



**LIQUID-SOLID TRANSITION IN CYCLOHEXANOL STUDIED  
BY NEUTRON TRANSMISSION**

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APPENDIX

FORTRAN IV C LEVEL 21

MAIN

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C     ALGEBRA TEORICO DA SECCAO DE CHOQUE TOTAL EM FUNCAO DA TEMPERATURA DE DEBYE
C     METODO DE KOTIARI-SINGWI
C     SIGMA=S/S/MINUSCULO (DEFINIDO PELA EQ 5) EM BARN
C     BK=CONSTANTE DE BOLTZMANN (EV/K)
C     HC=CONSTANTE DE PLANCK/2 PI (EV*5)
C     AMN=MASSA DO NEUTRON (AMU)
C     AMAT=MASSA DA AMOSTRA (AMU)
C     TEMP=TEMPERATURA DA AMOSTRA (K)
C     E=ENERGIA DO NEUTRON INCIDENTE (EV)
C     N=NUMERO DE PUNTOS A SEREM CALCULADOS
C     TEMPO(1)=TEMPERATURA DE DEBYE (K)
C     SIGMA(1)=SECCAO DE CHOQUE TOTAL (BARN)
C     ENTRADA DE DADOS
C     PRIMEIRO CARTAO- SIGMA BK HC AMN AMAT E TEMP-NO FORMATO 5E16 8
C     SEQUUNDO CARTAO- N NO FORMATO I3
C     A SEGUIR SAO LIDOS OS VALORES DA TEMPERATURA DE DEBYE NO FORMATO F8.1 (15
C     PIR CARTAO)
C     SAIDA DOS RESULTADOS
C     IMPRIME O VALOR DA TEMPERATURA DA AMOSTRA NO FORMATO F7.2 (K) E A SEGUIR
C     A TABELA COM O VALOR DA TEMPERATURA DE DEBYE (K) E A SECCAO DE CHOQUE EM
C     BARN
C     O PROGRAMA UTILIZA A SUBROTINA CALCO QUE CALCULA A INTEGRAL DE DEBYE *F(D)
C     METODO DE GAUSS-LE ENDRE
C     A SUBROTINA CALCO UTILIZA AS FUNCOES EFEL E VLEG
0001     DIMENSION SIGMA(100) Z(100) TEMPO(100),N(16)
0002     READ(5) SIGMA BK HC AMN AMAT E,TEMP
0003     READ(5) N
0004     READ(5) Z(TEMPO(1),1) N1
0005     WRITE(6) TEMP
0006     9 FORMAT(1X,12HTEMPERATURA= F7.2)
0007     WRITE(6) N1
0008     A=0
0009     J7 5 1-1,4
0010     Z(1)=TEMPO(1)/TEMP
0011     A=Z(1)
0012     CALL CALCO(A,R,NINT)
0013     F=Z5*HINT/(Z(1))**2
0014     TEMP(1)=TEMPO(1)
0015     ALFA=1 *HC**2 **Z(1)*TEMP
0016     SIGMA(1)=-4 *S/MO*AMN*(FA*E/HC**2 *AMAT)**3 *S/MO*AMN*HK*TEMP**4
** 5/(AMAT**3 *S)**4 *Z(1)-1 /Z(1)/54 )**E/(BK*TEMP)**5 /13 *Z(
**1)- 5*Z(1)/64 )+(E/BK*TEMP)**2 *17 /1+ *Z(1))-7 /24 *7 *Z(1)
**2/24 )+(E/BK*TEMP)**3 *3 /19 *Z(1)**3 /16 -Z(1)/36 )**S/MO**4
**5
0017     WRITE(6,6)SIGMA(1) TEMP(1)
0018     5 CONTINUE
0019     1 FORMAT(5F16.6)
0020     2 FORMAT(16F5.1)
0021     3 FORMAT(I3)
0022     4 FORMAT(11K,77,30X,16HSECCAO DE CHOQUE 19X,5HTEMP)
0023     6 FORMAT(3X,F8.2,15X,F5.1)
0024     STOP
0025     END

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# LIQUID SOLID TRANSITION IN CYCLOHEXANOL STUDIED BY NEUTRON TRANSMISSION\*

R. Fulfaro, L. A. Vinhas and  
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## ABSTRACT

The total cross section of the cyclohexanol was measured for neutrons with wavelength of  $\lambda = 6.13 \text{ \AA}$ , varying the sample temperature in a range that includes the temperature of melting. From these experimental results and by comparison with theoretical calculations based in the Placzek model it was possible to obtain the Debye temperatures for both states. These temperatures were used in the calculation of the disorder entropy variation near the fusion point.

