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The Cubic Relationship of the Molar Heat Capacity Cv and Debye's Temperature for Ethyl Fluoride (C2H5F)

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العلاقة التكعيبية للسعة الحرارية المولية ***Cv*** ودرجة حرارة ديباي لفلوريد الإيثايل ***(C2H5F)***

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Abstract:

This study employs Debye's theory to compute the constant-volume molar heat capacity (Cv) of solid ethyl fluoride (C2H5F) across cryogenic temperatures (5–140 K). Utilizing numerical integration of the reduced Debye integral implemented in MatLab, the theoretically derived Cv curve demonstrates the characteristic temperature-dependent behavior observed experimentally: enhanced heat absorption at low temperatures and an asymptotic approach to the classical limit near the melting point (129.95 K). The model rigorously validates the cubic temperature dependence (Cv ∝ T3) near absolute zero, exhibiting close agreement between Debye-derived values and the cubic function below the separation temperature (14.75 K). Beyond this threshold, deviations progressively increase with rising temperature. Crucially, calibration via the empirical approximation θD ≈ 10·Tsp yields a Debye temperature θD ≈147.5 K, aligning within 1.67% of the experimental value (θD=150 K) obtained from sound velocity measurements. This attests to the accuracy of the model parameters.

Keywords: Molar Heat Capacity, Ethyl Fluoride, Cubic relationship of Cv, Debye temperature.

الملخص:

تستند هذه الدراسة إلى نظرية ديباي لحساب السعة الحرارية المولية عند حجم ثابت (Cv) لفلوريد الايثايل الصلب (F5H2C) ضمن مجال درجات الحرارة المنخفضة (140 – 5 K). باستخدام التكامل العددي لتكامل ديباي المختزل المطبق في برنامج ماتلاب، يوضح منحنى Cv المستنتج نظريًا السلوك المميز المعتمد على درجة الحرارة الذي لوحظ تجريبيًا: امتصاص حراري معزز عند درجات الحرارة المنخفضة، واقتران تقاربي مع الحد الكلاسيكي بالقرب من نقطة الانصهار (129.95 K). يؤكد النموذج بشكل كبير اعتماد السعة الحرارية على درجة الحرارة المكعبة (Cv ∝ T3) بالقرب من الصفر المطلق، ويظهر توافقًا وثيقًا بين القيم المحسوبة وفق نموذج ديباي والدالة التكعيبية تحت درجة حرارة الفصل (14.75 K). ومع تجاوز هذه العتبة، تبدأ الانحرافات بالازدياد تدريجيًا مع ارتفاع درجة الحرارة. وعلاوة على

ذلك، فإن المعايرة عبر التقريب التجريبي θD ≈ 10·Tsp تُعطي درجة حرارة ديباي θD ≈147.5 K، وهو ما يتوافق بنسبة 1.67% مع القيمة التجريبية (θD=150 K) المستخلصة من قياسات سرعة الصوت، مما يعزز موثوقية معاملات النموذج ودقته.

الكلمات المفتاحية: السعة الحرارية المولية، فلوريد الإيثايل، العلاقة التكعيبية لـ Cv، درجة حرارة ديباي.

Introduction:

Ethyl halides, denoted by the chemical formula C_2H_5X (where X = F, Cl, Br, I), are organic compounds that exist as liquids under standard terrestrial conditions and transition to solids at very low temperatures. The resulting solid phase may be crystalline or amorphous, contingent upon the cooling rate during preparation. Slow cooling yields crystalline solids, whereas rapid cooling produces amorphous, glassy solids [1–4]. Ethyl fluoride (C_2H_5F), specifically, condenses at approximately 129.95 K (–143.2 °C) [5]. Its molecular structure comprises eight atoms: two carbon, five hydrogen, and one fluorine. It possesses a molar mass of 48.06 g/mol, a density of 0.8176 g/mL at –37 °C [5], and a refractive index of 1.3057 at –40 °C [6]. Despite extensive research employing multiple techniques, the crystalline structure of ethyl fluoride and ethyl halides generally remains unconfirmed experimentally. However, their crystallizability is well established [3,4]. Durig (1973) proposed a symmetrical crystal structure for ethyl halides based on far-infrared (FIR) lattice spectra frequencies and isotopic shifts [7]. Later, Mattug (1987) utilized Raman spectroscopy to conclude that light ethyl iodide (C_2H_5I) adopts either an orthorhombic or monoclinic structure [1]. This aligns with Taha's 2011 theoretical model, which integrated FIR spectra, Raman spectra, group theory, and calculations of crystal vibrational modes. Taha's results indicated an orthorhombic or monoclinic system and, based on symmetry considerations, specifically suggested a two-base-centered orthorhombic structure. Furthermore, Taha computed ethyl fluoride's crystal energy levels, observing splitting at low potential barriers and harmonic oscillator behavior at specific energies. These energy levels corroborated prior results, reinforcing Durig's proposal of a similar structural composition with two molecules per unit cell, as inferred from torsional patterns [2].

Molar heat capacity (C_v) is a fundamentally significant physical property due to its relationships with other material characteristics. Its investigation is thus essential for understanding matter and unraveling natural phenomena [8,9]. Theoretical C_v values provide a framework for future experimental comparisons with ethyl fluoride data and elucidate material behavior across temperatures up to the melting threshold. Key theories describing C_v as a function of absolute temperature include those of Dulong–Petit, Einstein, and Debye. Debye's theory is particularly robust, especially after Delaunay's simplification of its integral form. Its success stems from strong agreement with experimental data and its prediction of the cubic temperature dependence ($C_v \propto T^3$) at low temperatures [8,9]. Al Zawaly *et al.* (2025) previously applied this Debye model to compute the molar heat capacity of ethyl fluoride between 50 K and 500 K [10].

The present study likewise employs the Debye model to calculate C_v for ethyl fluoride at low temperatures (5 K to 140 K), encompassing its pre-melting regime. Additionally, it examines the adherence to the cubic relationship ($C_v \propto T^3$) at temperatures approaching absolute zero and evaluates the accuracy of ethyl fluoride's Debye temperature (θ_D) by comparing the theoretical value to the experimentally determined value of 150 K, obtained from sound velocity measurements versus temperature [11].

Debye's theory and reduced Delaunay calculations:

1. Debye's theory:

The total energy of phonons with angular frequencies between ω and $\omega + d\omega$, for one molecular mole is [12]

$$u = \int_0^{\omega_D} g(\omega)\langle\varepsilon\rangle_\omega d\omega = \frac{9}{2}\frac{ZN_A\hbar}{\omega_D^3}\int_0^{\omega_D}\omega^3 d\omega + \frac{9ZN_A\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3 d\omega}{e^{\hbar\omega/k_BT}-1}, \tag{1}$$

$$u = \frac{9}{8}ZR\theta_D + \frac{9\hbar ZN_A}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3 d\omega}{e^{\hbar\omega/k_BT}-1}, \tag{2}$$

$$\mathrm{C_v} = \left(\frac{\partial u}{\partial T}\right)_{\mathrm{v}} = \frac{9ZN_A\hbar^2}{\omega_D^3 k_B T^2}\int_0^{\omega_D}\frac{\omega^4 e^{\frac{\hbar\omega}{k_BT}} d\omega}{\left(e^{\frac{\hbar\omega}{k_BT}}-1\right)^2}, \tag{3}$$

Where: C_v is molar heat capacity at constant volume, Z is the number of atoms of one primitive cell, N_A is the Avogadro number, k_B is the Boltzmann constant, ω_D is the Debye's greatest angular frequency, T is the absolute temperature, and $\hbar = \mathrm{h}/2\pi$, where h is Planck's constant [12]. Equation (3) is one of the integral equations that is difficult to integrate mathematically, so it was treated using numerical methods and computer programs to find the molar heat capacity at different temperatures.

