I. INTRODUCTION

Because of the intensive use of carbon dioxide in industry and research [1], it has become necessary to determine its thermodynamic, physical and chemical properties on an extended range of temperatures. Significant effort has been deployed to build up a database through observations and theoretical calculations [2-12]. From the former point of view, we mention the case of the accurate measurements due to Giauque & Egan [3] and from the latter point of view, the derivation based on the classical version of the theory of lattice dynamics, which predicts the heat capacity of carbon dioxide in the range of temperatures $15<T<50$ K [4], is in a very good agreement with that obtained through observations [3]. However, such a good agreement is still out of reach for some other properties of carbon dioxide due to difficulties from both experimental and theoretical points of view. For instance, the empirical determination of the latent heat of sublimation at low temperatures remains a major obstacle because of the difficulty in eliminating the superheating of the gas [4]. Similarly, by way of example, the lagrangian classical treatment of the two-dimensional rigid rotor is intractable and the theoretical determination of the heat capacity, mentioned above, had been made possible at only sufficiently low temperatures ($T<50$ K) when the harmonic approximation is valid [6]. With that said, much work has to be done in order to determine further properties of carbon dioxide particularly at low temperatures, such properties are still missing in the best compendia.

We will exploit the data available in [3], which we refer to as G&E, and show that it is possible to evaluate the heat of sublimation $L$ and vapor pressure $p$ at temperatures $5\leq T\leq195$ K. A key prerequisite is the determination of the heat of sublimation at $T=0$ K ($L(0)=\epsilon_0$). Stull calculated an average value of $L$ by the method of least squares using the vapor pressure data measured by different workers [4] and obtained a value of 26.3 kJ·mol$^{-1}$ (=6286 cal·mol$^{-1}$) for $139\leq T\leq195$ K [10]. However, the literature citations listed in [4] show that Stull did not extract data from G&E, which is even more accurate and includes data concerning the heat capacity of the solid carbon dioxide and other data that could be used to obtain $L$ at different temperatures. By contrast, G&E have evaluated $L$ at 194.67 K using partly their measured data and available data for $L$ at lower temperatures [2]. They evaluated the integral of the heat capacity of the solid (change in the enthalpy) graphically from a smooth curve through their measured data and obtained a value for $L$ that is merely 10 cal·mol$^{-1}$ higher than their measured value $L_{\text{meas}}(194.67)=6030\pm5$ cal·mol$^{-1}$ (25230±21 J·mol$^{-1}$). They also evaluated the entropies of the gas and solid at 194.67 K and reached an excellent agreement between experimental data and statistics (the experimental & spectroscopic values of the entropy of the gas $s_g$ they obtained were 47.59 & 47.55 cal·K$^{-1}$·mol$^{-1}$, respectively, constituting a proof of the third law [14]). However, this cumbersome procedure had prevented them from carrying out a systematic evaluation of the latent heat and entropy at temperatures covering the range of their measured data. Furthermore, this procedure (the graphical evaluation) adds a human error, which is an unknown factor.
In this paper we will carry out a systematic evaluation of the fore-mentioned physical quantities on a more extended range of temperatures than that of G&E using 1) a computer algebra system (CAS), which eliminates the human error and allows an excellent adjustment of the parameters in order to achieve a better accuracy, as well as 2) an established formula for the vapor pressure. It will be shown below that our reevaluated value of $L(194.67)$ is 6030.4 cal·mol$^{-1}$ (25231 J·mol$^{-1}$). The data for the relevant quantities will be tabulated at temperatures incremented by 5 K and plotted. Moreover, the generating codes will be provided, which allow the evaluation of any quantity at any given temperature within minutes of time. In this work, we will be relying on measured data by different workers and on some empirical formulas derived by graphical interpolation. Since some of these data are provided without accuracy and some other lack accuracy due to personal error, it will be difficult to assign accuracy to our results, as is the case in most compendia. Some values of $p$ (in Torr) will be given with one significant digit while other values with 2 or 3 significant digits. The values of $L$ (of the order of 26000 J·mol$^{-1}$) will be given with five digits without decimals, assuming an error not higher than 0.35%. The accuracy of the results for $p$ and $L$ can be read by comparing with the available measured data.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{The vapor pressure vs. the temperature. Solid line: This work (TW) plotted for $110 \leq T \leq 195$, dotted line: G&E plotted for $155 \leq T \leq 196$.}
\end{figure}

\section{RESULTS AND DISCUSSIONS}

**Heat of sublimation at $T = 0$.** Throughout this paper, we use the units and symbols recommended by the *International Union of Pure and Applied Chemistry (IUPAC)* [15]. The energy is given in J and in cal = 4.184 J, the pressure in Torr, and the temperature in K. Since the original data were given in calories, we perform our evaluations in this unit, taking $R=1.98724$ cal·K$^{-1}$·mol$^{-1}$, then convert the results to joules.