## INTRODUCTION

Slow neutron transmission methods can be used to investigate physical properties such as freedom of motion of molecules and molecular groups in condensed states of matter<sup>(1, 6, 10, 11)</sup>. In this regard the plastic solids formed by globular molecules are of particular interest since their physical properties are intermediate between liquids and solids. These solids called organic globular compounds usually presents a very small entropy of melting<sup>(11)</sup> ( $< 5 \text{ cal/mole K}$ ) the term 'globular' is applied to them because the molecules involved possess a spherical symmetry about the center of mass as a result either of the distribution of the atoms or of the rotation of the molecule about its center. The solid formed by such a molecule when it freezes from the liquid state displays rather unusual physical properties that have been explained as resulting from practically unhindered rotation of the molecules about their lattice positions. The name 'plastic crystals' for the solids arises because among these properties one find the ease of plastic flow under only moderate pressures. In every case it is observed a transition at some definite temperature below the freezing point from the plastic solid form to a crystalline form that behaves like an ordinary solid<sup>(4)</sup>. In the rotational form stable at temperatures just below the freezing point the crystal structure is usually of the cubic family.

In the present work the cyclohexanol was selected for the studies because its solids state crystallizes in a cubic system and for its properties as a globular substance. The liquid-solid transition in cyclohexanol was investigated to obtain informations about the transition itself and also to obtain informations about the cyclohexanol in the liquid state. Atomic or molecular vibrational motion is one of the physical parameters whose changes play an important part in this transition. It can be successfully investigated by means of slow neutron transmission methods<sup>(10)</sup>. The total cross section measurements as a function of temperature of the sample in a range near the melting point allows a clear observation on changes in the molecular dynamics at state transition. In this paper from the slow neutron transmission measurements carried out on solid and liquid cyclohexanol near the melting point ( $25.5^\circ\text{C}$ ), it was possible to determine the Debye temperature for the liquid cyclohexanol and evaluate a disorder entropy at the melting point transition.

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## EXPERIMENTAL

Neutron transmission measurements in the temperature interval 3°C to 35°C were performed with neutrons of 6.13 Å wavelength selected using a single crystal spectrometer<sup>(3)</sup> at the IEA 2 MW light water reactor. A magnetite crystal monochromator and an appropriate choice of polycrystalline filters of Be and Pb were used to select only neutrons from first order Bragg's reflections; the elimination of higher order contamination was checked by total cross sections measurements of gold and water chosen as standard. At 6.13 Å the intensity was enough to have in one day a series of measurements covering the whole temperature interval of interest.

The sample was a commercial cyclohexanol (J. T. Baker Chemical) with purity better than 99%. It was in a aluminium holder with 0.253 cm internal spacing. The sample cooling was performed by circulation of cold air with variable flow in a isolated volume surrounding the sample; the temperatures were controlled within 2°C by thermocouples attached to the aluminium holder. The total neutron cross section is given by  $\sigma_T = \ln(T^{-1})/n$  where T is the measured neutron transmission and n is the number of molecules/cm<sup>2</sup> obtained from the sample thickness and bulk density. The melting point for cyclohexanol is 25.5°C and the curve of density vs. temperature is shown in figure 1. The density for solid cyclohexanol was calculated using the formula obtained from ultrasonic measurements<sup>(4)</sup> normalized for the experimental value  $\rho = 9624 \text{ g/cm}^3$  at 20°C<sup>(12)</sup> for the liquid cyclohexanol the density was obtained through the formula given in the International Critical Tables<sup>(8)</sup>. Also the experimental values given in the literature<sup>(13,8)</sup> is shown in figure 1.

Twenty independent series of independent measurements of neutron transmission were taken by cooling and/or heating the sample. Results obtained for  $\ln T^{-1}$  in function of temperature are displayed in figure 2 as average over series of cooling and heating. The indicated errors are obtained by propagation of the statistical errors of the several points measured at each temperature. Results indicate on cooling an step at 22.5°C the temperature difference from the tabulated melting point (25.5°C) is probably due to a small water contamination. On heating the variation occurred near 15°C. The temperature difference from heating and cooling cannot be ascribed to an error in the temperature measurement and may be due to a premelting phenomenon and partially due to further water contamination in the cooling process<sup>(11)</sup>.

The values of  $\sigma_T$  as a function of temperature in the interval 3°C to 35°C are shown in figure 3 for cooling and heating series. The densities were chosen from figure 1 considering the sample as being solid only below 22.5°C for the cooling and only below 15°C for the heating case. A mean value of  $\sigma_T = 1103$  barns can be ascribed for the cyclohexanol in the solid state and other mean value of  $\sigma_T = 1135$  barns for the liquid state.

## CALCULATION OF TOTAL CROSS SECTION VS DEBYE TEMPERATURE

The Debye approximation is also valid for molecular crystals when in computing thermodynamic functions only the lattice vibrations are considered. The cyclohexanol has a f.c.c. lattice<sup>(4)</sup> and belongs to the globular molecule class; then it can be likened to a monoatomic crystal whose atoms are changed in more complex units, i.e. molecules<sup>(10)</sup>.

