TRANSFORMATION OF THE EQUATIONS OF THERMODYNAMICS

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A simplified method is proposed and studied for deriving the equations of thermodynamics through automatic conversion (transformation) of an equation into a series of other equations through a replacement of variables on the basis of appropriate codes.

A large majority of the equations of thermodynamics, in particular, a large group of differential equations, can be formally derived from a small number of basic equations: the first and second laws of thermodynamics and equations defining the thermodynamic functions. Rows 1-5 in Table 4 show the basic equations, which relate the basic state functions P, V, T, S, U, I, F, and Φ with the process functions L, Q, L', and Q'.

The basic equations have certain formal properties, independent of their physical meaning; one such property is that when the variables in any equation are replaced by other variables according to certain recipes, this equation converts into another basic equation (or into itself). As a formal property, this variable-replacement property leads to equations which are derivable from the basic equations, and it can be used to abbreviate and simplify the derivation, discussion, and study of a large number of equations of thermodynamics. One equation can be converted into several others through an automatic replacement of variables. This conversion of one equation into another is a "transformation," and the recipe containing the

TABLE 1. The Basic Codes

0	1	2	3	4	5	6	7
P	V	P	V	T	T	S	S
V	$-P$	V	$-P$	$-S$	$-S$	T	T
T	T	S	S	P	V	P	V
S	S	$-T$	$-T$	$-V$	P	$-V$	P
U	I	F	Φ	U	I	F	Φ
I	U	Φ	F	F	Φ	U	I
F	Φ	U	I	I	U	Φ	F
Φ	F	I	U	Φ	F	I	U
L	L'	L	L'	$-Q$	$-Q$	$-Q'$	$-Q'$
L'	L	L'	L	$-Q'$	$-Q'$	$-Q$	$-Q$
Q	Q	Q'	Q'	$-L$	$-L'$	$-L$	$-L'$
Q'	Q'	Q	Q	$-L'$	$-L$	$-L'$	$-L$

TABLE 2. Code Combinations

0	1	2	3	4	5	6	7
1	0	3	2	5	4	7	6
2	3	0	1	6	7	4	5
3	2	1	0	7	6	5	4
4	6	5	7	0	2	1	3
5	7	4	6	1	3	0	2
6	4	7	5	2	0	3	1
7	5	6	4	3	1	2	0

Example. The combination of codes 1 and 2 yields code 3. Code 1 transforms U into I, and code 2 transforms I into Φ consequently, code 3 transforms U into Φ.

TABLE 3. Code 1 – Basic and Supplementary

0	P	V	T	S	U	I	F	Φ	L	L'	Q	Q'	C	R	k	n
1	V	$-P$	T	S	I	U	Φ	F	L'	L	Q	Q'	C	$-R$	$\frac{1}{k}$	$\frac{1}{n}$

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TABLE 4. Check of the Codes on the Basis of the Basic Equations of Thermodynamics

Equations				Codes				No.
Definition of the state functions								
$I = U + PV$	$F = U - TS$	$\Phi = F + PV$	$\Phi = I - TS$	0,1	4,6	2,3	5,7	1
Definition of the basic process functions								
$L' = L - \Delta(PV)$		$Q' = Q - \Delta(TS)$		0;1,2,3		4,5,6,7		2
The same in frictionless processes								
$dL = PdV$	$dL' = -VdP$	$dQ = TdS$	$dQ' = -SdT$	0,2	1,3	4,5	6,7	3
First law of thermodynamics								
$Q = \Delta U + L$	$Q = \Delta I + L'$	$Q' = \Delta F + L$	$Q' = \Delta\Phi + L'$	0,4	1,5	2,6	3,7	4
Combination of first and second laws								
$dU = TdS - PdV$		$dI = TdS + VdP$		0,4		1,5		5
$dF = -SdT - PdV$		$d\Phi = -SdT + VdP$		2,6		3,7		
According to Code 1								
Definition of supplementary functions								
$C = dQ/dT$				0,1				6
$n = -(V/P)(dP/dV)$				0,1				7
$k = (\partial I/\partial U)_S$				0,1				8
Equation of state of an ideal gas								
$PV = RT$				0,1				9

the various sets of variables is a "code." It is easy to see from Table 4 that correct results follow from the codes (for the basic functions) in Table 1, where there is also a "zeroth" code, containing a list of the variables which can be replaced. In general there are eight equations, including the original equation, which differ significantly in physical meaning, role, and range of application. In certain cases, the transformation does not alter the equation, or a transformation by means of two or more codes leads back to the same equation.

