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Thermodynamic Properties of Neopentane from 4°K to the Melting Point and Comparison with Spectroscopic Data[*1]

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Heat capacities, latent heats and vapor pressures of solid and liquid neopentane were measured and the following values were obtained; heat of transition $=628.7\pm0.3$ cal/mol, T(trans. pt.) $=140.498\pm0.05$°K, heat of fusion $=740.0\pm0.3$ cal/mol, T(triple pt.) $=256.750$°K, and P(triple pt.) $=268.47\pm0.13$ Torr. The amount of impurity in the sample after purification was estimated from a plot of the equilibrium temperature against the reciprocal of the fraction melted. From the result the impurity present was found to be 0.003_2 mol%. Despite of high purity, C_p value in the region below the melting point increases unexpectedly with temperature. This is interpreted as an effect of formation of vacancies in the crystals. The enthalpy required to form vacancies was estimated to be 3240 ± 220 cal/mol from the analysis of the heat capacity curve in the region below the melting point. The molal entropy of the ideal gas at the boiling point, calculated from the calorimetric data, was 71.24 ± 0.3 *e. u.* To bring this value into agreement with the value calculated from the infrared and Raman frequencies and the moments of inertia, requires the assumption of three equal potential energy maxima of 4.4 kcal/mol for hindered internal rotation of the methyl groups.

Non-polar tetrahedral molecules are grouped into two classes: one which undergoes phase transition in the solid state, and the other which does not.[1)] Probably, this can be mainly accounted for by interaction between molecular octupoles. We have treated neopentane first in a series of structural thermodynamic studies of tetrahedral molecular crystals.

Neopentane crystal is known to have a transition below its melting point, which was confirmed from the measurement of heat capacity by Aston *et al.*[2)] Also X-ray structural study of neopentane crystal[3)] shows that its unit cell is face-centered cubic with four molecules at -50 ± 5°C, and tetragonal at -150 ± 5°C. But no information about the orientations of the molecular axes in the unit cell is given yet. Aston *et al.* measured heat capacity of neopentane from 13.22°K to the boiling point, the amount of impurity in their specimen used being 0.727 mol%. And the premelting phenomenon observed was ascribed to the impurities involved in the specimen.

The present paper will describe some results of the measurement of the thermodynamic properties of highly purified neopentane from 4 to 260°K.

The heat capacity curve in the region below the melting point was analyzed so as to study the premelting phenomenon of neopentane crystal. And a comparison of the entropy calculated from spectroscopic data with calorimetric data was made based on the third law of thermodynamics.

Experimental

Material. A chemically pure-grade reagent neopentane obtained from Philips Co., Ltd. (purity; 99.52 mol%[4)]) was further purified by means of the "Spinning band fractional distillation column" SB618 (effective height of column is 3 m and the number of theoretical plates is 180) developed by Tokyo Kagaku Seiki Co., Ltd. and a Molecular Sieve 5A adsorption column. The resulting material was twice distilled, at dry ice temperature, through pyrex glass fractionating bulb A (Fig. 1), in which fractionation could be carried out in the absence of air in a vacuum system. The middle fraction was collected in the sample bulb B with a cock connected to the vacuum line by a pyrex glass joint. This sample was cooled to liquid nitrogen temperature and pumped out to less than 5×10^{-4} Torr, melted, cooled again and repumped to remove the trace of air from the sample. The cock attached to the sample bulb was closed and the weight of the sample together with the bulb was measured. For introduction of the sample into the calorimeter, the sample bulb

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1) I. Nitta, *Z. Krist.*, **112**, 234 (1959).

2) J. G. Aston and G. H. Messerly, *J. Am. Chem. Soc.*, **58**, 2354 (1936).

3) A. H. Mones and B. Post, *J. Chem. Phys.*, **20**, 755 (1952).