For cubic monoatomic polycrystals it is possible to compute the total scattering cross sections using the Debye temperature as a parameter<sup>(5)</sup>. In the Placzek expansion the total scattering cross section is the sum of individual cross sections for 0, 1, 2, ... phonon processes, i.e.

$$\sigma_s = \sum_{\ell=0}^{\infty} \sigma_{\ell} \quad (1)$$

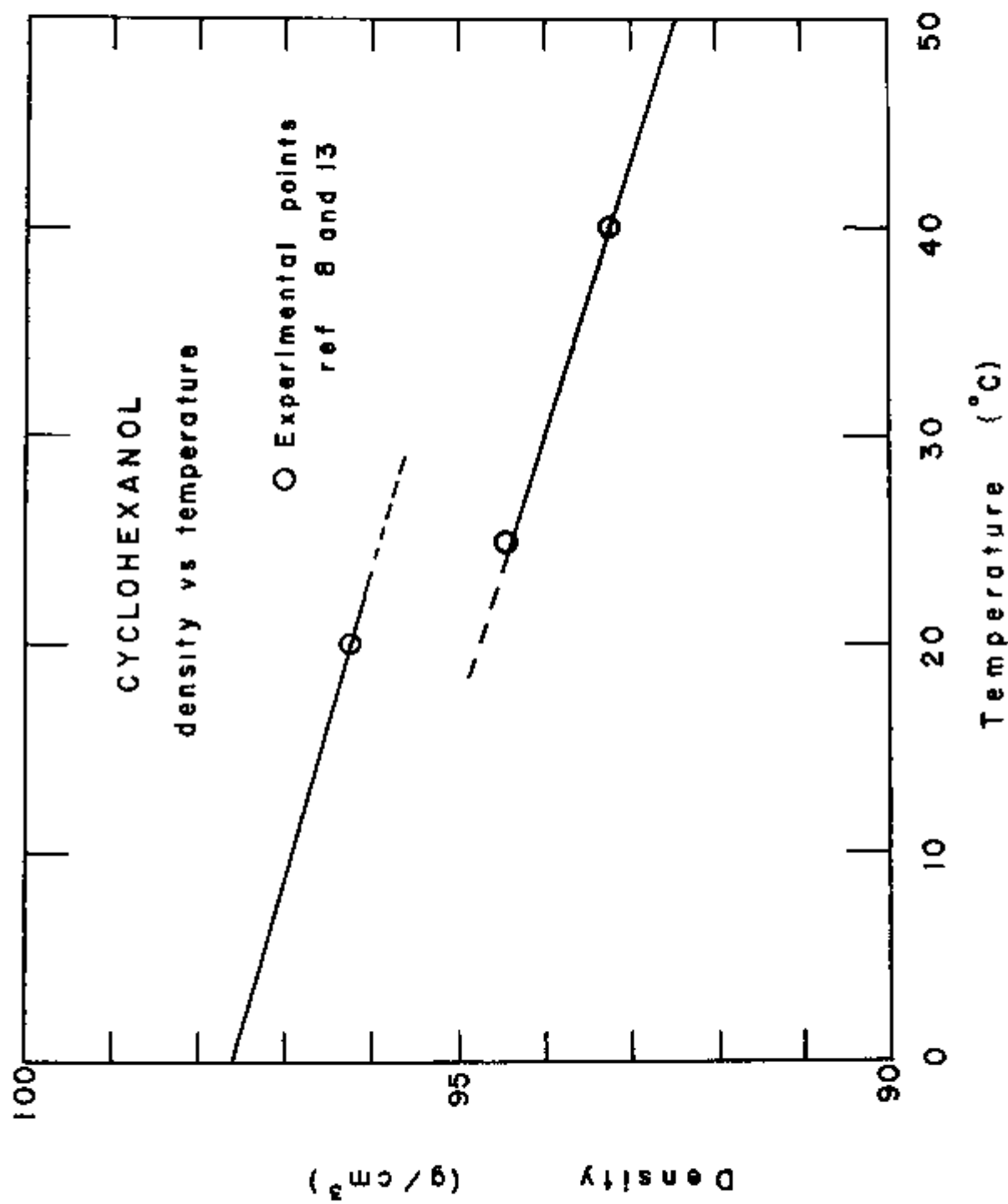


Figure 1 — Density of cyclohexanol as a function of temperature.



where  $\sigma_{\ell}$  is the total incoherent cross section in the Debye approximation generalized to the case of  $\ell$  phonons involved in the scattering process. In the case of heavy nuclei the Debye-Waller factor occurring in  $\sigma_{\ell}$  is expanded in powers of  $1/M$ . Collecting terms of same power in  $M^{-1}$  one can write

$$\sigma_{\ell} = \sum_{n=0} \frac{\sigma_{\ell}^{(n)}}{M^n} \quad (2)$$

with

$$\sigma_{\ell}^{(n)} = \sum_{\ell=0} \sigma_{\ell}^{(n)} \quad (3)$$

Alternating terms in equation (3) are of opposite sign cancel the contribution of each others. Because of this the series of equation (2) converges very rapidly. For sufficiently large  $M$  it is not necessary to go beyond the first inverse power of  $M$ .