Comparing the results of the Debye's model with experiment facts:

Some mathematical substitutions have been made to simplify the comparison, assuming that $t = \hbar\omega/k_B\mathrm{T}$, i. e. $\omega = (k_B\mathrm{T}/\hbar)\,t$, and from it $d\omega = (k_B\mathrm{T}/\hbar)\,dt$, and by substituting in equation (2), we find that:

$$u = \frac{9}{8}ZR\theta_D + \frac{9ZRT}{t_D^3}\int_0^{t_D}\frac{t^3dt}{e^t - 1}, \tag{4}$$

We will study what the molar heat capacity C_v becomes at very high and very low temperatures as follows [13]:

1. At very high temperatures ($\mathbf{T \gg \theta_D}$):

Which means $t \rightarrow 0$, so the following approximation can be adopted:

$$e^t \approx t + 1 \qquad or \qquad t \approx e^t - 1,$$

According to Taylor's expansion, **equation (4) can be written as follows:**

$$u = \frac{9}{8}ZR\theta_D + \frac{9ZRT}{t_D^3}\int_0^{t_D}\frac{t^3dt}{t} = \frac{9}{8}ZR\theta_D + \frac{9ZRT}{t_D^3}\int_0^{t_D}t^2dt,$$

$$u = \frac{9}{8}ZR\theta_D + 3ZRT, \tag{5}$$

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v = 3ZR, \tag{6}$$

This is the same result obtained by experimental measurements at high temperatures.

2. At very low temperatures ($\mathbf{T \ll \theta_D}$):

Tends $\boldsymbol{t}$ to infinity ($t \rightarrow \infty$), so the limits of integration become $0 \sim \infty$. From the Taylor series expansion:

$$\frac{1}{e^t - 1} = \frac{e^{-t}}{1 - e^{-t}} = \sum_{I=1}^{\infty} e^{-It}$$

Equation (4) becomes:

$$u = \frac{9}{8}ZR\theta_D + \frac{9ZRT}{t_D^3}\sum_{I=1}^{\infty}\left[\left|\int_0^{t_D} t^3 e^{-It}dt\right|\right],$$

Through gamma integrals, Raman zeta functions, and since $t_D = \frac{\hbar\omega_D}{k_BT} = \frac{\theta_D}{T}$, we get:

$$u = \frac{9}{8}ZR\theta_D + \frac{3\pi^4 ZR}{5\theta_D^3}T^4, \tag{7}$$

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{12\pi^4 ZR}{5\theta_D^3}T^3, \tag{8}$$

This is what the experimental results have shown, which confirm that the molar heat capacity C_v is directly proportional to T^3 [13]. Despite the great convergence between the Debye's model and the experimental results and its achievement of the cubism relationship at low temperatures, there are some deviations in the results of this model from experimental values near absolute zero. However, the Debye's model is one of the best models that can be adopted for calculating the theoretical molar heat capacity of substances that do not have experimental values and are in their solid state at very low temperatures.

Delaunay's mathematically reduced calculations :

The scientist Delaunay succeeded in calculating the Debye integral of the molar heat capacity C_v, analytically numerically. He stripped that integral relationship of physical constants by reducing it to mathematical substitutions not related to one type of material. He substituted $\omega = P\omega_D$, from it $d\omega = \omega_D\, dP$ and $P = 0 \rightarrow 1$, so that the relationship (3) becomes as follows [14]:

$$C_v = \frac{9ZN_A\hbar^2{\omega_D}^2}{k_BT^2}\int_0^1 \frac{P^4 e^{(\hbar\omega_D/k_BT)P}\,dP}{(e^{(\hbar\omega_D/k_BT)P}-1)^2}, \tag{9}$$

