

# Equivalence of thermodynamical fundamental equations

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**Abstract.** The Gibbs function, which depends on the intensive variables  $T$  and  $P$ , is easier to obtain experimentally than any other thermodynamical potential. However, textbooks usually first introduce the internal energy, as a function of the extensive variables  $V$  and  $S$ , and then proceed, by Legendre transformations, to obtain the Gibbs function. Here, taking liquid water as an example, we show how to obtain the internal energy from the Gibbs function. The two fundamental equations (Gibbs function and internal energy) are examined and their output compared. In both cases complete thermodynamical information is obtained and shown to be practically the same, emphasizing the equivalence of the two equations. The formalism of the Gibbs function is entirely analytical, while that based on the internal energy is, in this case, numerical. Although it is well known that all thermodynamic potentials contain the same information, usually only the ideal gas is given as an example. The study of real systems, such as liquid water, using numerical methods, may help students to obtain a deeper insight into thermodynamics.

## 1. Introduction

Thermodynamic potentials are an important topic in any course of thermodynamics. According to the first and second laws, for a hydrostatic, monocomponent, one-phase and closed system, the equation  $du = T ds - P dv$  indicates that the specific internal energy  $u = u(s, v)$  exists as a function of the specific entropy,  $s$ , and of the specific volume,  $v$  ([1], pp 1–2 and p 33). These are known as *natural variables* of  $u$  ([2], p 41). Other state variables, such as temperature and pressure, are readily obtained from  $u(s, v)$ :  $T(s, v) = (\partial u / \partial s)_v$  and  $P(s, v) = -(\partial u / \partial v)_s$ . Eliminating  $s$  from  $T(s, v)$  and  $P(s, v)$ , one finds the *thermal equation of state*  $P = P(T, v)$ .

In fact, *all* thermodynamical properties may be derived from  $u = u(s, v)$  or, in other words, such an equation, the so-called *fundamental equation* in the energy representation ([3], p 41), contains complete thermodynamical information for a given system. We note that neither the thermal equation of state nor the internal energy equation of state,  $u = u(T, v)$ , nor even the entropy equation of state,  $s = s(T, v)$ , which can all be derived from the fundamental equation, contains complete thermodynamical information about a system ([1], pp 33–4).

Other fundamental equations, such as the specific enthalpy,  $h = h(s, P)$ , the specific Helmholtz function,  $f = f(T, v)$ , and the specific Gibbs function,  $g = g(T, P)$ , can be used instead of  $u = u(s, v)$ . They are called fundamental equations in the enthalpy, Helmholtz function and Gibbs function representations, respectively. These thermodynamical potentials are equivalent in the sense that they contain, and may provide, the same (full) thermodynamical

information. It is well known that any fundamental equation can be obtained from any other by means of a Legendre transformation ([2], ch 4). In particular,

$$h(s, P) = u(s, P) + Pv(s, P) \quad (1)$$

$$f(T, v) = u(T, v) - Ts(T, v) \quad (2)$$

$$g(T, P) = u(T, P) - Ts(T, P) + Pv(T, P) \quad (3)$$

are Legendre transformations of  $u(s, v)$  ([4], ch 10 and [3], ch 5). Such transformations just operate a change of natural variables. Hence, it is merely a matter of convenience to use one fundamental equation or another. Thermodynamics alone does not provide fundamental equations for a particular system and, therefore, these should be obtained from appropriate experiments (yielding property tables [5]) or from theoretical models (in the framework of statistical mechanics [6]).

In most textbooks for undergraduate courses the ideal gas is used as an example (normally unique) of a system described by a fundamental equation, where  $u = u(s, v)$  is often used as such an equation. For the ideal gas, all Legendre transformations upon  $u$  can be performed promptly, but this exercise may seem rather more like a mathematical manipulation than a physically meaningful operation. Real systems, for which fundamental equations are more intricate, are usually not referred to. For real systems in the laboratory, however, the normal starting point is not the internal energy but the Gibbs function  $g = g(T, P)$ , since its natural variables  $T$  and  $P$  are much easier to measure and control. In the present paper, we show how to obtain the fundamental equation in the internal energy representation from a fundamental equation in the Gibbs function representation, which was fitted to real data for liquid water. Moreover, we show the operability of both fundamental equations,  $g = g(T, P)$  and  $u = u(s, v)$ , in obtaining, for our system, the complete thermodynamical set of properties.