4) T. Shinoda, H. Enokido and Y. Mashiko, *Japan Analysst*, **17**, 1358 (1968).

weighed was attached again to the filling line which was evacuated to less than 10^{-5} Torr. After condensing the neopentane into the calorimeter vessel, the neopentane left in the vacuum line was collected in the sample bulb cooled to liquid nitrogen temperature and weighed together with the bulb. The weight of the actual specimen was estimated by subtracting the leavings from the weight measured first. A schematic diagram of the calorimeter filling system which attaches to the vapor pressure measurement and purification apparatus is shown in Fig. 1. As grease of cock a particular 'Phynal' which is soluble in water was employed instead of silicone grease, since the latter is dissolved by hydrocarbon liquid and vapor.

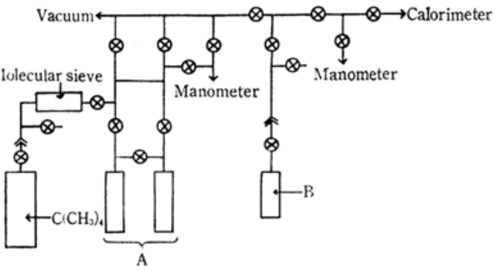

Fig. 1. Schematic diagram of the calorimeter filling system which attaches to the vapor pressure measurement and purification apparatus.

The amount of impurity in the specimen was determined from measurements of the melting point range.

Apparatus. The cryostat and the calorimeter vessel were the same as described previously.[5] The heat input and the resistances of the thermometers were recorded on a Hitachi recorder and a Rubicon six-dial double microvolt potentiometer as a function of time, respectively. The monitoring and control of the adiabatic conditions were automatically made. For this purpose, the highly sensitive *d. c.* amplifier which was possible to detect $\pm 2\times 10^{-9}$ V was designed and constructed. When the thermocouple signaled, the current in the heater circuit was regulated so as to be proportional to the temperature difference between the calorimeter and the adiabatic shield. All adjusting operations of the intercept and slope of the proportion were carried out according to the conditions of measurement. These adiabatic controls were separately adjusted in three parts of the shield. The controlling operations for measurement below 15°K were carried out manually, since the temperature difference thermocouple tended to lose its sensitivity rapidly at low temperatures.

The working thermometer for $T<13.5$°K was a germanium resistor (Minneapolis-Honeywell Reg. Co.) calibrated by thermodynamic temperature scale. We shall describe below the procedure by which the temperature scales were fixed.

Measurement for the calibration was reported previously.[5] Recently Plumb *et al.*[6] attempted to fit the resistance-temperature data for germanium resistors to a polynomial of the form

$$\log_{10} R = \sum_{n=0}^{m} A_n (\log_{10} T)^n \tag{1}$$

where the upper limit of m is varied from 3 to 8 depending on individual resistor. Owing to the difficulty of computation we attempted to find four formulas which would fit separately to the regions; 12.00—15.00°, 9.75—12.00°, 6.36—9.75° and 1.50—6.36°. The formulas are given in the following:

$$\begin{aligned} \log_{10} R &= (-K)/(\log_{10} R) + A + (B/T'), \\ T - T' &= a(T-b)(T-c)(T-d)(T-e) + f. \end{aligned} \tag{2}$$

Coefficients determined are given in Table 1. The deviations of the observed values from the calculated curve, by using the formulas Eq. (2) are within ±0.01° as shown in Fig. 2.

TABLE 1. COEFFICIENTS DETERMINED BY FITTING EQ. (1) TO THE CALIBRATION DATA OF Ge-RESISTOR

T (°K)	1.50—6.36	6.36—9.75	9.75—12.00	12.00—15.00
A	4.676183	3.352358	2.124168	2.191166
B	1.355019	3.542044	7.257872	6.589340
K	5.943370	3.352985	1.505155	1.528695
a	0.00357	0.0129	0.0193	0.00756
b	1.560	6.249	9.364	12.107
c	3.980	7.651	11.031	13.440
d	6.104	9.164	12.367	15.011
e	1.268	$(T-e)=1$	$(T-e)=1$	$(T-e)=1$
f	−0.001	0.0	0.002	0.0