Table 1 shows three sets of four variables, in each of which sets the upper variable can be specified (taking signs into account) in four versions, since a simultaneous change of the sign in the pair P, V or in the pair T, S or in both pairs does not alter the basic equations or those derived from them. All versions are equivalent in terms of the results of the transformation, so it is sufficient to use the sets in Table 1. That these other versions are possible is important only for a clarification of the next point.

By transforming two or more times successively with the same code or different codes, we produce a transformation according to a new code, which we can treat as the result of "combining" these other codes. Table 2 shows the numbers of the codes which are combinations of two codes: first the code whose number appears at the top of this table is used, and then the code whose number appears in the left column. We see that combinations do not result in any codes other than the eight in Table 1. Although the version of the code may be different, this fact (as was mentioned in the previous paragraph) does not affect the results of the transformation. The result of combining codes sometimes depend on the order of this combination (e.g., codes 4 and 5). Successive use of codes 1, 2, 3, 4, or 7 leads to a "zeroth" code (in one of the versions), i.e., converts any equation into itself. These codes are symmetric; i.e., two equations are converted into each other, and some equations, symmetric in structure, convert into themselves.

Indices indicating that a given variable is held constant during a process or during a partial differentiation and processes including cycles can also be transformed (without an account of signs). However, transfer of the role played by the original equation to the equation resulting from the transformation may be

TABLE 5. Examples of the Transformation of Thermodynamic Equations by Means of All the Codes