In fact, extensive variables such as  $U$ ,  $S$  and  $V$ , although they might be useful for isolated systems, are not appropriate for systems which exchange energy with the surroundings. Intensive variables such as temperature and pressure are far more convenient, and, in practice, we are obliged to use the (natural) variables  $T$  and  $P$  and, therefore, the specific Gibbs function,  $g = g(T, P)$ .

We use here the analytic specific Gibbs function  $g = g(P, T)$  for liquid water proposed by Thomsen and Hartka [7]. Water is chosen since it is a common substance for which a lot of thermodynamical data are available. The fit made by Thomsen and Hartka is a nice exercise in extracting a simple equation of state directly from the data. The dependence of  $v$  on  $T$  and  $P$  is quadratic. On the other hand, the dependence of the specific heat  $c_P$  on  $T$  is linear at normal pressure. The dependence of  $c_P$  on  $P$  (also linear) is derived from a thermodynamic compatibility condition between the specific heat and the thermal equation of state. The Gibbs function is then readily obtained. From the Gibbs function we can proceed the other way around extracting the complete set of thermal coefficients and specific heats.

In order to determine the fundamental equation in the internal energy representation,  $u = u(s, v)$ , which is presumably more familiar to students in the context of the second law, we apply a Legendre transformation to the Gibbs function, a procedure which, in the present case, has to be performed numerically. We then apply the thermodynamical formalism to  $u = u(s, v)$  in order to obtain the same set of thermal coefficients and specific heats as before. Unlike for the Gibbs function, we now have to compute all derivatives numerically. Finally, we compare the results arising from  $g = g(T, P)$  and from  $u = u(s, v)$ , finding good agreement between them. In this way, we emphasize the equivalence of the results, irrespective of the fundamental equation used and of the techniques involved. In our opinion, the use of numerical tables and methods may help students to acquire a deeper insight into thermodynamics, going beyond classical examples, such as the ideal gas [8, 9].

The outline of this paper is as follows. In section 2 we present the Gibbs function for water as a fundamental equation and present the formalism for obtaining thermal coefficients and specific heats. In section 3 we derive the internal energy from the Gibbs function and extract the same coefficients and specific heats as before. Comparison of the two sets of results is

performed in section 4. The conclusions are presented in section 5. Some technical details about numerical derivatives are given in the appendix.

## 2. The Gibbs function of liquid water as its fundamental equation: explicit expression

We take the fundamental equation  $g = g(T, P)$  for liquid water as given in the following analytic form due to Thomsen and Hartka [7]:

$$g(T, P) = -(c_0 + bT_0) T \ln \left( \frac{T}{T_0} \right) + (c_0 + bT_0) (T - T_0) + \frac{1}{2} b (T - T_0)^2 + v_0 \left[ P - \frac{1}{2} k_0 P^2 \right] + \lambda v_0 P \left[ (T - T_0)^2 + aP (T - T_0) + \frac{1}{3} a^2 P^2 \right] \quad (4)$$

where  $v_0 = 1.00008 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ ,  $\lambda = 8 \times 10^{-6} \text{ K}^{-2}$ ,  $T_0 = 277 \text{ K}$ ,  $a = 2 \times 10^{-7} \text{ K Pa}^{-1}$ ,  $k_0 = 5 \times 10^{-10} \text{ Pa}^{-1}$ ,  $c_0 = 4205.7 \text{ J kg}^{-1} \text{ K}^{-1}$ ,  $b = 2.6 \text{ J kg}^{-1} \text{ K}^{-2}$ . The state  $T = T_0$  and  $P = 0$  was chosen as the reference state for which  $g(T_0, 0) = 0$ . The parametrization (4) for the specific Gibbs function was obtained from experimental data on  $v = v(T, P)$  and  $c_P = c_P(T, P_0)$ , with  $P_0$  the atmospheric pressure. More accurate fits to the experimental data can be found, but equation (4) is sufficient for the pedagogical purposes of the present work. One recognizes in equation (4) the similarity of the first two terms to the corresponding ones in the ideal or the van der Waals gases with constant  $c_V$ , but the rest is quite different.

