CALCULATING THE PROPERTIES OF A REAL GAS FROM TABLES OF THERMODYNAMIC FUNCTIONS

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The feasibility of applying numerical differentiation methods to tables of thermodynamic functions is demonstrated on several numerical examples.

For analyzing many thermodynamic processes of a real gas, it is necessary to calculate the derivatives of p, v, T as well as the specific heats and the adiabatic exponents. As a source of data for starting the calculations one may use tables of thermodynamic functions, which represent the relations $v = v(p, T)$, $s = s(p, T)$, $h = h(p, T)$, etc. As the standard procedure for calculating the properties of a real gas, which would not require a very qualified person, one may apply here the techniques of numerical analysis and thus make it easier to calculate the said properties of a real gas. We will discuss these techniques on specific examples, with the derivatives represented in dimensionless form: in terms of deviation factors [2]. It has been shown in [2] that two deviation factors involving the partial derivatives $(\partial v/\partial p)_T$ and $(\partial v/\partial T)_p$ can be independent as, for example,

$$\mu_T = \frac{(\partial v/\partial p)_T}{(\partial v/\partial p)_{T,\text{ideal}}} = -\frac{p^2}{RT}\left(\frac{\partial v}{\partial p}\right)_T; \quad \mu_p = \frac{(\partial v/\partial T)_p}{(\partial v/\partial T)_{p,\text{ideal}}} = \frac{p}{R}\left(\frac{\partial v}{\partial T}\right)_p.$$

All other deviation factors are expressible in terms of any of the independent ones.

Let us calculate μ_p and μ_T at the point p = 600 bars and T = 850°K for nitrogen [3]. Particularly convenient for calculating the partial derivatives are formulas applicable to equidistant points, expressed in terms of values of the functions at these points. The formula for calculating μ_p can, for instance, look as follows [1]:

$$\mu_p = \frac{p_0}{12R\tau}(v_{-2} - 8v_{-1} + 8v_1 - v_2). \tag{1}$$

With the temperature step $\tau = 100$°K, we find from [3] that $v_{-2} = 0.004178$; $v_{-1} = 0.004713$; $v_0 = 0.005241$; $v_1 = 0.005763$; $v_2 = 0.006281$ m³/kg. This yields $\mu_p = 1.060$.

The properties of a real gas which involve the derivative $(\partial v/\partial p)_T$, including μ_T, can be expediently determined by differentiating not the specific volume but the density instead:

$$(\partial v/\partial p)_T = -v^2(\partial \rho/\partial p)_T, \tag{2}$$

since, in accordance with the thermal equation of state of a real gas in virial form, the isotherms are hyperbolas with respect to the specific volume. Accordingly,

$$\mu_T = \frac{(p_0 v_0)^2}{12RT_0\pi}\left(\frac{1}{v_{-2}} - \frac{8}{v_{-1}} + \frac{8}{v_1} - \frac{1}{v_2}\right).$$

With the pressure step $\pi = 50$ bars, we find along the $T_0 = 850$°K isotherm: $v_{-2} = 0.006079$; $v_{-1} = 0.005622$; $v_0 = 0.005241$; $v_1 = 0.004918$; $v_2 = 0.004642$ m³/kg. As a result, $\mu_T = 0.997$.

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Next we can determine μ_V [2]:

$$\mu_v = \frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_v = \frac{\mu_p}{\mu_T} = \frac{1.060}{0.997} = 1{,}064.$$

A direct calculation of μ_V is complicated, inasmuch as isochores are not expressed explicitly in tables.

Other properties of a real gas can be calculated after they have been represented as combinations of partial derivatives $(\partial/\partial p)_T$ and $(\partial/\partial T)_p$ or deviation factors. For example, the volume exponent of the adiabatic process [2] can be expressed as

$$\frac{1}{k_v} = -\frac{p}{v}\left(\frac{\partial v}{\partial p}\right)_s = -\frac{p}{v}\left[\left(\frac{\partial v}{\partial p}\right)_T + \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p^2\right]. \tag{3}$$

For the considered point $k_V = 1.740$.

