Review by Pascal Marquet of the paper "acp_2020_361"

entitled: Reappraising the appropriate calculation of a common meteorological quantity: Potential Temperature.

by Manuel Baumgartner, Ralf Weigel, Ulrich Achatz, Allan H. Harvey, and Peter Spichtinger.

1 General Major Comments / Recommendations

The paper of Baumgartner, Weigel, Achatz, Harvey and Spichtinger submitted to the Atmospheric Chemistry and Physics examines the impact of temperature variation in specific heat capacity $c_p(T)$ on the calculation of the potential temperature θ and entropy of dry air.

The authors show that, through integration and a cumulative effect, the impacts of $c_p(T)$ on θ appear to be significant above 10 to 20 km height. The authors show that modified calculations of θ for dry air can induce "non-negligible" differences in predicting the altitude of gravity wave breaking, "although not excessive".

It is undeniable that the hypothesis of constant values of c_p for dry air and water vapour is only a first approximation that deserves to be studied further, even if the variations of c_p with temperature is by far greater for the liquid and solid phases of water.

It seems to me, however, that the authors should comment on and/or answer a series of questions that arise on reading their article.

(1) – the authors present in section 3 a range of possible dry-air values of c_p that appear to be greatly exaggerated, ranging from 994 to 1011 J/K/kg. I show in this review that the uncertainty interval must be much smaller (1004.5 to 1007.5 J/K/kg), which must imply impacts on values of θ about 7 times smaller than those considered at high altitude in the document. The authors should modify sections 2 to 5 and Figures 2, 3 and 4, by reducing the uncertainty on c_p and by retaining only the more recent and realistic values.

(2) – I show from copies of previously published papers, tables and figures that the observed values of $c_p(T)$ for T < 320 K contradict values above 1007.5 J/K/kg, those under 1004.5 J/K/kg and the (ideal gas) formulations of Lemmon et al. (2000) and Dixon (2007) considered in section 4 by the authors. Observed values of $c_p(T)$ for T < 320 K are rather consistent with the (real gas) NIST-REFPROP formulation considered in section 6 and with the IAPWS-TEOS10 formulation.

(3) – In this sense, the approach followed by the authors to calculate first values of θ_{ref} from the ideal-gas formulation of $c_p(T)$ by Lemmon et al (2000), and then those of θ_{real} for the real-gas NIST-REFPROP formulation, seems attractive, with however a comparison to irrelevant and too extreme constant values of 1011 and 994 J/K/kg in Figure 4 of the paper.

(4) – Moreover the results of your section 6 seem strange to me, because the comparison of $\theta_{\rm ref}$ deduced from the ideal-gas Lemmon's formulation (purple curve in your figure 3) with $\theta_{\rm real}$ deduced from the real-gas NIST-REFPROP's formulation (yellow discs in your figure

3) gives very small differences on figures 8. Indeed, the differences $\theta_{\text{real}} - \theta_{\text{ref}}$ of less than 0.05 K for $\theta > 700$ K above 20 km (less than 0.007%) seem unrealistic and not consistent with differences of 4.5 J/K/kg (or 4.5 %) for $c_p(T)$ at 200 K, 2.8J/K/kg (or 2.8%) at 250K and 1.3 J/K/kg (or 1.3 %) at 300 K (values deduced from the yellow discs and the purple curve in your figure 3).

I guess that the relative differences $(\theta_{\text{real}} - \theta_{\text{ref}})/\theta_{\text{ref}}$ should be of the order of a few percent above 25 km and should increase with height, as indicated by a rough analysis of the differences between curves of your Figure 4b (to be checked by you, however, from direct computations and/or from a version with a linear scale of your figure 4b).

Differences of several percent between ideal-gas and real-gas formulations of $c_p(T)$ should lead to larger differences in the gap between θ_{real} and θ_{ref} . This should result in a likely change in the conclusion in your section 6 and the use of formulations from IAPWS-TEOS10 (free) or INIST-REFPROP (to buy), rather than the analytical formula of Lemmon et al (2000, Eq.18, page 345) that is contradict by the values of $c_p(T)$ published in Table A2 (pages 366-367) of the same paper (see Fig.9 in section 3 bellow)

(5) – In fact, after reflection and analysis of this aspect (4), this is probably a false problem. Indeed, everything seems to be explained by the fact that the major differences for your θ come from values of c_p for highest T temperatures, say between 400 K and 2000 K. This aspect is not documented in your figure 3, where the values of c_p are only plotted up to 485 K.

The fact that the values of your θ_{real} and θ_{ref} are very close must be explained by a low sensitivity of your θ to values of c_p for ambient temperatures (let's say those ranging from 200 K to 320 K and which define how the physical parameterizations should influence the weather parameters), with, on the other hand, a strong sensitivity of your θ to values of c_p for temperatures above 400 K (temperatures that are not observed in the real atmosphere but that intervene numerically in the calculation of your θ when passing from high altitudes where the pressure is very low and returning adiabatically towards the ground level through very high artificial temperatures).

Therefore, if you are interested in the values of θ calculated by an adiabatic evolution from a very low pressure p to a (surface) pressure $p_0 = 1000$ hPa, you should better describe the accuracy of the values of $c_p(T)$ for T > 400 K.

(6) – Another aspect should be addressed in this article. One of the goals of our community is to provide efficient and applicable numerical methods for climate and numerical weather prediction models. In this sense, it would be useful to quantify the iterative processes designed and tested in this article: what is the extra cost (in CPU) for the calculation of $\theta_{\rm ref}$ and $\theta_{\rm real}$ compared to the direct calculation θ_{c_p} for a constant c_p ? (make this evaluation for example for a set of vertical columns of standard atmosphere)

(7) – For me, the most problematic aspect concerns the application you chose in section 7, by assuming that the squared Brunt-Väisälä frequency could be

$$N^2 = \frac{g}{\theta} \frac{\partial \theta}{\partial z} \,, \tag{1}$$

where θ would be calculated by the particle method (by an adiabatic evolution from a very low pressure p to a surface pressure $p_0 = 1000$ hPa).

Differently, we recalled in Marquet and Geleyn (2013, MG13) that N^2 should be calculated from the local gradients of basic meteorological parameters (temperature and pressure if dry air is considered), and not from the variable θ that you study in your article (by an adiabatic evolution from a very low pressure p to a surface pressure $p_0 = 1000$ hPa).

In fact N^2 corresponds to adiabatic fluctuations of the density, before anything else. Accordingly, equations (B2) and (1) of MG13 applied to dry air give the corresponding expression of N^2 as a function of local vertical gradients of density (ρ) and specific entropy (s):

$$N^{2} = \left. \frac{g}{\rho} \left. \frac{\partial \rho}{\partial z} \right|_{s} - \left. \frac{g}{\rho} \left. \frac{\partial \rho}{\partial z} \right|_{s} = \left. \left(-\frac{g}{\rho} \left. \frac{\partial \rho}{\partial s} \right|_{p} \right) \left. \frac{\partial s}{\partial z} \right. \right|_{s}$$

where the first vertical derivative (of density with respect to z) is computed at constant entropy and the second vertical derivative (of density with respect to s) is computed at constant pressure. The local state equation $p = \rho RT$ and $\rho = p/(RT)$ with constant R and p implies

$$\left. \frac{\partial \rho}{\partial s} \right|_p = \left. - \frac{\rho}{T} \left. \frac{\partial T}{\partial s} \right|_p$$

The dry-air Gibbs equation writes $T ds = dh - dp/\rho$, with $dh = c_p(T) dT$ and with possibly $c_p(T)$ depending on absolute temperature. For constant pressure, this Gibbs equation reduces to $T ds|_p = c_p(T) dT|_p$, leading to $dT/ds|_p = T/c_p(T)$, and thus to $d\rho/ds|_p = -\rho/c_p(T)$. The squared dry-air Brunt-Väisälä frequency is therefore equal to

$$N^2 = \frac{g}{c_p(T)} \frac{\partial s}{\partial z}.$$
 (2)

The dry-air Gibbs equation can then be used again to write $T \partial s/\partial z = c_p(T) \partial T/\partial z - (1/\rho)\partial p/\partial z$ which is valid for vertical oscillations. If moreover hydrostatic conditions prevail, then $\partial p/\partial z = -\rho g$, leading to

$$N^2 = \frac{g}{T} \left(\frac{\partial T}{\partial z} + \frac{g}{c_p(T)} \right)$$
(3)

This equation corresponds to the dry-air version of (22) in MG13, and it is Equation (1a) in the previous famous paper of Durran and Klemp (1982) about computations of the Brunt-Väisälä frequency (a key paper that you do not cite).

An expected result is that $N^2 = 0$ for the dry-air adiabatic lapse rate $\partial T/\partial z = -g/c_p(T)$.