The G&E heat capacity measurements, shown in the codes (appendix), extend from 15.52 to 189.78 K. On such a large interval there is no best equation that will represent the data [14]. G&E worked on a smooth curve through the data but did not describe it. In order to represent the data, the alternative is to subdivide the interval into sufficiently small intervals and represent the data by a polynomial on each sub-interval in such a way that the polynomial pieces blend smoothly making a spline [16].

MATLAB provides spline curve via the command `spline(x,y)` (see Appendix Section). It returns the piecewise polynomial form of the cubic spline interpolant with the not-a-knot end conditions, having two continuous derivatives and breaks at all interior data sites except for the leftmost and the rightmost one. The values of the spline at the
FIG. 2: The heat of sublimation vs. the temperature. Solid line: This work (TW) plotted using the derived Eq. [12], dotted line: plotted using the same equation with $p_{G&E}$, dash-dot line: arc of the spline through the data $(T_{TW}, L_{TW})$ & $T=5n$ K $(0 \leq n \leq 31$, positive integer) shown in Table II. This arc extrapolates the solid line to temperatures below 5 K.

The excellent agreement between the experimental & spectroscopic values of $s_g$ at 194.67 K is due to G&E accurate measurements and to the success of Debye’s theory at low temperatures$^1$. G&E used Debye’s formula to evaluate $s_s$ for $0 \leq T \leq 15$ K. However, they did not explain their choice for Debye’s temperature $\theta_D$. In this work, the energy and entropy of the solid for temperatures below 15.52 K are extrapolated by substitution of the Debye heat capacity formula. Moreover, we will rely on Suzuki & Schnepp’s assertion that the molar heat capacities of the solid carbon dioxide ($c_v$ & $c_p$) are equal within an error of $10^{-5}$ per cent for such small temperatures$^2$. Finally, we fix $\theta_D$ by equating the heat capacity due to Debye with that measured by G&E at 15.52 K (0.606 cal·K$^{-1}$·mol$^{-1}$). Solving the equation using a CAS we find $\theta_D=139.59$ K.

The MATLAB codes provided in the appendix are split into three parts. In Part (I), cd represents the Debye heat capacity. The vectors $t$ & $cp$ show the temperature data sites used by G&E (15.52→189.78 K) and the corresponding measured heat capacities (0.606→13.05 cal·K$^{-1}$·mol$^{-1}$), respectively. These G&E data sites are extended by the temperature vector $u$ and the corresponding Debye heat capacity vector $v$, respectively. The last two lines evaluate, at the temperature vector $Tn$, the spline through the extended data sites $(t$, $cp)$, the integrals $\int_0^T c_p \, dT'=h_s(T)$ + $\epsilon_0=\Delta h_s(T)$ (vector I) and $\int_0^T (c_p/T') \, dT'=s_s(T)$ (vector J), with $T \in Tn$.

The heat of sublimation $\epsilon_0$ is determined upon solving the equation $\mu_g=\mu_s$ at any given temperature for which the

---

$^1$ The more advanced theory elaborated in$^3$ reduces at low temperatures to Debye’s theory.
measured $L$ is known. The lead we had followed seeking for higher accuracy led us to select the value of $L=6190$ cal-mol$^{-1}$ at 170 K \[2\]. Eucken & Donath \& \[3\]. We find $\epsilon_0=6273.4$ cal-mol$^{-1}$ and the calculation is shown below.