Since the $k_B\theta_D = \hbar\omega_D$, θ_D is the Debye's temperature. The Debye characteristic temperature θ_D, is an important parameter in the study of a large number of solid state problems involving lattice vibrations, such as thermal conductivity, electrical resistivity and scattering of thermal neutrons. Because of its importance and the scarcity of available low temperature heat capacity data, several methods have been developed to calculate it[15]. By putting $x = T/\theta_D$ and $y = C_v/3ZR$, R is the gas constant, using integration by parts, we get [14]:

$$y = \frac{12}{x}\int_0^1 \frac{P^3\,dP}{e^{P/x}-1} - \frac{3}{x}\left(\frac{1}{e^{1/x}-1}\right), \tag{10}$$

This is a mathematical integration that does not depend on the type of material and its physical properties, as we see [14]. Based on this integration, Delaunay was able to calculate 40 points using numerical methods and accurately. The reason for the limited number of points is the lack of development of computer software at that time, or perhaps it did not exist, which made the work dependent on manual calculations for many, many steps. Currently, based on the numerical Simpson (3/8) method used by Algeidi and Aldeeb [16] to integrate the Debye integral law, and which the agreement of its results with those of Delaunay's (40points), it will be relied upon to extend the range of Delaunay's results for the reduced molar heat capacity mathematically as a function of the reduction temperature. Using computer programming, we set the jumps of the reduced molar heat capacity points to be 0.010, which is smaller than the Delaunay jumps (0.05), we obtained 300points, as shown in figure (1), compared with the manually calculated Delaunay points. These points help in extracting the molar heat capacity points of solids and calibrating their Debye temperature values.

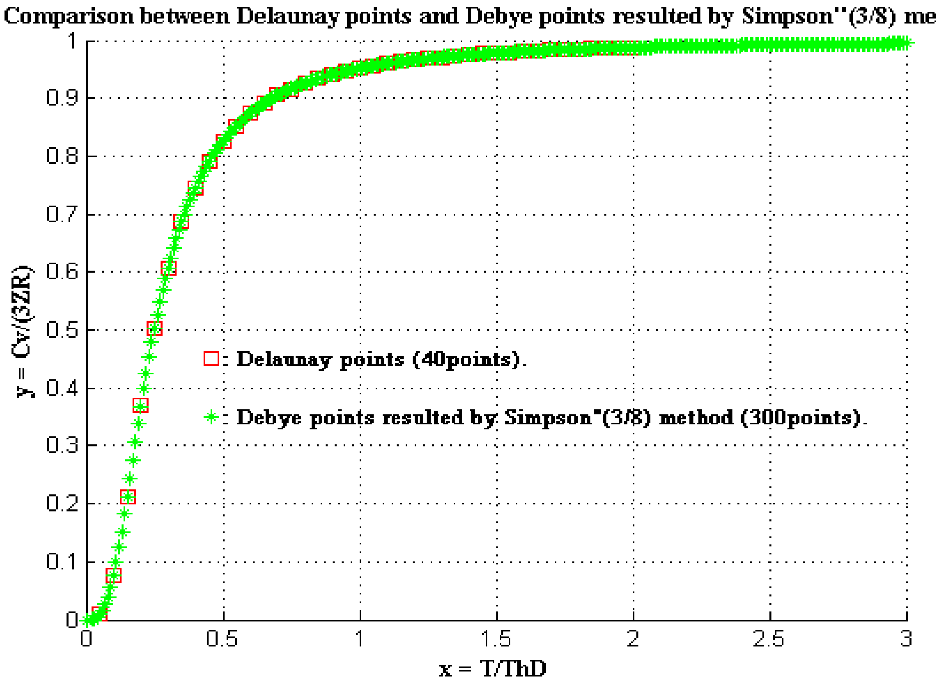

Figure (1): Comparison of Delaunay ponts with those obtained from Simpson's method for the reduced molar heat capacity as a function of the reduced temperature.