The important finding for your study is that there is no need to use the gradient of any potential temperature for computing N^2 . Really, only the vertical gradient of T has to be calculated in (3), where it is possible to take into account the variations of $c_p(T)$ with the temperature you want to study in your paper. It is thus "possible", but not "mandatory", to use (2) and a possible entropy formulation $s = c_p \ln(\theta) + const$ for the entropy to get the form (1) $N^2 = (g/\theta) \frac{\partial \theta}{\partial z}$ you have considered in your paper, but if and only if c_p is a constant. And this is not possible if $c_p(T)$ depends on the temperature, with in this case the need to stick with the formulation (3) recalled above in terms of the gradient $\frac{\partial T}{\partial z}$.

The other important result here is that it is the local temperature that is involved in $c_p(T)$, so those between 1004.5 J/K/kg and 1007.5 J/K/kg for 200 K < T < 320 K, and especially not the ones at the higher temperatures that you studied in your paper to calculate $\theta_{\rm ref}$ or $\theta_{\rm real}$, which are not needed for computing N^2 by (3). It therefore seems to me that the application described in your section 7 is inaccurate, since the formulation (1) that you use for N^2 is not the right one (3). If so, can you show another application where values of your formulation of θ_{ref} or θ_{real} would intervene in meteorological science?

(8) – My recommendation is that the document deserves acceptance only if the impacts described in section 7 concerning gravity waves are real.

Therefore, the authors must provide evidence that it is indeed their formulations of θ_{ref} or θ_{real} (obtained by an adiabatic evolution between the pressures p and p_0) that intervenes in the Brunt-Väisälä frequency formula, and not the local vertical gradients of temperature and pressure derived in Durran and Klemp (1982) and Marquet and Geleyn (2013).

If the authors can provide this evidence, then their paper would merit to be published subject to taking all the major recommendations and specific comments into account, or explaining why they do not need to take them into account.

2 Specific Comments

- Line 1: add dry in: "... it is conserved for dry air's adiabatic ..."

- Lines 10 to 22: I do not have access to Wegener's book (1911) and I confess that I was not aware of Köppen's oral contribution (1888). I have cited only the contributions of von Helmholtz and von Bezold in my papers (Marquet 2011, 2017, 2019b, Marquet and Dauhut 2018). I have been able to verify, however, Kutzbach's sentence (1979, page 143) in which Köppen's (1988) oral contribution is mentioned (see the excerpts in the Figure 1 in section 3 bellow). However, the title of the 1888 lecture of Köppen is written in Kutzbach (1979) as: "Ueber die Luftmischung und potentielle Temperatur", which might be different from the one in your bibliography: "Über Luftmischung..."? Moreover, I have not found the paper (or a copy of this lecture) of Köppen: do you have a copy of this lecture, or are you just citing the sentence of Kutzbach? Finally, I do not understand why you cite the URL: http://snowcrystals.com/?

- Lines 10 to 28: It would be useful to refer to the papers by Poisson (1833) and Thomson (1862-65) who had clearly imagined, before von Helmoltz and von Bezold in 1888, this idea of adiabatic variation on the vertical and the calculation of temperature for an air particle brought back to the surface (see section 5 of Marquet and Dauhut, 2018, and Marquet 2019b). I give copies of these articles on Figures 2 and 3.

- Lines 10 to 28: It would be useful to refer to Bauer's paper (1908-1910), where the link between entropy and the potential temperature of dry air is made for the first time (see citations in Marquet 2011, Marquet and Dauhut 2018 and Marquet 2019b). I give copies of this paper of Bauer on Figures 4 and 5

- Lines 53 to 61: You should mention the basic references for the definition and the use of $PV(\theta)$: Ertel (1940) and Hoskins (1987) at least (see also Schubert et al. 2004 cited in Marquet 2014).

- Lines 65-67: The studies of the moist-air entropy by Hauf and Höller (1987) and Marquet (2011) do not start from the Gibbs' equation " $Tds = dh - dp/\rho - \sum_n \mu_n dq_n$ ". On the contrary, they start from the moist-air entropy $s = \sum_n q_n s_n$ expressed as the weighted sum of the entropies s_n for its n = 0, ..., 3 constituents (dry air, water vapour, liquid water and ice) with concentrations q_n (specific contents).

- Lines 68-69: The assumption of "local equilibrium" and use of latent heats release (of vaporization L_v and sublimation L_s) are also included in the definition of Hauf and Höller (1987) and Marquet (2011), not only in the formulation of Emanuel (1994).

- Lines 69-70: It is not true that "These formulations always rely on the assumption of reversible processes (i.e. conserved entropy)". On the contrary, the formulation $s(\theta_s)$ of Marquet (2011, ...) makes it possible to measure and quantify the losses or increases in moist-air entropy associated with irreversible processes such as the removal of precipitations that you mention. See in particular Eq.(59) in Marquet and Geleyn (2015), where the change in moist-air entropy associated with pseudo-adiabatic (von Bezold, 1888) processes writes:

$$ds = c_{pd} \frac{d\theta_s}{\theta_s} = (s - s_l) \left(\frac{-dr_{sw}}{1 + r_{sw}}\right)$$

- Lines 82-83: You say: "the potential temperature is commonly used as a prognostic variable in numerical models for the formulation of the energy equation". Could you explain in which models θ is used as a prognostic variable? As far as I know, the prognostic variables associated with energy is either the temperature T or the combination $c_p T$, with the moistair definition for c_p . In particular, your reference to Richardson et al (2007) on line 105 seems incorrect, since page 25 of this article the equations are: " $DT/Dt = F_q$ " or " $\partial T/\partial t = ... + F_q$ " or " $\partial (\rho T)/\partial t = ... + \rho F_q$ ".

- Lines 105: You say: "it was pointed out by Li and Chen (2019) that this approach could suffer from not accounting for the temperature dependence of the isobaric specific heat capacity c_p of the respective atmospheres gas composition". I spent some time checking this out in Li and Chen (2019), and I find (page 2): "Furthermore, the expressions of potential temperature and equivalent potential temperature become complicated when the heat capacity of the atmosphere varies with temperature or when multiple condensing species exist in the atmosphere. Here as elsewhere, could you quote the pages and/or equations corresponding to your citations, to help the reader find his way around in articles or books with very many pages?

- Lines 117: It is customary, at the end of the introduction, to present the outline of the article, with a summary of the content of each forthcoming sections. This should be included at the end of your Section 1.

- Lines 134: Your value for $R_a = R/M_{\text{mol},a}$ is known with R given up to ± 0.0001 I believe? You could retain the value 8.31446 for example? Anyhow you have to give the resulting value $R_a = 287.115$ at least, with perhaps the associated precision ± 0.005 ? - Lines 183: It was indeed indicating by WMO that the variability of c_p ranges from 994 J/K/kg to 1011 J/K/kg. But the real recommendation is rather a value close to 1005 J/K/kg, in line with the values presently used in most General Circulation (GCM) and Numerical Weather Prediction (NWP) models:

$ \begin{array}{c} \\ c_p \ (J/K/kg) \\ \end{array} \ $	GCM and/or NWP models
1005.0	Unified-Model (UKMO, UK, from Adrian Lock)
1005.0	COSMO (DWD, Germany, from Dmitrii Mironov)
1004.7	IFS (ECMWF, Reading, UK, from "sucst.F90")
1004.7	ARPEGE (Meteo-France, Toulouse, France, from "sucst.F90")
1004.7	AROME (Meteo-France, Toulouse, France, from "sucst.F90")
1004.7	Meso-NH (L.A.+Meteo-France, Toulouse, France, from "sucst.F90")
1004.7	LMD-Z (IPSL, Paris, France, from "suphec.F90")
1004.6	ICON (DWD, Germany, from Dmitrii Mironov)
1004.6	GFS (USA, from "physcons.f")

- Lines 191-192: These old WMO values of 994 J/K/kg and 1011 J/K/kg are too extreme and unrealistic, because they are not used in any current GCM and NWP model. Or could you indicate the models where these values might be used?

- Page 8, Table 1: The values of 994 J/K/kg, 1000 J/K/kg, 1003 J/K/kg and 1011 J/K/kg do not seem relevant.

- The value 994 J/K/kg comes from an old book I couldn't find, and the accuracy of the data obtained before 1933 can be questioned. This is like the measurement of the speed of light, the accuracy of which cannot be the "meeting of all possibilities", including for example the measurements of Romer and Huygens in 1675 (220,000 km/s), Bradley in 1729 (301,000 km/s), Fizeau in 1849 (315,000 km/s) or Foucault in 1862 (298,000 km/s)? It is the same for the measurement of the numerical values of $\gamma = c_p/c_v$ for diatomic gases, where the value of 1.421 retained by Poisson in 1833 or of 1.41 by Thomson in 1862 cannot be compared with the modern value of 7/5 = 1.40? It is the same for the measurement of absolute scale of temperature, with a constant corresponding to 267 K in Gay-Lussac (1802) and Carnot (1824), to 273.22 K in Thomson (1848), before to be presently fixed to 273.15 K (see the review in Marquet, 2019a).
- The value of 1000 J/K/kg attributed to Valis (2009) seems to be easily questionable: see the legend in Figure 6 in section 3 bellow.
- I don't know where the value of 1003 J/K/kg published in Tripoli and Cotton (1981) comes from. But one can also have doubts about their values of c_p for ice (2100 J/K/kg instead of 2106 J/K/kg) and liquid water (4187 J/K/kg instead of 4218 J/K/kg), with important differences for both dry air, liquid water and ice from the values commonly used in GCM and NWP model.
- Other than the mention in the WMO recommendations, I have never seen an application of the value 1011 J/K/kg. Could you indicate such an application of the value $c_p = 1011 \text{ J/K/kg}$ for dry air?

