THE LATENT HEAT OF FUSION

OF

CIS AND TRANS

DECAHYDRONAPHTHALENE

by

Robert Gordon Pyle, B.A.Sc.

A thesis submitted in partial fulfilment of

the requirements for the degree of

MASTER OF APPLIED SCIENCE

in the Department

of

CHEMICAL ENGINEERING

THE UNIVERSITY OF BRITISH COLUMBIA

May, 1947

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INTRODUCTION

The object of this research was, in general, to obtain further scientific data concerning the two isomers, cis and trans decahydronaphthalene. More specifically, it was to determine the Latent Heat of fusion of the two isomers over the range of temperature from the respective freezing points of the pure isomers to the eutectic point of their solutions. It, furthermore, produced an opportunity to study the mesomorphic state or, as it is more commonly called, the "liquid crystal" behavior of the isomers.

METHOD OF DETERMINING THE LATENT HEATS

The method used in determining the latent heats was essentially that outlined by J. H. Hildebrand, Ph. D. in his text, " Solubilities of Non-electrolytes." This method depends upon the fact that the two substances under consideration, must obey Raoult's law. Since it is the determination of the latent heats of two isomers which are mutually soluable in all proportions, it can, within reason, be assumed they will be sufficiently alike to obey Raoult's law. Therefore, assuming the law does hold, the partial vapor pressure of

the solute may be defined by the equation as follows

$$p = p^0 N$$

where
p = the partial pressure of the solute

p^0 = the pressure of the solute in its pure liquid
form which has been supercooled

N = the mol fraction of the solute

Since the solid is the more stable form below the melting point of a substance, p^0 must be greater than p^S, the vapor pressure of the solid at the same temperature, and we can have equilibrium only when the partial pressure of the solute in the liquid phase is reduced by the pressure of the solvent until it is numerically equal to that of the solid. When this equilibrium has been reached, we may equate the partial pressure of the solute, p, to be equal to the vapor pressure of the solid, p^S.

These relationships may be shown by Figure 1. The vapor pressure curves of the pure liquid and solid forms are represented along the temperature axis and will intersect at the melting point, T_m. The pressure-composition relations are shown at the three temperatures, T, T' and T_m. At T and T', since the vapor pressure of the solid, p^S, is less than that of the pure liquid, p^0, it is required in order to have equilibruim that p^0 be reduced to $p = p^S$ by dilution with a solvent to the mol fractions N and N' respectively. The variation of

solubility with temperature is shown on the basal plane of the figure, having the values N, N' and 1 at the temperatures T, T' and T_m respectively.
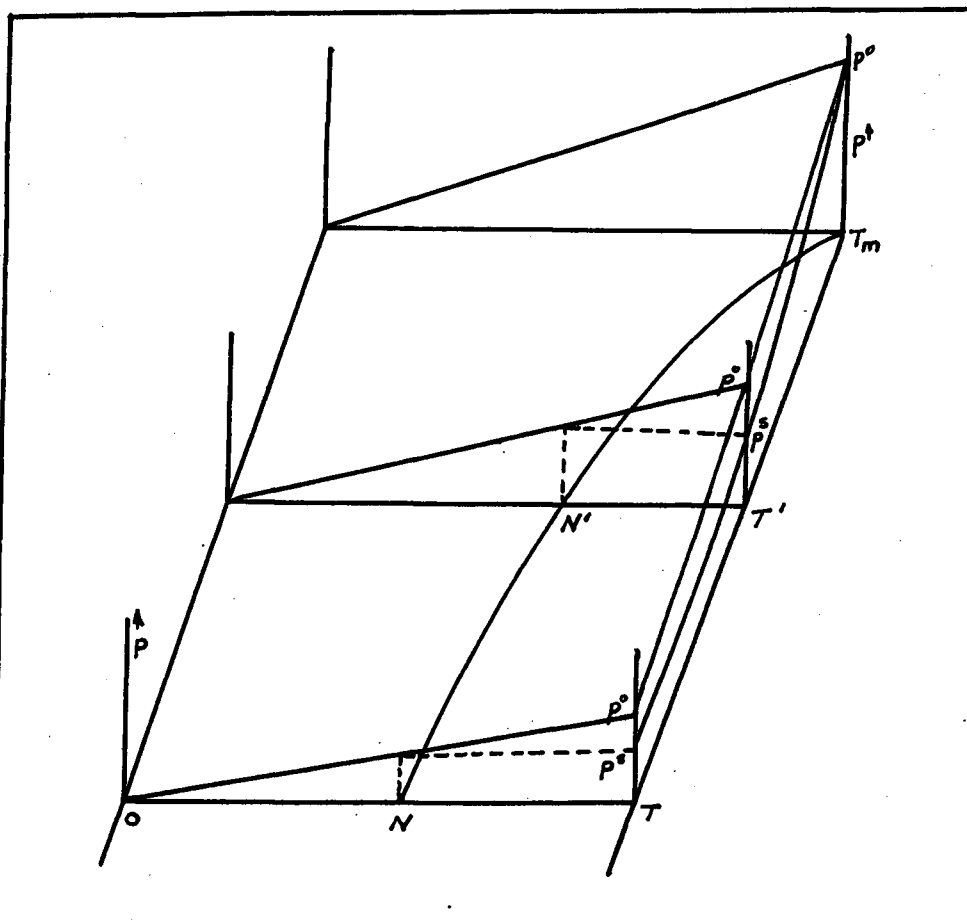

Figure 1.　Relationship between vapor pressure, temperature and mol fraction.

The solubility, N, at any temperature can be calculated from the ratio p^S / p^0 .