From the first and second laws,  $dg = -sdT + v dP$ , and therefore

$$s(T, P) = - \left( \frac{\partial g}{\partial T} \right)_P \quad (5)$$

$$v(T, P) = \left( \frac{\partial g}{\partial P} \right)_T. \quad (6)$$

The entropy equation of state,  $s = s(T, P)$ , and the thermal equation of state,  $v = v(T, P)$ , are evaluated from equation (4), leading to

$$s(T, P) = (c_0 + bT_0) \ln \frac{T}{T_0} - b(T - T_0) - 2\lambda v_0 P (T - T_0) - \lambda v_0 a P^2 \quad (7)$$

and

$$v = v_0 \left[ 1 + \lambda (T - T_0 + aP)^2 - k_0 P \right]. \quad (8)$$

From the entropy equation of state, the specific heat at constant pressure is evaluated. Since  $\delta q = T ds$ , from the definition  $c_P = (\delta q / dT)_P$ ,

$$c_P(T, P) = T \left( \frac{\partial s}{\partial T} \right)_P = c_0 - b(T - T_0) - 2\lambda v_0 P T \quad (9)$$

where we have taken the derivative of the entropy equation of state (7) with respect to the temperature at constant pressure. From the thermal equation of state the (cubic) expansion coefficient,  $\alpha$  and the isothermal compressibility,  $\kappa_T$ , are obtained from their definitions:

$$\alpha(T, P) = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P = \frac{2\lambda (T - T_0 + aP)}{1 + \lambda (T - T_0 + aP)^2 - k_0 P} \quad (10)$$

$$\kappa_T(T, P) = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T = \frac{k_0 - 2\lambda a (T - T_0 + aP)}{1 + \lambda (T - T_0 + aP)^2 - k_0 P} \quad (11)$$

where we have taken the derivatives of the thermal equation of state (8). In section 4 the outcome of equations (9)–(11) will be compared with the results for the same quantities in the framework of the internal energy representation.

### 3. The internal energy of liquid water as its fundamental equation: explicit expression

All thermodynamic potentials contain the same information. As an alternative fundamental equation we consider  $u = u(s, v)$  which can be obtained from (4) in the following way. The internal energy,  $u = g + Ts - Pv$ , as a function of  $T$  and  $P$ , is obtained from (4), (7) and (8), and reads as

$$u(T, P) = c_0(T - T_0) - \frac{1}{2}b(T - T_0)^2 + \frac{1}{2}v_0k_0P^2 - 2\lambda v_0P \left[ T^2 - T(T_0 - aP) - \frac{1}{2}aPT_0 + \frac{1}{3}a^2P^2 \right] + u_0 \quad (12)$$

where  $u_0$  is a constant.

It is not possible to obtain an analytic expression for  $u = u(s, v)$  from  $g = g(T, P)$  given by equation (4), i.e. the Legendre transformation of  $g(T, P)$  into  $u(s, v)$  cannot be performed analytically. Therefore, we have to resort to numerical methods.