- Lines 194-199 and Figure 2: Assuming new extreme values of 1004.5 J/K/kg and 1007.5 J/K/kg (later demonstrated), I was able to redo your figures 2 (a) and (b) with the same US standard atmosphere profile: see Figure 7 in section 3 bellow, with indeed the same difference $\Delta \theta_{c_p} = \theta_{994} - \theta_{1011}$ (in black) as in your paper. The new differences $\theta_{1004.5} - \theta_{1007.5}$ (in red) are much smaller, by an order of magnitude or so (divided by a factor of about 5 to 7). The new differences are less than 2 K at 20 km, 5 K at 35 km and 14 K (instead of 75 K) at 50 km. These new differences $\theta_{1004.5} - \theta_{1007.5}$ may modified your comments and conclusions in your section 3.

- Section 4, Lines 226-260 and Figure 3: I disagree with many of the points you've drawn on your figure 3. So I redid your figure 3 by deleting the old and questionable data (see Figure 8 in section 3 bellow). I kept the values of 1004 J/K/kg, 1004.832 J/K/kg, 1005 J/K/kg and 1005.7 J/K/kg, the data of Vassermann et al (1966) and NIST-REFPROP as well as the two curves of Lemmon et al (2000) and Dixon (2007). This new figure shows that constant values of c_p between 1004.5 J/K/kg and 1007.5 J/K/kg agree with the selected points for the range of temperatures observed in the atmosphere (say 200 to 320 K). The two curves of Lemmon et al (2000) and Dixon (2007) are retained here because they are valid for the approximation of ideal gases and allow to measure the differences with formulations for real gases, such as Vassermann et al (1966) and NIST-REFPROP. The impact of real gases properties on c_p increases with decreasing values of T bellow 260 K, and is larger than 4 J/K/kg at 200 K.

- Lines 245, legend of Fig 3, lines 315-321 and Eqs.(18) and (19): It should be mentioned that your formula (18) with the coefficients (19) of Lemmon et al (2000) disagrees with the observed values given in Table A2 of the same article Lemmon et al (2000). And indeed, while formula (18) leads to decreasing values of $c_p(T)$ for decreasing T, the values of $c_p(T)$ in Table A2 show a minimum around 250 K and become increasing for decreasing temperatures up to 81.72 K (see Figs.9 and 10 in section 3 bellow). It should also be mentioned that your equation (18) corresponds to equation (18) (page 345) in Lemmon et al (2000).

- Lines 246 and 325-329: You should mention that the equation of Dixon (2007, p.376) used to compute the dry-air value $c_p(T)$ plotted in your Fig.3 is

 $c_p(T) = 1002.5 + 275. \ 10^{-6} \ (T - 200)^2 \ \text{J/K/kg}$

(see Figure 11 in section 3 bellow).

- Lines 356 / Eq.(11): The gaz constant " R_a " is missing before the integral $\int_{p_0}^p dp'/p'$

- Lines 356 / Eq.(21), Lines 359 / Eq.(22), Lines 374 / Eq.(23), Lines 411 / Eq.(25), Line 426 and 429, Line 691 / Eq.(C1), Line 693 / Eq.(C2): You should used the same dummy variable "T'" as in your Eq.(11) line 153 ($\int_{T_0}^T dT'/T'$) to write all the integrals of the kind $\int_{\theta}^T c_p(T')dT'/T'$. The use of the dummy variable "z" can lead to unfortunate confusion with the altitude variable, which is then used in the rest of your paper to describe the true vertical coordinate.

- Page 11 / Fig 3: I have plotted in Figure 12 (top, see section 3 bellow) the equivalent of your Figure 3, but with different formulations that correspond to observed ("real gases") values of $c_p(T)$, with a zoom (Figure 12 bottom) around the usual atmospheric temperatures.

I first reported (from your Fig.3) the points of your calculations made with the (paid) application of NIST-REFPROP. These NIST-REFPROP values are comparable to those I have computed with the (free) SIA software (http://www.teos-10.org/software.htm) corresponding to the IAPWS-2010 (Feistel et al, 2010) and TEOS-10 (Feistel, 2018) formulations. There is a similar minimum $c_p(T) \approx 1005.5$ to 1005.7 J/K/kg at around 250 K and with the same higher values of about 1007 J/K/kg at 320 K and 1006.7 J/K/kg at 200 K.

The values published in Table A2 of Lemmon et al. (2000) are fairly comparable to those of NIST-REFPROP and IAPWS-TEOS10, with a similar minimum of $c_p(T)$ at around 250 K.

The same applies to the values of $c_p(T)$ for N2 and O2 published in Marquet (2015), with the values for dry air completed with the values of $c_p(T)$ for Argon.

The minimum of $c_p(T)$ for N2 is at around 290 K in both Stewart and Jacobsen (1989, Table 5.73, see Fig.13 bellow) and Span et al. (2000, page 1410, see Fig.14 bellow). The resulting figure 5 for N2 published in Marquet (2015) is recalled in Fig.15 bellow.

The minimum of $c_p(T)$ for O2 is at around 220 K in Jacobsen et al. (1997, Table 5.79, see Figs.16 and 17). The resulting figure 4 for O2 published in Marquet (2015) is recalled in Fig.18 below.

Values of $c_p(T)$ for Argon increases for decreasing T for both Tegeler et al. (1999, Table 34, see Fig.19) and Stewart and Jacobsen (1989, Table 15, Figs.20 and 21). The unpublished Fig.22 plotted below shows that values for Tegeler et al. (1999) and Stewart and Jacobsen (1989) fairly coincide for 150 < T < 300 K.

The unpublished Fig.23 below shows that it is equivalent to use $c_p(T)$ computed for N2, O2 and H20 vapour by using Statistical and Quantum Physics (dashed lines) or by the "calorimetric method" (third law and integration of $c_p(T')/T'$ from 0 K to T, sum of $L(T_k)/T_k$ for all changes of phases at T_k , add the Pauling-Nagle residual entropy at 0 K for H2O). It thus appears that it is for these temperature-dependent values of $c_p(T)$ for gases that the agreement between the calorimetric and quantum methods can be obtained, an agreement which is not obtained with "ideal gas" formulations.

I have also plotted on Figure 12 bellow the constant values used in many GCM and NWP models (1004.6, 1004.7, 1005 J/K/kg, depicted by coloured horizontal dashed lines). It appears, considering all these values of c_p constant or dependent on T, and in the range of atmospheric temperatures (200 < T < 320 K), that the imprecision on $c_p(T)$ is between 1004.5 and 1007.5 J/K/kg. These extreme values have been used earlier in this review to plot several figures, instead of the (old) WMO extreme values 994 and 1011 J/K/kg you used in your study.

Regarding the search for an accurate average value $c_p(T) \approx c_p^0$, it appears that $c_p^0 \approx 1005.8 \text{ J/K/kg}$ could be more realistic (for 200 < T < 320 K) than those presently used in GCM and NWP models (1004.6, 1004.7, 1005 J/K/kg).

However, the impact of these new formulations $(c_p(T) \text{ or } c_p^0)$ should be small in our CMGs and NWP models. Moreover, taking into account the dependence of $c_p(T)$ on temperature, not only for dry air but also for water vapor, liquid water and ice, would greatly complicate the writing of the physical parameterizations of these models, and would greatly increase the cost of these physical parameterizations.

3 Additional Figures

Thus Bezold reached the same conclusion as Hann.

In order to facilitate the discussion of this result and the analysis of similar processes, Bezold introduced a number of terms borrowed from physics into the meteorological vocabulary, the most important being "potential temperature."⁸⁹ This quantity stood for the heat content of air which in 1888 Helmholtz had defined as the temperature that the parcel of air assumes when being compressed or expanded adiabatically to a standard pressure.⁹⁰ It quickly became part of standard meteorological terminology. Using this convenient quantity, Bezold briefly and plainly described what he had expressed graphically:

88 Bezold, Gesammelte Abhandlungen, p. 124.

89 Also specific moisture, pseudo-adiabatic process, entropy.

⁹⁰ Helmholtz, "Ueber atmosphärische Bewegungen," *Sitzber. Ak. Berlin* (1888), 652–653, translated in Abbe's second collection (1891), 78–111. According to A. Wegener, (*Thermodynamik der Atmosphäre*, Leipzig, Barth, 1911, p. 111) early in 1888 (before publication of Bezold's paper) Köppen had already used the term potential temperature in a talk in Hamburg, entitled "Ueber die Luftmischung und potentielle Temperatur, in Anlehnung an die neueste Abhandlung von Herrn v. Helmholtz."