By the use of the Clapeyron-Clausius equation, the relationship between the vapor pressures, p^s and p^o, may be found. Since the volume of the liquid is small in comparison to the vapor, it is neglected and the Clapeyron-Clausius equation becomes

$$\frac{d\ p^o}{d\ T} = \frac{L_e}{T\ V_v} \qquad\qquad (\ 1\ )$$

where L_e = latent heat of evaporation

V_v = volume of the vapor

Furthermore, in regions well below the critical temperature, the vapor pressure is relatively small and we may assume that the ideal gas laws may be applied. Since the volume of the vapor is still large in comparison to the volume of the liquid, the equation becomes

$$\frac{d\ p^o}{d\ T} = \frac{L_e\ p^o}{R\ T^2} \qquad\qquad (\ 2\ )$$

By simplication, the equation becomes

$$\frac{d\ \ln\ p^o}{d\ T} = \frac{L_e}{R\ T^2} \qquad\qquad (\ 3\ )$$

The vapor pressure of the solid may also be found by a similar method. The volume of the solid may be neglected and since the vapor pressure will be less than that of the liquid,

we may assume that the ideal gas laws will be, in this case, even more accurate. Therefore, for the vapor pressure of the solid, we have the following equation

$$\frac{d \ln p^S}{d T} = \frac{L_S}{R T^2} \qquad (4)$$

where L_S = the latent heat of sublimation.

The latent heat of fusion, L_f, is related to the latent heats of vaporization and sublimation by the first law of thermodynamics. That is

$$L_S = L_f + L_e \qquad (5)$$

since the same amount of heat must be absorbed in the conversion of a given quantity of solid directly to the vapor (L_S) as it would for the change in two stages, first from the solid to the liquid (L_f) and then from the liquid to vapour(L_e).

The latent heat of fusion can be found by subtracting equation (3) from equation (4).

$$\frac{d \ln p^S}{d T} - \frac{d \ln p^0}{d T} = \frac{L_S - L_e}{R T^2}$$

$$\frac{d \ln (p^S/p^0)}{d T} = \frac{L_f}{R T^2} \qquad (6)$$

Since the relationship p^S/p^0 is equal to the mol fraction

if Raoult's law is appicable, the equation then becomes

$$\frac{d \ln x}{d T} = \frac{L_f}{R T^2} \qquad (7)$$

Although I do not agree with the following derivation, it is entered here in order that it may be discussed later with regard to the experimental results.

If the difference in the specific heats of the solid and liquid at the freezing point is small, the latent heat of fusion can be assumed independant of the temperature and equation (7) integrated.

$$\ln x = - \frac{L_f}{R T} + I$$

The constant of integration can be evaluated since at the melting point, $T = T_m$, and x becomes unity.

$$I = \frac{L_f}{R T_m}$$

Therefore,

$$\ln x = - \frac{L_f}{R T} + \frac{L_f}{R T_m}$$

$$\ln x = \frac{L_f (T - T_m)}{R T T_m}$$

Thus,

$$L_f = \frac{R T T_m \ln x}{T - T_m} \qquad (8)$$

If, however, the more exact value of the latent heat is required, the change of latent heat of fusion with temperature may be accounted for by using the differences between the molal specific heats of the liquid and solid forms, c^0 and c^S respectively. This influence of temperature on the latent heat of fusion can be expressed by Kirchhoff's equation as follows;

$$\frac{d\,(L_0 - L_S)}{d\,T} = \frac{d\,L_f}{d\,T} = c^0 - c^S \qquad (9)$$

Therefore,

$$L_m^0 - L_m^S - (L^0 - L^S) = (c^0 - c^S)(T_m - T) \qquad (10)$$

where the subscripts, m, refer to the values at the melting point.

Substituting the value of L_f from equation (10) into equation (7) and integrating

$$\frac{d\,\ln x}{d\,T} = \frac{L_f}{R\,T^2} = \frac{(L_m^0 - L_m^S) - (c^0 - c^S)(T_m - T)}{R\,T^2}$$

$$\int_{1}^{x} d\,\ln x = (L_m^0 - L_m^S)\int_{T_m}^{T} \frac{dT}{R\,T^2} - \int_{T_m}^{T} \frac{(c^0 - c^S)(T_m - T)\,dT}{R\,T^2}$$

$$\ln x = -\frac{(L_m^0 - L_m^S)(T_m - T)}{R\quad TT_m} + \frac{(c^0 - c^S)(T_m - T)}{R\quad T}$$

$$-\frac{(c^0 - c^S)}{R}\,\ln\frac{T_m}{T} \qquad (11)$$

Equation (8) and the more exact equation (11) vary only slightly and are usually within two or three percent of each other, with equation (11) giving a lower value for the latent heat of fusion. However, the results of this work indicate that the latent heat varies considerably with temperature, much more than be accounted for by the difference in the molal specific heats, and therefore, equation (7) which does not assume that the latent heats should be constant, has been used for the calculations.

APPARATUS   AND   EXPERIMENTAL   PROCEDURE

The latent heats of fusion of cis and trans decahydro-naphthalene were determined by first accurately measuring the depression of the freezing points of various mixtures of the two isomers. The mixtures of decalin were weighed in a small bulb which was then sealed off from the atmosphere and placed in an acetone bath. The acetone had been previously dried with calcium chloride to remove any water which may be present and would tend to freeze out on the glass bulb and obscure the visible signs of crystal growth. The acetone bath was cooled by solid CO_2 until the desired temperature was reached, with a horizontal stirrer mixing the acetone to maintain the temperature constant throughout. The temperature was measured and controlled by the use of a platinum resistance thermometer. The thermometer gave control of the temperature in that it was measuring the temperature at all times during an experimental

run and the galvanometer, in series with it, recorded immed-
iately any variation of temperature of magnitude of .005° C
and it could be corrected immediately.

