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Low-temperature Data for Carbon Dioxide

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Summary. We investigated empirical data for the vapor pressure ($154 \leq T \leq 196\,\mathrm{K}$) and the heat capacity ($12.52 \leq T \leq 189.78\,\mathrm{K}$) of solid carbon dioxide. A computer algebra system (*CAS*) was used for all calculations. From the numerical point of view, we have adopted a cubic piecewise polynomial representation for the heat capacity and reached an excellent agreement between the available empirical data and the calculated ones. Furthermore, we have obtained values for the vapor pressure and heat of sublimation at temperatures below 195 right down to 0 K. The theoretical key prerequisites are: 1) Determination of the heat of sublimation of $26250\,\mathrm{J \cdot mol^{-1}}$ at vanishing temperature and 2) Elaboration of a 'linearized' vapor pressure equation that includes all the relevant properties of the gaseous and solid phases. It is shown that: 1) The empirical vapor pressure equation derived by *Giauque* & *Egan* remains valid below the assumed lower limit of 154 K (a similar argument holds for *Antoine*'s equation), 2) The heat of sublimation reaches its maximum value of $27211\,\mathrm{J \cdot mol^{-1}}$ at 58.829 K and 3) The vapor behaves as a (polyatomic) ideal gas even for temperatures below 150 K.

Keywords. Thermodynamics; Phase transitions; Computer chemistry; Spline.

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 over an extended range of temperatures. Significant effort has been deployed to build up a database through observations and theoretical calculations [2–13]. From the former point of view, we mention the accurate measurements due to *Giauque* and *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 capacities of carbon dioxide in the range of temperatures between 15 and 50 K [5], in very good agreement with those 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

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eliminating the superheating of the gas [3]. 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 only at sufficiently low temperatures ($T < 50\,\mathrm{K}$) 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 Ref. [3], which we refer to as *G&E*, and show that it is possible to evaluate the heat of sublimation L ($\Delta_{\text{sub}}H$) and vapor pressure p at temperatures $5 \le T \le 195\,\mathrm{K}$. A key prerequisite is the determination of the heat of sublimation at $T = 0\,\mathrm{K}$ ($L(0) = \varepsilon_0$). *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 $26.3\,\mathrm{kJ \cdot mol^{-1}}$ ($6286\,\mathrm{cal \cdot mol^{-1}}$) for $139 \le T \le 195\,\mathrm{K}$ [10]. However, the literature citations listed in Ref. [4] show that *Stull* did not extract data from *G&E*, which are even more accurate and include data concerning the heat capacity of solid carbon dioxide and other data that could be used to obtain L at different temperatures. By contrast, *G&E* have evaluated L at $194.67\,\mathrm{K}$ 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 $10\,\mathrm{cal \cdot mol^{-1}}$ higher than their measured value $L_{\text{meas}}(194.67) = 6030 \pm 5\,\mathrm{cal \cdot mol^{-1}}$ ($25230 \pm 21\,\mathrm{J \cdot mol^{-1}}$). They also evaluated the entropies of the gas and solid at $194.67\,\mathrm{K}$ and reached an *excellent* agreement between experimental data and statistics (the experimental and spectroscopic values of the entropy of the gas s_g they obtained were 47.59 and $47.55\,\mathrm{cal \cdot K^{-1} \cdot mol^{-1}}$, 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 afore-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 $6030.4\,\mathrm{cal \cdot mol^{-1}}$ ($25231\,\mathrm{J \cdot mol^{-1}}$). 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 will be given with 2 or 3 significant digits. The values of L (of the order of $26000\,\mathrm{J \cdot mol^{-1}}$) 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.

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 $R = 1.98724\,\mathrm{cal}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$, 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 subinterval 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). 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 breaks `spline (x, y, x(i))` coincide with the data values `y (i)`. Cubic splines are more attractive for interpolation purposes than higher-order polynomials [16].