<table>
<tr><th colspan="6">Equation</th><th colspan="4">Codes</th><th>No.</th></tr>
<tr><td colspan="6">Consequences of the first law of thermodynamics</td><td></td><td></td><td></td><td></td><td rowspan="3">10</td></tr>
<tr><td>For $L = 0$</td><td>$Q = \Delta U$</td><td>$Q' = \Delta F$</td><td>For $L' = 0$</td><td>$Q = \Delta I$</td><td>$Q' = \Delta \Phi$</td><td>0</td><td>2</td><td>1</td><td>3</td></tr>
<tr><td>For $Q = 0$</td><td>$L = -\Delta U$</td><td>$L' = -\Delta I$</td><td>For $Q' = 0$</td><td>$L' = -\Delta \Phi$</td><td>$L = -\Delta F$</td><td>4</td><td>5</td><td>6</td><td>7</td></tr>
<tr><td colspan="6">Differential equations of thermodynamics</td><td colspan="4"></td><td rowspan="9">11</td></tr>
<tr><td colspan="6">$(\partial U/\partial P)_T = -T\,(\partial V/\partial T)_P - P\,(\partial V/\partial P)_T$</td><td colspan="4">0</td></tr>
<tr><td colspan="6">$(\partial I/\partial V)_T = T\,(\partial P/\partial T)_V + V\,(\partial P/\partial V)_T$</td><td colspan="4">1</td></tr>
<tr><td colspan="6">$(\partial F/\partial P)_S = -S\,(\partial V/\partial S)_P - P\,(\partial V/\partial P)_S$</td><td colspan="4">2</td></tr>
<tr><td colspan="6">$(\partial \Phi/\partial V)_S = S\,(\partial P/\partial S)_V + V\,(\partial P/\partial V)_S$</td><td colspan="4">3</td></tr>
<tr><td colspan="6">$(\partial U/\partial T)_P = P\,(\partial S/\partial P)_T + T\,(\partial S/\partial T)_P$</td><td colspan="4">4</td></tr>
<tr><td colspan="6">$(\partial I/\partial T)_V = V\,(\partial S/\partial V)_T + T\,(\partial S/\partial T)_V$</td><td colspan="4">5</td></tr>
<tr><td colspan="6">$(\partial F/\partial S)_P = -P\,(\partial T/\partial P)_S - S\,(\partial T/\partial S)_P$</td><td colspan="4">6</td></tr>
<tr><td colspan="6">$(\partial \Phi/\partial S)_V = -V\,(\partial T/\partial V)_S - S\,(\partial T/\partial S)_V$</td><td colspan="4">7</td></tr>
<tr><td colspan="3">$(\partial S/\partial V)_T = (\partial P/\partial T)_V$</td><td colspan="3">$(\partial S/\partial P)_T = -(\partial V/\partial T)_P$</td><td colspan="2">0,7</td><td colspan="2">1,6</td><td rowspan="2">12</td></tr>
<tr><td colspan="3">$(\partial T/\partial V)_S = -(\partial P/\partial S)_V$</td><td colspan="3">$(\partial T/\partial P)_S = (\partial V/\partial S)_P$</td><td colspan="2">2,5</td><td colspan="2">3,4</td></tr>
<tr><td colspan="3">$U = F - T\,(\partial F/\partial T)_V$</td><td colspan="3">$I = \Phi - T\,(\partial \Phi/\partial T)_P$</td><td colspan="2">0</td><td colspan="2">1</td><td rowspan="4">13</td></tr>
<tr><td colspan="3">$F = U - S\,(\partial U/\partial S)_V$</td><td colspan="3">$\Phi = I - S\,(\partial I/\partial S)_P$</td><td colspan="2">2</td><td colspan="2">3</td></tr>
<tr><td colspan="3">$U = I - P\,(\partial I/\partial P)_S$</td><td colspan="3">$I = U - V\,(\partial U/\partial V)_S$</td><td colspan="2">4</td><td colspan="2">5</td></tr>
<tr><td colspan="3">$F = \Phi - P\,(\partial \Phi/\partial P)_T$</td><td colspan="3">$\Phi = F - V(\partial F/\partial V)_T$</td><td colspan="2">6</td><td colspan="2">7</td></tr>
<tr><td colspan="6">$U = \Phi - T\,(\partial \Phi/\partial T)_P - P\,(\partial \Phi/\partial P)_T$</td><td colspan="4">0,4</td><td rowspan="4">14</td></tr>
<tr><td colspan="6">$I = F - T\,(\partial F/\partial T)_V - V\,(\partial F/\partial V)_T$</td><td colspan="4">1,5</td></tr>
<tr><td colspan="6">$F = I - S\,(\partial I/\partial S)_P - P\,(\partial I/\partial P)_S$</td><td colspan="4">2,6</td></tr>
<tr><td colspan="6">$\Phi = U - S\,(\partial U/\partial S)_V - V\,(\partial U/\partial V)_S$</td><td colspan="4">3,7</td></tr>
<tr><td colspan="3">$(\partial^2 U/\partial S^2)_V = (\partial T/\partial S)_V$</td><td colspan="3">$(\partial^2 I/\partial S^2)_P = (\partial T/\partial S)_P$</td><td colspan="2">0</td><td colspan="2">1</td><td rowspan="4">15</td></tr>
<tr><td colspan="3">$(\partial^2 F/\partial T^2)_V = -(\partial S/\partial T)_V$</td><td colspan="3">$(\partial^2 \Phi/\partial T^2)_P = -(\partial S/\partial T)_P$</td><td colspan="2">2</td><td colspan="2">3</td></tr>
<tr><td colspan="3">$(\partial^2 U/\partial V^2)_S = -(\partial P/\partial V)_S$</td><td colspan="3">$(\partial^2 I/\partial P^2)_S = (\partial V/\partial P)_S$</td><td colspan="2">4</td><td colspan="2">5</td></tr>
<tr><td colspan="3">$(\partial^2 F/\partial V^2)_T = -(\partial P/\partial V)_T$</td><td colspan="3">$(\partial^2 \Phi/\partial P^2)_T = (\partial V/\partial P)_T$</td><td colspan="2">6</td><td colspan="2">7</td></tr>
</table>

erroneous; e.g., a Carnot cycle is transformed by code 4 into an isochore–isobar cycle, but the role of the Carnot cycle is not transferred to the latter cycle.