The procedure during a run was as follows: the cis
and trans decalin were weighed very accurately and then run
through a small funnel into a glass bulb. The bulb was then
sealed off from the atmosphere with only a small portion of
the neck remaining. An inch air gap was allowed between the
neck and a glass handle to prevent the passage of heat from the
atmosphere to the decalin in the bulb. The mixture was then
shaken intermittently for several hours and the allowed to
stand for 24 or 48 hours to insure complete mixing. The mixture
was then frozen and placed in the acetone bath and the temper-
ature raised slowly until only one or two small crystals
remained. The temperature was then held constant until the
crystals showed signs of growing or disappearing whereupon
the temperature was varied according to the result. During this
time, the bulb was shaken continuously to prevent the formation
of surface films and thus cause a temperature gradient from
the acetone bath to the decalin in the bulb. The temperature
was then held constant for ninety minutes after which time,
if there was no visible signs of the crystals growing or
disappearing, this temperature was assumed to be the melting
or freezing point. The mixture was then checked 24 hours later
and each succeeding day until the results became constant. It
is this final temperature that has been recorded as the freezing
point of the solution.

The mixture was then raised to 20° C and the refractive index taken with a Pulfrich refractometer. This was done in order to discover if, at low temperatures, the cis or trans decalin was unstable and converted to the other isomer. The results are plotted with the refractive index against the percentage volume of trans decalin.

The platinum resistance thermometer was checked at various times and at no time varied from the ice point by more than $.004^{\circ}$ C. It was necessary to balance the Wheatstone bridge daily as a slight change in atmospheric conditions made it vary considerably.

EXPERIMENTAL READINGS

RUN	MOL FRACTION		TEMPERATURE
	Trans	Solvent	^{o}C
1	0.00000	1.00000	- 43.275
2	0.02428	0.97572	- 44.226
3	0.05361	0.94639	- 45.560
4	0.08558	0.91442	- 47.044
5	0.17520	0.82480	- 51.255
6	0.25250	0.74750	- 55.128
7	0.34786	0.65236	- 59.369
8	0.40008	0.40008*	- 57.714
9	0.50236	0.50236	- 54.346
10	0.56614	0.56614	- 50.075
11	0.61998	0.61998	- 47.494
12	0.67905	0.67905	- 45.291
13	0.80000	0.80000	- 39.001
14	0.89970	0.89970	- 34.050
15	0.96880	0.96880	- 31.820
16	1.00000	1.00000	- 30.659

* According to the curve of the freezing points, this point is on the trans decalin side of the eutectic point. However, since these two isomers are mutually soluable in each other, it is only convention which states that the substance in the larger proportion is called the solvent. Furthermore,

FIGURE 2

11 A

FREEZING POINT CURVE

Temperature ° Centigrade

Mol Fraction Trans
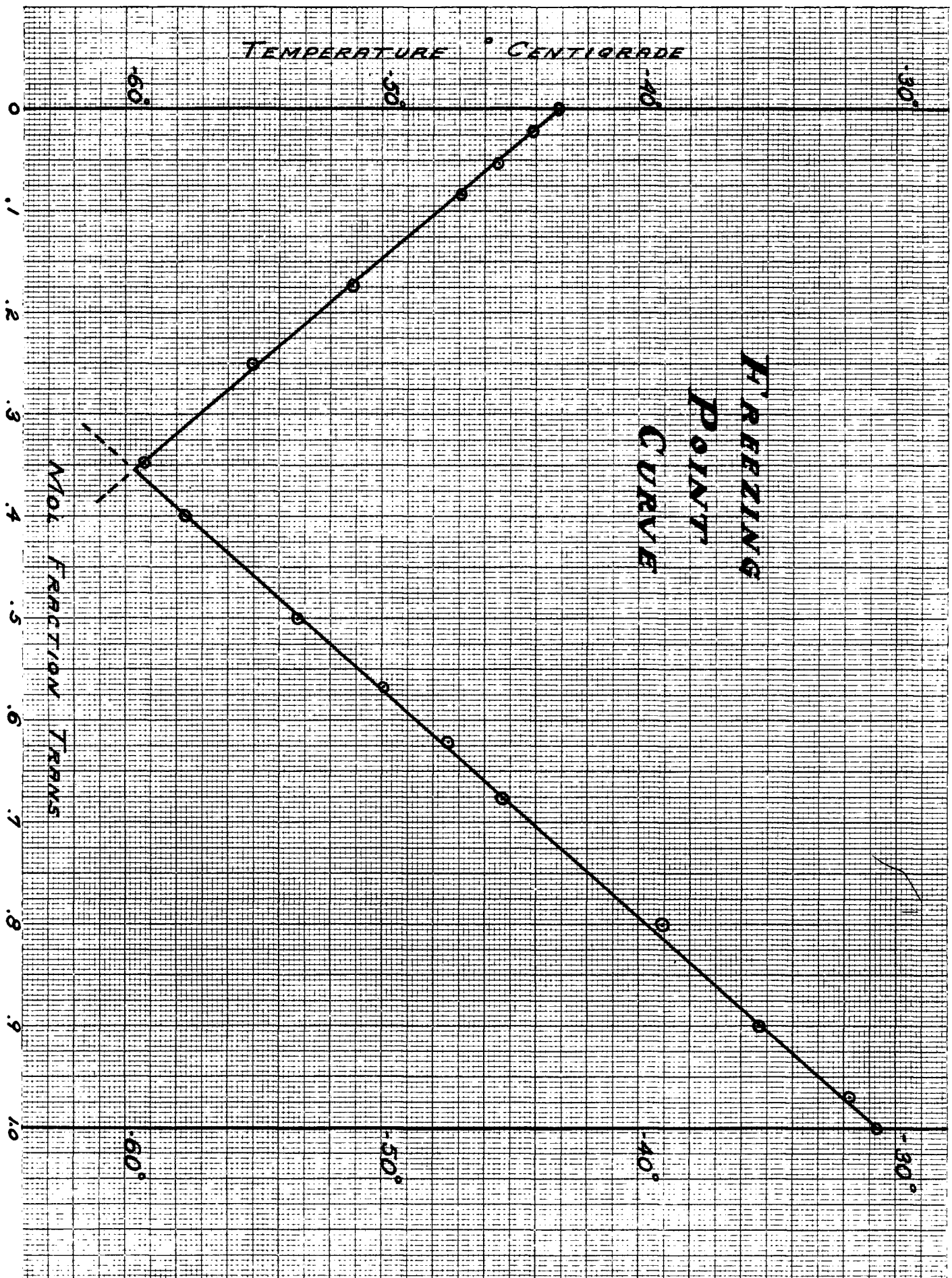
Hildebrand, in his text, calls the substance that freezes out of solution as the solute but in this thesis, it is more convenient to look upon the substance freezing out of the solution as the solvent.