Results and discussion:

- Molar Heat Capacity Calculation:

The molar heat capacity C_v of ethyl fluoride was calculated as a function of absolute temperature (T) in the low-temperature range of 5–140 K using Equation (10):

$$y = \frac{C_v}{3ZR}$$

where Z denotes the number of atoms in a primitive cell. The Debye temperature θ_D = 150K was adopted for these calculations, consistent with experimental sound velocity measurements [11]. Given that molar heat capacity depends on atomic degrees of freedom per primitive cell, and recognizing that the ethyl fluoride molecule (C_2H_5F) constitutes the fundamental structural unit, the molecule itself was treated as the primitive cell. This approach is justified because the molecule cannot be subdivided into smaller symmetric units. Consequently, Z=8 atoms (2 C, 5 H, 1 F) were assigned to the primitive cell. The computations were implemented using MatLab, with results tabulated in Table 1. Figure 2 graphically represents these theoretical C_v values as a function of absolute temperature. As depicted, the MatLab-derived data exhibits the characteristic functional form of conventional molar heat capacity curves, validating the theoretical framework.

Table (1): Theoretical values of the molar heat capacity C_v of ethyl fluoride (C_2H_5F) according to the Debye's model.

T [K]	C_v [J/(mol.K)]	T [K]	C_v [J/(mol.K)]
5.00000	0.5759325563	75.00000	164.7079685749
10.00000	4.6038137346	80.00000	168.4407910029
15.00000	15.1298785611	85.00000	171.6268570360
20.00000	32.3603506563	90.00000	174.3636103842
25.00000	52.9991495474	95.00000	176.7287430022
30.00000	73.5600940582	100.00000	178.7845243246
35.00000	92.1023129376	105.00000	180.5811560342
40.00000	107.9879785929	110.00000	182.1593600473
45.00000	121.2654688466	115.00000	183.5523744336
50.00000	132.2515968211	120.00000	184.7874962133
55.00000	141.3235167789	125.00000	185.8872784575
60.00000	148.8329663440	130.00000	186.8704635692
65.00000	155.0790444748	135.00000	187.7527147418
70.00000	160.3056727540	140.00000	188.5471924443

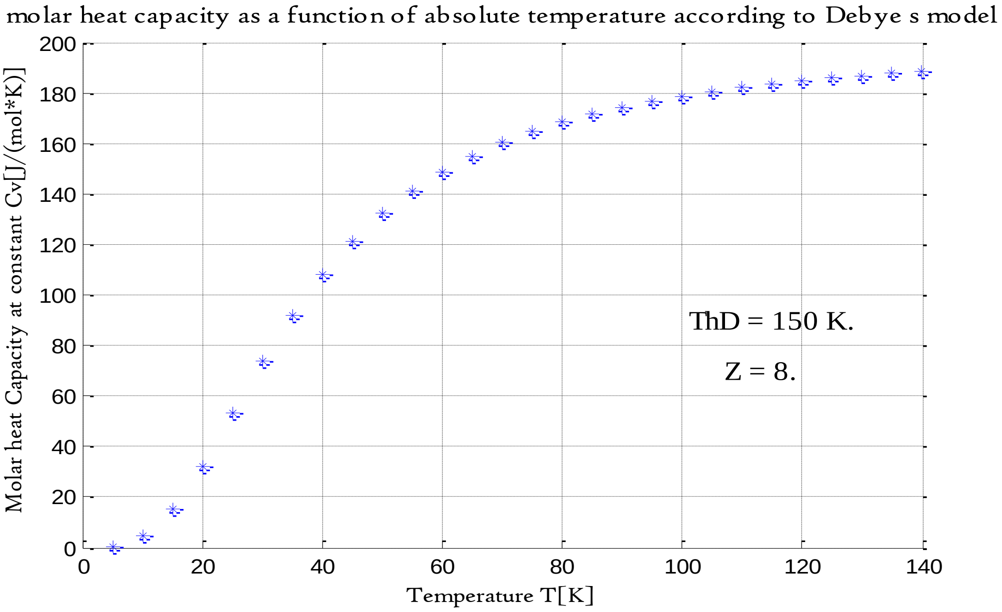

Figure (2): Theoretical values of the molar heat capacity C_v resulting from Debye's model for C_2H_5F at $\theta_D = 150K$, using a special MatLab program.

