



First order derivatives of thermodynamic functions under assumption of no chemical changes revisited



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ABSTRACT

In the field of experimental chemistry, it is extremely useful and necessary to have fast access to equations that link the physical and chemical parameters to the state. In this regard, starting with Bridgman's equations, an online application had been projected and implemented in order to generate all equations of first order derivatives of thermodynamic parameters for a closed system. MathJax open source and PHP language have been used for implementation. So a framework was conceived and implemented to automatically generate the first order derivatives of the thermodynamic parameters for closed system.

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1. Introduction

The principles of thermodynamics as they are stated today combine classical thermodynamics whose formulation is based on experimental observation of macroscopic quantities measured in laboratory thermodynamic systems. To mark the history of classical thermodynamics, we have to go back to 1960, when Otto von Guericke created the first vacuum pump [1]. Thermodynamics has evolved as a science of gaseous states by establishing the (ideal) gas laws till apparition in 1761 of 'heat capacity' and 'latent heat' concepts [2]. At this point in time thermodynamics became the science of states and transformation of matter in any state of aggregation. More than 50 years later, Sadi Carnot published his reflections on the combustion engine [3]. Carnot's idealization (Carnot cycle) marked the apparition of a new approach: statistical thermodynamics. Successively, Clausius [4], Maxwell [5], Boltzmann [6], and Planck [7] defined the elements of statistical thermodynamics. Through a series of papers published between 1873 and 1876, Gibbs completes thermodynamics by adding its appropriate mathematical apparatus [8]. In 1914, Bridgman [9] showed that all relations between variations of thermodynamic quantities can be expressed as functions of three parameters: C_p – heat capacity (at constant

pressure), α_V – coefficient of thermal expansion, and β_T – isothermal compressibility.

Based on the relations given by Bridgman, a program able to generate the variation equations between all fundamental thermodynamic quantities has been implemented. Our aim was to have all equations in the same web-page without needing any program or any 'add-on' in this sense.

2. Materials and methods

2.1. Thermodynamic parameters

The total differential of a function f of several variables is the sum of all partial differentials [10]. In the absence of chemical changes, all state thermodynamic parameters are total differentials and depend on two variables (Table 1).

Identifying the heat from reversible process $dQ_{rev} = T \cdot dS$ and the mechanical work derived from quasi-static processes $dW_{cvs} = -p \cdot dV$, also heat (dQ) and work (dW) thermodynamic quantities became total differentials. The condensed collection of the Bridgman's thermodynamic equations [9] was implemented in our web-page using a series of modification schemas to translate these equations in their first order partial derivatives [11] (Table 2).

For example, using isothermal compressibility (β_T) and isobaric dilatation (α_V) the following expressions could be identified: $VpT = -V \cdot \beta_T$, $VTp = V \cdot \alpha_V$, and rest of the combinations containing V (volume), p (pressure), and T (temperature) letters could result

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Table 1
Differentials of thermodynamic parameters.

| | |
|--|-------------------------------------|
| $dE = T \cdot dS - p \cdot dV + \sum_i \mu_i \cdot dn_i$ | In the presence of chemical changes |
| $dn_i = 0$ for each i | Provided that no chemical changes |
| $dE = T \cdot dS - p \cdot dV$ | In the presence of chemical changes |

E = internal energy; S = entropy; V = volume; n = number of particles; p = pressure.

from these two expressions. If the function f is total energy (E), then using specific heat at constant volume ($C_V = ETV$) and internal pressure ($\pi_T = EVT$) and starting from equation numbered as 1 in Table 2 to equation numbered as 6, all remaining partial derivatives of the energy when any two of the temperatures (T), pressures (p) and volumes (V) are kept constant could be identified.

2.2. System implementation

The MathJax open source [12], JavaScript platform for displaying of mathematics, has been used to implement the Bridgman's differentials in a web-page. A program has been developed and implemented using PHP language [13] to simplify and automate displaying of the equations.

The web-page was structured in two main parts: introduction and main part of the page.

- Introductory elements have been included in the first part of the page to allow utilization of equations without navigation on specialized pages. This part of the web-page provides the measures and relations used in thermodynamics.
- The main part of the page contains the relationships between first order derivatives of thermodynamic quantities. As implementation it was chosen to create an 'array' with equations, in a form similar to that of Bridgman. The first two fields of the array contain the variable and constant quantities from the expression of differential (these two quantities are interchangeable [9]) while the third field of the array stored the compacted form (removing signs from the definition of differentials) of the differentials (Implementation 1).

Implementation 1. First part from the definition of the array containing half-relationships between thermodynamic quantities.

Step 0. Instantiate 'Bridgman' as an array (of arrays, see below)

```
bridgman=array();
```

Step 1. Add to 'Bridgman' array the list of half partial derivatives (see [9])

```
bridgman[]=array("T","p","1");
bridgman[]=array("V","p","-VTp");
bridgman[]=array("S","p","-HTp/T");
.../(45 equations in total)
```

To speed up the process of displaying the equations, interchanged equations can also be stored in this array (Implementation 2).