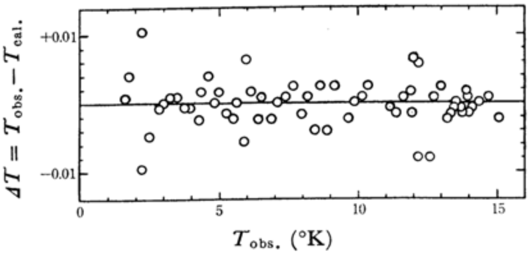

Fig. 2. Deviation of observed temperature of a germanium thermometer from the calculated temperature by using Eq. (2).

Results and Discussion

Heat Capacity of $C(CH_3)_4$. The calorimeter contained 7.4675 g (=0.10350 mol) in measurement series I and 14.4073 g (=0.19968 mol) in measurement series II. Series I and II were taken from separate filling from the same sample. The measured values of the heat capacity in the region of 4 to 260°K are listed in Table 2. The second virial coefficient of gaseous neopentane has not been determined experimentally below 300°K. Therefore its value at low temperatures was estimated by extrapolation of high temperature results using

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[5] T. Shinoda, T. Atake, H. Chihara, Y. Mashiko and S. Seki, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **69**, 1619 (1966).

[6] G. Cataland and H. Plumb, *J. Rev. NBS*, **70A**, 243 (1966).

Table 2. Heat capacity of neopentane
(Molecular weight 72.151; 1 cal = 4.1840 absolute joules; 0°C = 273.15°K)

T (°K)	C_p (cal/deg mol)	T (°K)	C_p (cal/deg mol)	T (°K)	C_p (cal/deg mol)	T (°K)	C_p (cal/deg mol)
4.141	0.03662	75.473	13.44	139.335	27.01	206.082	28.42
4.535	0.05003	77.485	13.74	140.498	'Transition'	208.108	28.55
4.927	0.06307	79.462	14.08	141.715	34.58	210.210	28.72
5.304	0.08185	81.405	14.38	142.424	26.28	211.885	28.78
5.825	0.1197	83.319	14.70	142.552	25.74	212.496	28.88
6.409	0.1688	85.303	15.00	143.338	24.32	214.667	29.04
6.985	0.2348	87.359	15.29	144.082	24.38	216.187	29.17
7.593	0.3095	89.391	15.60	144.887	24.39	216.827	29.26
8.241	0.4117	91.394	15.84	146.085	24.47	218.274	29.40
8.857	0.5189	92.956	16.03	146.887	24.52	218.963	29.46
9.444	0.6313	94.911	16.30	148.882	24.65	220.360	29.55
10.043	0.7766	96.936	16.61	150.849	24.85	221.268	29.61
10.661	0.9432	99.127	17.02	152.884	25.05	222.443	29.75
11.290	1.101	101.293	17.43	155.007	25.23	223.646	29.88
11.872	1.263	103.333	17.81	157.116	25.41	224.605	29.95
12.497	1.415	105.355	18.19	159.221	25.56	226.844	30.18
13.004	1.576	107.352	18.56	161.296	25.77	229.081	30.38
13.309	1.665	109.325	18.94	163.379	25.97	231.275	30.51
14.176	1.956	111.277	19.34	165.450	26.12	235.589	30.93
14.951	2.223	113.113	19.69	167.509	26.25	237.738	31.07
14.972	2.219	115.027	20.20	169.554	26.37	239.880	31.21
15.739	2.508	116.922	20.51	170.175	26.42	242.013	31.39
15.939	2.565	118.883	20.96	172.219	26.54	243.634	31.50
17.167	2.995	120.903	21.44	174.228	26.64	245.738	31.68
18.587	3.467	122.985	21.91	176.240	26.75	247.842	31.87
20.164	4.010	125.124	22.40	178.287	26.82	249.939	32.07
61.576	11.56	126.395	22.67	180.398	26.95	252.009	32.33
63.489	11.76	128.571	23.19	182.043	27.07	254.044	32.86
65.161	11.97	130.720	23.72	184.272	27.17	255.166	34.04
65.642	12.03	132.764	24.26	186.461	27.29	255.446	34.81
67.148	12.24	134.780	24.93	188.292	27.39	255.807	37.11
67.549	12.31	136.216	25.43	195.516	27.77	256.750	'Fusion'
69.202	12.53	136.775	25.65	197.662	27.91	258.051	36.21
69.417	12.55	137.887	26.10	199.788	28.01	258.132	36.43
71.330	12.81	138.290	26.23	201.904	28.14	259.929	36.59
73.424	13.12	139.014	26.60	204.011	28.31		