Figure 1: Excerpts from Kutzbash (1979) page 143, with the title of the 1888 lecture of Köppen written as: "Ueber die Luftmischung und potentielle Temperatur", which might be different from the one in your bibliography: "Über Luftmischung...". Moreover, I have not found the paper (or a copy of this lecture) of Köppen, and I do not understand why you cite the URL: http://snowcrystals.com/.



Figure 2: Excerpts from the book "Treatise on Mechanics" by Poisson (1833). On the top: These equations (6) contain the "law of elastic force" and of "the temperature of gases", either compressed or expanded without any changes in their "quantity of heat" (say adiabatic). These laws are based on the sole hypothesis that the ratio γ of the specific heat (capacities, say c_p/c_v) does not depend, for a given fluid, on both pressure and temperature (here " θ + 266.67" corresponds to the absolute temperature defined 15 years after in 1848 by W. Thomson, next Lord Kelvin, now set to: "T = t + 273.15 K"). With modern notations, these "adiabatic" laws are: $p' = p (\rho'/\rho)^{\gamma}$ and $T' = T (\rho'/\rho)^{\gamma-1}$. On the bottom: ... we can consider γ as a constant ... Dulong found that, for a perfectly dry air, $\gamma \approx 1.421$ (which is not so different from the modern value 1.40 for the diatomic gases).



Figure 3: Excerpts from the paper "On the convctive equilibrium of temperature in the atmosphere" by W. Thomson (lecture 1862, published 1865), next Lord Kelvin. This lecture was read a few years before Clausius' article (1865) in which he defined entropy. With modern notations, Eq.(1) writes $(p/p_0)^{\kappa} = T/\theta$, where θ is the (absolute) temperature when the parcel of temperature T and pressure p is brought to the surface pressure p_0 via an adiabatic transformation. This is the definition of the "potential temperature". Here $\kappa = 1 - 1/k = 1 - 1/\gamma \approx 0.291$, where $\gamma = c_p/c_v \approx 1.41$ is an improved value since Poisson (1833).

No. 2.] "POTENTIAL TEMPERATURE" AND "ENTROPY." 177

THE RELATION BETWEEN "POTENTIAL TEMPERA-TURE" AND "ENTROPY."¹

By L. A. BAUER.

IN 1888 the late Professor von Helmholtz incidentally introduced the term "waermegehalt" in connection with his investigations,² "On Atmospheric Motions." According to him the "waermegehalt" or the actual heat contained in a given mass of air is to be measured by the absolute temperature which the mass would assume if it were brought adiabatically to the normal or standard pressure. It remained for the late Professor von Bezold, however, to perceive the full significance of this term and to reveal its important bearing in the discussion of meteorological phenomena.

As the quantity really involved in this new term is not a quantity of heat, von Bezold suggested that the term be replaced by the evidently more appropriate one of "potential temperature."³ This met with von Helmholtz's approval.

With the aid of this happy idea of "potential temperature" von Bezold was enabled to draw in a simple and beautiful manner a number of important conclusions governing thermodynamic phenomena taking place in the atmosphere. Thus, for example, he found that :

"Strict adiabatic changes of state in the atmosphere leave the potential temperature unchanged, whereas pseudo-adiabatic ones invariably increase the same, the increase being in proportion to the amount of aqueous evaporation."

Von Bezold called attention to the fact that this law bears a strik-

¹ Presented before the Philosophical Society of Washington, March 16, 1907.

² Sitzungsberichte Berliner Akademie, 1888, V. XLVI., p. 652, "Ueber atmospherische Bewegungen," see translation in Abbe's Mechanics of the Earth's Atmosphere, Washington, 1891, p. 83. The symbol θ is used to denote the "Waermegehalt."

³ Sitzb. Berliner Akad., 1888, V. XLVI., p. 1189, "Zur Thermodynamik der Atmosphaere"; also in von Bezold's "Gesammelte Abhandlungen," Vieweg und Sohn, Braunschweig, 1906, p. 128. A translation will be found in Abbe's Mechanics, etc., p. 243. 178 L. A. BAUER. [VOL. XXVI.

ing resemblance to the well-known theorem of Clausius, now commonly known as the second law of thermodynamics, viz.: "that the entropy strives towards a maximum;" but, he says, "it is not identical with it."

The purpose of this paper is to examine into the precise relationship between the two functions "potential temperature" and "entropy" and to see whether any use could be made advantageously of the former in the treatment of certain thermodynamic problems as well as to ascertain wherein the potential temperature law fails to give full expression of the second law of thermodynamics. To my knowledge no application has as yet been made of the new term in treatises on thermodynamics. The substance of this paper was communicated to the American Association for the Advancement of Science at the Springfield meeting in 1895, but publication pending opportunity for further elaboration was deferred.

The "potential temperature" of a body is defined as the absolute temperature assumed when the body is brought adiabatically to standard pressure.

Defining the thermodynamic state per *unit of mass* of a body by the three variables, T, the absolute temperature, v, the volume per unit of mass, p, the pressure supposed uniform, the following characteristic equation subsists between them : T = f(v, p).

If the body be brought now adiabatically to standard pressure p_0 , then the temperature assumed at the end of the process is the so-called *potential temperature* as above defined and is designated by the symbol θ . Hence,

$$\theta = f(v, p_0). \tag{1}$$

For a perfect gas, since kT = pv, k being a constant for any particular gas,

$$\theta = \frac{p_0}{b} \cdot v = k_0 \cdot v, \tag{2}$$

or the potential temperature for any particular gas is directly proportional to the volume and, hence, as von Bezold showed, the potential temperature readily admits of a graphical representation on the usual pv diagram, being simply proportional to the v abscissæ of points of intersection of the line of standard pressure, $p = p_0$, with the adiabats.

Figure 4: The first two pages of Bauer (lecture 1907; printed 1910). The origin of the name "potential temperature" is clearly credited to von Bezold with von Helmholtz's approval (and this is confirmed by the reading of von Bezold's papers of 1888), but without mention to the lecture of Köppen in this paper, nor in those of von Helmoltz and von Bezold.

 c_p and c_v are, respectively, the specific heats at constant pressure and at constant volume; k is a constant for any particular gas. Utilizing equation (3) and remembering that

 $\varepsilon = \frac{c_p}{c_v}$ and $k = (c_p - c_v)$

we get

or

$$s = c_p \log \theta + (\varepsilon - 1) \log \frac{k}{p_0} + \text{const.},$$
$$s = c_p \log \theta + \text{const.}$$

This gives us the relation sought between potential temperature and entropy. Since c_p is invariably a positive quantity, it follows at once that for any process the potential temperature varies in precisely the same direction as the entropy. If the entropy is increased, as it invariably is for irreversible processes in accordance with the second law of thermodynamics, then is the potential temperature likewise increased. When the entropy remains constant, as for reversible processes, e. g., a strict adiabatic process, then the potential temperature likewise remains constant. In other words as far as perfect gases are concerned it is possible to express the entropy function in its simplest form by means of a quantity — the potential temperature — not only readily interpretable but also easy of direct graphical representation.

Figure 5: The page 180 of Bauer (lecture 1907; printed 1910), where the link between (dryair) entropy and potential temperature " $s = c_p \ln(\theta) + const$ " appear for the first time in meteorological science.

For an ideal gas (and the air in the Earth's atmosphere is very close to ideal) the conventional equation of state is

$$p = \rho RT, \tag{1.55}$$

(5)

where *R* is the gas constant for the gas in question and *T* is temperature. (*R* is related to the universal gas constant R_u by $R = R_u/m$, where *m* is the mean molecular weight of the constituents of the gas. Also, R = nk, where *k* is Boltzmann's constant and *n* is the number of molecules per unit mass.) For dry air, $R = 287 \text{ Jkg}^{-1} \text{ K}^{-1}$ Air has virtually constant composition except for variations in water vapour content. A measure of this is the water where *k* is the Boltzmann constant and *R* the gas constant. The diatomic molecules N_2 and O_2 that comprise most of our atmosphere have two rotational and three translational degrees of freedom, so that $I \approx 5RT/2$, and so $c_v \approx 5R/2$ and $c_p \approx 7R/2$, both being constants. These are in fact very good approximations to the measured values for the Earth's atmosphere, and give $c_p \approx 10^3 \text{ Jkg}^{-1}\text{ K}^{-1}$. The internal energy is simply $c_v T$ and the

Figure 6: Excerpts from the paper Valis (2009) pages 14 and 21. It is clearly explained that $R_d \approx 287 \ J/K/kg$ and $c_p = (7/2) \ R_d$, leading to $c_p \approx 1004.5 \ J/K/kg$, and not $c_p \approx 1000 \ J/K/kg$ as suggested in your Fig.3 and Table 1. This value $c_p \approx 1000 \ J/K/kg$ is here only a rough indication, a very simple "order of magnitude".



Figure 7: The vertical profiles of $\theta_{1004.5}$ and $\theta_{1007.5}$, and the difference of them (in red), plotted for the same US Standard Atmosphere as used in your paper, and compared to the same difference $\Delta \theta_{c_p} = \theta_{994} - \theta_{1011}$ (in black) as in your paper.