To construct  $u(s, v)$  we chose five equally spaced entropies, ranging between  $650.0 \text{ J kg}^{-1} \text{ K}^{-1}$  and  $750.0 \text{ J kg}^{-1} \text{ K}^{-1}$ , and five equally spaced specific volumes, between  $1.0130 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$  and  $1.0170 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ . For any equilibrium state, say  $(s_i, v_j)$ , we solve numerically  $s(T_{ij}, P_{ij}) = s_i$  and  $v(T_{ij}, P_{ij}) = v_j$ , with  $s$  and  $v$  given by equations (7) and (8), and find  $T_{ij}$  and  $P_{ij}$ . Hence, the equilibrium state defined by  $(s_i, v_j)$  is also defined by  $(T_{ij}, P_{ij})$ . The numerical determination of  $(T_{ij}, P_{ij})$  was accurately performed using *Mathematica* (this can also be done with any other algebraic manipulation software). The values for  $(T_{ij}, P_{ij})$  are presented in table 1. Introducing these values for the temperature and pressure into equation (12), we obtained the results for  $u(s, v)$  presented in table 2. The constant  $u_0$  in equation (12) is chosen in order to set to zero the energy of the equilibrium state ( $s_1 = 650.0 \text{ J kg}^{-1} \text{ K}^{-1}$ ,  $v_1 = 1.0170 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ ), i.e.  $u(s_1, v_1) = 0$ .

**Table 1.** Absolute temperatures, in K, and pressures, in MPa, obtained from [7] for liquid water. The specific entropies,  $s$ , are in  $\text{J kg}^{-1} \text{ K}^{-1}$  and the specific volumes,  $v$ , in  $\text{m}^3 \text{ kg}^{-1}$ .

$v/10^{-3}$	$s = 650.0$	$s = 675.0$	$s = 700.0$	$s = 725.0$	$s = 750.0$
	$T$	$T$	$T$	$T$	$T$
1.0130	325.04	327.54	330.23	333.18	336.61
1.0140	324.80	327.27	329.89	332.76	336.02
1.0150	324.58	327.00	329.58	332.37	335.49
1.0160	324.37	326.75	329.28	331.00	335.01
1.0170	324.16	326.51	328.99	331.65	334.57
	$P$	$P$	$P$	$P$	$P$
1.0130	16.2583	22.7173	30.4737	40.1405	53.0646
1.0140	12.7340	18.9071	26.2657	35.3237	47.1357
1.0150	9.2728	15.1816	22.1793	30.7020	41.5953
1.0160	5.8705	11.5340	18.2023	26.2494	36.3665
1.0170	2.5233	7.9582	14.3243	21.9451	31.3948

In principle, one could obtain  $u = u(s, v)$  directly in the laboratory, although the experiments would be difficult to perform. Actually, one should conduct experiments at constant specific volume for different specific entropies, but volume is a variable which is quite difficult to keep constant. On the other hand, variations of entropy are also difficult to measure. One could imagine very small energy transfers to the system (using e.g. a resistor). The entropy variation would then be the sum of each energy transfer divided by the absolute temperature of the system. The sum of the tiny energies would be the variation of the internal energy. To obtain the Gibbs function as a function of its natural variables is much easier in practice.

**Table 2.** Specific internal energy,  $u(s, v)$ , in  $\text{J kg}^{-1}$ , for liquid water. The units of  $s$  and  $v$  are as in table 1.

$v/10^{-3}$	$s = 650.0$	$s = 675.0$	$s = 700.0$	$s = 725.0$	$s = 750.0$
	$u$	$u$	$u$	$u$	$u$
1.0130	37.248 60	8194.259 32	16 415.996 95	24 708.018 22	33 079.175 71
1.0140	22.757 87	8173.454 44	16 387.637 95	24 670.303 55	33 029.112 01
1.0150	11.759 55	8156.416 72	16 363.425 01	24 637.305 82	32 984.775 23
1.0160	4.926 21	8143.065 15	16 343.242 84	24 608.843 24	32 945.817 72
1.0170	0.000 00	8133.324 80	16 326.987 19	24 584.757 57	32 911.956 58

Several properties will now be obtained and compared in order to show the equivalence of the formalisms used in the two fundamental equations used here (the Gibbs function, handled analytically, and the internal energy, handled numerically).

From  $du = T ds - P dv$ , one obtains

$$T(s, v) = \left( \frac{\partial u}{\partial s} \right)_v \quad (13)$$

$$P(s, v) = - \left( \frac{\partial u}{\partial v} \right)_s \quad (14)$$

In order to determine  $T$  and  $P$  from  $u$  given in table 2 we computed numerically the derivatives on the right-hand side of these equations using a five-point algorithm [10]. This algorithm, also used in [8], is described in the appendix. The resulting temperatures and pressures are given in table 3.