- **Cubic Temperature Dependence Near Absolute Zero:**

As established, the molar heat capacity at constant volume (C_v) for solids universally follows a cubic relationship with absolute temperature (T) at very low temperatures:

$$C_v = \frac{12\pi^4 ZR}{5\theta_D^3} T^3,$$

This study confirms that solid ethyl fluoride adheres to this fundamental law near absolute zero. The validity of the experimental Debye temperature (θ_D =150K) [11]) and its calibration were further evaluated. Using MatLab, **computations were performed with the following parameters:**

- Melting point (T_m=129.95K).
- Experimental Debye temperature (θ_D=150K).
- Number of atoms per primitive cell (Z=8).

The resulting C_v values are cataloged in Table 2. Figure 3 illustrates that the C_v curve for C_2H_5F, derived from the Debye model, aligns closely with the cubic function from T ≈ 0 K to 14.75 K. Beyond this threshold, the curves diverge, with discrepancies increasing as temperature rises.

Table (2): Delaunay values for the molar reduction heat capacity of C_2H_5F obtained from the Debye's model compared with the experimental cubism relationship for C_v at T using a special MatLab program.

T	C_v (Delaunay)	C_v (T^3)	T	C_v (Delaunay)	C_v (T^3)
0.25	0.000071992	0.000071992	8.25	2.586986827	2.587161043
0.50	0.000575933	0.000575933	8.50	2.829265882	2.829556658
0.75	0.001943772	0.001943772	8.75	3.086167421	3.086638554
1.00	0.004607460	0.004607460	9.00	3.358095789	3.358838679
1.25	0.008998946	0.008998946	9.25	3.645446447	3.646588984
1.50	0.015550179	0.015550179	9.50	3.948604123	3.950321417
1.75	0.024693108	0.024693108	9.75	4.267940822	4.270467927
2.00	0.036859684	0.036859684	10.00	4.603813735	4.607460465
2.25	0.052481854	0.052481854	10.25	4.956563069	4.961730980
2.50	0.071991570	0.071991570	10.50	5.326509869	5.333711421
2.75	0.095820779	0.095820779	10.75	5.713953837	5.723833738
3.00	0.124401433	0.124401433	11.00	6.119171218	6.132529880
3.25	0.158165479	0.158165479	11.25	6.542412778	6.560231796
3.50	0.197544867	0.197544867	11.50	6.983901910	7.007371435
3.75	0.242971548	0.242971548	11.75	7.443832907	7.474380749
4.00	0.294877470	0.294877470	12.00	7.922369421	7.961691684
4.25	0.353694582	0.353694582	12.25	8.419643135	8.469736192
4.50	0.419854835	0.419854835	12.50	8.935752664	8.998946222
4.75	0.493790177	0.493790177	12.75	9.470762695	9.549753722
5.00	0.575932556	0.575932558	13.00	10.024703372	10.122590643
5.25	0.666713920	0.666713928	13.25	10.597569930	10.717888933
5.50	0.766566208	0.766566235	13.50	11.189322569	11.336080543
5.75	0.875921344	0.875921429	13.75	11.799886575	11.977597421
6.00	0.995211215	0.995211461	14.00	12.429152657	12.642871517
6.25	1.124867633	1.124868278	14.25	13.076977509	13.332334781
6.50	1.265322258	1.265323830	14.50	13.743184567	14.046419162
6.75	1.417006483	1.417010068	**14.75**	**14.427564948**	**14.785556608**
7.00	1.580351239	1.580358940	15.00	15.129878561	15.550179071
7.25	1.755786714	1.755802395	15.25	15.849855356	16.340718499
7.50	1.943741952	1.943772384	15.50	16.587196706	17.157606841
7.75	2.144644304	2.144700855	15.75	17.341576897	18.001276047
8.00	2.358918715	2.359019758	16.00	18.112644710	18.872158067