On the other hand, transformation can bring out new physical relations and new quantities, whose physical meaning and roles should be studied separately. Although nearly all the variables and equations used here are known [1-4], including L' [5], formal transformation led to the new variable $Q' = Q - \Delta(TS)$, which, by analogy with the free energy and free enthalpy [1], can be called the "free heat" and treated as part of the heat expended on a change in the free energy (in addition to the energy converted into work). The role of this variable and its possible applications in calculations should be studied separately. New variables may appear during transformation of supplementary functions, e.g., the heat capacity, by means of various codes.

Code 1 is slightly more important than the others, since it can also be used for the equation of state of an ideal gas and thus for all equations which follow from the ideal-gas equation (and from the basic equations). Table 3 shows for code 1 the method of replacing the "supplementary" variables C, R, n, k. Where necessary, the table can be fleshed out with thermal coefficients, Joule coefficients, or variables characterizing polytropic processes [6].

The equations of state for real gases and the equations derived from them, equations involving the discharge of material, and certain other equations cannot be transformed by this method.

TABLE 6. Examples of the Transformation of Thermodynamic Equations by Code 1 (basic and supplementary)

<table>
<tr><th colspan="4">Equations</th><th>No.</th></tr>
<tr><td colspan="4">Differential equation of thermodynamics</td><td></td></tr>
<tr><td colspan="2">$C_V = (\partial U/\partial T)_V$</td><td colspan="2">$C_P = (\partial I/\partial T)_P$</td><td>16</td></tr>
<tr><td colspan="2">$C_V = T\,(\partial S/\partial T)_V$</td><td colspan="2">$C_P = T\,(\partial S/\partial T)_P$</td><td>17</td></tr>
<tr><td colspan="2">$(\partial C_V/\partial T)_V = (\partial^2 U/\partial T^2)_V$</td><td colspan="2">$(\partial C_P/\partial T)_P = (\partial^2 I/\partial T^2)_P$</td><td>18</td></tr>
<tr><td colspan="2">$(\partial C_V/\partial V)_T = T\,(\partial^2 P/\partial T^2)_V$</td><td colspan="2">$(\partial C_P/\partial P)_T = -T\,(\partial^2 V/\partial T^2)_P$</td><td>19</td></tr>
<tr><td colspan="2">$(\partial^2 U/\partial V^2)_S = kP/V$</td><td colspan="2">$(\partial^2 I/\partial P^2)_S = -V/(kP)$</td><td>20</td></tr>
<tr><td colspan="4">$C_P - C_V = T\,(\partial V/\partial T)_P\,(\partial P/\partial T)_V$ (symm.)</td><td>21</td></tr>
<tr><td colspan="2">$C_P - C_V = -T\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V^2$</td><td colspan="2">$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P^2$</td><td>22</td></tr>
<tr><td colspan="2">$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]$</td><td colspan="2">$\left(\frac{\partial T}{\partial P}\right)_I = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$</td><td>23</td></tr>
<tr><td colspan="4">Equations referring to a polytropic process</td><td></td></tr>
<tr><td>$n_{(PV)} = 1$ (symm.) $n_P = 0$</td><td colspan="2">$1/n_V = 0$</td><td>$k = n_T\,C_P/C_V$ (symm.)</td><td>24, 25, 26</td></tr>
<tr><td colspan="2">$n_U = n_T\,[1 - (\partial T/\partial V)_U\,(\partial V/\partial T)_P\,]$</td><td colspan="2">$n_I = n_T\,/[1 - (\partial T/\partial P)_I\,(\partial P/\partial T)_V\,]$</td><td>27</td></tr>
<tr><td colspan="4">Equations refering to an ideal gas (the equations are denoted to show their relationship with those above).</td><td></td></tr>
<tr><td colspan="2">$(\partial S/\partial V)_T = R/P$</td><td colspan="2">$(\partial S/\partial P)_T = -R/V$</td><td>12 i</td></tr>
<tr><td colspan="4">$C_P - C_V = R$ (symm.)</td><td>21 i</td></tr>
<tr><td colspan="2">$n_T = 1$ (symm.)</td><td colspan="2">$k = C_P/C_V$ (symm.)</td><td>24i, 26i</td></tr>
<tr><td colspan="2">$n_U = 1$</td><td colspan="2">$n_I = 1$</td><td>27 i</td></tr>
<tr><td colspan="4">Equations referring to an ideal gas with constant C_V</td><td></td></tr>
<tr><td>For $S = \text{const}$</td><td colspan="3">$PV^k = \text{const}$ (symm.)</td><td>28 i</td></tr>
<tr><td>For $S = \text{const}$</td><td colspan="2">$TV^{k-1} = \text{const}$</td><td>$T/P^{\frac{k-1}{k}} = \text{const}$</td><td>29 i</td></tr>
<tr><td>For $n = \text{const}$</td><td colspan="3">$n = (C_n - C_P)/(C_n - C_V)$ (symm.)</td><td>30 i</td></tr>
</table>