**Table 3.** Temperatures, in K, and pressures, in MPa, for liquid water obtained from the data given in table 2 using equations (13) and (14). The units of  $s$  and  $v$  are as in table 1.

$v/10^{-3}$	$s = 650.0$	$s = 675.0$	$s = 700.0$	$s = 725.0$	$s = 750.0$
	$T$	$T$	$T$	$T$	$T$
1.0130	325.02	327.54	330.22	333.19	336.58
1.0140	324.79	327.27	329.89	332.76	336.00
1.0150	324.57	327.01	329.58	332.37	335.48
1.0160	324.36	326.75	329.28	332.00	335.00
1.0170	324.16	326.51	328.99	331.65	334.56
	$P$	$P$	$P$	$P$	$P$
1.0130	16.2583	22.7170	30.4732	40.1396	53.0593
1.0140	12.7340	18.9073	26.2658	35.3239	47.1369
1.0150	9.2728	15.1816	22.1793	30.7018	41.5946
1.0160	5.8706	11.5340	18.2024	26.2497	36.3676
1.0170	2.5235	7.9582	14.3244	21.9441	31.3911

It is instructive to compare these temperatures and pressures with those obtained for the same equilibrium states  $(s, v)$  given in table 1. Comparing the data in tables 1 and 3, one confirms the accuracy of the algorithm used to compute the derivatives.

Considering again table 3, coefficients such as the specific heat at constant volume,  $c_V = (\delta q/dT)_v$ , the relative pressure coefficient,  $\beta = (1/P)(\partial P/\partial T)_v$ , the adiabatic compressibility coefficient,  $\kappa_S = (1/v)(\partial v/\partial P)_s$ , are obtained by numerical derivation of  $T$  and  $P$  with respect to  $v$  (at constant  $s$ ) or with respect to  $s$  (at constant  $v$ ).

Since  $\delta q = T ds$ , for a reversible isochoric process,

$$c_V = T \left( \frac{\partial s}{\partial T} \right)_v = T \left[ \left( \frac{\partial T}{\partial s} \right)_v \right]^{-1} \quad (15)$$

which is readily computed from table 3. The relative pressure coefficient, or, equivalently,  $B = P\beta$ , is again obtained from table 3 using

$$B = \left( \frac{\partial P}{\partial T} \right)_v = \left( \frac{\partial P}{\partial s} \right)_v \left( \frac{\partial s}{\partial T} \right)_v = \left( \frac{\partial P}{\partial s} \right)_v \left[ \left( \frac{\partial T}{\partial s} \right)_v \right]^{-1}. \quad (16)$$

The adiabatic compressibility coefficient,

$$\kappa_S = \frac{1}{v} \left[ \left( \frac{\partial P}{\partial v} \right)_s \right]^{-1} \quad (17)$$

also follows directly from table 3.

The coefficients,  $c_V$ ,  $B$  and  $\kappa_S$  are related to the second derivatives of the specific internal energy,  $u$  ([4], ch 9). Of the four second-order derivatives, only three are independent (owing to the equality of mixed derivatives) and we have chosen  $c_V$ ,  $B$  and  $\kappa_S$ . The derivatives in equations (15)–(17) have been computed numerically, using the five-point algorithm mentioned above, from the  $T$  and  $P$  data in table 3. The resulting values are displayed in table 4 for the equilibrium states ( $s$ ,  $v$ ) considered in the previous tables.

**Table 4.** Coefficients  $c_V$  (in  $\text{kJ kg}^{-1} \text{K}^{-1}$ ),  $B$  (in  $\text{MPa K}^{-1}$ ) and  $\kappa_S$  (in  $\text{MPa}^{-1}$ ) for liquid water obtained from equations (15)–(17) using the five-point algorithm to compute the derivatives of  $T$  and  $P$  given in table 3. The units of  $s$  and  $v$  are as in table 1.