TREATMENT OF THE RESULTS

The following tables have been calculated by the normal method of determining molal latent heats of fusion. Equation 7 that is

$$L_f = \frac{R\, T\, T_m}{T - T_m} \ln x \quad ,$$

has been used since the molal specific heats of the liquid and solid forms are not available for the use of the more exact equation. Also, in the following tables, the corrected temperature has been taken from the freezing point curve and it is this value that has been used to calculate the latent heat.

Latent Heat of Fusion of Cis Decalin

Run	Mol Fraction Cis	Temperature Reading	Corrected	ln Solvent	L_f cal/mol
1	1.00000	− 43.275	− 43.275	0.00000	2235
2	0.97572	− 44.226	− 44.412	−.02458	2249
3	0.94639	− 45.560	− 45.786	−.05511	2275
4	0.91442	− 47.044	− 47.283	−.08945	2300
5	0.82480	− 51.255	− 51.480	−.19264	2376
6	0.74750	− 55.128	− 55.100	−.29115	2452
7	0.65214	− 59.369	− 59.566	−.42749	2559

The value of the pure cis decalin has been taken from the graph on page 13 A.

Latent Heat of Fusion of Trans Decalin

Run	Mol Fraction Trans	Ln Solvent	Temperature Reading	Temperature Corrected	Latent Heat Cal/mol
8	0.40008	-0.91610	-57.714	-57.602	3512
9	0.50236	-0.68848	-53.346	-53.007	3314
10	0.56614	-0.56895	-50.075	-50.143	3189
11	0.61998	-0.47793	-47.494	-47.725	3099
12	0.67905	-0.38702	-45.291	-45.073	3018
13	0.80000	-0.22301	-39.001	-39.631	2779
14	0.89970	-0.10543	-34.550	-35.163	2683
15	0.96880	-0.03170	-31.820	-32.060	2622
16	1.00000	00.00000	-30.659	-30.659	2605

The molal latent heat of trans decalin was interpolated from the graph of the latent heats plotted with temperature on page 13 A.

Sample Calculation

$$L_f = \frac{R\,T\,T_m}{T - T_m}\, \ln x$$

where

R = 1.9868

T_m = -43.275°C = 229.910°A

T = -45.786°C = 227.394°A

ln x = ln .94639 = -0.05511

FIGURE 3   13 A

Latent Heat of Fusion — Latent heat of fusion in kcal/mol vs Temperature °A, showing Trans and Cis curves.