Figure 8: **Top:** The copy of your Fig.3; **Bottom:** a modified version of it, where the "questionable data" are removed. The idealized curves of Lemmon (2000) and Dixon (2007) are kept here, although they should also be deleted and replaced by the real cases depicted in the next figure (IAPWS, TEOS10, Lemmon 2000 Table A2, Jacobsen et al. 1997, ...), as explained in the text.

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Temperature	Density	Internal energy	Enthalpy	Entropy	<i>c</i> _v	c _p	Speed of sound
(K)	(mol/dm ³)	(J/mol)	(J/mol)	J/(mol-K)	J/(mol-K)	J/(mol-K)	(m/s)
			0.101 325 MP	a isobar			
59.77	33.069	-4713.1	-4710.0	70.905	34.01	55.05	1030.6
60	33.036	-4700.3	-4697.2	71.119	33.96	55.05	1028.8
62	32.750	-4590.2	-4587.1	72.924	33.52	55.05	1012.6
64	32.462	-4480.1	-4477.0	74.672	33.09	55.07	996.3
66	32.171	-4369.9	-4366.8	76.367	32.69	55.11	9/9.6
08	31.8/8	- 4259.7	- 4256.5	78.013	32.30	55.25	962.7
70	31.301	- 4149.5	-4140.1	81 172	31.56	55 37	945.5
74	30.078	- 3027.0	- 3024.6	87 601	31.22	55 51	920.1
76	30.670	- 3816.7	- 3813.4	84.173	30.89	55.68	892.3
78	30.358	- 3705.2	- 3701.9	85.622	30.57	55.88	874.0
78.90	30.215	- 3654.7	- 3651.4	86.266	30.43	55.99	865.6
81.72	0.155 27	1628.3	2280.9	160.41	21.73	31.56	177.2
82	0.15467	1634.6	2289.8	160.52	21.71	31.52	177.5
84	0.150 5 3	1679.4	2352.5	161.28	21.58	31.26	180.0
86	0.14663	1723.8	2414.8	162.01	21.48	31.04	182.4
88	0.14295	1767.9	2476.7	162.72	21.40	30.85	184.8
90	0.13947	1811.7	2538.2	163.41	21.33	30.69	187.1
92	0.13617	1855.4	2599.5	164.09	21.27	30.55	189.4
94	0.133 03	1898.8	2660.4	164.74	21.22	30.42	191.7
96	0.130 05	1942.1	2721.2	165.38	21.17	30.32	193.9
98	0.12/21	1985.2	2/81.7	166.00	21.13	30.22	196.1
100	0.124 49	2028.2	2842.1	167.21	21.09	30.13	198.2
102	0.121 90	20/1.0	2902.2	167.21	21.00	30.03	200.5
104	0.117.04	2115.6	3022.3	168 36	21.05	29.90	204.5
108	0.114 76	2199.0	3082.0	168.92	20.98	29.86	204.5
110	0.112 57	2241.5	3141.6	169.47	20.96	29.81	208.6
112	0.110 47	2284.0	3201.2	170.01	20.94	29.76	210.5
114	0.108 44	2326.3	3260.7	170.53	20.93	29.72	212.5
116	0.106 49	2368.6	3320.1	171.05	20.91	29.68	214.5
118	0.104 62	2410.9	3379.4	171.56	20.90	29.64	216.4
120	0.102 81	2453.1	3438.7	172.05	20.89	29.61	218.3
122	0.101 06	2495.3	3497.8	172.54	20.87	29.58	220.2
124	0.099 377	2537.4	3557.0	173.02	20.86	29.55	222.1
126	0.097 748	2579.5	3616.0	173.50	20.85	29.52	223.9
128	0.096 174	2621.5	3675.1	173.96	20.84	29.50	225.8
130	0.094 650	2663.5	3734.0	174.42	20.84	29.48	227.6
132	0.093 175	2705.5	3793.0	174.87	20.83	29.45	229.4
134	0.091 747	2747.5	3851.9	175.31	20.82	29.43	231.2
136	0.090 363	2789.4	3910.7	175.75	20.82	29.42	232.9
136	0.089 021	2031.3	4028.3	176.18	20.81	29.40	234.7
140	0.086 455	2015.1	4023.3	177.02	20.81	29.38	230.4
142	0.085 227	2915.1	4087.1	177.43	20.80	29.37	230.2
146	0.084 035	2998.7	4204.5	177.83	20.79	29.34	241.6
148	0.082 877	3040.5	4263.1	178.23	20.79	29.33	243.3
150	0.081 750	3082.3	4321.8	178.62	20.78	29.32	244.9
155	0.079 065	3186.8	4468.3	179.59	20.78	29.29	249.1
160	0.076 553	3291.1	4614.7	180.51	20.77	29.27	253.1
165	0.074 198	3395.4	4761.0	181.41	20.76	29.25	257.1
170	0.071 985	3499.6	4907.2	182.29	20.76	29.23	261.1
175	0.069 902	3603.8	5053.3	183.13	20.75	29.22	264.9
180	0.067 937	3707.9	5199.3	183.96	20.75	29.20	268.7
185	0.066 081	3812.0	5345.3	184.76	20.75	29.19	272.5
190	0.064 324	3916.0	5491.2	185.54	20.75	29.18	276.2
193	0.062 659	4020.0	5782.0	186.29	20.75	29.17	2/9.8
210	0.061 079	4124.0	5782.9	187.03	20.74	29.10	283.4
220	0.055 486	4551.9	6365.9	100.43	20.74	29.15	290.5
230	0.053.050	4747 6	6657 3	101.01	20.74	29.14	304 1
240	0.050 836	4955 4	6948.6	192.35	20.75	29.13	310 7
	0.000 000		0.40.0	1,74.33	and 15	wy .1.3	510.7

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Figure 9: Values of $c_p(T)$ at 1013.25 hPa for dry air (above 81.72 K) from Lemmon et al. (2000, Table A2).

THERMODYNAMIC PROPERTIES OF AIR

TABLE A2. Thermodynamic properties of air-Continued

Temperature (K)	Density (mol/dm ³)	Internal energy (J/mol)	Enthalpy (J/mol)	Entropy J/(mol-K)	c _v J/(mol-K)	с _р J/(mol-K)	Speed of sound (m/s)
250	0.048 793	5163.2	7239.9	193.53	20.75	29.13	317.1
260	0.046 908	5371.1	7531.1	194.68	20.76	29.13	323.4
270	0.045 164	5578.9	7822.4	195.78	20.76	29.13	329.6
280	0.043 546	5786.8	8113.7	196.84	20.77	29.13	335.6
290	0.042 040	5994.8	8405.1	197.86	20.78	29.14	341.5
300	0.040 634	6203.0	8696.5	198.85	20.80	29.15	347.4
310	0.039 320	6411.2	8988.1	199.80	20.81	29.16	353.1
320	0.038 089	6619.5	9279.8	200.73	20.83	29.18	358.7
330	0.036 932	6828.1	9571.6	201.63	20.85	29.19	364.2
340	0.035 844	7036.8	9863.6	202.50	20.87	29.21	369.7
350	0.034 818	7245.7	10 156.0	203.34	20.89	29.23	375.0

Figure 10: Values of $c_p(T)$ at 1013.25 hPa for dry air (above 81.72 K) from Lemmon et al. (2000, Table A2) (continued).

The specific thermal capacity at constant pressure $c_{\rm P}$ is given by the empirical expression

$$c_{\rm P} = 1002.5 + 275 \times 10^{-6} (T_{\rm K} - 200)^2 \,{\rm J/kg} \,{\rm K}$$

Figure 11: The equation of Dixon (2007, p.376) used to compute the dry-air value $c_p(T)$ plotted in your Fig.3: $c_p(T) = 1002.5 + 275. 10^{-6} (T - 200)^2 J/K/kg$. You may help the reader by including this formula? Or helping the reader by giving the page 376? You may help the reader by indicating that the accuracy would be of 0.1 % from 200 K to 450 K?

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Figure 12: The same as your Fig.3 and with your NIST-REFPROP (1013.25 hPa) datasets, but with other "real gases" formulations of $c_p(T)$ depending on T: IAPWS + TEOS10, Lemmon 2000 Table A2, Jacobsen et al. 1997 / Marquet 2015. Constant values used in many GCM and NWP models (1004.6, 1004.7, 1005) are depicted by coloured horizontal dashed lines, with the value 1005.8 a possible new "mean value"?