Implementation 2. First part from second half of the definition of the array containing half-relationships between thermodynamic quantities.

Step 2. Add to 'Bridgman' array the list of half partial derivatives with the reversed order of the variable and the constant ($\partial x|_{y=ct} = -\partial y|_{x=ct}$, see [9])

```
bridgman[]=array("p","T","-1");
bridgman[]=array("p","V","-VTp");
bridgman[]=array("p","S","-HTp/T");
.../(again 45 equations in total)
```

From this point, it is only a matter of manipulation of the equations, to provide in full the desired equations. Three algorithms have been implemented to accomplish this task (Algorithms 1–3).

Algorithm 1. Function used to generate a partial derivative.

Returns the code sequence (text-based) needed for MathJax to display a partial derivatives; take as input an array and returns a string containing the elements of the array according to the MathJax syntax.

```
function pd(x){
return("\left. \frac{\partial "+x[0]+"}{\partial "+x[1]+"} \right|_{ "+x[2]+"=ct.}");
}
```

An instance of the Algorithm 1 will produce first (left) part of an equation. For instance $pd(array('E','G','A'))$ returns the text corresponding to the image of the derivative of the E by G when A is constant:

```
"\left. \frac{\partial E}{\partial G} \right|_{A=ct.}"
text image
```

Algorithm 2. This algorithm implements the first function assembling the right part of the differential equation.

The function takes as input one string (function $lt(x)$)
Step 1. Replace "*" character (sign) with "\cdot" string (TeX encoding for multiplication)

```
y=str_replace(""," \cdot",x);
```

Step 2. Split the fractions into nominator and denominator

```
(z=explode("/",y))
```

Step 3. If the split leads to only one element, then it is the nominator (and it should be returned as is) else go to the next step

```
(if(count(z)<2)return(z[0]))
```

Step 4.

```
4.1. Find first position of the "+" sign (i1=strpos(z[0],"+"))
```

```
4.2. Find first position of the "-" sign (i2=strpos(z[0],"-"))
```

```
4.3. Decide whatever comes first
```

```
i3===FALSE;if(i2===FALSE)i3=i1;if(i1===FALSE)i3=i2;
if(!((i1===FALSE)&&! (i2===FALSE)))if(i2>i1)i3=i2;else
i3=i1;
```

Table 2
Gradients after pressure (p), volume (V) and temperature (T) of an unknown function (f): the case of total energy ($f=E$).

| Variable | $\frac{\partial f}{\partial x} \Big _{z=ct} = \frac{\partial f}{\partial x} \Big _{y=ct} + \frac{\partial f}{\partial y} \Big _{x=ct} \cdot \frac{\partial y}{\partial x} \Big _{z=ct}$ | $\frac{\partial f}{\partial z} \Big _{x=ct} = \frac{\partial f}{\partial y} \Big _{x=ct} \cdot \frac{\partial y}{\partial z} \Big _{x=ct}$ | Order* |
|----------|---|--|---------|
| z | $fxz = fxy + fyx \cdot yxz$ | $fzx = fyx \cdot yzx$ | $f = E$ |
| p | $fpV = fpT + fTp \cdot TpV$ | $fVp = fTp \cdot TVp$ | 6 |
| p | $fpT = fpV + fVp \cdot VpT$ | $fTp = fVp \cdot VTP$ | 5 |
| T | $fTV = fTp + fTp \cdot pTV$ | $fVT = fTp \cdot pVT$ | 2 |
| T | $fTp = fTV + fVT \cdot VTP$ | $fTp = fVT \cdot VpT$ | 4 |
| V | $fVT = fVp + fVp \cdot pVT$ | $fTV = fVp \cdot pTV$ | 1 |
| V | $fVp = fVT + fTV \cdot TVp$ | $fVp = fTV \cdot TpV$ | 3 |

*Order identifies the possible order applied to identify the terms starting from the known toward unknowns using the relations between partial derivatives. Note that the derivatives in the top of the second and third columns are true only for functions that fulfil the following conditions: $f=f(x,y)$ and $y=y(x,z)$.

4.4. If no sign found, then sign part (z_0 variable) is empty else extract from $z[0]$ its sign part

```
if (i3===FALSE) z0=""; else{
  z0=substr(z[0], 0, i3)+z[0][i3]; z[0]=substr(z[0], i3+1);
}
```

Step 5. Repeat the steps 4.1. to 4.3. for denominator ($z[1]$) in place of nominator ($z[0]$)

5.4. Take in $z[1]$ the sign and its following part if any

```
if (i3===FALSE) z1=""; else{
  z1=z[1][i3]+substr(z[1], i3+1); z[1]=substr(z[1], 0, i3);
}
```

Step 6. Construct according to the MathJax (Math TeX) syntax the expression and return it as a string

```
(return(z0+"\frac{"+z[0]+"}{"+z[1]+"}"+z1;)
```

Algorithm 3. This algorithm implements the second function assembling the right part of the differential equation.