CALCULATED FROM

$$L_f = \frac{R \, T \, T_m}{T - T_m} \ln x$$
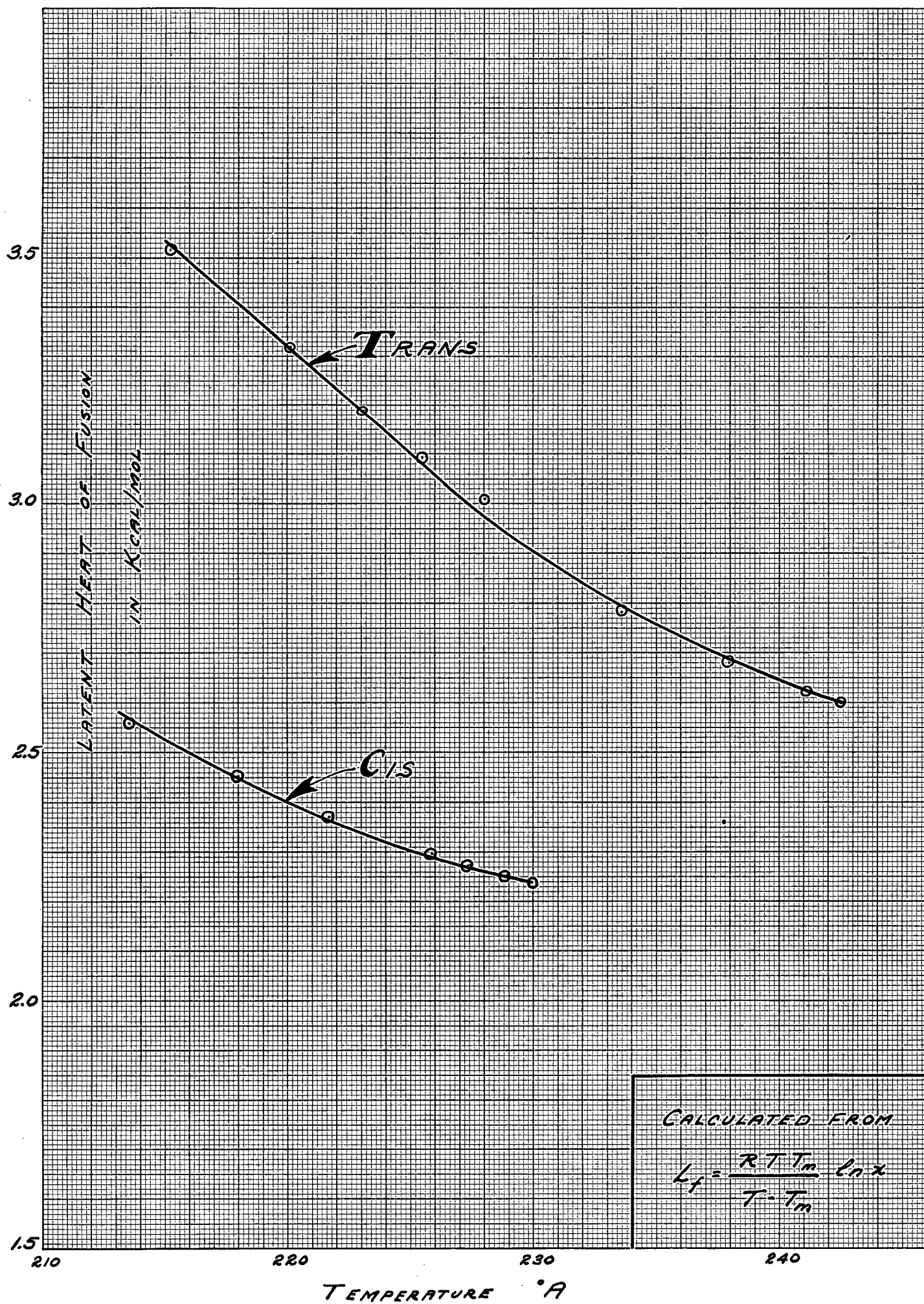
$$L_f = \frac{1.9868\ (229.910)(227.394)(-.05511)}{-2.516}$$

$$= 2275\ cal/mol\ at\ -45.786^{\circ}\ C$$

From the preceding two tables of latent heats, it appears rather obvious that the latent heats of fusion is not a constant value but varies considerably with temperature. One of the initial assumptions in the derivation of this formula was that the molal specific heats of the liquid and the solid at the freezing point will be almost equal. Therefore, from inspection of the more exact equation (11), it does not appear that the differences in the molal specific heats could possibly bring about a constant for the value of the latent heat.

Thus, if the equation is used where there was no restriction placed upon the latent heat, a more exact value for the latent heat should be obtained. In the following table , the equation

$$\frac{d\ ln\ x}{d\ T} = \frac{L_f}{R\ T^2}$$

has been used and the slope of the ln solvent against the temperature found at the required temperatures from the graph on page 15 A.

Calculations of Latent Heat
from Ln Solvent - Temperature Curve

Run N°	Temperature T	T²	Slope	Latent Heat Cis
1	229.910	52,858	0.02100	2204
2	228.768	52,335	0.02135	2229
3	227.394	51,708	0.02212	2272
4	225.897	51,029	0.02294	2325
5	221.700	49,151	0.02542	2492
6	218.080	47,559	0.02842	2685
7	213.614	45,631	0.03200	2900

Latent Heat of Trans

Run N°	Temperature T	T²	Slope	Latent Heat Cis
8	215.180	46,302	0.04770	4386
9	220.173	48,476	0.04100	3949
10	223.037	49,745	0.03765	3725
11	225.455	50,830	0.03436	3469
12	228.107	52,033	0.03125	3229
13	233.549	54,545	0.02725	2955
14	238.017	56,652	0.02400	2706
15	241.180	58,168	0.02252	2600
16	242.526	58,812	0.02187	2552

The values of these latent heats are plotted on the following graph on page 15 B.