With $\mu_g=\mu_p+v_g$ and $\mu_a=\mu_a-T s_a$, the equation $\mu_g=\mu_a$ reduces to $\epsilon_0=\Delta h_a-T s_a-\alpha_g-p v_g$. Upon solving the Clapeyron equation for $p v_g$ we obtain $p v_g=[L/(T d \ln p/dT)]+p v_s$, and finally

$$
\epsilon_0 = \Delta h_a - T s_a - \alpha_g - \frac{L}{T(d \ln p/dT)} - p v_s . \quad (1)
$$

We will make use of the G&E empirical equation to evaluate $p$ and $d \ln p/dT$ at 170 K

$$
p_{\text{G&E}}(\text{Torr}) = 10 \exp[(a_1/T) + b_1 + c_1 T + d_1 T^2] \quad (154 \leq T \leq 196 \text{ K}),
$$

(2) $a_1=-1354.210 \times \ln 10$, $b_1=8.96990 \times \ln 10$, $c_1=0.015188 \times \ln 10$, $d_1=-4.5107 \times \ln 10$, and obtain $p(170)=74.59$ Torr. Since $v_s=25.55$ cm$^3$-mol$^{-1}$ \[5\], the last term $p v_s=0.06$ cal-mol$^{-1}$ is neglected. The term including $L$ equals 6190/(170×0.108021)=337.08 cal-mol$^{-1}$, and $\Delta h_a(170)$ & $s_a(170)$ are the 85000th components of the vectors 1 & J: $\Delta h_a(170) - 170 \times s_a(170)=1(85000)-170 \times 1(85000)=1227.8$ cal-mol$^{-1}$.

Now, we make our first hypothesis concerning the vapor. We assume the validity of the first order virial expansion neglecting thus the next terms, and this has always been the case for carbon dioxide \[3\] at such low temperatures. We have then

$$
p v_g = RT + B(T) p , \quad (3)
$$

thereby we can show that the term $\alpha_g$ in \[1\] is the free energy of an ideal\(^2\) gas evaluated at the point $(T,p)=(170 \text{ K}, 74.59 \text{ Torr})$. For the molecule of CO\(_2\) we have $\alpha_g=a_t + a_v + a_r$, which is the sum of the translational, rotational and four vibrational contributions $a_v=2 a_{v1} + a_{v2} + a_{v3}$ \[17\] \[18\]. With our choice of the origin of the energy, these contributions write

$$
a_t = -RT \ln(C e T^{5/2}/p) ; \quad a_v = R \{ -T \ln[T/(2 \theta_v)] + \theta_v/3 \} ; \quad (T > 5 \text{ K}) \quad (i = 1 - 3) , \quad (4)
$$

with $C=7.75545 \times 10^5$ in SI units $=(2 \pi m/h^2)^{3/2} k^{5/2}$ and $\theta_v=0.561$, $\theta_{v1}=954$, $\theta_{v2}=1890$, $\theta_{v3}=3360$ K. We have then $\alpha_g(170)=-7838.2$ cal-mol$^{-1}$ leading with the previously evaluated terms to $\epsilon_0=6273.4$ cal-mol$^{-1}$.

**Vapor pressure.** From now on we will assume $\epsilon_0=6274$ cal-mol$^{-1}$ (26250 J-mol$^{-1}$). Upon substituting \[3\] & \[1\] into $\epsilon_0=\Delta h_a - T s_a - \alpha_g - p v_g$ ($\mu_g=\mu_a$) and rearranging the terms we obtain

$$
p = C T^{5/2} Z_r Z_v \exp\{[\Delta h_a - T s_a - \epsilon_0 - B(T) p]/RT\} , \quad (5)
$$

where $Z_v=Z_{v1} Z_{v2} Z_{v3}$, $Z_{v1}=1/[1 - \exp(-\theta_{v1}/T)]$ (i=1 - 3), and\(^3\) $Z_r=[T + \theta_r/3]/(2 \theta_r)$. Assuming that $B(T)$ follows Berthelot’s equation \[3\] \[11\]

$$
B(T) p = R \ell_1[1 - (\ell_2/T^2)] p(\text{Torr}) \quad (6)
$$

(\text{where } \ell_2=6 \times 304.1^2 \text{ K}^2 \text{ and, in order to express } B(T) p \text{ in cal-mol}^{-1}, \text{we take } \ell_1=9 \times 304.1/(128 \times 72.8 \times 760) \text{ K/Torr}, \text{we have solved numerically both equation (5) and its linearized form and the results coincide up to an insignificant error. Upon substituting } \exp[-B(T) p/RT]=1-B(T) p/RT \text{ into (5), the linearized equation yields}