Considering the complete expression<sup>(5)</sup> for  $\sigma_{\ell}^{(n)}$  and using the equations (2) and (3) one can write

$$\sigma_{\ell} = \sigma^{(0)} + \frac{\sigma^{(1)}}{M} \quad (4)$$

with

$$\sigma^{(0)} = \sigma_0^{(0)} = S + s \quad (5)$$

that is the sum of coherent and incoherent scattering cross sections of hydrogen atoms in the cyclohexanol molecule; where  $S = 4\pi a^2$  and  $s = 4\pi(a^2 - \bar{x}^2)$  being  $a$  the scattering length.

For the limiting case  $E \ll k_0 \theta_D$  and  $T \gg \theta_D$  some approximations can be performed. For  $M > 10$  amu it is not necessary to consider  $\sigma^{(2)}$  since its contribution to total cross section would not amount more than one per cent.

For the case  $T \gg \theta_D$  the  $\sigma^{(1)}$  is given by<sup>(6)</sup>

$$\begin{aligned} \sigma^{(1)} = & -2(S+s) 2 \frac{m_0}{4f_1^2} \alpha E + \frac{3(S+s)m_0}{\sqrt{E}} (k_0 \theta_D)^{1/2} \left[ \left( -\frac{2}{5} \frac{T}{\theta_D} - \frac{1}{7} + \frac{1}{54} \frac{\theta_D}{T} \right) + \right. \\ & + \frac{E}{k_0 \theta_D} \left( \frac{5}{3} \frac{T}{\theta_D} - \frac{1}{2} + \frac{5}{84} \frac{\theta_D}{T} \right) + \frac{E^2}{k_0^2 \theta_D^2} \left( \frac{7}{4} \frac{T}{\theta_D} - \frac{7}{24} + \frac{7}{240} \frac{\theta_D}{T} \right) + \frac{E^3}{k_0^3 \theta_D^3} \left( \frac{3}{8} \frac{T}{\theta_D} + \right. \\ & \left. \left. + \frac{3}{16} - \frac{1}{96} \frac{\theta_D}{T} \right) \right] \end{aligned} \quad (6)$$

The theoretical scattering cross section  $\sigma_{\ell}$  is calculated from equations (4), (5) and (6). Here  $M$  is the molecular mass,  $m_0$  is the neutron mass and  $E$  is the neutron energy.

where

$$\alpha = \frac{34\pi^2}{k_0 \theta_D} \text{ with } F = \frac{1}{4} + \frac{T}{\theta_D} \phi\left(\frac{\theta_D}{T}\right) \quad \phi(z) = \frac{1}{z} \int_0^z \frac{x}{e^x - 1} dx \quad (7)$$

$\theta_D$  is the Debye temperature,  $T$  is the absolute temperature  $h = h/2\pi$  and  $k_B$  are the Planck and Boltzmann constants respectively. In the present work for the fixed  $\lambda = 6.13 \text{ \AA}$  corresponds  $E = 0.02176 \text{ eV}$ . The temperature interval for solid cyclohexanol was  $273^\circ\text{K} - 290^\circ\text{K}$   $M = 100.16$  amu for the cyclohexanol ( $\text{C}_6\text{H}_{12}\text{O}$ ) and having twelve hydrogen atoms result  $S + s = 978$  barns. The total cross section  $\sigma_T = \sigma_s + \sigma_a$  where  $\sigma_s$  is computed according to formula(4) and  $\sigma_a$  is the absorption cross section. In  $\sigma_s$  are included the contribution to  $\sigma_T$  of all atoms different of hydrogen presents in the cyclohexanol molecule for the fixed neutron energy  $E$  this total contribution is equal to 46.5 barns.

The theoretical  $\sigma_T(T)$  was calculated using the mean tabulated value  $\theta_D \sim 60^\circ\text{K}$  as a parameter for all the temperature interval for solid cyclohexanol the maximum variation of the calculated values of  $\sigma_T(T)$  was 0.2%. Therefore the  $\sigma_T(\theta_D)$  was calculated as a function of Debye temperature  $\theta_D$  in the interval  $0^\circ\text{K} - 100^\circ\text{K}$  using the fixed value  $T = 283^\circ\text{K}$  as a parameter. The range of variation for  $\theta_D$  was chosen according to reference<sup>(4)</sup>, the resulting plot of  $\sigma_T$  versus  $\theta_D$  is displayed in figure 4. To the experimental mean value  $\sigma_T = 1.103$  barns obtained for the solid cyclohexanol (figure 3) corresponds two values of Debye temperatures in the figure 4  $\theta_s = 23^\circ\text{K}$  and  $\theta_L = 65^\circ\text{K}$  this last value agree with the values usually tabulated<sup>(4)</sup>. From the same figure 4 the experimental mean value  $\sigma_T = 1.135$  barns obtained for the liquid cyclohexanol (figure 3) near the break leads to a Debye temperature value  $\theta_L = 20^\circ\text{K}$  for the liquid cyclohexanol.