Tables 5 and 6 show illustrative transformations. Tables 4 and 5 show the basic notation for the equations, which is intended to bring out the essence of the transformation. All the equations which transform into each other have the same number but different code numbers, corresponding to the codes used to obtain them. The original equation (which could be any one of the group) is denoted by code 0, and an equation obtained by means of two or more codes is denoted by two or more code numbers. In Table 6, which deals only with code 1, the code numbers are not shown, since all the equations are given in pairs by codes 0 and 1; if both codes lead to the same equation, the latter is symmetric ("symm.").

The number of examples could be greatly increased, since the number of equations, especially differential equations, which can be treated is huge.* Many of these equations have been used for a long time,

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*It is easy to show that the number of first-order partial derivatives which can be formed from the eight state functions listed in the text is $8 \cdot 7 \cdot 6 = 336$; the number of second-order partial derivatives with respect to a single variable is also 336; and the number of second-order partial derivatives with respect to two variables is $336 \cdot 0.5 = 168$. The total of 840 partial derivatives leads to a huge number of possible differential equations relating first- and second-order partial derivatives.

but most have not been used at all. This transformation method is proposed in order to abbreviate and simplify the derivation of equations, but we must again caution the reader that this transformation is only of a formal nature. For example, the thermal efficiency is transformed into the mechanical energy efficiency by code 4, but it would be a mistake to conclude that the two efficiencies play equivalent roles in evaluating thermodynamic cycles [7].

Transformation of the equations of thermodynamics offers a shorter path for their formal derivation from the basic equations; because of the particular structure of these basic equations, this transformation procedure is peculiar to thermodynamics.

NOTATION

C	is the heat capacity, J/deg;
F	is the free energy, J;
I	is the enthalpy, J;
K	is the ratio of specific heats;
L	is the work, J;
L'	is the available work, J;
n	is the polytropy index;
P	is the pressure, N/m^2;
Q	is the heat, J;
Q'	is the free heat, J;
R	is the universal gas constant, J/deg;
S	is the entropy, J/deg;
T	is the temperature, °K;
U	is the internal energy, J;
V	is the volume, m^3;
Φ	is the thermodynamic potential (or free enthalpy), J. Additive quantities can be attributed to the entire system (in which case they have the dimensionality indicated above), to 1 mole, or to 1 kg of the working medium. In the latter case (except for R), they are usually represented by lower case letters in the literature.

LITERATURE CITED

1. N. I. Belokon', Thermodynamics [in Russian], GÉI (1954).
2. M. P. Vukalovich and I. I. Novikov, Engineering Thermodynamics [in Russian], GÉI (1958).
3. V. V. Sushkov, Engineering Thermodynamics [in Russian], GÉI (1960).
4. A. S. Yastrzhembskii, Engineering Thermodynamics [in Russian], GÉI (1953).
5. D. P. Kolodnyi, "Available work in a thermodynamic process," in: Scientific-Research Works of the Tashkent Textile Institute [in Russian], No. 3, Tashkent (1956).
6. D. P. Kolodnyi, "Polytropic process of an ideal gas with a variable specific heat at constant volume," in: Scientific-Research Works of the Tashkent Textile Institute [in Russian], No. 1, Tashkent (1953).
7. D. P. Kolodnyi, Izv. Vuzov, Énergetika, 9 (1959).