$$
p_{\text{TW}}(\text{Torr}) = \frac{p_{\text{ideal}}}{\{1 + \ell_1[1 - (\ell_2/T^2)]p_{\text{ideal}}/T\}} \quad (T \geq 5 \text{ K}) \quad (7)
$$

where $p_{\text{ideal}}$ (in Torr) is the corresponding pressure for an ideal gas

$$
p_{\text{ideal}}(\text{Torr}) = (760/101325) C T^{5/2} Z_i Z_v \exp\{[\Delta h_a - T s_a - \epsilon_0]/RT\} . \quad (8)
$$

\(^2\) In fact, we can show that the correction for gas imperfection to $\mu_g$ is under the above assumption $p v_g - RT$, implying $\alpha_g=\alpha_g_{\text{ideal}}$.

\(^3\) Because of the symmetry requirements of the total wave function under the interchange of the two identical nuclei \[17\] \[18\]. $Z_r$ is coupled with the nuclear partition function and the above expression of $Z_r$ no longer holds for $T$ of the order of $\theta_r$. However, as $T$ increases the separation of the two partition functions becomes possible \[17\]. The above formula for $Z_r$ has been derived using the Euler-MacLaurin expansion and can be used safely for $T$ of the order of 5 K and higher values.
Table I & FIG. 1 compare values of the vapor pressure derived in this work (TW) with those of G&E (Eqs. (7) & (2)). We have evaluated (2) at temperatures below the left-end point 154 K, as shown in Table I, and the formula remains applicable, however, for temperatures above 110 K; below this temperature, equation (2) diverges from (7). The third column (A) of Table I shows values of the vapor pressure evaluated using Antoine’s equation [14]. The constants 
\[ A_1 = 6.81228, \quad B_1 = 1301.679, \quad C_1 = -3.494 \]

of Antoine’s equation have been evaluated by the National Institute of Standards and Technology (NIST) [10] from G&E data. The equation writes
\[ p_A(T) = \left( \frac{760}{1.01325} \right) \exp \left\{ \bar{A}_1 - \left[ \bar{B}_1 / (A_1 T + C_1) \right] \right\} \quad (154.26 \leq T \leq 195.89 \text{ K}), \]  
(9)

where \( \bar{A}_1 = A_1 \ln 10, \quad \bar{B}_1 = B_1 \ln 10. \)

TABLE I: Vapor pressure data. The values of the pressure shown in italics are evaluated at temperatures beyond the assumed range of validity of the corresponding formula. The table compares our results TW: This work (Eq. (7)) with those of G&E (Eq. (2)) [3] and Antoine’s equation (Eq. (9)) [10]. Nomenclature: NA=Not Applicable. Conventions: 1) E–n=10^{-n}; 2) a letter C shown on the right of a p-value indicates that a small correction for gas imperfectation has been added; if, otherwise, the values of \( p \) with and without correction are equal (\( p=p_{\text{ideal}} \)). Since the G&E and A data are empirical, a letter C has been added to all of them including those values evaluated beyond the assumed range of validity.

| T/K | \( p_{TW}/\text{Torr} \) | \( p_{G&E}/\text{Torr} \) | \( p_A/\text{Torr} \) |
|-----|----------------|----------------|----------------|
| 65  | 3.4E–12       | NA             | 3.3E–12(C)     |
| 70  | 1.2E–10       | NA             | 1.3E–10(C)     |
| 75  | 2.8E–9        | NA             | 3.0E–9(C)      |
| 80  | 4.2E–8        | NA             | 4.7E–8(C)      |
| 85  | 4.7E–7        | NA             | 5.2E–7(C)      |
| 90  | 3.9E–6        | NA             | 4.3E–6(C)      |
| 95  | 2.6E–5        | NA             | 2.8E–5(C)      |
| 100 | 1.4E–4        | NA             | 1.5E–4(C)      |
| 105 | 6.8E–4        | NA             | 7.3E–4(C)      |
| 110 | 0.003         | 0.003(C)       | 0.003(C)       |
| 115 | 0.01          | 0.01(C)        | 0.01(C)        |
| 120 | 0.03          | 0.03(C)        | 0.03(C)        |
| 125 | 0.09          | 0.09(C)        | 0.09(C)        |
| 130 | 0.2           | 0.2(C)         | 0.2(C)         |
| 135 | 0.6           | 0.6(C)         | 0.6(C)         |
| 140 | 1.4           | 1.4(C)         | 1.4(C)         |
| 145 | 3.1           | 3.1(C)         | 3.1(C)         |
| 150 | 6.4           | 6.4(C)         | 6.3(C)         |
| 155 | 12.5          | 12.6(C)        | 12.5(C)        |
| 160 | 23.6          | 23.6(C)        | 23.5(C)        |
| 165 | 42.8(C)       | 42.7(C)        | 42.4(C)        |
| 170 | 74.6(C)       | 74.6(C)        | 74.1(C)        |
| 175 | 126(C)        | 126(C)         | 125(C)         |
| 180 | 206(C)        | 207(C)         | 205(C)         |
| 185 | 320(C)        | 330(C)         | 328(C)         |
| 190 | 513(C)        | 513(C)         | 511(C)         |
| 195 | 776(C)        | 781(C)         | 777(C)         |