#### CALCULATION OF A DISORDER ENTROPY AT THE MELTING POINT

The melting of a crystal is accompanied by an abrupt change in internal energy, molar volume and entropy. When the crystal is that of a molecular compound, contributions to the increase of internal energy and entropy arise from change in the character of the vibrations among the unit molecules, disorder of the structure, change in the internal vibrations within each molecule and acquisition of rotational degrees of freedom. A simpler case to treat is relative to crystals made up of atoms that possess an entropy of melting with only the two first mentioned contributions since the atoms do not have internal degrees of freedom. Another interesting case where there is no change in the internal coordinates during melting is that of the organic and inorganic crystals whose molecules possess free rotation in three dimensions in the crystalline state<sup>(8)</sup>.

At the melting there is a discontinuous change in properties accompanying the discontinuous change in volume. A volume expansion in a crystal and in a liquid is accompanied by an increase in entropy chiefly due to the change in the vibrational degrees of freedom of the assembly while the configuration remains essentially unchanged. On the other hand at the crystal-liquid transition there is in addition an entropy change associated with the change in the structure since the liquid lacks the long range regularity of the crystal<sup>(9)</sup>. It is possible to compute the change in entropy associated with the volume change together with the change in vibrational character  $\Delta S_v$  by subtracting this entropy change from the experimental entropy of fusion  $\Delta S_f$  one can obtain the entropy change associated with the disordering melting  $\Delta S_D$ <sup>(8)</sup>.

As a consequence of the foregoing arguments one can write

$$\Delta S_D = \Delta S_f - \Delta S_v \quad (8)$$

#### THE $\Delta S_v$ CALCULATION

From the statistical definition of entropy and using some approximations one can write the expression on entropy for an Einstein solid<sup>(2)</sup>