$v/10^{-3}$	$s = 650.0$	$s = 675.0$	$s = 700.0$	$s = 725.0$	$s = 750.0$
	$c_V$	$c_V$	$c_V$	$c_V$	$c_V$
1.0130	3266.40	3176.27	2948.07	2640.65	2311.42
1.0140	3331.38	3233.16	3020.57	2739.44	2434.89
1.0150	3389.97	3287.55	3088.75	2829.94	2547.19
1.0160	3443.74	3339.60	3153.08	2913.50	2650.13
1.0170	3493.82	3389.47	3213.93	2991.17	2745.18
	$B$	$B$	$B$	$B$	$B$
1.0130	2.344 19	2.740 88	3.052 58	3.489 75	4.168 94
1.0140	2.304 42	2.657 58	2.958 37	3.363 56	3.964 58
1.0150	2.259 15	2.579 54	2.868 99	3.246 58	3.784 75
1.0160	2.210 80	2.506 10	2.784 23	3.138 37	3.627 34
1.0170	2.161 36	2.436 43	2.703 35	3.036 35	3.483 89
	$\kappa_S/10^{-4}$	$\kappa_S/10^{-4}$	$\kappa_S/10^{-4}$	$\kappa_S/10^{-4}$	$\kappa_S/10^{-4}$
1.0130	2.775 23	2.561 58	2.311 08	2.006 34	1.609 34
1.0140	2.824 08	2.618 22	2.379 15	2.091 62	1.723 65
1.0150	2.871 48	2.673 13	2.444 80	2.173 34	1.833 36
1.0160	2.917 19	2.725 93	2.507 27	2.249 75	1.933 33
1.0170	2.960 95	2.776 20	2.565 76	2.318 97	2.017 87

Other coefficients, such as the (cubic) thermal expansion coefficient,  $\alpha = (1/v)(\partial v/\partial T)_P$ , the specific heat at constant pressure,  $c_P = (\delta q/dT)_P$ , and the isothermal compressibility,  $\kappa_T = -(1/v)(\partial v/\partial P)_T$ , can be obtained. For this, we use (see [8]) the reciprocity theorem, which leads to

$$B = \frac{\alpha}{\kappa_T} \quad (18)$$

Mayer's relation, which can be written as

$$c_P = c_V + \frac{T v \alpha^2}{\kappa_T} \quad (19)$$

and Reech's relation, which is given by

$$\frac{c_P}{c_V} = \frac{\kappa_T}{\kappa_S}. \quad (20)$$

Solving the system of these three equations with respect to  $c_P$ ,  $\kappa_T$  and  $\alpha$  one finds

$$c_P = c_V \left[ 1 - \frac{T v B^2 \kappa_S}{c_V} \right]^{-1} \quad (21)$$

$$\kappa_T = \kappa_S \frac{c_P}{c_V} = \kappa_S \left[ 1 - \frac{T v B^2 \kappa_S}{c_V} \right]^{-1} \quad (22)$$

$$\alpha = B \kappa_T = B \kappa_S \left[ 1 - \frac{T v B^2 \kappa_S}{c_V} \right]^{-1}. \quad (23)$$

#### 4. Comparison of results

In table 5 we present the results for the coefficients (21)–(23). Any other thermodynamic coefficient can now be obtained from them [11]. These results obtained in the internal energy representation should be compared with those obtained in the Gibbs function representation.

In table 6 we present the results, in the framework of the Gibbs function representation, for  $c_P$ ,  $\alpha$  and  $\kappa_T$  obtained from equations (9)–(11), using the pressures and temperatures of table 3.

**Table 5.** Coefficients  $c_P$  (in  $\text{kJ kg}^{-1} \text{K}^{-1}$ ),  $\alpha$  (in  $\text{K}^{-1}$ ) and  $\kappa_T$  (in  $\text{MPa}^{-1}$ ) for liquid water obtained in the internal energy representation from equations (21)–(23), using  $c_V$ ,  $B$  and  $\kappa_S$  of table 4. The units of  $s$  and  $v$  are as in table 1.