From Table I we establish the following results. Equations (2) & (9) are still valid beyond their assumed ranges of validity; the ranges are now extended right down below their left-end points to include temperatures above 110 and 65 K, respectively. Moreover, the vapor behaves as a polyatomic ideal gas for temperatures below 155 K.

An instance of calculation is provided in the codes provided in Part(II) of the appendix, which show the evaluation of the ideal-gas pressure equation (8) & the real-gas pressure equation (7) at 160, 180 & 194.67 K. The evaluated pressures are represented by the 3-vectors \( \mathbf{p_I} \) and \( \mathbf{p_{TW}} \), respectively.

**Heat of sublimation.** Combining different thermodynamic entities we establish the equation
\[ L(T) = \epsilon_0 - \Delta h_s(T) + h_g(T) + [B(T) - (T dB/dT)] p(T), \]  
(10)

where the last two terms add a correction for gas imperfection, \( p(T) \) is the vapor pressure and \( h_g \) is the ideal-gas enthalpy given by \( h_g = R \left( \frac{7T}{2} - \frac{\theta_r}{3} \right) - T^2 d(a_v/T)/dT \) (Eq. (4)).

Looking for extreme values we can first ignore the correction for gas imperfection then justify it later. We have solved graphically the equation \( dL/dT = 0 \) (\( c_{p_s} = c_{p,g} \)) and obtained the values 57.829 K for \( T \) & 6503.58 cal·mol⁻¹ for \( L \) as shown in FIG. 2. We will assume \( L_{\text{max}} = 6503.6 \) cal·mol⁻¹ (27211 J·mol⁻¹). Tables II & III however, show that at 57.829 K the vapor behaves as an ideal gas, and this justifies the omission of the correction terms in \( dL/dT = 0 \).
Substituting (6) into (10), this latter splits into two equations whether we evaluate the vapor pressure using (2) or (7):

\[ L_{G&E} = \epsilon_0 - \Delta h_s + h_g + R \ell_1 [1 - (3\ell_2/T^2)] p_{G&E} \quad (154 \leq T \leq 196 \text{K}), \]  
\[ L_{TW} = \epsilon_0 - \Delta h_s + h_g + R \ell_1 [1 - (3\ell_2/T^2)] p_{TW} \quad (T \geq 5 \text{K}). \]

Equations (11) & (12) are plotted in FIG. 2. In the codes provided in Part (III) of the appendix, we evaluate the r.h.s of (12) at 160, 180 & 194.67 K (3-vector LTW). The value of the latent heat obtained at 194.67 K is 6030.4 cal \cdot mol^{-1} (25231 J \cdot mol^{-1}) or 6030.6 cal \cdot mol^{-1} (25232 J \cdot mol^{-1}) whether we calculate the r.h.s of (12) or (11).