the (7, 28) Lennard-Jones potential.[7] The heat capacity of gaseous neopentane used was those estimated from experimental equation obtained by Spencer *et al.*[8] The density taken for the liquid was given by Whitmore *et al.*,[9] and that for the solid was ascertained by the reference data of X-ray analysis.[3] The value of heat of vaporization was that obtained by Aston *et al.*[2] Corrections were made for curvature where necessary.

The results of measurements of the heat capacity are plotted in Fig. 3 along with those given by Aston *et al.*[2] Their results deviate considerably from ours, particularly in the ranges of melting point and transition point. This is probably due to the fact that the higher amount of impurity was involved in the specimen employed by them.

The time required for the calorimeter system to reach equilibrium after heating was a few seconds at $4 < T < 6$°K, a few minutes at $10 < T < 20$°K and about ten minutes at $T > 60$°K. But in the middle point of the transition and the melting duration, the time for equilibration after heating became about an hour and 20—30 min, respectively.

The transition, the maximum of which is at 140.498±0.05°K, should in principle be second-

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[7] S. D. Hamann and J. A. Lawbert, *Australian J. Chem.*, **7**, 1 (1954); S. D. Hamann, J. A. Lambert and R. B. Thomas, *ibid.*, **8**, 149 (1955).

[8] H. M. Spencer and G. N. Flannagan, *J. Am. Chem. Soc.*, **64**, 2511 (1942).

[9] F. C. Whitmore and G. H. Fleming, *ibid.*, **55**, 3803 (1933).

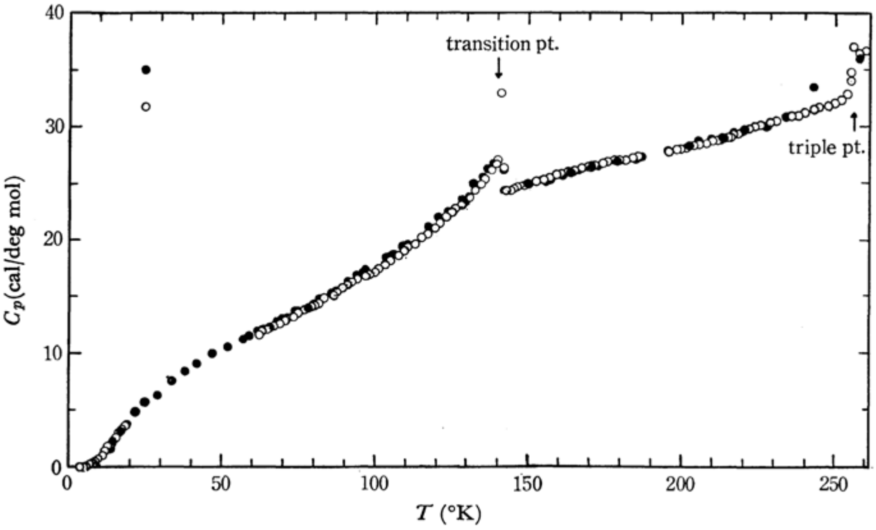

Fig. 3. Heat capacity curve of neopentane.
●: Aston *et al.* ○: Present research

TABLE 3. THE TRIPLE POINT OF NEOPENTANE

Fraction melted	T (°K)		P (Torr)
0.20214	256.7284		268.40
0.27607	256.7341		268.43
0.36610	256.7401		268.45
0.55641	256.7454		268.60
0.81611	256.7493		268.49
		average	268.47±0.13
T_{tr} (pure neopentane)	256.756		
Lwow[9] (1871)	253		
Whitmore and Fleming[9] (1933)	253.7		
Aston and Messerly[2] (1936)	256.53±0.10		