We will deal with molar physical quantities labeled by the subscripts s and g to differentiate between the solid and gaseous phases. We denote by L the latent heat of sublimation and by u_i, a_i, μ_i, v_i, h_i, s_i ($i = s, g$), the internal energy, free energy, chemical potential, volume, enthalpy, and entropy, respectively. We take the zero of rotational energy to be that of the $J = 0$ state and the zero of vibrational energy to be that of the ground state, meaning that a molecule at rest in the gas has an energy of zero at vanishing temperature ($u_g(0) = 0$). Let ε_0 be the heat of sublimation at $T = 0$ which is, according to our energy convention, the binding energy of the particles of the solid ($u_s(0) = a_s(0) = h_s(0) = \mu_s(0) = -\varepsilon_0 < 0$).

The excellent agreement between the experimental and 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[a]. *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 the *Debye* temperature θ_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* and *Schnepp*'s assertion that the molar heat capacities of the solid carbon dioxide (c_v and c_p) are equal within an error of 10^{-5} per cent for such low temperatures [5]. Finally, we fix θ_D by equating the heat capacity due to *Debye* with that measured by *G&E* at 15.52 K ($0.606\,\mathrm{cal}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$). Solving the equation using a *CAS* we find $\theta_D = 139.59$ K.

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[a] The more advanced theory elaborated in Ref. [5] reduces at low temperatures to *Debye*'s theory

The MATLAB codes provided in the appendix are split into three parts. In Part(I), `cd` represents the *Debye* heat capacity. The vectors `t` and `cp` show the temperature data sites used by *G&E* (15.52 → 189.78 K) and the corresponding measured heat capacities ($0.606 \rightarrow 13.05\,\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), 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 $\int_0^T c_p\,\mathrm{d}T' = h_s(T) + \varepsilon_0 = \Delta h_s(T)$ (vector `I`) and $\int_0^T (c_p/T')\,\mathrm{d}T' = s_s(T)$ (vector `J`), with $T \in$ `Tn`.

The heat of sublimation ε_0 is obtained upon solving the equation $\mu_g = \mu_s$ at any given temperature for which the measured L is known. The lead we had followed seeking for higher accuracy led us to select the value of $L = 6190\,\text{cal}\cdot\text{mol}^{-1}$ at 170 K [2, 3]. We find $\varepsilon_0 = 6273.4\,\text{cal}\cdot\text{mol}^{-1}$ and the calculation is shown below.

With $\mu_g = a_g + pv_g$ & $\mu_s = h_s - Ts_s$, the equation $\mu_g = \mu_s$ reduces to $\varepsilon_0 = \Delta h_s - Ts_s - a_g - pv_g$. Upon solving the *Clapeyron* equation for pv_g we obtain $pv_g = [L\cdot(T\,\mathrm{d}\ln p/\mathrm{d}T)^{-1}] + pv_s$, and finally Eq. (1).

$$\varepsilon_0 = \Delta h_s - Ts_s - a_g - \frac{L}{T(\mathrm{d}\ln p/\mathrm{d}T)} - pv_s \tag{1}$$

We will make use of the *G&E* empirical equation (Eq. (2)) to evaluate p and $\mathrm{d}\ln p/\mathrm{d}T$ at 170 K.

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

By using $a_1 = -1354.210\times\ln 10$, $b_1 = 8.69903\times\ln 10$, $c_1 = 0.001588\times\ln 10$, $d_1 = -4.5107\times 10^{-6}\times\ln 10$, we obtain $p(170) = 74.59$ Torr. Since $v_s = 25.55\,\text{cm}^3\cdot\text{mol}^{-1}$ [5], the last term $pv_s = 0.06\,\text{cal}\cdot\text{mol}^{-1}$ is neglected. The term including L equals $6190/(170\times 0.108021) = 337.08\,\text{cal}\cdot\text{mol}^{-1}$, and $\Delta h_s(170)$ and $s_s(170)$ are the 85000th components of the vectors `I` and `J`: $\Delta h_s(170) - 170\times s_s\,(170) =$ `I(85000)` $-$ `170*J(85000)` $= -1227.8\,\text{cal}\cdot\text{mol}^{-1}$.