TABLE II: Heat of sublimation data. The values of the latent heat shown in italics are evaluated at temperatures beyond the assumed range of validity of the corresponding formula. The table compares our results TW: This work (Eq. (12)) with those derived from Eq. (11) using G&E pressure equation. Nomenclature: NA=Not Applicable. Convention: a letter C shown on the right of a \( L \)-value indicates that a small correction for gas imperfection has been added; if, otherwise, the values of \( L \) with and without correction are equal.

| T/K | \( L_{TW}/J\cdot mol^{-1} \) | \( L_{G&E}/J\cdot mol^{-1} \) |
|-----|-------------------------------|-------------------------------|
| 0   | 26250                         | NA                            |
| 5   | 26394                         | NA                            |
| 10  | 26538                         | NA                            |
| 15  | 26676                         | NA                            |
| 20  | 26804                         | NA                            |
| 25  | 26914                         | NA                            |
| 30  | 27005                         | NA                            |
| 35  | 27077                         | NA                            |
| 40  | 27133                         | NA                            |
| 45  | 27172                         | NA                            |
| 50  | 27197                         | NA                            |
| 55  | 27209                         | NA                            |
| 60  | 27210                         | NA                            |
| 65  | 27201                         | NA                            |
| 70  | 27183                         | NA                            |
| 75  | 27158                         | NA                            |
| 80  | 27128                         | NA                            |
| 85  | 27091                         | NA                            |
| 90  | 27048                         | NA                            |
| 95  | 27002                         | NA                            |
| 100 | 26951                         | NA                            |
| 105 | 26896                         | NA                            |
| 110 | 26836                         | 26836                         |
| 115 | 26773                         | 26773                         |
| 120 | 26707                         | 26707                         |
| 125 | 26637                         | 26637                         |
| 130 | 26565                         | 26565                         |
| 135 | 26488                         | 26488                         |
| 140 | 26408                         | 26408                         |
| 145 | 26325                         | 26325                         |
| 150 | 26329(C)                      | 26329(C)                      |
| 155 | 26149(C)                      | 26149(C)                      |
| 160 | 26055(C)                      | 26055(C)                      |
| 165 | 25958(C)                      | 25958(C)                      |
| 170 | 25855(C)                      | 25855(C)                      |
| 175 | 25745(C)                      | 25745(C)                      |
| 180 | 25629(C)                      | 25629(C)                      |
| 185 | 25504(C)                      | 25504(C)                      |
| 190 | 25368(C)                      | 25368(C)                      |
| 195 | 25221(C)                      | 25221(C)                      |

In concluding, it was of interest to further compare our results for the pressure with those used by Stull [4] that, as already stated, are less accurate than G&E values. At temperatures 138.8, 148.7, 153.6, 158.7 K, we read from [4] the values 1, 5, 10, 20 Torr for the pressure, while our evaluated values (Eq. (7)) are 1.16, 5.30, 10.42, 20.12 Torr, respectively. Finally, values of the entropy of the solid at the tabulated temperatures \( T = 5j \text{K} \) (\( 1 \leq j \leq 39 \), positive integer) form a sub-vector of \( J \) and are obtainable upon executing the codes \( q = 2500:2500:97500; J(q) \). For instance, \( s_s(160) = J(80000) = 14.07 \), \( s_s(180) = J(90000) = 15.50 \) and \( s_s(194.67) = J(97335) = 16.52 \text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) (58.87, 64.85 & 69.12 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}, respectively).
III. METHODS

Concerning the numerical approach, given the accurate data for the heat capacity at constant pressure of carbon dioxide and some available data for the heat of sublimation, we employed the method of splines to generate and evaluate a smooth curve representing the heat capacity data. Dealing with a large number of data sites, we preferred to use cubic splines, which are more attractive for interpolation purposes than higher-order polynomials [16]. Once the curve set, we proceeded to the evaluation of the change of the enthalpy and entropy of the solid. The evaluation of the relevant physical quantities concerning the vapor was rather straightforward using almost fresh formulas from the thermodynamic literature [17, 18]. We used MATLAB to execute the task and the calculated entities were used in subsequent vapor pressure and heat of sublimation evaluations.

Now, concerning the theoretical approach, we mainly derived a formula for the vapor pressure including a correction for gas imperfection and effects for internal structure, as well as a formula for the heat of sublimation with same purposes.

IV. ACKNOWLEDGMENTS

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Appendix

This section is devoted to provide the main MATLAB codes, as a part of the numerical method, leading to the results shown in this paper.