$v/10^{-3}$	$s = 650.0$	$s = 675.0$	$s = 700.0$	$s = 725.0$	$s = 750.0$
	$c_P$	$c_P$	$c_P$	$c_P$	$c_P$
1.0130	3859	3975	3901	3839	3934
1.0140	3911	3990	3925	3866	3921
1.0150	3952	4007	3949	3893	3925
1.0160	3987	4024	3972	3918	3936
1.0170	4018	4042	3993	3941	3941
	$\alpha/10^{-5}$	$\alpha/10^{-5}$	$\alpha/10^{-5}$	$\alpha/10^{-5}$	$\alpha/10^{-5}$
1.0130	76.8	87.8	93.3	101.8	114.2
1.0140	76.4	85.8	91.4	99.2	110.0
1.0150	75.6	84.0	89.6	97.0	106.9
1.0160	74.6	82.3	87.9	94.9	104.2
1.0170	73.6	80.6	86.1	92.7	100.9
	$\kappa_T/10^{-4}$	$\kappa_T/10^{-4}$	$\kappa_T/10^{-4}$	$\kappa_T/10^{-4}$	$\kappa_T/10^{-4}$
1.0130	3.279	3.206	3.058	2.917	2.739
1.0140	3.315	3.231	3.092	2.952	2.776
1.0150	3.348	3.258	3.126	2.989	2.825
1.0160	3.378	3.285	3.158	3.026	2.871
1.0170	3.405	3.310	3.188	3.055	2.897

**Table 6.** Coefficients  $c_P$ ,  $\alpha$  and  $\kappa_T$  (units as in table 5) for liquid water obtained in the Gibbs function representation from equations (9)–(11) for temperatures and pressures of table 3. The units of  $s$  and  $v$  are as in table 1.

$v/10^{-3}$	$s = 650.0$	$s = 675.0$	$s = 700.0$	$s = 725.0$	$s = 750.0$
	$c_P$	$c_P$	$c_P$	$c_P$	$c_P$
1.0130	3996	3955	3906	3845	3764
1.0140	4015	3975	3929	3872	3798
1.0150	4033	3996	3952	3898	3830
1.0160	4052	4016	3973	3923	3859
1.0170	4069	4035	3995	3947	3887
	$\alpha/10^{-5}$	$\alpha/10^{-5}$	$\alpha/10^{-5}$	$\alpha/10^{-5}$	$\alpha/10^{-5}$
1.0130	81.0	87.0	93.7	101.4	110.9
1.0140	79.4	85.2	91.7	99.1	108.0
1.0150	77.9	83.6	89.8	96.9	105.3
1.0160	76.4	81.9	88.0	94.8	102.8
1.0170	75.0	80.4	86.3	92.9	100.4
	$\kappa_T/10^{-4}$	$\kappa_T/10^{-4}$	$\kappa_T/10^{-4}$	$\kappa_T/10^{-4}$	$\kappa_T/10^{-4}$
1.0130	3.315	3.195	3.062	2.907	2.717
1.0140	3.342	3.225	3.096	2.948	2.770
1.0150	3.367	3.254	3.128	2.987	2.819
1.0160	3.392	3.281	3.160	3.023	2.865
1.0170	3.416	3.308	3.190	3.058	2.907

Comparison of tables 5 and 6 confirms the equivalence of the two fundamental equations and the accuracy of the numerical methods used to compute derivatives. The best agreement is obtained in the interior of the tables. At the borders, as expected (errors are greater at the extreme points [10]), the discrepancies are larger. Although  $u(s, v)$  (table 2) was obtained with high accuracy (the indicated digits are all significant), the algorithm to compute its derivatives ( $T$  and  $P$ ) introduces errors. These are amplified by the numerical derivatives of  $T$  and  $P$  (note that these derivatives occur in the denominators (see equations (15)–(17) and (21)–(23))), explaining the deviations between the entries of tables 5 and 6. The maximum relative error is 5%. We verified that in some regions of the  $(s, v)$  plane outside the range explored in this paper, the five-point algorithm is not enough to keep the numerical inaccuracies with a relative error of less than 5%.