FIGURE 4   15A

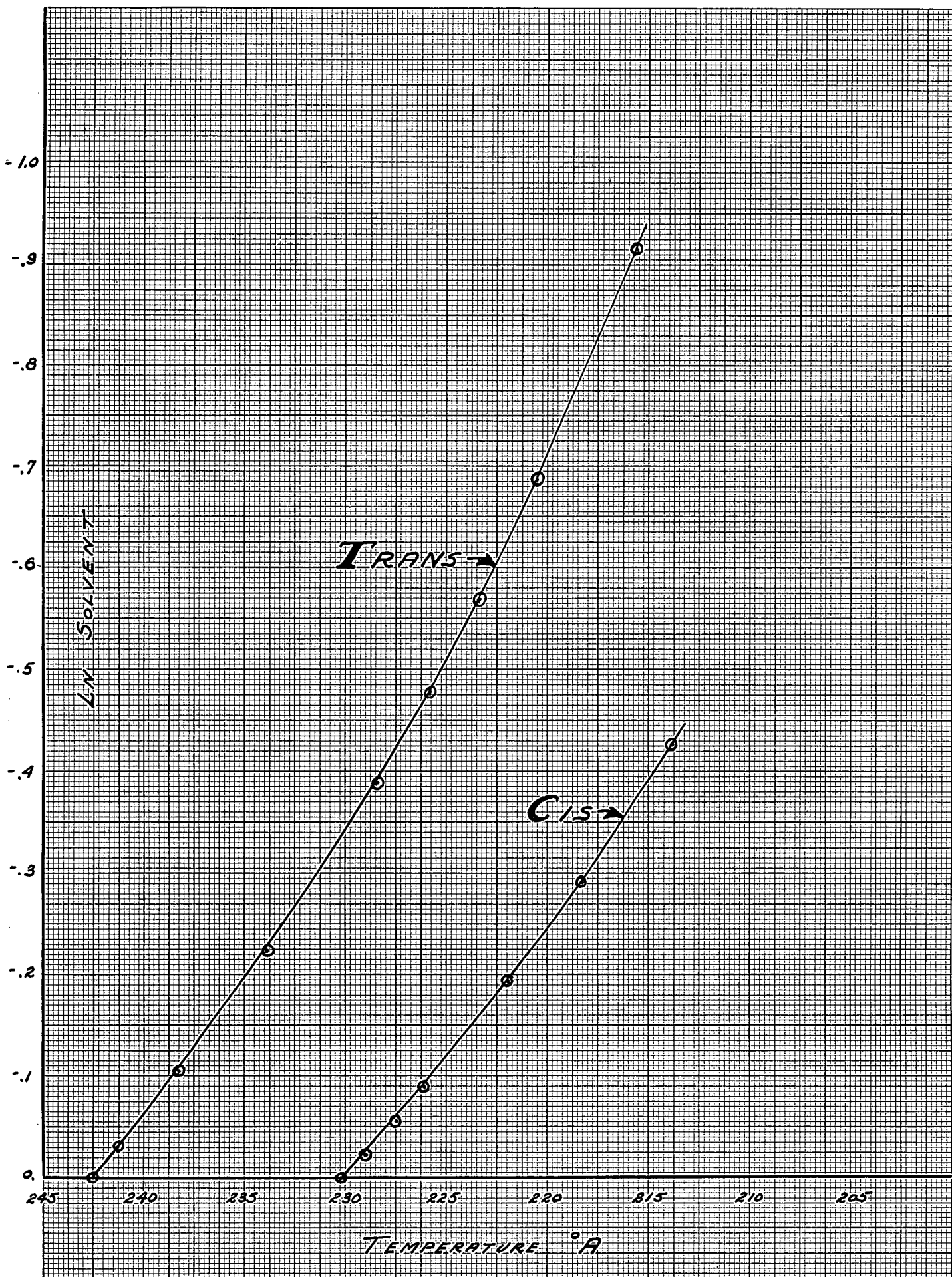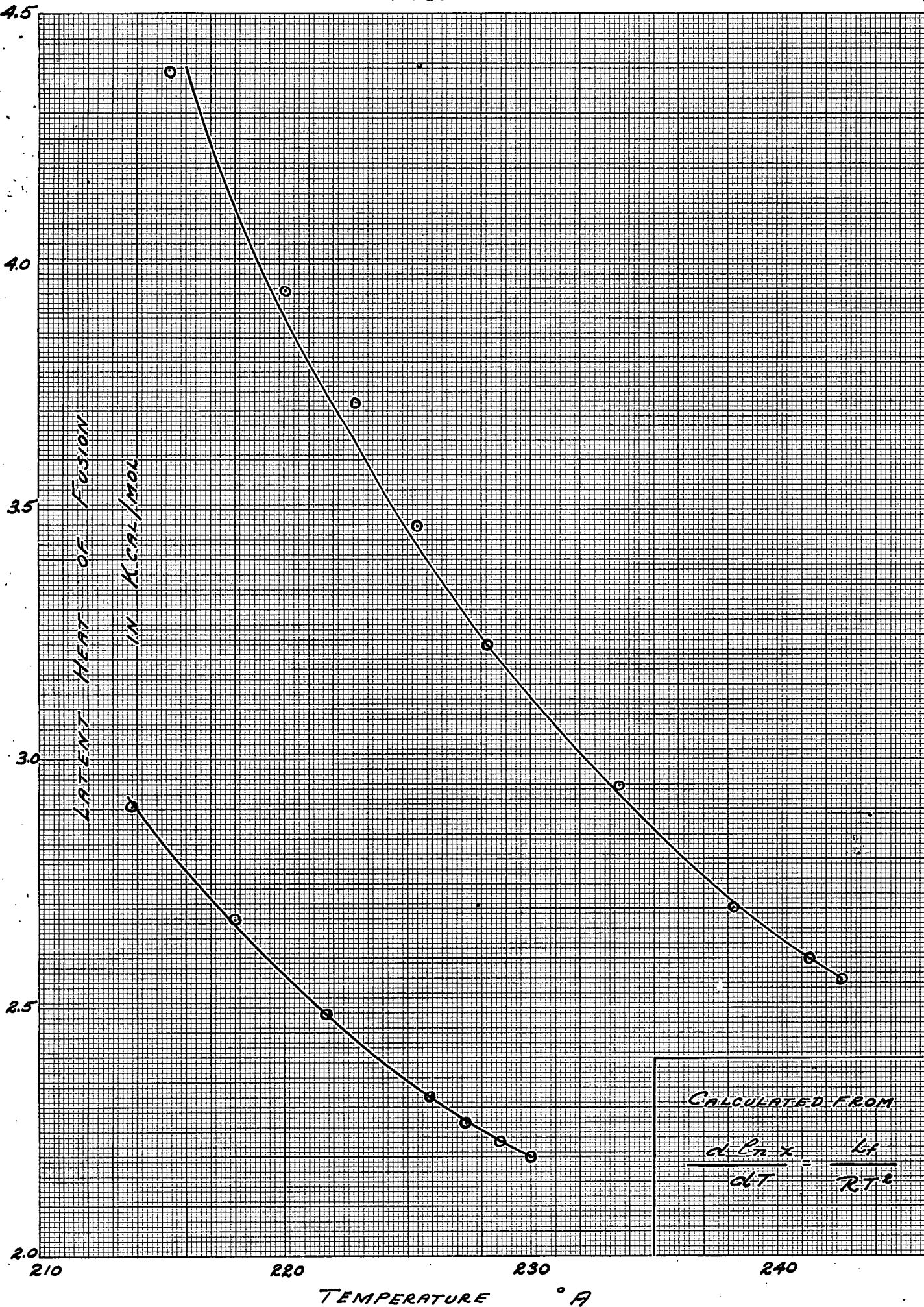FIGURE 5   15 B