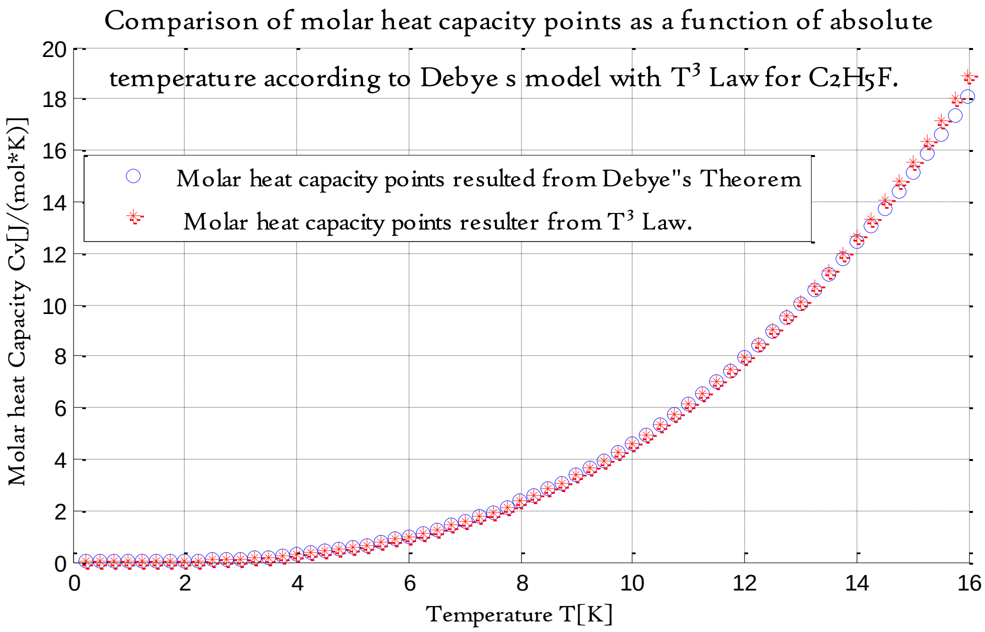

Figure (3): The extent to which the values of molar heat capacity C_v extracted from the Debye's model are consistent with the cubic significance at absolute temperature near absolute zero for C_2H_5F.

The separation temperature (Tsp=14.75 K) correlates with the Debye temperature via the relation:

$$\theta_D \approx 10 \cdot T_{sp}$$

Applying this empirical relation yields:

$$\theta_D \approx 10 \ x \ 14.75 = 147.5 \ K$$

This value is in excellent agreement with the experimental θ_D=150 K used in this study. The minor deviation (1.67%) is statistically insignificant, confirming the robustness of the experimental Debye temperature and its negligible impact on the model.

Conclusion:

The molar heat capacity (C_v) of solid ethyl fluoride was theoretically determined as a function of absolute temperature across the range 5–140 K using the Debye integral formulation and computational methods. The resulting C_v curve exhibits the characteristic shape consistent with experimentally derived heat capacity profiles. Furthermore, the cubic temperature dependence of C_v near absolute zero ($C_v \propto T^3$) was rigorously examined. Calculations based on the Debye integral demonstrate close agreement with this cubic relationship for ethyl fluoride at temperatures approaching absolute zero, with convergence increasing as T→0 K. Deviation from the cubic law becomes discernible above 14.75 K and intensifies with rising temperature. This analysis yields a Debye temperature of $\theta_D \approx 147.5$ K for ethyl fluoride, validating the experimental parameter (θ_D = 150 K) used in this study and confirming the robustness of the theoretical model.

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