Now, we make our first hypothesis concerning the vapor. We assume the validity of the first order virial expansion neglecting thus the higher order terms, and this has always been done for carbon dioxide [3] at such low temperatures. We have then Eq. (3), thereby we can show that the term a_g in Eq. (1) is the free energy of an ideal[b] gas evaluated at the point $(T, p) = (170\,\text{K}, 74.59\,\text{Torr})$.

$$pv_g = RT + B(T)\,p \tag{3}$$

For the molecule of CO_2 we have $a_g = a_\text{t} + a_\text{r} + a_\text{v}$, which is the sum of the translational, rotational, and four vibrational contributions $a_\text{v} = 2a_{\text{v}1} + a_{\text{v}2} + a_{\text{v}3}$ [17, 18]. With our choice of the origin of the energy, these contributions can be written as shown by Eq. (4) with $C = 7.575455\times 10^5$ in SI units ($= (2\pi m/h^2)^{3/2} k^{5/2}$) and $\theta_\text{r} = 0.561$, $\theta_{\text{v}1} = 954$, $\theta_{\text{v}2} = 1890$, $\theta_{\text{v}3} = 3360\,\text{K}$.

$$a_\text{t} = -RT\ln(C\mathrm{e}\,T^{5/2}/p); \qquad a_\text{r} = R\{-T\ln[T/(2\,\theta_\text{r})] + \theta_\text{r}/3\};$$
$$a_{\text{v}i} = RT\ln[1 - \exp(-\theta_{\text{v}i}/T)]; \quad (T \geq 5\,\text{K}) \quad \text{and} \quad (i = 1\text{–}3) \tag{4}$$

We have then $a_g(170) = -7838.2\,\text{cal}\cdot\text{mol}^{-1}$ leading with the previously evaluated terms to $\varepsilon_0 = 6273.4\,\text{cal}\cdot\text{mol}^{-1}$.

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[b] In fact, we can show that the correction for gas imperfection to μ_g is under the above assumption $pv_g - RT$, implying $a_g = a_{g\,\text{ideal}}$

Vapor Pressure

From now on we will assume $\varepsilon_0 = 6274\,\mathrm{cal}\cdot\mathrm{mol}^{-1}$ ($26250\,\mathrm{J}\cdot\mathrm{mol}^{-1}$). Upon substituting Eqs. (3) and (4) into $\varepsilon_0 = \Delta h_s - Ts_s - a_g - pv_g$ ($\mu_g = \mu_s$) and rearranging the terms we obtain Eq. (5) where $Z_\mathrm{v} = Z_{\mathrm{v}1}{}^2 Z_{\mathrm{v}2} Z_{\mathrm{v}3}$, $Z_{\mathrm{v}i} = [1 - \exp(-\theta_{\mathrm{v}i}/T)]^{-1}$ ($i = 1$–3), and[c] $Z_\mathrm{r} = [T + \theta_\mathrm{r}/3] \cdot (2\,\theta_\mathrm{r})^{-1}$.

$$p = CT^{5/2} Z_\mathrm{r} Z_\mathrm{v} \exp\{[\Delta h_s - Ts_s - \varepsilon_0 - B(T)p]/RT\} \tag{5}$$

Assuming that $B(T)$ follows *Berthelot*'s equation (Eq. (6)) [13, 14] where $\ell_2 = 6\times 304.1^2\,\mathrm{K}^2$ and, in order to express $B(T)\,p$ in $\mathrm{cal}\cdot\mathrm{mol}^{-1}$, we take $\ell_1 = 9\times 304.1/(128\times 72.8\times 760)$ K/Torr, we have solved numerically both Eq. (5) and its linearized form and the results coincide up to an insignificant error.

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

Upon substituting $\exp[-B(T)p/RT] = 1 - B(T)p/RT$ into Eq. (5), the linearized equation yields Eq. (7) where p_ideal (in Torr) is the corresponding pressure for an ideal gas (Eq. (8)).