$$S = k [ (q + 3N) \ln (q + 3N) - q \ln q - 3N \ln 3N ] \quad (9)$$

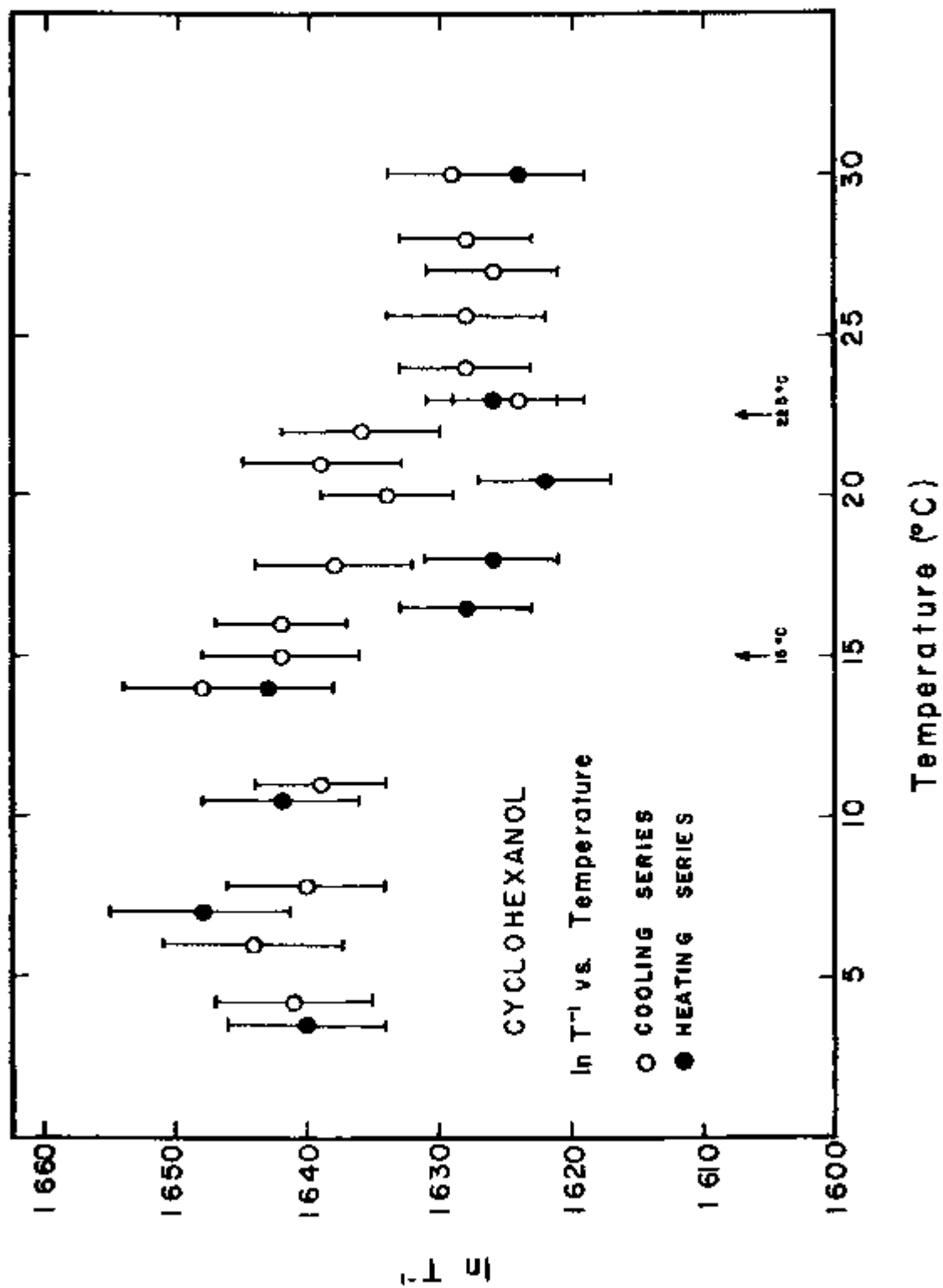


Figure 2 — Results obtained for  $\ln T^{-1}$  for cyclohexanol in function of temperature averages over several series of cooling and heating

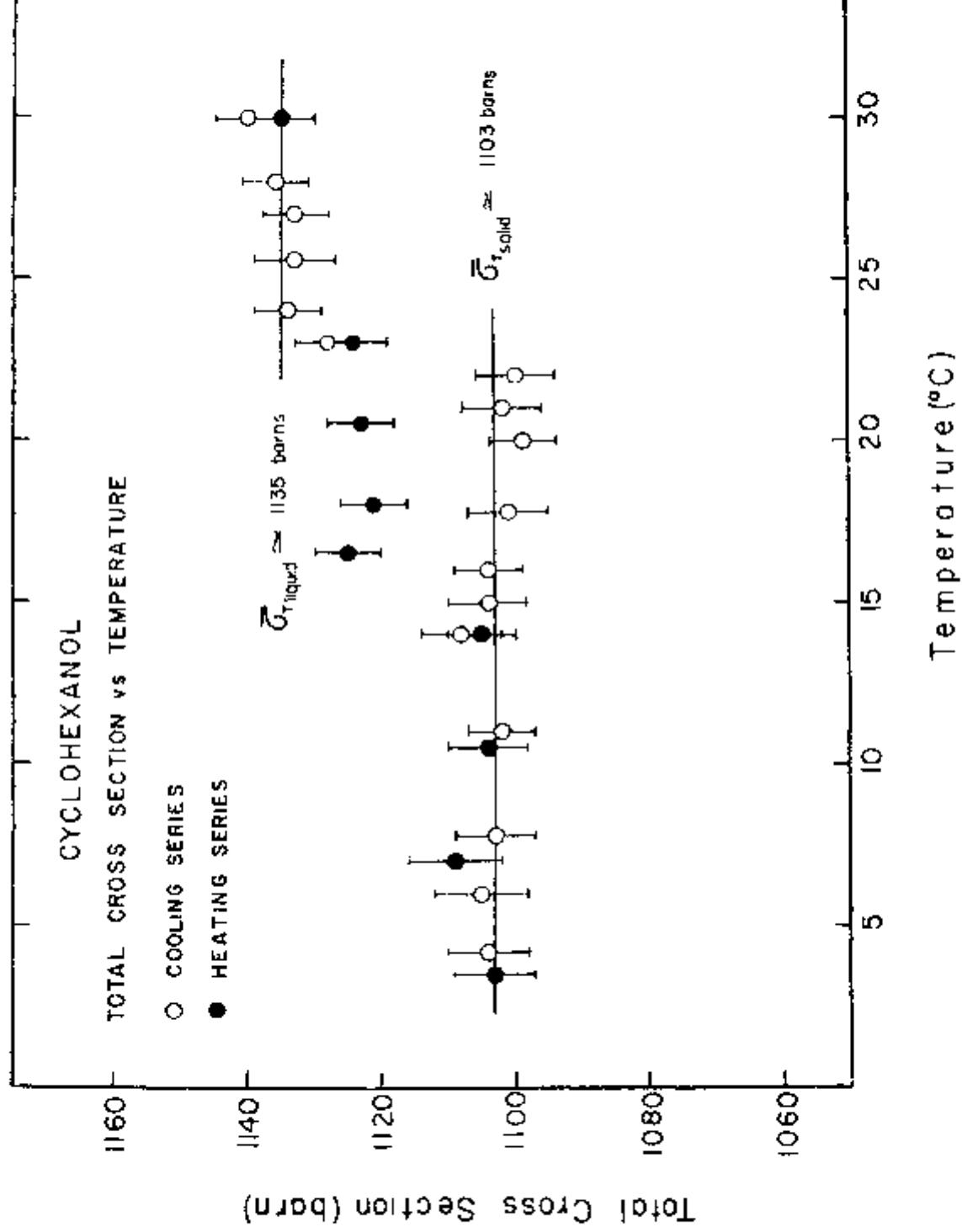


Figure 3 — Values of  $\sigma_T$  as a function of temperature. The mean values for cyclohexanol in the solid and liquid state are indicated