The coefficients  $c_V$ ,  $B$  and  $\kappa_S$  are readily obtained from table 6 and from equations (18)–(20). The comparison of the resulting values with those obtained in the  $u = u(s, v)$  representation (table 4) is as good as the comparison between tables 5 and 6.

## 5. Conclusions

Motivated by the fact that few examples are available to illustrate that thermodynamical potentials, as functions of their natural variables, contain the same information, we studied two fundamental equations for the same real system. We carried out *numerically* the Legendre transformation of the Gibbs function for water in order to obtain the fundamental equation in the internal energy representation. We obtained a set of thermal coefficients and specific heats in the two representations (Gibbs function and internal energy) and showed their agreement.

Water was considered since it is well known experimentally but other substances for which we have empirical or theoretical equations of state  $v = v(T, P)$  and a specific heat  $c_P = c_P(T, P)$  could have been taken. The classical examples of the ideal gas or the van der Waals gas, described by equations  $P = P(v, T)$  and usually taken with constant  $c_V$ , are



different from our present example. For the van der Waals gas the function  $g = g(T, P)$  cannot be obtained analytically (the thermal equation of state has to be inverted numerically). Therefore, unlike in the present work, the internal energy  $u = u(s, v)$  is analytical and the Gibbs function  $g = g(T, P)$  is numerical. The extraction of thermodynamical coefficients in the case of the van der Waals model is an interesting exercise for students.

From the experimental point of view, the Gibbs function plays a crucial role in a large variety of situations (phase equilibria, chemical equilibrium, electrochemistry, solutions, etc) since its natural variables  $T$  and  $P$ , which are the intensive variables characterizing the thermal and mechanical equilibrium, are the most easy to control. It is therefore desirable that students become acquainted with that function and work with it as early as possible. Of course, in an introductory course of thermodynamics there are many new concepts which have to be introduced before the Gibbs function. However, in a second course of thermodynamics (alone or with statistical mechanics) in undergraduate or graduate studies, the usefulness of thermodynamic potentials should be emphasized with practical examples right from the outset. One such possible line of approach was presented in this paper. In fact, we used numerical techniques which are straightforward to implement on a computer. We believe that the use of computational methods may help students to analyse real systems and to better understand the power of thermodynamics.

## Appendix

To compute numerically derivatives of  $u$  (or of  $T$  or  $P$ ) with respect to  $s$  and  $v$  we used a five-point algorithm [8, 10]. Given  $N \geq 5$  equally spaced data points  $1, 2, \dots, i, \dots, N-1, N$  for the variable  $x$ , the derivatives of the function  $y(x)$ , at the data point  $j$ ,  $(dy/dx)_j$ , are obtained numerically as follows:

$$\left(\frac{dy}{dx}\right)_1 = \frac{1}{24\Delta x}(-50y_1 + 96y_2 - 72y_3 + 32y_4 - 6y_5) \quad (24)$$

$$\left(\frac{dy}{dx}\right)_2 = \frac{1}{24\Delta x}(-6y_1 - 20y_2 + 36y_3 - 12y_4 + 2y_5) \quad (25)$$

$$\left(\frac{dy}{dx}\right)_i = \frac{1}{24\Delta x}(2y_{i-2} - 16y_{i-1} + 16y_{i+1} - 2y_{i+2}) \quad (26)$$

$$\left(\frac{dy}{dx}\right)_{N-1} = \frac{1}{24\Delta x}(-2y_{N-4} + 12y_{N-3} - 36y_{N-2} + 20y_{N-1} + 6y_N) \quad (27)$$

$$\left(\frac{dy}{dx}\right)_N = \frac{1}{24\Delta x}(6y_{N-4} - 32y_{N-3} + 72y_{N-2} - 96y_{N-1} + 50y_N). \quad (28)$$

The algorithm, which also applies to partial derivatives, is more reliable inside the interval of  $x$  [10]. Computing these numerical derivatives requires modest knowledge of computer programming and the process can be easily implemented in spreadsheets such as *Excel*.

We checked that a three-point algorithm leads to larger numerical errors.

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