TABLE 4. HEATS OF FUSION AND TRANSITION OF NEOPENTANE

	Temperature interval (°K)	Corrected heat input (cal/mol)	$\int C_p dT$ (cal/mol)	Premelting (cal/mol)	ΔH (cal/mol)
	"Fusion"				
	(mol wt 72.151; (i) 0.10350 mol, (ii) 0.19968 mol)				
(i)	256.119—257.202	779.1	38.9	—	740.2
(ii)	256.455—258.901	828.0	88.3	—	739.7
				average	740.0±0.3
	Aston and Messerly (1936) (mol wt 72.09; 0.25778 mol)				
	240.407—259.847	1609.9	854.1	23.5	779.3
	240.913—261.442	1662.7	910.7	25.0	777.0
				average	778.2±3.5
	"Transition" (140—142°K)				
	139.374—143.046	728.8	100.4		628.4
	139.562—143.358	759.5	130.5		629.0
				average	628.7±0.3

order as was shown in Fig. 3, but actually nearly first-order. We observed no dependence of the heat capacity anomaly of the sample on its thermal history.

The Triple Point and Purity Determination. The equilibrium temperature and pressure of the system were observed during the fusion. The results are given in Table 3. The triple point of pure neopentane, given as 256.756°K, was estimated from a plot of the equilibrium temperature against the reciprocal of the fraction melted. The amount of impurity present in the specimen was also found to be 0.003_2 mol% from the plot.

The present result for the triple point temperature of neopentane deviates considerably from the other results except from that of Aston *et al.* as shown in Table 3. This is also interpreted as an effect induced by impurities.

The Heats of Fusion and of Transition. Two measurements of the heat of fusion are summarized in Table 4, and the average result is compared with that obtained by Aston *et al.* In spite of their correction for premelting, their average result deviates remarkably from the present result.

Aston *et al.* treated the abnormal rise in the heat capacity curve at about 140°K as an isothermal transition. However, we obtained that the transition may be in principle second-order type, with very high heat capacity (*i. e.* 34.58 cal/mol at 141.715°K) over a narrow temperature range. As to the heat of transition, two determinations of the heat supplied to the specimen in the region between 140 and 142°K were made, and the results are also given in Table 4. This average value is to be compared with the heat of transition of 615.9±0.6 cal/mol reported by Aston *et al.*

Heat Capacities in the Premelting Range. Using highly purified neopentane we reexamined the existence of premelting effect found by Aston *et al.* The measurements of the heat capacity in the vicinity of the melting point were made several times with various temperature rise (0.5—1°C) to determine the detailed shape of the heat capacity curve in this region. The result is plotted in Fig. 4, and analysed by ascribing to it several causes.

In the region far below the melting point the data of C_p (normal) can be expressed with sufficient accuracy in the form $A+BT$. Thus, we first attempted to find a formula which would fit to the observed values of heat capacity in the region from 195 to 215°K. The formula obtained is the following:

$$C_p(\text{normal}) = 14.369 + (0.068327)T, \qquad (3)$$

and the plots of C_p(normal) *versus* T as determined from the formula (3) in the region below the melting point are shown with small open circles connected with solid line in Fig. 4.

We, then, estimated[10] the effect on the heat capacity induced by impurities that we determined in the previous section, and the results are shown by the dashed curve in Fig. 4, which is still below the observed values.