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

$$p_\mathrm{ideal}(\mathrm{Torr}) = (760/101325)\,C\,T^{5/2} Z_\mathrm{r} Z_\mathrm{v} \exp\{[\Delta h_s - Ts_s - \varepsilon_0]/RT\} \tag{8}$$

Table 1 and Fig. 1 compare values of the vapor pressure derived in this work (TW) with those of *G&E* (Eqs. (7) and (2)). We have evaluated Eq. (2) at temperatures below the left-end point 154 K, as shown in Table 1, and the formula remains applicable, however, for temperatures above 110 K; below this temperature, Eq. (2) diverges from Eq. (7). The third column (A) of Table 1 shows values of the vapor pressure evaluated using *Antoine*'s equation [14]. The constants $A_1 = 6.81228$, $B_1 = 1301.679$, and $C_1 = -3.494$ of *Antoine*'s equation have been evaluated by the *National Institute of Standards and Technology* (*NIST*) [10] from *G&E* data. The equation writes as shown by Eq. (9) where $\bar{A_1} = A_1 \ln\ 10$ and $\bar{B_1} = B_1 \ln\ 10$.

$$p_\mathrm{A}(\mathrm{Torr}) = (760/1.01325)\ \exp\{\bar{A_1} - [\bar{B_1}/(A_1 T + C_1)]\} \quad (154.26 \leq T \leq 195.89\,\mathrm{K}) \tag{9}$$

From Table 1 we establish the following results. Equations (2) and (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 given in Part(II) of the appendix, which show the evaluation of the ideal-gas pressure Eq. (8) and the real-gas pressure Eq. (7) at 160, 180, and 194.67 K. The evaluated pressures are represented by the 3-vectors `PI` and `PTW`, respectively.

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[c] 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 θ_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 1. 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 imperfection 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	$p_{\text{TW}}/\text{Torr}$	$p_{G\&E}/\text{Torr}$	p_A/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	329(C)	330(C)	328(C)
190	511(C)	513(C)	511(C)
195	776(C)	781(C)	777(C)

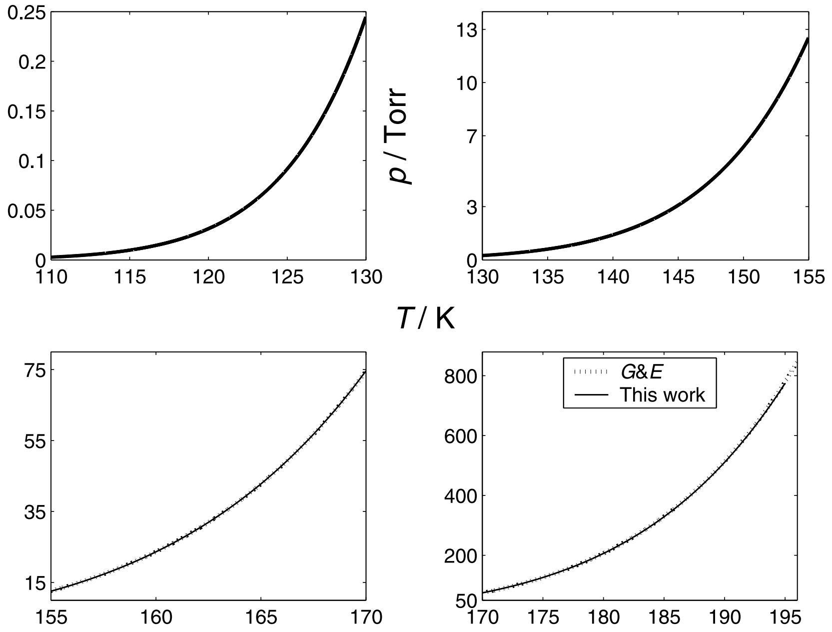

Fig. 1. The vapor pressure *vs*. the temperature; solid line: this work (TW) plotted for $110 \leq T \leq 195$, dotted line: *G&E* plotted for $155 \leq T \leq 196$

Heat of Sublimation

Combining different thermodynamic entities we establish Eq. (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 $h_g = R[(7T/2) - (\theta_\mathrm{r}/3)] - T^2[\mathrm{d}(a_\mathrm{v}/T)/\mathrm{d}T]$ (Eq. (4)).

$$L(T) = \varepsilon_0 - \Delta h_s(T) + h_g(T) + [B(T) - (T\,\mathrm{d}B/\mathrm{d}T)]\,p(T) \qquad (10)$$