Figure 5. Latent Heat of Fusion in K CAL/MOL vs. Temperature °A. Calculated from $\dfrac{d\ln x}{dT} = \dfrac{L_f}{RT^2}$

REFRACTIVE INDICES

The following are the refractive indices of the various mixtures of cis and trans decalin.

Run N°	Mol Fraction Trans	Percent Trans by volume	Refractive Index at 20° C
1	0.00000	0.000	1.48116
2	0.02428	2.359	1.48090
3	0.05361	5.209	1.48054
4	0.08558	8.340	1.48021
5	0.17520	17.115	1.47917
6	0.25250	24.700	1.47826
7	0.34786	34.120	1.47727
8	0.40008	39.280	1.47662
9	0.50236	49.500	1.47542
10	0.56614	55.880	1.47487
11	0.61998	61.350	1.47401
12	0.67905	67.250	1.47347
13	0.80000	79.600	1.47202
14	0.89970	89.720	1.47090
15	0.96880	96.840	1.47017
16	1.00000	100.000	1.46968

The above values are plotted on the following graph on page 16 A.
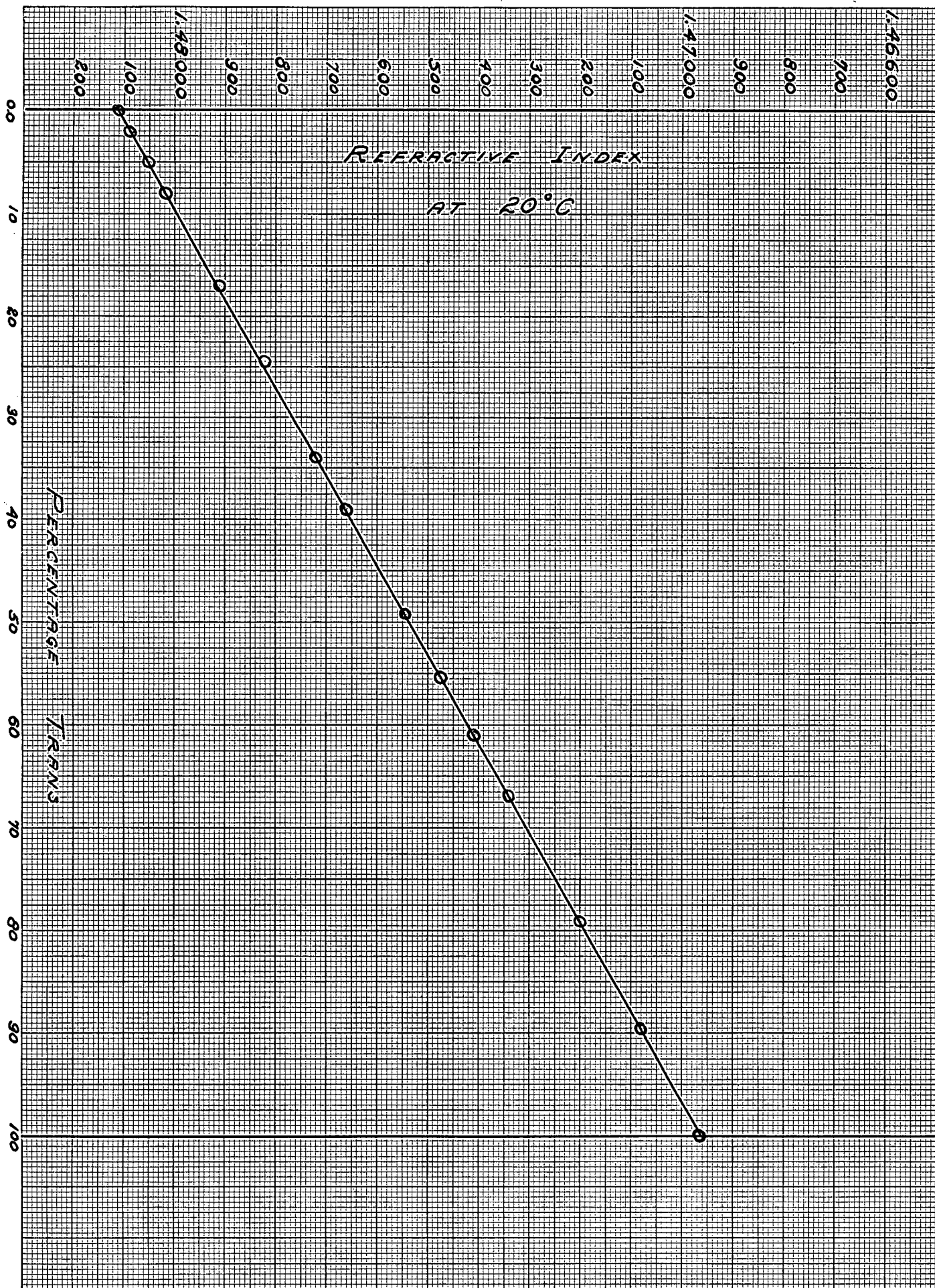
Densities at 20° C