Knowing k_V, one can easily find the velocity of sound at the considered point:

$$a = \sqrt{k_v p v} = \sqrt{1.740 \cdot 600 \cdot 10^5 \cdot 0.005241} = 739 \text{ m/sec}$$

The temperature exponent of the adiabatic process will be determined according to the Rozen formula [2]:

$$\varkappa = \frac{c_p}{c_p - R\mu_p}. \tag{4}$$

At the considered point $\varkappa = 1.360$.

For determining the specific heat c_p, if it is not listed in tables, one may use two formulas:

$$c_p = (\partial i/\partial T)_p = T(\partial s/\partial T)_p.$$

Let us calculate c_p at the point p = 1000 bars and T = 450°K for air [3] from the values of enthalpy:

$$c_p = \frac{1}{12\tau}(h_{-2} - 8h_{-1} + 8h_1 - h_2)$$

$$= \frac{1}{12 \cdot 25}(405{,}0 - 8 \cdot 435{,}4 + 8 \cdot 495{,}0 - 524{,}4) = 1.1916 \text{ kJ/kg} \cdot \text{deg}.$$

In [3] we find $c_p = 1.192$ kJ/kg · deg.

In Table 1 are listed the values of c_p for air, calculated from the values of enthalpy (I), entropy (II), or taken from [3] along the p = 50 bars isobar (III). The differences between the values of the specific heat on the left-hand side in Table 1 indicate a poor matching between values of enthalpy, entropy and specific heat within this range.

For determining the specific heat c_V one may use the expression in [2]:

$$c_v = c_p - R\mu_p\mu_v. \tag{5}$$

The differential throttling effect is determined according to the formula

$$\alpha_i = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] = \frac{z\mu_p - 1}{v c_p}. \tag{6}$$

TABLE 1. Comparison between Values of c_p Calculated from the Enthalpy, the Entropy, and Taken from Tables in [3]

Item No.	p = 50 bars, T (°K)						
	140	150	160	170	180	190	200
I	5,5608	3,3067	1,8317	1,6083	1,4592	1,3600	1,2858
II	7,1806	3,3338	1,8080	1,6065	1,4616	1,3467	1,2833
III	8,694	2,721	1,927	1,620	1,457	1,356	1,288

TABLE 2. Values of c_p (J/kg · deg) Calculated along an Isotherm; $c_{p0} = 1187$ J/kg · deg

Formulas	T = 450° K, p (bars)				
	350	375	400	425	450
$-T(\partial^2 v/\partial T^2)_p \cdot 10^5$	0,20	0,18	0,18	0,14	0,14
Δc_p	5,2	9,6	14,9	19,1	21,8
$c_p = c_{p0} + \Delta c_p$	1192,2	1196,6	1201,9	1206,1	1208,8
c_p [3]	1192	1197	1202	1206	1209

TABLE 3. Comparison between Values of k_{TT} and k_{pp} Calculated and Found by Graphical Differentiation

t, °C	p, atm	v	ρ	k_{TT}	k_{pp}
Nitrogen [4]					
		(cm^3/g)	(g/cm^3)		
200	100	14,48	0,06905	0,950 0,9412	1,017 1,0218
	200	7,637	0,1309	0,895 0,8925	1,003 1,0105
	300	5,389	0,1856	0,835 0,8246	0,970 0,9735
	400	4,287	0,2333	0,775 0,7670	0,923 0,9238
	500	3,622	0,2761	0,720 0,7222	0,875 0,8812
Carbon monoxide [5]					
		(cm^3/mole)	(g/cm^3)		
200	100	406,3	0,06893	0,951 0,9505	1,040 1,040
	200	213,9	0,1309	0,892 0,8924	1,038 1,021
	300	150,7	0,1858	0,830 0,8308	1,014 1,008
	400	119,7	0,2340	0,769 0,7706	0,962 0,9600
	500	101,4	0,2763	0,718 0,7189	0,908 0,9096
Hydrogen [6]					
		(cm^3/mole)	(g/liter)		
200	100	404,7	4,980	0,958 0,9626	0,9653 0,9649
	200	211,0	9,554	0,918 0,9164	0,9316 0,9352
	300	146,4	13,77	0,885 0,8859	0,8996 0,8993
	400	113,9	17,70	0,855 0,8575	0,8690 0,8697
	500	94,42	21,35	0,827 0,8186	0,8395 0,8384