Thermodynamic Properties of Cryogenic Fluids

Temperature (K)	Density (kg/m ³)	Internal energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)	C, (kJ/kg-K)	C _p (kJ/kg-K)	Velocity of sound (m/s)
			0.1 MPa	isobar			
63.159	869.82	-150.90	-150.78	2.4232	1.117	2.019	1022.
70.000	839.96	-137.13	-137.01	2.6303	1.094	2.015	934.
77.237	807.14	-122.47	-122.34	2.8296	1.068	2.042	851.
77.237	4.5655	54.738	76.642	5.4059	0.9373	1.340	172.
80.000	4.3796	57.275	80.108	5.4500	0.8294	1.191	177.
90.000	3.8449	65.241	91.250	5.5813	0.7536	1.081	191.
100.00	3.4361	72.871	101.97	5.6943	0.7480	1.067	202.
110.00	3.1089	80.440	112.61	5.7957	0.7465	1.060	212.
120.00	2.8402	87.976	123.18	5.8877	0.7456	1.056	222.
130.00	2.6153	95.490	133.73	5.9721	0.7450	1.053	231.
140.00	2.4241	102.99	144.24	6.0500	0.7444	1.050	240.
150.00	2.2593	110.47	154.73	6.1224	0.7440	1.048	249.
160.00	2.1158	117.94	165.21	6.1900	0.7437	1.047	257.
170.00	1.9896	125.41	175.67	6.2534	0.7435	1.046	265.
180.00	1.8778	132.87	186.12	6.3132	0.7433	1.045	273.
190.00	1.7780	140.32	196.57	6.3696	0.7431	1.044	281.
200.00	1.6883	147.77	207.00	6.4232	0.7430	1.043	288.
210.00	1.6073	155.22	217.44	6.4741	0.7429	1.043	295.
220.00	1.5338	162.66	227.86	6.5226	0.7429	1.043	302.
230.00	1.4667	170.11	238.29	6.5689	0.7428	1.042	309.
240.00	1.4053	177.55	248.71	6.6133	0.7428	1.042	316.
250.00	1.3488	184.99	259.13	6.6558	0.7428	1.042	322.
260.00	1.2967	192.42	269.54	6.6966	0.7428	1.042	329.
270.00	1.2485	199.86	279.96	6.7360	0.7428	1.041	335.
280.00	1.2038	207.30	290.37	6.7738	0.7429	1.041	341.
290.00	1.1621	214.74	300.78	6.8104	0.7430	1.041	347.
300.00	1.1233	222.17	311.20	6.8457	0.7431	1.041	353.
310.00	1.0870	229.61	321.61	6.8798	0.7433	1.041	359.
320.00	1.0529	237.05	332.02	6.9129	0.7435	1.041	365.
330.00	1.0210	244.49	342.44	6.9449	0.7438	1.042	370.
340.00	0.99090	251.94	352.86	6.9760	0.7441	1.042	376.
350.00	0.96254	259.39	363.28	7.0062	0.7445	1.042	381.
360.00	0.93577	266.84	373.70	7.0356	0.7449	1.043	387.
370.00	0.91045	274.29	384.13	7.0642	0.7454	1.043	392.
380.00	0.88646	281.76	394.56	7.0920	0.7460	1.044	397.
390.00	0.86371	289.22	405.00	7.1191	0.7467	1.044	402.
400.00	0.84209	296.70	415.45	7.1456	0.7474	1.045	408.
450.00	0.74847	334.20	467.80	7.2689	0.7523	1.050	432.
500.00	0.67359	371.99	520.45	7.3798	0.7592	1.056	455.
600.00	0.56131	448.82	626.98	7.5740	0.7781	1.075	496.
700.00	0.48113	527.77	735.62	7.7414	0.8011	1.098	534.

Table 5.73. Thermodynamic Properties of Nitrogen

Figure 13: Values of $c_p(T)$ at 1000 hPa for Nitrogen. Dataset for vapour (N2, above 77.237 K) is from Jacobsen et al. (1997, Table 5.73).

SPAN ET AL.

Thermodynamic properties of nitrogen

K	ρ mol/dm ³	J/mol	J/mol	J/(mol K)	J/(mol K)	J/(mol K)	m/s
			0.	1 MPa			
63.170	30.960	-4222.8	-4219.6	67.955	32.95	56.02	995
65	30.690	-4120.2	-4117.0	69.556	32.60	56.11	976.
70	29.937	-3839.0	-3835.7	73.724	31.65	56.42	926
75	29.155	-3555.9	-3552.5	77.632	30.76	56.89	875
77.244	28.793	-3428.0	-3424.6	79.313	30.39	57.17	852.
77.244	0.162 65	1544.3	2159.1	151.60	21.60	31.46	174.
80	0.156 33	1605.7	2245.4	152.70	21.48	31.15	178
85	0.146 15	1715.8	2400.0	154.57	21.31	30.72	184
90	0.137 32	1824.5	2552.8	156.32	21.20	30.41	190
95	0.129 56	1932.4	2704.3	157.96	21.11	30.19	196
100	0.122 68	2039.6	2854.7	159.50	21.05	30.01	201
105	0.116 52	2146.2	3004.4	160.96	21.00	29.88	206
110	0.110 98	2252.5	3153.5	162.35	20.97	29.77	212.
115	0.105 96	2358.4	3302.2	163.67	20.94	29.68	217.
120	0.101 38	2464.0	3450.4	164.93	20.92	29.61	222
125	0.097200	2569.5	3598.3	166.14	20.90	29.55	226
130	0.093355	2674.8	3745.9	167.30	20.88	29.50	231
135	0.089809	2779.9	3893.3	168.41	20.87	29.46	235.
140	0.086528	2884.9	4040.6	169.48	20.86	29.43	240
145	0.083482	2989.8	4187.6	170.51	20.85	29.40	244
150	0.080647	3094.6	4334.5	171.51	20.85	29.37	249
160	0.075524	3303.9	4628.0	173.40	20.84	29.33	257
170	0.071021	3513.1	4921.1	175.18	20.83	29.29	265
180	0.067029	3722.0	5213.9	176.85	20.82	29.27	273
190	0.063466	3930.8	5506.5	178.44	20.82	29.25	280.
200	0.060265	4139.5	5798.9	179.93	20.81	29.23	288
210	0.057374	4348.2	6091.1	181.36	20.81	29.22	295
220	0.054749	4556.7	6383.2	182.72	20.81	29.21	302
230	0.052355	4765.2	6675.2	184.02	20.81	29.20	309
240	0.050162	4973.6	6967.1	185.26	20.81	29.19	315
250	0.048147	5182.0	7259.0	186.45	20.81	29.18	322
260	0.046287	5390.4	7550.8	187.60	20.81	29.18	328
270	0.044567	5598.7	7842.5	188.70	20.81	29.17	335
280	0.042970	5807.1	8134.3	189.76	20.81	29.17	341.
290	0.041484	6015.4	8426.0	190.78	20.81	29.17	347
300	0.040098	6223.8	87177	191 77	20.82	29.17	353
310	0.038801	6432.2	9009.4	192.73	20.82	29.17	359
320	0.037586	6640.6	9301.2	193.65	20.83	29.18	364
330	0.036445	6849.1	9593.0	194.55	20.84	29.18	370
340	0.035371	7057.7	9884.8	195.42	20.85	29.19	375
350	0.024359	7266.3	10 177	196.27	20.86	29.20	291
400	0.030060	8311.6	11 638	200.17	20.00	29.20	301.
450	0.026718	9362.1	13 105	203.63	21.08	29.40	421
500	0.024045	10 421	14 580	206.73	21.27	29.59	454
550	0.021858	11 490	16 065	209.57	21.51	29.84	476
600	0.020027	12 573	17 564	212.17	21.80	30.12	40.6
700	0.017175	14 795	20.607	216.96	22.00	30.76	400
800	0.015028	17 063	23 717	2210.00	23.12	31.44	568
900	0.013359	19 409	26.894	224.76	23.78	32.10	600
W	0.010000	21 917	20 125	229.17	24.39	22.70	631

Figure 14: Values of $c_p(T)$ at 1000 hPa for Nitrogen. Dataset for vapour (N2, above 77.244 K) is from Span et al. (2000, Table p.1410).



Figure 5. Specific heat capacity at constant pressure for N₂ corresponding to Table BII. Units of c_p are J K⁻¹kg⁻¹. The latent heats are in units of kJ kg⁻¹.

		N ₂ (vapour). U	Jnit J K^{-1} kg ⁻¹		
77.4	1340	120	1056	200	1043
80	1191	140	1050	250	1042
90	1081	160	1047	300	1041
100	1067	180	1045		

Figure 15: Values of $c_p(T)$ at 1000 hPa for Nitrogen (solids α and β , liquid, gas) from Marquet (2015).