We assumed finally, that the excess heat capacity

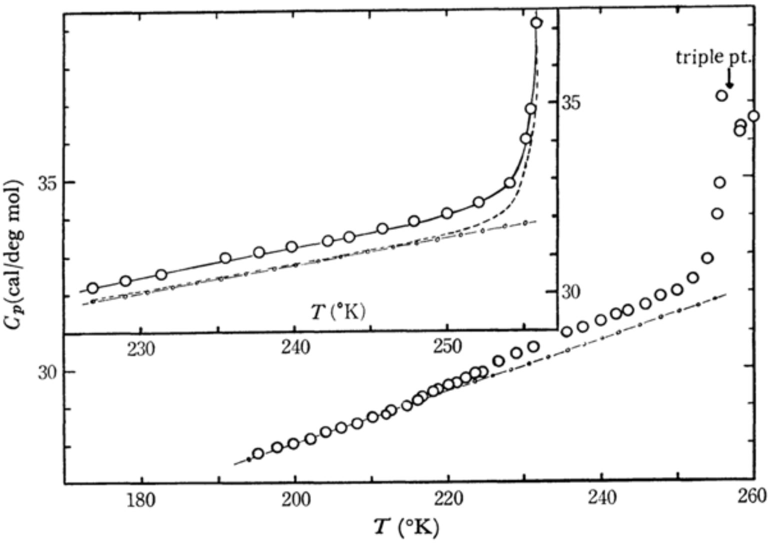

Fig. 4. Heat capacity in the premelting range.
○ : C_p(obs.)
———: C_p(normal) + C_p(impurity) + C_p(vac.)
—○—○—: C_p(normal) = 14.369 + 0.068327T
– – – –: C_p(normal) + C_p(impurity)

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[10] Y. Mashiko, *Japan Analyst,* **15,** 1151 (1966).

remained in subtracting C_p(normal) and C_p (impurity) from the total is caused by the thermal creation of imperfections, asssuming such as the Schottky-type vacancies. The assumption may be supported by the facts that neopentane crystal transforms to a plastic crystal phase below its melting point, and self-diffusion was observed by the experiment of proton T_1(spin lattice relaxation time) in this phase.[11]

The enthalpy to form the vacancies was calculated from the theory of Schottky vacancy. $\log_{10}(\Delta C_p \times T^2)$ was plotted against $1/T$, where $\Delta C_p = C_p$ (obs.) $- C_p$(normal) $- C_p$(impurity), and a straight line was obtained as shown in Fig. 5. By using the information contained in the intercept and slope of its line, we obtained the following expression:

$$n/N = 4 \times \exp\left[\frac{-3240(\pm 220)}{RT}\right], \qquad (4)$$

where n is the number of vacancies, and N Avogadro's number. The value of 3240±220 cal/mol is the enthalpy of formation of vacancies obtained from the plot. Using the Eq. (4) it is calculated the vacancies of $(n/N)_{\mathrm{T.P.}} = 0.69\%$ are to be formed in the crystal at the tiple point.

If the excess heat capacity due to vacancy formation is denoted by C_p(vac.), the plots of C_p (normal) $+ C_p$(impurity) $+ C_p$(vac.) *versus* T are shown by the solid cruve in Fig. 4. The observed values (open circles) of heat capacity for $C(CH_3)_4$ may be found to be in excellent agreement with the calculated values. Although there is no example of the creation of vacancies in molecular crystals except for inert gas crystals investigated by Morrison *et al.*,[12] the consideration of lattice vacancies seems to be important in treating premelting phenomenon as shown in this experiment.