Part(I)

Part(I) shows the data sites used by G&E (15.52→189.78 K) & (0.606→13.05 cal·K⁻¹·mol⁻¹). We evaluate the spline through the extended data sites (t, cp), the integrals \( \int_0^T c_p \, dT' = h_s(T) + \epsilon_0 = \Delta h_s(T) \) (vector I) and \( \int_0^T (c_p/T') \, dT' = s_s(T) \) (vector J), with \( T \in T_n \).

```matlab
syms x z real;
f=(12/(x^3))*int((z^3)/(exp(z)-1),z,0,x);
g=(3*x)/(exp(x)-1); A=f-g; cd=3*1.98724*A;
u=0.01:0.01:15.25; xn=139.59./u;
v=real(double(subs(cd,x,xn))); t=[0 u 15.52 17.30 19.05 21.15 23.25 25.64 27.72 29.92 32.79 35.99 39.43 43.19 47.62 52.11 56.17 61.26 66.24 71.22 76.47 81.94 87.45 92.71 97.93 103.26 108.56 113.91 119.24 124.58 130.18 135.74 141.14 146.48 151.67 156.72 162.00 167.62 173.36 179.12 184.58 189.78]; cp=[0 v 0.606 0.825 1.081 1.419 1.791 2.266 2.676 3.069 3.555 4.063 4.603 5.195 5.794 6.326 6.765 7.269 7.302 7.707 8.047 8.370 8.703 8.984 9.189 9.421 9.671 9.893 10.07 10.27 10.44 10.69 10.88 11.08 11.27 11.45 11.64 11.84 12.07 12.32 12.57 12.82 13.05]; Tn=0.001:0.002:196.001; spcp=spline(t,cp,Tn); I=0.002*cumsum(spcp); J=0.002*cumsum(spcp./Tn);
```

Part(II)

We evaluate the ideal-gas and real-gas pressures (Eqs. \( \text{(8)} \) & \( \text{(7)} \)) at 160, 180 & 194.67 K. The evaluated pressures are represented by the 3-vectors \( \Pi \) and \( \text{PTW} \), respectively.

```matlab
Eps=6274; T=[159.999 179.999 194.669]; m=[80000 90000 97335]; ms=I(m)-(T.*J(m)); P=7.575455*(10^5); l1=9*304.1/(128*72.8*760); l2=6*(304.1^2); S=exp(ms./(1.98724*T)); Ztr=(1/(2*0.561))*(T.^(7/2)).*
```

\begin{align}
\text{ones(size(T))} &+ ((0.561/3)./T)); \\
Zv &=(1./((\text{ones(size(T))-exp(-954./T)).^2}).* \\
& (1./((\text{ones(size(T))-exp(-1890./T))).) * \\
& (1./((\text{ones(size(T))-exp(-3360./T))).) * \\
\text{PI} &=(760/101325)*PC).*((Ztr.*Zv).* \\
& (S.*exp(-Eps./(1.98742*T)))) \\
\text{V} &=(11*((\text{ones(size(T))-12./(T.^2))).*(PI./T)).+ \\
\text{ones(size(T)); PTW}=\text{PI}.//V; \\
\text{T} & = 160 \quad 180 \quad 194.67 \\
\text{PI} & = 23.604 \quad 204.845 \quad 739.817 \\
\text{PTW} & = 23.632 \quad 206.308 \quad 754.942 \\
\end{align}

**Part(III)**

We evaluate the the heat of sublimation (Eq. (12)) 160, 180 & 194.67 K. The output is the 3-vector $LTW$.

\begin{align}
\text{IT} & = \text{ones(size(T)); h1}=954./(\exp(954./T)-\text{IT}); \\
\text{h2} & = \exp(1890./T)-\text{IT}; \\
\text{h3} & = \exp(3360./T)-\text{IT}; \\
\text{hv} & = 1.98724*(2*h1)+h2+h3; \\
\text{hg} & = ((3.5+1.98724).*T)+hv-(((1.98724*0.561)/3)*\text{IT}; \\
\text{GI} & = (1.98724*11).*\text{IT}-(3*12./(T.^2))).*\text{PTW}; \\
\text{LTW} & = \text{Eps}-I(m)+\text{hg}+\text{GI}; \\
\text{T} & = 160 \quad 180 \quad 194.67 \\
\text{LTW(cal/mol)} & = 6227.4 \quad 6125.5 \quad 6030.4 \\
\text{LTW(J/mol)} & = 26055 \quad 25629 \quad 25231 \\
\end{align}

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