Quantities involving the second derivatives of thermodynamic functions are calculated just as simply, for example:

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p = -\frac{T_0}{12\tau}\left(-v_{-2} + 16v_{-1} - 30v_0 + 16v_1 - v_2\right). \tag{7}$$

From here, knowing the initial values $c_p(p_0)$ and $h(p_0)$, one can calculate $c_p(p)$ and $h(p)$ tables along isotherms by successive numerical integration of the $(\partial c_p/\partial p)_T = f(p)$ table thus obtained. In Table 2 are shown the results of c_p calculations along a segment of the T = 450°K isotherm for nitrogen [3]. Although $(\partial c_p/\partial p)_T$ does not appear monotonic, evidently due to errors in rounding off the values of specific volume, the accuracy of the c_p calculations becomes satisfactory because of the smoothing effect of integration.

For clarity, all calculations in this article were made to one extra decimal place (i.e., without rounding off to three decimal places, corresponding to the accuracy of the numerical differentiation): thus, for example, the specific heat at constant pressure for air is here $c_p = 1.1916$ and the rounded off value $c_p = 1.192$ is exactly the value tabulated in [3]. Furthermore, the number 1.192 and similar numbers with unity have essentially three decimal places, like 0.999, inasmuch as the number of significant places increases stepwise with higher absolute values, while the relative error varies smoothly as the absolute rounding off error remains constant. This fact is not always considered in constructing tables of thermodynamic functions (see [3], for instance).

It would be interesting to compare the calculated derivatives of p, v, T for a real gas with the results of graphical differentiation (Table 3). The quantities $k_{TT} = -(p/v)(\partial v/\partial p)_T$ and $k_{pp} = (T/v)(\partial v/\partial T)_p$ (second rows in the respective columns) have been found from the values of specific volume and density. In [4-6] the deviation of the specific heat from the ideal-gas law

$$\alpha = v_{id} - v = RT/p - v,$$

was differentiated.

The algorithm of numerical differentiation, which involves interpolating n considered points by means of an (n−1)-th-degree polynomial and subsequently calculating the derivative of this polynomial at a given point, suggests a higher accuracy and reliability of these results. An advantage of numerical differentiation is also the possibility of estimating the error incurred by this operation.

The number of reliable decimal places to which a derivative has been calculated by numerical differentiation is approximately equal to the number of decimal places in the difference between two consecutive values of specific volume [1]. Thus, if the considered thermodynamic quantity contains an absolute error Δ, then increasing the τ-step or the π-step results in a smaller relative error in the derivative – which agrees with the statements in [7] concerning the accuracy of graphical differentiation – inasmuch as a larger step results in a longer isobar or isotherm segment on which the derivative is sought and this is equivalent to a larger curvature of the given isoline relative to the error Δ.

A shortcoming of existing tables is that the values have been calculated to not enough significant places, with a corresponding low accuracy in the determination of the respective thermodynamic quantity. For instance, the tables in [8] have been constructed in steps of 1°C temperature and 1 bar pressure. An approximation of the derivative by the half-step difference yields in this case a negligible error due to replacing the tangent by a secant (truncation error), but the difference $v_{i+1} - v_{i-1}$ is given to two decimal places and, consequently, the rounding off error is of the order of 1%. In order to obtain this difference to 3 or 4 decimal places, it is necessary to increase the step and this, in turn, makes it necessary to use multipoint formulas of numerical differentiation because of the now increasing truncation error. Tables of thermodynamic functions representing the equation of state to 7 or 8 decimal places would have made it much simpler to calculate the derivatives of real-gas properties.

NOTATION

p	is the pressure;
T	is the absolute temperature;
v	is the specific volume;
ρ	is the density;
s	is the specific entropy;
h	is the specific enthalpy;
μ_T, μ_p, μ_v	are the deviation factors;
z	is the compressibility;
R	is the universal gas constant;
$\varkappa$, k_v	are the exponents of the adiabatic process;
c_p	is the specific heat at constant pressure;
c_v	is the specific heat at constant volume;
a	is the velocity of sound.

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