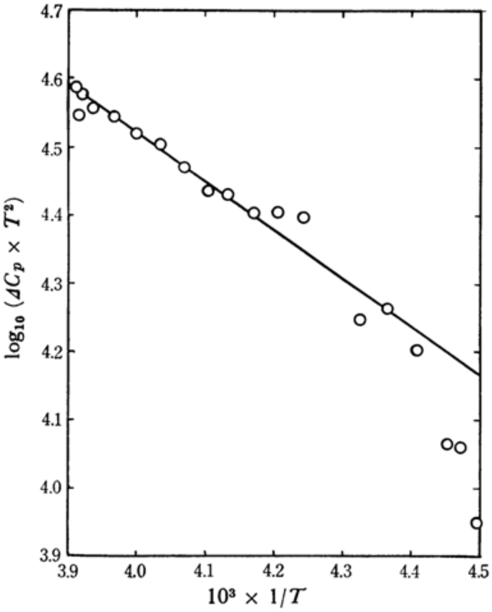

Fig. 5. Plot of $\log_{10}(\Delta C_p \times T^2)$ against $1/T$ for neopentane.

TABLE 5. VAPOR PRESSURE OF SOLID AND LIQUID NEOPENTANE

T (°K)	P (Torr)	$P-P$ (Eqs. (5) and (6)) (Torr)
Solid		
194.448	3.71	−0.12
196.585	4.73	+0.09
198.726	5.67	+0.07
200.848	6.66	−0.07
202.960	8.13	+0.08
205.065	9.60	+0.02
207.097	11.32	+0.03
209.120	13.38	+0.12
211.303	15.67	−0.03
213.589	18.61	−0.07
217.898	25.57	−0.07
220.039	29.77	−0.09
223.493	37.93	+0.01
224.801	41.43	−0.01
225.734	44.07	−0.05
227.971	51.13	0.00
230.182	58.97	−0.02
232.364	67.72	−0.02
234.495	77.38	+0.07
236.664	88.30	+0.07
238.812	100.32	+0.06
240.952	113.75	+0.06
243.075	128.43	0.00
244.694	140.75	0.00
246.800	158.27	+0.04
248.896	177.63	+0.03
250.979	198.99	+0.62
253.038	221.97	+0.88
254.959	245.36	+1.14
255.064	246.73	+1.25
255.925	257.57	+0.97
256.116	260.38	+1.29
256.537	265.70	+1.01
Liquid		
257.126	273.21	−0.19
257.108	273.93	+0.75
257.205	274.03	−0.34
258.994	297.06	−0.18
259.058	297.67	−0.38
260.875	323.17	+0.31

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[11] E. O. Stejskal, D. E. Woessner, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.*, **31**, 55 (1959).

[12] R. H. Beaumont, H. Chihara and J. A. Morrison, *Proc. Phys. Soc.* (*London*) **A74**, 1462 (1961).

The Vapor Pressure Measurements. The measurements were made in the region of 194 to 260°K as already described,[5] and the results are listed in Table 5.

An attempt was made to find coefficients which would fit the equation based on the theory of ideal gas, liquid and crystal to the observed values. The final equations are given in the following:

i) $194°\mathrm{K} < T <$ triple point

$$\log_{10} P + 2(\log_{10} T) + \exp(-g_s/RT) = -1672.65/T + 13.76190, \quad (5)$$

where the third term on the left hand side is the contribution due to the creation of vacancies described in the previous section, and g_s is the Gibbs energy of formation of the vacancies.

ii) $T >$ triple point

$$\log_{10} P + 2(\log_{10} T) = -(1517.19)/T + 13.15766. \quad (6)$$

The deviations of the calculated values (horizontal line), using Eqs. (5) and (6), from the observed one are shown by the open circles in Fig. 6. Also in Fig. 6 are illustrated the deviations between the pressures observed by Whitmore *et al.*[9] and by Aston *et al.* and those calculated. The other results show strong deviation from the present results, and this may arise from the facts that the sample used in the measurements by Aston *et al.* was stated to be 99.273 mol% pure, but the amount of impurity in the sample used by Whitmore *et al.* was not reported.