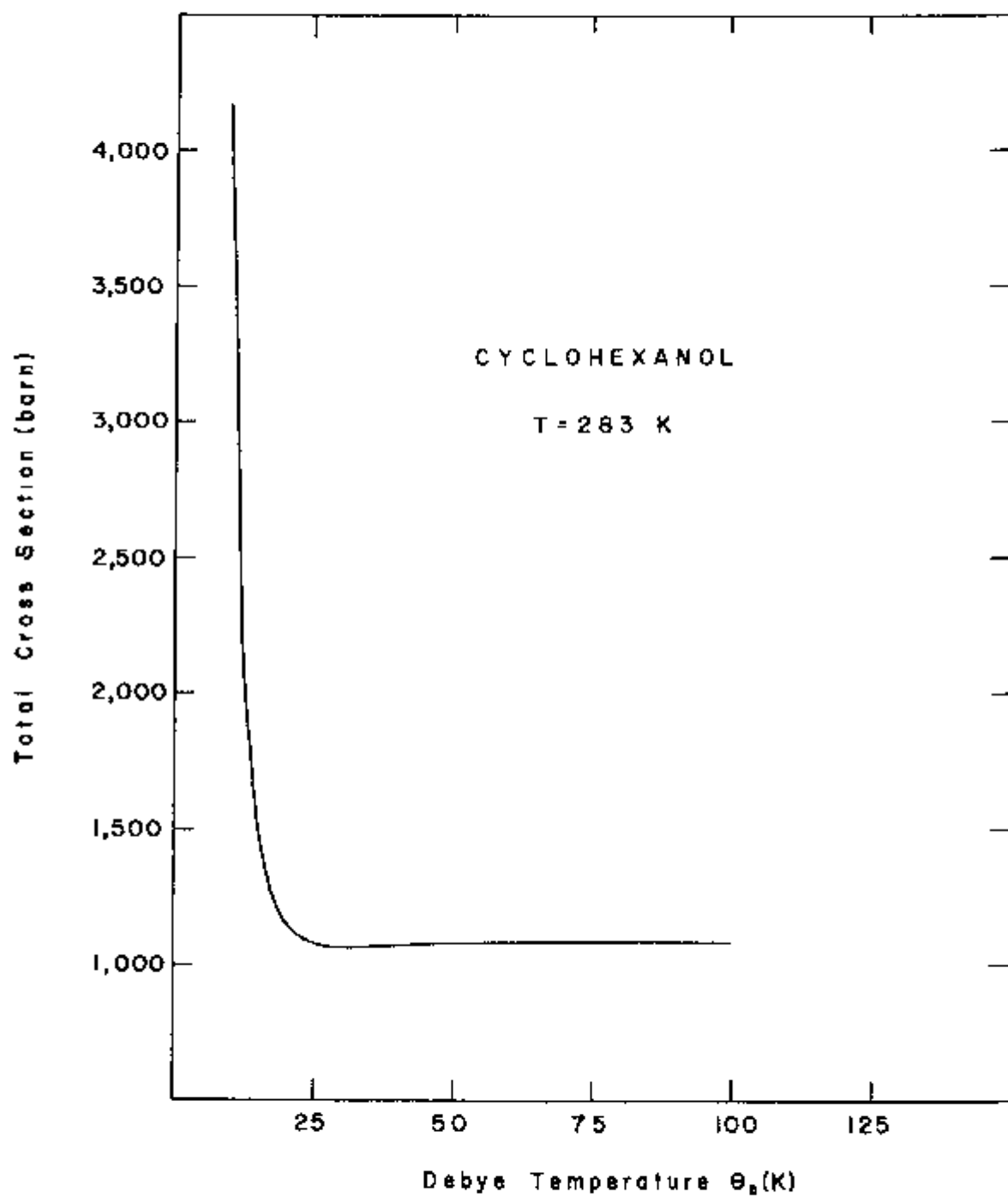


Figure 4 — Total cross section as a function of Debye temperature for  $T = 283$  K calculated using the computer program in Appendix

where  $N$  is the number of atoms (or molecule)  $q$  is the number of energy quanta or phonons of magnitude  $h\nu$  and  $k$  is the Boltzmann constant

The thermodynamic function free energy  $F$  is given by  $F = U - TS$  where  $U = qh\nu$  is the amount of energy raised above the zero point energy after the absorption of  $q$  vibrational quanta by the solid. So,  $F$  can be written as

$$F = qh\nu - kT [(q + 3N) \ln (q + 3N) - q \ln q - 3N \ln 3N] \quad (10)$$

The number of quanta  $q$  is determined regarding that no quanta at all would be absorbed if the solid were able to submit completely to its striving towards a minimum value of energy. On the other hand if it were governed completely by the striving towards maximum entropy the number of quanta absorbed would continue to increase<sup>(2)</sup>. The equilibrium state lies at the point where the free energy is a minimum thus where

$$\frac{dF(q)}{dq} = 0 \quad (11)$$

Combining equations (10) and (11) follows

$$h\nu - kT \ln \frac{q + 3N}{q} = 0$$

or

$$q = \frac{3N}{e^{h\nu/kT} - 1}$$

Rearranging the eq (9)

$$S = k \left[ q \ln \left( \frac{q + 3N}{q} \right) + 3N \ln \left( \frac{q + 3N}{3N} \right) \right] \quad (12)$$

or

$$S = 3Nk \left[ \frac{(h\nu/kT)}{e^{h\nu/kT} - 1} + \ln(1 - e^{-h\nu/kT})^{-1} \right] \quad (13)$$

