volume, pressure and temperature respectively - in fact the reduced equation of state appears as a relation between the three dimensionless quantities  $v/v_0$ ,  $p/p_0$ ,  $T/\theta$  and is dependent on the values of  $m$  and  $n$ . The experimental equation of state is a relation between the quantities  $v$ ,  $p$  and  $T$ ,  $f_{\text{min}}(v, p, T) = 0$  say, which must be reduced

(56)

to the form  $F_{mn} (v/v_0, p/p_0, T/\theta) = 0$  before comparison with the theoretical curves is possible. The transformation is most easily effected by means of the equations

$$u = k\theta$$

and  $p_0 V_0 = \mathcal{R}\theta$  where  $\mathcal{R} = kN$

If the dissociation energy  $u$  and the volume at zero temperature  $V_0$  are found by observation,  $p_0$  and  $\theta$  can then be found. Thus the reduced equation of state

$$F_{mn} (v/v_0, p/p_0, T/\theta) = 0$$

can be derived and the experimental isobars and isotherms drawn and comparison made with the theoretical curves above. From them we can find the variation of the thermal expansion and the compressibility with temperature and pressure. Similarly, experimental curves of the elastic constants as functions of temperature and pressure can be reduced so that comparison with the theoretical curves is possible. Experimental curves of the elastic constants as functions of temperature have

actually been found by Hunter and Siegel (7) and they show qualitative agreement with the above.

The theoretical curves are drawn as far as the turning points and in some cases slightly beyond them, but it has been ascertained that the method of approximation used to derive the results given is only accurate up to the point of maximum  $T/\theta$ . After that the approximation gives no reliable results. For this reason the  $c_{44}$  curves cannot give any indication whether Born's hypothesis that  $c_{44} = 0$  is a criterion for melting gives accurate results.

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