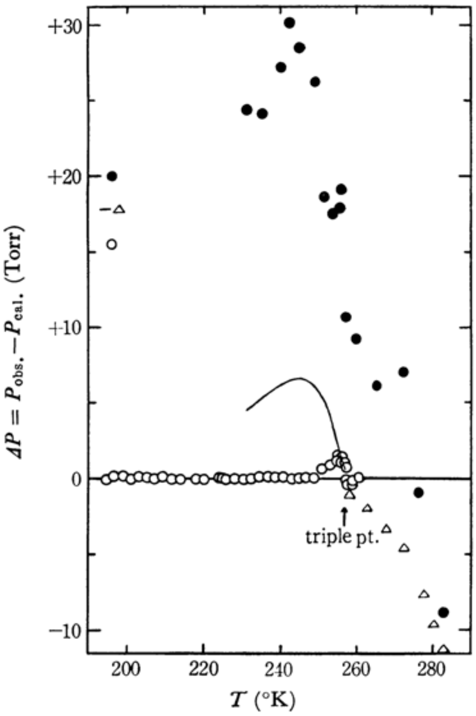

Fig. 6. Deviation of observed vapor pressure of neopentane from the calculated one by using Eqs. (5) and (6).
●: Whitmore *et al.* −△: Aston *et al.*
○: Present research

The Entropy. The calculation of the entropy of neopentane gas at the boiling point from the calorimetric data was made, and the result is summarized and compared with the result obtained by Aston *et al.* in Table 6. The entropy below

TABLE 6. THE ENTROPY OF NEOPENTANE GAS AT THE BOILING POINT

'Calorimetric'

Aston *et al.*	e.u.	Present research	e.u.
0—13.14°K	0.56	0—13.14°K	0.55
13.14—140.02°K	24.13	13.14—140.00°K	23.81
Transition	4.39	Transition (140.00—142.00°K)	4.47
140.02—256.53°K	16.55	142.00—256.75°K	16.47
Fusion	3.03	Fusion	2.88
265.53—282.61°K	3.63	256.75—282.61°K	3.64±0.05
Vaporization	19.24	Vaporization	19.24±0.20
Ideal gas correction	0.18	Ideal gas correction	0.18
	71.71±0.3		71.24±0.3

'Spectroscopic'

	Aston *et al.*	Present research
Translational and Rotational	73.34	73.09
Vibrational (carbon skelton)	5.38	5.34
Vibrational (other modes)	0.17	0.25
Total	78.89	78.68
Calorimetric	71.71	71.24
$(S_f - S) \times 4$ (difference from the value for free rotation)	7.18	7.44

4°K was estimated by using the values of Debye characteristic temperature obtained from the extrapolation of plots of Debye temperature *versus* *T*. The entropy from 260°K to the boiling point was estimated by using the thermal data observed by Aston *et al.*

The spectroscopic entropy of neopentane gas at the boiling point calculated from its infrared and Raman spectra[13)] and the moment of inertia ($I=186.2\times10^{-40}\,\mathrm{g\cdot cm^2}$), are given in Table 6 along with that obtained by Aston *et al.* The difference of the vibrational entropy between the present result and their one is due to the difference of the spectroscopic data used in the calculations; in their calculation earlier data by Rank *et al.*[14)] were employed.

To bring the calorimetric value into agreement with the spectroscopic, requires the assumption of three equal potential energy maxima of 4.4 kcal/mol for hindered internal rotation of the methyl groups (moment of inertia $I_{\mathrm{Me}}=5.14\times10^{-40}\,\mathrm{g\cdot cm^2}$). This value of hindering potential is reasonable in comparison with the observed value of 5.2 kcal/mol, for solid neopentane obtained by cold neutron scattering.[15)]

[13)] D. H. Rank, B. D. Saksaena and E. R. Shull, *Discussions Faraday Soc.*, **9**, 187 (1950).

[14)] D. H. Rank and E. R. Bordner, *J. Chem. Phys.*, **3**, 248 (1935).

[15)] J. J. Rush, *ibid.*, **46**, 2285 (1967).