Trans — 0.8700 gm/cc   Cis — 0.8967 gm/cc

FIGURE 6 16A

REFRACTIVE INDEX

AT 20°C

PERCENTAGE TRANS

DISCUSSION OF THE RESULTS

The results for the latent heats of fusion, found over the range from the melting points of cis and trans decalin to their eutectic temperature, appear to be reasonable although not in agreement with papers which have been published on the subject. These papers give no indication that the latent heat should vary with a change in temperature. Hildebrand, who appears more interested in the solubilities of the compounds than their latent heats, assumes the latent heat to be constant and interprets the variations in solubilities to be due to the change in the molal specific heats of the liquid and solid phases. This may be done for small temperature ranges of two or three degrees where the latent heat of fusion does not vary considerably but the variation for trans decalin from 2552 cal/mol at -30° C to 4386 cal/mol at - 58° C can scarcely be accounted for by the difference in specific heats since in most texts, it is assumed that these values are very close at the melting points.

F. A. Lindemann, in 1910, published a paper on the kinetics of fusion which was capable of quantitative treatment and, although it cannot be used in that sense in this paper, it is possible to show that the heat of fusion should vary considerably with temperature. He assumed that as the heat is applied, the amplitude of vibration of the atoms or molecules in a crystal lattice increased until it became equal to the

average distance between the atoms and collisions occurred.
Thus the energy was shared and the destruction of the crystal,
or melting, occurred. Lindemann assumed the particles to be
classical oscillators and the motion of the vibrating particles
to be simple harmonic.

The mean vibrational energy is then given by

$$U_{vib} = \int_{0}^{r_0} f\, x\, dx$$

where r_0 = the vibrational amplitude when melting occurs

f = the restoring force per cm displacement and

is determined by the equation

$$2\pi \nu = (f/m)^{\frac{1}{2}}$$

where ν = the frequency

m = the mass of the particle.

Although Lindemann goes further with his theory of the
kinetics of fusion, it is not of interest at this point. If,
the energy required to cause the destruction of the crystal
must come from the heat supplied, then the amount of heat will
vary upon the restoring force on the particles. Now when a
substance is at a temperature close to its melting point, it
is soft and pliable since the attraction between the molecules
is small and the restoring force is almost negligable. However,
as the temperature of the substance is lowered from its melting

point, the attraction or the restoring force on the molecules
becomes greater. Now since the restoring force will vary
considerably the further the substance is away from its freezing
point, the energy required to ~~the~~ destroy the crystal will
vary considerably also. The latent heat of fusion which is a
measurement of the energy, will therefore vary with the larger
values as the temperature is lowered. Thus the results which
have been obtained, appear to be reasonable.

When the natural log. of the solvent is plotted
against the temperature, the slope of this curve is, in the
beginning, almost a straight line and it is possibly this fact
that in previous papers, they assume the latent heat to be a
constant value. However, if the range of the freezing points
is increased, it can be seen that this curve is not straight
but varies greatly as the temperature is lowered. It is for
this reason also that, although they do not agree with the
other papers, the results of these experiments seem to be
reasonable.

Although the temperatures of the freezing points
were measured as accurately as possible, it was necessary
to correct them as shown on page 12. This correction was
caused by the formation of the mesomorphic state of the cis
decalin which hindered the observation of the crystals.
Although cis and trans decahydronaphthalene are not long
chain hydrocarbons that are usually associated with liquid
crystals, the decrease in the transparency of the cis decalin
near its melting point could well be attributed to the arrange-

-ment of the molecules into "swarms" as they were called by
E Bose to indicate a non-permenant grouping. Pure trans decalin
does not, however, show any signs of the formation of "liquid
crystal" but cis will be found in a variable range. The "liquid
crystal" will be found over a variable range of 4 - 4.5° C at
the freezing point of pure cis (-43.275°C) while at the eutectic
point, the swarms will be found over a range of 27°C and
possibly even a larger range. The range was measured because
of the difficulty in freezing the eutectic mixture and, by
allowing it to stand in an acetone bath at - 87°C for 24 hours,
the mixture was finally frozen. At this temperature, the swarms
appeared readily and remained until the solution froze completely.
If a lower temperature could have been used, the range may have
been still larger.

From the measurements of the refractive indices and the
straight line graph of the plotted results, there is no indi-
cation of the isomers changing at the lower temperatures. This
however, is not actually proven as the decalin was measured
at 20°C in which case the isomers, if changed at all due to
stresses set up at the low temperature, could convert back to
the original as the temperature is raised.

BIBLIOGRAPHY

Hildebrand, J.H., Ph.D. textbook, "Solubilities of Non-
    electrolytes," second edition, 1936.

Glasstone, Samuel, Ph.D. "Text-book of Physical Chemistry"

Fischl, F.B. and Naylor, B.F., paper, " The Heat Capacity,
    Heat of Fusion and Entropy of 11-n-Decylheneicosane,"
    Penn. State College, Journal of American Chemical
    Society, Vol. 67 p 2075, 1945.

Schumann, S.C. and Aston, J.G. paper, "The Heat Capacity
    and Entropy, Heats of Transition, Fusion and
    Vaporization and Vapor Pressure of Cyclopentane,"
    J. of Am. Chem. Soc., Vol 65 p 341, 1943.

Negishi, G.R., " The Heat of Fusion and Vapor Pressure of
    Stannic Iodide," U of California, J. of Am. Chem.
    Soc., Vol 58 p 2180, 1936.