Temperature (K)	Density (kg/m ³)	Internal energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)	C, (kJ/kg-K)	C _p (kJ/kg-K)	Velocity of sound (m/s)
-			0.1 MPa	isobar			
54 371	13061	- 193 61	- 193 53	2 0922	1 195	1 673	1124
55,000	1303.6	- 192 56	- 192.48	21114	1 176	1.671	1127
60,000	1282.1	- 184 21	- 184 13	2 2569	1 089	1 673	1128
65,000	1259.8	-175.83	-175.75	2 3910	1.046	1.677	1102
70.000	1237.1	-167.44	-167.36	2.5153	1.017	1.678	1067.
75.000	1214.0	-159.05	-158.97	2.6311	0.9922	1.679	1028.
80.000	1190.6	-150.66	-150.57	2.7395	0.9699	1.681	988.
85,000	1166.7	-142.24	-142.15	2.8416	0.9490	1.688	947.
90,000	1142.1	-133.78	-133.69	2.9383	0.9296	1.699	906.
90.062	1141.8	-133.67	-133.58	2.9395	0.9293	1.699	905.
90.062	4.4135	56.939	79.597	5.3065	0.6757	0.9705	177.
95.000	4.1642	60.284	84.298	5.3573	0.6549	0.9413	183.
100.00	3.9411	63.612	88.986	5.4054	0.6527	0.9352	188.
105.00	3.7418	66.931	93.656	5.4510	0.6534	0.9332	193.
110.00	3.5625	70.247	98.318	5.4944	0.6541	0.9316	198.
115.00	3.4001	73.561	102.97	5.5357	0.6544	0.9298	203.
120.00	3.2524	76.870	107.62	5.5753	0.6543	0.9280	207.
125.00	3.1174	80.174	112.25	5.6131	0.6540	0.9262	212.
130.00	2.9935	83.473	116.88	5.6494	0.6537	0.9246	216.
135.00	2.8793	86.767	121.50	5.6843	0.6533	0.9231	220.
140.00	2.7736	90.056	126.11	5.7178	0.6530	0.9218	225.
145.00	2.6756	93.342	130.72	5.7502	0.6527	0.9207	229.
150.00	2.5845	96.624	135.32	5.7814	0.6524	0.9196	233.
155.00	2.4994	99.903	139.91	5.8115	0.6521	0.9188	237.
160.00	2.4199	103.18	144.50	5.8407	0.6519	0.9180	241.
165.00	2.3453	106.45	149.09	5.8689	0.6517	0.9173	244.
170.00	2.2752	109.73	153.68	5.8963	0.6516	0.9167	248.
175.00	2.2093	113.00	158.26	5.9228	0.6514	0.9162	252.
180.00	2.1471	116.26	162.84	5.9486	0.6513	0.9158	255.
185.00	2.0883	119.53	167.42	5.9737	0.6513	0.9154	259.
190.00	2.0328	122.80	171.99	5.9981	0.6512	0.9151	262.
195.00	1.9801	126.07	176.57	6.0219	0.6512	0.9148	266.
200.00	1.9301	129.33	181.14	6.0451	0.6513	0.9146	269.
205.00	1.8826	132.60	185.71	6.0676	0.6513	0.9144	273.
210.00	1.8374	135.86	190.29	6.0897	0.6514	0.9143	276.
215.00	1.7943	139.12	194.86	6.1112	0.6515	0.9142	279.
220.00	1.7532	142.39	199.43	6.1322	0.6516	0.9142	283.
225.00	1.7139	145.65	204.00	6.1527	0.6518	0.9142	286.
230.00	1.6764	148.92	208.57	6.1728	0.6520	0.9143	289.
235.00	1.6405	152.19	213.14	6.1925	0.6522	0.9144	292.
240.00	1.6062	155.45	217.71	6.2118	0.6525	0.9145	295.
250.00	1.5416	161.99	226.86	6.2491	0.6531	0.9150	301.

Table 5.79. Thermodynamic Properties of Oxygen

Figure 16: Values of $c_p(T)$ at 1000 hPa for Oxygen. Dataset for vapour (O2, above 90.062 K) is from Jacobsen et al. (1997, Table 5.79).

Thermodynamic Properties of Cryogenic Fluids

Table	5.79	(continued)

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Temperature (K)	Density (kg/m ³)	Internal energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (kJ/kg-K)	C _v (kJ/kg-K)	C _p (kJ/kg-K)	Velocity of sound (m/s)
260.00	1.4820	168.54	236.02	6.2850	0.6539	0.9156	307.
270.00	1.4269	175.09	245.17	6.3196	0.6549	0.9164	313.
280.00	1.3757	181.65	254.34	6.3529	0,6560	0.9174	319.
290.00	1.3281	188.23	263.52	6.3851	0.6573	0.9185	324.
300.00	1.2837	194.81	272.71	6.4163	0.6587	0.9199	330.

Figure 17: Values of $c_p(T)$ at 1000 hPa for Oxygen. Dataset for vapour (O2, above 90.062 K) is from Jacobsen et al. (1997, Table 5.79, continued).



Figure 4. Specific heat capacity at constant pressure for O_2 corresponding to Table BI. Units of c_p are $J K^{-1} kg^{-1}$. The latent heats are in units of $kJ kg^{-1}$.

10 20	(D ₂ (vapour), U	Jnit I K ⁻¹ kg ⁻¹		
90	970.5	135	923.1	240	914.5
95	941.3	140	921.8	250	915.0
100	935.2	145	920.7	260	915.6
105	933.2	150	919.6	270	916.4
110	931.6	170	916.7	280	917.4
115	929.8	190	915.1	290	918.5
120	928.0	210	914.3	300	919.9
125	926.2	230	914.3		
130	924.6	235	914.4		

Figure 18: Values of $c_p(T)$ at 1000 hPa for Oxygen (solids α , β and γ , liquid, gas) from Marquet (2015).

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Temperature (K)	Density (kg m ⁻³)	Internal energy (kJ kg ⁻¹)	Enthalpy (kJ kg ⁻¹)	Entropy (kJ kg ⁻¹ K ⁻¹)	c_v (kJ kg ⁻¹ K ⁻¹)	с _р (kJ kg ⁻¹ К ⁻¹)	w (m s ⁻¹)
			0.1 N	1Pa isobar			
83.814 ^a	1416.80	-276.61	-276.54	-2.5440	0.549 61	1.1156	862.52
85	1409.57	- 275.29	-275.22	-2.5283	0.544 83	1.1157	854.35
87.178 ^b	1396.16	-272.86	-272.79	-2.5000	0.536 57	1.1171	839.20
87.178 ^b	5.7043	-129.08	-111.55	-0.650 58	0.327 91	0.565 41	170.77
90	5.5077	- 128.12	-109.97	-0.63265	0.325 70	0.560 00	173.85
95	5.1933	- 126.44	-107.19	-0.602 59	0.322 73	0.552 56	179.11
100	4.9152	-124.78	-104.44	-0.574 39	0.320 58	0.547 02	184.16
105	4.6669	- 123.14	-101.71	-0.54781	0.318 99	0.542 79	189.04
110	4.4436	-121.51	-99.008	-0.522 64	0.317 78	0.539 48	193.76
115	4.2416	-119.89	-96.317	-0.498 72	0.316 85	0.536 85	198.34
120	4.0577	-118.28	-93.639	-0.47592	0.316 12	0.534 72	202.80
125	3.8896	-116.68	-90.969	-0.45412	0.315 53	0.532 98	207.15
130	3.7352	-115.08	-88.308	-0.433 25	0.315 06	0.531 53	211.39
135	3.5929	- 113.49	-85.654	-0.413 21	0.314 68	0.530 31	215.54
140	3.4613	-111.90	- 83.005	- 0.393 95	0.314 36	0.529 28	219.60
145	3.3392	-110.31	-80.361	-0.375 39	0.314 10	0.528 40	223.59
150	3.2255	-108.72	-77.721	-0.357 49	0.313 88	0.527 64	227.49
155	3.1194	-107.14	-75.084	-0.340 20	0.313 69	0.526 98	231.33
160	3.0202	-105.56	-72.451	-0.323 48	0.313 53	0.526 41	235.10
165	2.9272	-103.98	-69.820	-0.307 29	0.313 39	0.525 91	238.80
170	2.8398	-102.40	-67.192	-0.291 59	0.313 27	0.525 46	242.45
175	2.7576	-100.83	-64.565	-0.276 37	0.313 17	0.525 07	246.03
180	2.6800	- 99.254	-61.941	-0.261 58	0.313 08	0.524 72	249.57
185	2.6067	-97.680	- 59.318	-0.247 21	0.313 00	0.524 41	253.05
190	2.5374	-96.108	-56.697	-0.233 23	0.312 94	0.524 12	256.48
195	2.4716	-94.536	-54.077	-0.219 61	0.312 87	0.523 87	259.87
200	2.4093	- 92.964	-51.458	-0.206 35	0.312 82	0.523 64	263.21
210	2.2936	-89.824	-46.224	-0.18082	0.312 73	0.523 24	269.76
220	2.1885	- 86.686	-40.993	-0.15648	0.312 66	0.522 91	276.15
230	2.0927	- 83.550	- 35.765	-0.13324	0.312 60	0.522 64	282.40
240	2.0050	-80.415	-30.540	-0.11101	0.312 55	0.522 40	288.50
250	1.9244	- 77.281	-25.317	-0.089 69	0.312 51	0.522 20	294.48
260	1.8500	-74.149	-20.096	-0.069 21	0.312 48	0.522 02	300.33
270	1.7812	-71.018	-14.877	-0.04951	0.312 45	0.521 87	306.07
280	1.7174	-67.887	-9.6585	-0.03053	0.312 42	0.521 74	311.70
290	1.6579	-64.757	-4.4417	-0.012 23	0.312 40	0.521 62	317.24
300	1.6025	-61.628	0.77404	0.005 46	0.312 38	0.521 52	322.67
310	1.5507	- 58,499	5.9888	0.022 56	0.312 37	0.521 43	328.02
320	1.5021	- 55.371	11.203	0.039 11	0.312 35	0.521 35	333.27
330	1.4565	- 52.244	16.416	0.055 15	0.312 34	0.521 28	338.45
340	1.4135	-49.116	21.628	0.070 71	0.312 33	0.521 21	343.55
350	1.3731	-45.990	26.840	0.085 82	0.312 32	0.521 15	348.57
375	1.2814	-38.174	39.867	0.121 77	0.312 30	0.521 03	360.81
400	1.2012	- 30.359	52.892	0.155 39	0.312 29	0.520 93	372.65

TABLE 34. Thermodynamic properties of argon

Figure 19: Values of $c_p(T)$ at 1000 hPa for Argon vapour (above 87.178 K) from Tegeler, Span and Wagner (1999, Table 34).