Looking for extreme values we can first ignore the correction for gas imperfection then justify it later. We have solved graphically the equation $\mathrm{d}L/\mathrm{d}T = 0$ ($c_{p\,s} = c_{p\,g}$) and obtained the values 57.829 K for T and 6503.58 $\mathrm{cal\cdot mol^{-1}}$ for L as shown in Fig. 2. We will assume $L_\mathrm{max} = 6503.6\,\mathrm{cal\cdot mol^{-1}}$ ($27211\,\mathrm{J\cdot mol^{-1}}$). Tables 2 and 1, however, show that at 57.829 K the vapor behaves as an ideal gas, and this justifies the omission of the correction terms in $\mathrm{d}L/\mathrm{d}T = 0$.

Substituting Eq. (6) into Eq. (10), this latter splits into two equations (Eqs. (11) and (12)) whether we evaluate the vapor pressure using Eqs. (2) or (7).

$$L_{G\&E} = \varepsilon_0 - \Delta h_s(T) + h_g(T) + R\ell_1[1 - (3\ell_2/T^2)]p_{G\&E} \quad (154 \le T \le 196\,\mathrm{K}) \quad (11)$$

$$L_\mathrm{TW} = \varepsilon_0 - \Delta h_s(T) + h_g(T) + R\ell_1[1 - (3\ell_2/T^2)]\,p_\mathrm{TW} \quad (T \ge 5\,\mathrm{K}) \qquad (12)$$

Equations (11) and (12) are plotted in Fig. 2. In the codes provided in Part(III) of the appendix, we evaluate the r.h.s of Eq. (12) at 160, 180, and 194.67 K (3-vector `LTW`). The value of the latent heat obtained at 194.67 K is 6030.4 $\mathrm{cal\cdot mol^{-1}}$

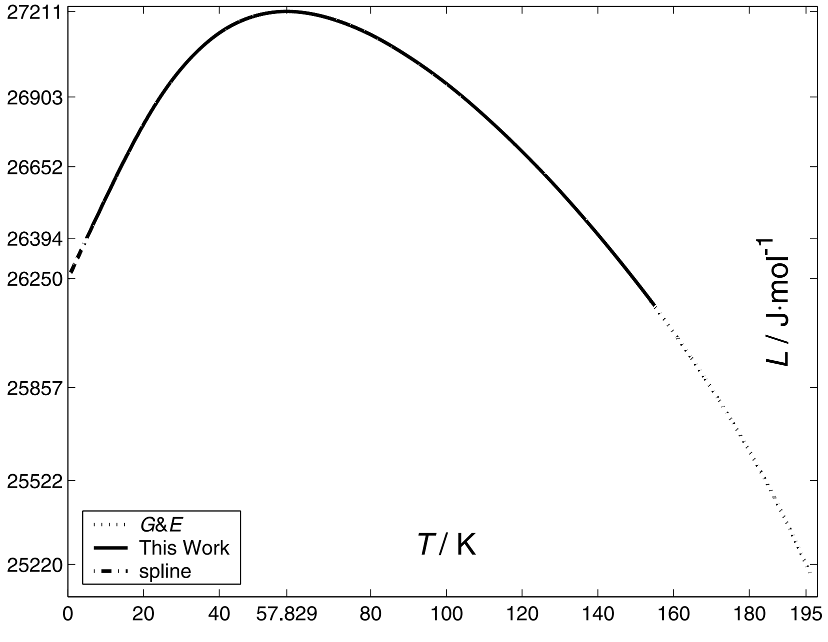

Fig. 2. The heat of sublimation *vs.* the temperature; solid line: this work (TW) plotted using the derived Eq. (12), dotted line: plotted using the same equation with $p_{G\&E}$, dash-dot line: arc of the spline through the data (T, L_TW) and $T = 5n$ K ($0 \le n \le 31$, positive integer) shown in Table 2; this arc extrapolates the solid line to temperatures below 5 K