Since the Debye temperatures do not differ greatly from the Einstein temperatures<sup>(2)</sup> the former defined for a solid as  $\theta_s = \frac{h\nu_s}{k}$  one can put the equation (13) for the entropy of an Einstein solid in the form

$$S_{sol} = 3Nk \left[ \frac{\theta_s/T}{e^{\theta_s/T} - 1} + \ln(1 - e^{-\theta_s/T})^{-1} \right] \quad (14)$$

The main interest is to determine  $\Delta S_v$  in the melting temperature  $T_m$ . In a solid the atoms vibrate about mean positions which are fixed but in a liquid at temperatures near the melting point it is generally recognized that the atoms vibrate about mean positions which though not fixed move slowly compared with the velocity with which the atoms vibrate. Then one can assume the liquid phase to be quasi-crystalline with weaker binding forces i.e. with a Debye temperature  $\theta_L$  for liquid lower than in the solid state  $\theta_s$ <sup>(7)</sup>. The entropy for the liquid phase  $S_{liq}$  can be calculated using the same equation (14) but now introducing the  $\theta_L$ .

The  $\Delta S_v = S_{liq} - S_{sol}$  is given by

$$\Delta S_v = 3Nk \left[ \frac{\theta_L/T_m}{e^{\theta_L/T_m} - 1} - \frac{\theta_s/T_m}{e^{\theta_s/T_m} - 1} + \ln \frac{1 - e^{-\theta_s/T_m}}{1 - e^{-\theta_L/T_m}} \right] \quad (15)$$

### THE $\Delta S_D$ CALCULATION

According with equation (8) to obtain  $\Delta S_D$  it is necessary to have the experimental entropy of fusion defined as<sup>(12)</sup>

$$\Delta S_F = \frac{\Delta H_F}{T_m} \quad (16)$$

where  $\Delta H_F$  is the gram atomic heat of fusion

For the cyclohexanol where  $T_m = 298.5^\circ\text{K}$  and  $\Delta H_F = LM = 419.67 \text{ cal/mole}$   $\Delta S_F = 1.408 \text{ cal/mole}^\circ\text{K}$ . Here  $L$  is the latent heat of fusion equal to  $4.19 \text{ cal/gram}$  and  $M$  is the cyclohexanol molecular mass

The equation (8) for the disorder entropy at the melting point can be rewritten in the form

$$\Delta S_D = \frac{H_F}{T_m} - 3Nk \left[ \frac{\theta_L/T_m}{e^{\theta_L/T_m} - 1} - \frac{\theta_s/T_m}{e^{\theta_s/T_m} - 1} + \ln \frac{1 - e^{-\theta_s/T_m}}{1 - e^{-\theta_L/T_m}} \right] \quad (17)$$

where  $Nk = R = 1.987 \text{ cal/mole}^\circ\text{K}$  is the Gas constant

The experimental values  $\theta_L$  and  $\theta_s$  obtained from the total cross sections measurements in cyclohexanol were used to perform the calculation of the eq (17)

The first set of experimental Debye temperatures  $\theta_s = 65^\circ\text{K}$  and  $\theta_L = 20^\circ\text{K}$  for solid and liquid cyclohexanol respectively gives a computed  $\Delta S_v = 7.015 \text{ cal/mole}^\circ\text{K}$  this value is larger than experimental entropy of fusion  $\Delta S_F$ . Although the value  $\theta_s = 65^\circ\text{K}$  is within the range of values usually found for the solid cyclohexanol<sup>(4)</sup> the employment of this  $\theta_s$  in the calculations lead to a negative value of  $\Delta S_D$ . Since the condition  $\Delta S_v < \Delta S_F$  must be satisfied<sup>(9)</sup> the  $\Delta S_v$  was calculated for the second set of Debye temperatures  $\theta_s = 23^\circ\text{K}$  and  $\theta_L = 20^\circ\text{K}$  obtaining  $\Delta S_v = 833 \text{ cal/mole}^\circ\text{K}$  and the value  $\Delta S_D = 573 \text{ cal/mole}^\circ\text{K}$

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## RESUMO

Foi medida a seção de choque total do ciclohexanol para neutrons com comprimento de onda fixo de  $\lambda = 6.13 \text{ \AA}$ , variando-se a temperatura da amostra no intervalo que inclui a temperatura da mudança de estado. A partir destes resultados experimentais e comparando com cálculos teóricos baseados no modelo de Placzek, foram obtidos valores das temperaturas de Debye do ciclohexanol para ambos os estados. Estas temperaturas foram utilizadas no cálculo da variação de entropia de desordem próximo ao ponto de fusão.

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