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Temperature	Density	Internal Energy	Enthalpy	Entropy	c,	c _p	Velocity of Sound
ĸ	mol/dm ³	J/mol	J/mol	J/mol K	J/mol K	J/mol K	m/s
		0.	101325 MPa	Isobar			
84	35.449	-4829.8	-4826.9	53.39	21.31	42.63	852
86	35.150	-4744.3	-4741.4	54.39	21.06	42.90	839
* 87.29	34,953	-4688.7	-4685.8	55.04	20.90	43.08	830
* 87.29	0.14460	1044.8	1745.5	128.71			192
88	0.14337	1050.6	1757.3	128.84			186
	0 10005	1071 0	1205 0	100 07			170
90	0.13995	10/1.3	1/95.3	129.27			1/9
92	0.13664	1096.0	1837.5	129.74			177
94	0.1334/	1122.5	1881.7	130.21			178
90	0.13044	1149.8	1926.6	130.68			1/9
98	0.12/56	11/7.4	19/1.7	131.15			181
100	0.12481	1204.9	2016.8	131.60			183
102	0.12218	1232.3	2061.6	132.05			185
104	0.11967	1259.5	2106.2	132.48			187
106	0.11727	1286.5	2150.5	132.90			189
108	0.11497	1313.2	2194.6	133.31			191
110	0.11276	1339.8	2238.4	133.72	12.94	21.86	193
112	0.11065	1366.2	2282.0	134.11	12.89	21.76	195
114	0.10861	1392.5	2325.4	134 49	12.84	21.68	197
116	0.10665	1418.7	2368.7	134 87	12.79	21.60	199
118	0.10476	1444.7	2411.9	135.24	12.76	21.54	201
120	0 10295	1470 6	2454 9	135 60	19 79	21 48	203
120	0 10119	1406 5	2494.9	135.00	12.72	21.40	205
124	0.00050	1522 3	2497.0	136 30	12.70	21.45	204
124	0.09990	1548 0	2583 3	136.50	12.65	21.30	208
128	0.09629	1573.6	2626.0	136.98	12.64	21.31	210
120	0 00476	1500 2	2669 6	127 21	12 62	21 28	211
130	0.09478	1694.2	2008.0	137.51	12.62	21.26	213
134	0.09326	1650 3	2752 5	137.04	12.01	21.23	215
134	0.09164	1630.5	2755.5	137.93	12.60	21.22	215
138	0.09046	1701 3	2838 4	138 58	12.59	21.20	218
200	0.00711	1/01.5	2000.4	100.00	12100	CALLO	
140	0.08780	1726.7	2880.7	138.88	12.57	21.16	220
142	0.08654	1752.1	2923.0	139.18	12.56	21.14	221
144	0.08531	1777.5	2965.3	139.48	12.56	21.13	223
146	0.08411	1802.8	3007.5	139.77	12.55	21.11	224
148	0.08295	1828.2	3049.7	140.06	12.55	21.10	226
150	0.08182	1853.5	3091.9	140.34	12.54	21.08	227
152	0.08072	1878.8	3134.0	140.62	12.54	21.07	229
154	0.07965	1904.1	3176.2	140.89	12.53	21.06	231
1.54	0.0/965	1904.1	51/0.2	140.09	12.55	21.00	201

Table 15 Thermodynamic properties of argon-Continued

Figure 20: Values of $c_p(T)$ at 1013.25 hPa for Argon vapour (above 87.29 K) from Stewart and Jacobsen (1989, Table 15). Missing values between 87.29 K and 108 K can be computed from the difference in enthalpies $\Delta h = c_p \Delta T$, and thus $c_p = \Delta h/\Delta T$ (increasing from 15.9 J/K/mol at 87.29 K to 22.6 J/K/mol at 97–99 K, then decreasing toward 21.91 J/K/mol at 109 K).

THERMODYNAMIC PROPERTIES OF ARGON

Temperature K	Density mol/dm ³	Internal Energy J/mol	Enthalpy J/mol	Entropy J/mol K	C _v J/mol K	C _p J/mol K	Velocity of Sound m/s
158	0.07760	1954.6	3260.4	141.43	12.53	21.04	234
160	0.07661	1979.9	3302.5	141.70	12.53	21.03	235
162	0.07565	2005.1	3344.5	141.96	12.52	21.02	237
164	0.07471	2030.4	3386.6	142.22	12.52	21.02	238
166	0.07380	2055.6	3428.6	142.47	12.52	21.01	240
168	0.07291	2080.8	3470.6	142.72	12.52	21.00	241
170	0.07204	2106.0	3512.6	142.97	12.51	20.99	242
172	0.07119	2131.2	3554.6	143.22	12.51	20.99	244
174	0.07036	2156.4	3596.5	143.46	12.51	20.98	245
176	0.06955	2181.5	3638.5	143.70	12.51	20.98	247
178	0.06875	2206.7	3680.4	143.94	12.51	20.97	248
180	0.06/98	2231.9	3722.4	144.17	12.51	20.96	250
185	0.06612	2294.7	3827.2	144.75	12.50	20.95	253
190	0.06436	2357.6	3931.9	145.30	12.50	20.94	256
195	0.06269	2420.4	4036.6	145.85	12.50	20.93	260
200	0.06111	2483 2	4141.2	146.38	12.50	20.92	263
205	0 05961	2545 9	4245 8	146 89	12 50	20 91	266
210	0.05818	2608.6	4350.3	147.40	12.49	20.91	270
215	0.05681	2671.3	4454.8	147.89	12.49	20.90	273
220	0.05551	2734.0	4559.3	148.37	12.49	20.89	276
225	0.05427	2796.7	4663.7	148 84	12.49	20.89	279
230	0.05308	2859 3	4768 2	149 30	12 49	20 88	282
235	0.05195	2922 0	4872 6	149 75	12 49	20.88	285
240	0.05086	2984.6	4976.9	150.19	12.49	20.87	288
245	0.04981	3047.2	5081.3	150.62	12 49	20.87	291
250	0.04881	3109 8	5185 6	151 04	12 49	20.86	294
255	0.04785	3172 4	5289.9	151.45	12 48	20.86	297
260	0.04693	3234 9	5394 2	151 86	12 48	20 86	300
265	0.04604	3297.5	5498.4	152.26	12.48	20.85	303
270	0 04518	3360 0	5602 7	152 64	12 48	20 85	306
275	0.04/36	3422 6	5706 0	152.04	12.40	20.05	300
280	0.04356	3485 1	5811 2	153 40	12.40	20.85	312
285	0.04279	3547 6	5015 4	153 77 .	12.40	20.84	314
290	0.04205	3610.2	6019.6	154.13	12.48	20.84	317
205	0 04124	2670 7	6100 0	154 40	10 40	20 94	200
295	0.04134	30/2./	6123.8	154.49	12.48	20.84	320
300	0.04065	3/35.2	0227.9	154.84	12.48	20.83	323
320	0.03933	3860.2	6436.3	155.52	12.48	20.83	328
330	0.03694	4110.1	6852.8	156.83	12.48	20.83	333
2/0	0.03505	1005 0	70(1) 0	157 / 5	10.10	00.00	
340	0.03585	4235.0	7061.0	157.45	12.48	20.82	344

Table 15 Thermodynamic properties of argon-Continued

Figure 21: Values of $c_p(T)$ at 1013.25 hPa for Argon vapour (above 87.29 K) from Stewart and Jacobsen (1989, Table 15, continued).



Figure 22: Unpublished figure plotted by me in 2016. Values of $c_p(T)$ for Argon at 1000 hPa (solid, liquid, gas). Datasets for vapour are from Tegeler, Span and Wagner (1999, TSW99, in red) and Stewart and Jacobsen (1989, SJ89, in blue). The asymptotic value 4.966 cal/K/mol corresponds to the "ideal-gas" value 520.3 = (5/2) 8.31432 / 0.039948 J/K/kg. Values of $c_p(T)$ for solid and liquid phases are from other papers and books.



Figure 23: Unpublished figure plotted by me in 2020. The purple dashed curves computed for N2, O2 and H20 vapour by using Statistical and Quantum Physics compare well with the solid curves that correspond to the "calorimetric method" (third law and integration of $c_p(T')/T'$ from 0 K to T, sum of $L(T_k)/T_k$ for all changes of phases at T_k , add the Pauling-Nagle residual entropy at 0 K for H2O).

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