Table 2. Heat of sublimation data; the values of the heat of sublimation 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 Eq. (2); 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	$L_{\mathrm{TW}}/\mathrm{J\cdot mol^{-1}}$	$L_{G\&E}/\mathrm{J\cdot mol^{-1}}$	T/K	$L_{\mathrm{TW}}/\mathrm{J\cdot mol^{-1}}$	$L_{G\&E}/\mathrm{J\cdot mol^{-1}}$
0	26250	NA	100	26951	NA
5	26394	NA	105	26896	NA
10	26538	NA	110	26836	*26836*
15	26676	NA	115	26773	*26773*
20	26804	NA	120	26707	*26707*
25	26914	NA	125	26637	*26637*
30	27005	NA	130	26565	*26565*
35	27077	NA	135	26488	*26488*
40	27133	NA	140	26408	*26408*
45	27172	NA	145	26325	*26325*
50	27197	NA	150	26239(C)	*26239*(C)
55	27209	NA	155	26149(C)	26149(C)
60	27210	NA	160	26055(C)	26055(C)
65	27201	NA	165	25958(C)	25958(C)
70	27183	NA	170	25855(C)	25855(C)
75	27158	NA	175	25745(C)	25745(C)
80	27128	NA	180	25629(C)	25629(C)
85	27091	NA	185	25504(C)	25504(C)
90	27048	NA	190	25368(C)	25368(C)
95	27002	NA	195	25221(C)	25220(C)

($25231\,\mathrm{J\cdot mol^{-1}}$) or $6030.6\,\mathrm{cal\cdot mol^{-1}}$ ($25232\,\mathrm{J\cdot mol^{-1}}$) whether we calculate the r.h.s of Eqs. (12) or (11).

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 Ref. [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 $T = 5j\,\mathrm{K}$ ($1 \leq j \leq 39$, positive integer) form a subvector of `J` (see Part(I) of the appendix) 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)` = $16.52\,\mathrm{cal\cdot K^{-1}\cdot mol^{-1}}$ (58.87, 64.85, and $69.12\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, respectively).

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 was 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 appropriate 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 of internal structure, as well as a formula for the heat of sublimation with similar intentions.

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) and (0.606 → 13.05 $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). We evaluate the spline through the extended data sites (`t, cp`), the integrals $\int_0^T c_p \, \mathrm{d}T' = h_s(T) + \varepsilon_0 = \Delta h_s(T)$ (vector `I`), and $\int_0^T (c_p/T') \, \mathrm{d}T' = s_s(T)$ (vector `J`), with $T \in$ `Tn`.

```
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 60.86 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. (8) and (7)) at 160, 180, and 194.67 K. The evaluated pressures are represented by the 3-vectors `PI` and `PTW`, respectively.

```
Eps = 6274; T = [159.999 179.999 194.669];
m = [80000 90000 97335]; ms = I(m) − (T.*J(m));
PC = 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)).*
(ones(size(T)) + ((0.561/3)./T)));
```

```
Zv = (1./((ones(size(T)) − exp(−954./T)).^2)).*
(1./(ones(size(T)) − exp(−1890./T))).*
(1./(ones(size(T)) − exp(−3360./T)));
PI = ((760/101325)*PC).*((Ztr.*Zv).*
(S.*exp(−Eps./(1.98742*T))));
V = (l1*((ones(size(T)) − (l2./(T.^2))).*(PI./T))) +
ones(size(T)); PTW = PI./V;
T   = 160    180     194.67
PI  = 23.604 204.845 739.817
PTW = 23.632 206.308 754.942
```

Part(III)

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

```
IT = ones(size(T)); h1 = 954./(exp(954./T) − IT);
h2 = 1890./(exp(1890./T) − IT);
h3 = 3360./(exp(3360./T) − IT);
hv = 1.98724*((2*h1) + h2 + h3);
hg = ((3.5*1.98724).*T) + hv − (((1.98724*0.561)/3)*IT);
GI = (1.98724*l1).*(IT − ((3*l2)./(T.^2))).*PTW;
LTW = Eps − I(m) + hg + GI;
T            = 160    180    194.67
LTW(cal/mol) = 6227.4 6125.5 6030.4
LTW(J/mol)   = 26055  25629  25231
```

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