The function takes as input one string previous processed by [Algorithm 2](#) (**function** `ltx2(x)`)

Do to an indefinite loop the following steps (**for** $i=0; i++$):

Step 1. If end of the string was reached then exit (**if** $i>=strlen(x)$) **break**;

Step 2. If $x[i]$ is not one of the characters "+-." then continue the loop

```
if (!(strpos("+-.", x[i])===FALSE) continue;
```

Step 3. If $x[i]$ is a slash then continue (**if** $x[i]=="/"$) **continue**;

Step 4. If in the string are less than 3 characters remained from the position i to the end of the string then continue (**if** $i>strlen(x)-3$) **continue**;

Step 5. If the found sign is preceded by other sign then continue

```
if (i>0) if (strpos("+-.", x[i-1])===FALSE) continue;
```

Step 6. If the found sign is followed by other sign(s) then continue

```
if (!(strpos("+-.", x[i+1])===FALSE) continue;
if (!(strpos("+-.", x[i+2])===FALSE) continue;
```

Step 7. Split the string (x) in parts at current position (i) and reassemble it using `pd` function for writing the partial derivative (three consecutive letters are here)

```
x1=substr(x, 0, i); x2=substr(x, i, 3); x3=substr(x, i+3);
y=x1.pd(x2); i=strlen(y); x=y.x3;
```

Step 8. Return the new string (**return** x)

3. Implementation algorithm for thermodynamic parameters

The goal of our application was to translate the first order derivatives associated to thermodynamic functions to provide users with a reliable system able to link the physical and chemical parameters with the phase.

The implemented algorithm able to generate two hundred and forty equations between thermodynamic quantities is illustrated in [Algorithm 4](#).

Algorithm 4. The devised main program implemented for thermodynamic quantities.

Step 1. Instantiate 4 empty arrays (**b1=b2=b3=bz=array()**)

Step 2. For each entry in `bridgman` table add one entry in each array - first, second and third element and use first two ones as indexes to add the third in the last (`bz`) array. Please note that `bz` array keeps the association between elements.

```
for (i=0; i<count(bridgman); i++){
  b1[i]=bridgman[i][0]; b2[i]=bridgman[i][1]; b3[i]=bridgman[i][2];
  bz[b1[i]][b2[i]]=b3[i];
}
```

Step 3. Sort (ascending using the alphabet) simultaneously the `b1`, `b2` and `b3` arrays by the values of the second (`b2`) array

```
(array_multisort(b2, SORT_ASC, b1, b3))
```

Step 4. Instantiate one array with the symbols of thermodynamic functions and counts them

```
termo=array("A", "E", "G", "H", "Q", "S", "T", "V", "p", "w");
n=count(termo);
```

Step 5. Set a counter to 0 ($u=0$)

Step 6. For each (thermodynamic) function (**for** $i=0; i<n; i++$)

```
For each different function (for (j=i; j<n; j++)) if (i==j) continue;
For each different function
(for (k=i; k<n; k++) if (i==k||j==k) continue)
Step 6.1. Display a html break line (echo("<hr>"))
Step 6.2. Display the left part of an equation
echo("\[" +pd(termo[j]+termo[k]+termo[i])+" = ")
Step 6.3. Display the right part of the equation
if (bz[termo[j]][termo[i]]=="0") echo("0 \]");
elseif (bz[termo[k]][termo[i]]=="0") echo("\infty \]");
else{
  echo("\frac{" .ltx2(ltx(bz[termo[j]][termo[i]])) .
  echo("}" .ltx2(ltx(bz[termo[k]][termo[i]])) ."} \]");
}
Step 6.4. Increment the counter
```

4. Application interface

4.1. Interface

The results of our implementation are freely available at the following URL: <http://l.academicdirect.org/Chemistry/ChemPhys/>. The inputs of the application are state parameters, process differentials, thermodynamic equations and gradients ([Fig. 1](#)).

The first order partial derivatives, counting a number of two hundred and forty equations, are displayed as the output ([Fig. 2](#)).

4.2. Open tool

The web portal is a static interface on which the information is already displayed and can be visualized. The program is free and its speed is directly dependent on data transfer rate, processing speed of the client and processing speed of the server. Under a data transfer rate of 100 Mb/s using an Intel Core Duo 2.33 GHz and 1 GB of RAM, all equations are displayed in less than 2 min (1 min and 50 s).

The implemented system is applicable only on closed systems (see [Table 2](#)). However, the equations presented in [Table 1](#) express the equations presented in [Table 2](#) for varying the amount of substance. Linking together the equations presented in [Table 1](#) with those presented in [Table 2](#), the implementation for irreversible thermodynamics is possible. The implementation of the general case in our system is our further plans of developing this open access tool.

The transformation of an interactive interrogation is also conducted in our lab in order to allow selecting the function, the variable and the constant before generation of the thermodynamic equation of first order derivatives.

The tool has complex computational need. The application runs on a web server (<http://l.academicdirect.org/Chemistry/ChemPhys/>). The process of loading the thermodynamic equation of first order derivatives expressed as percentage is displayed in the left lower corner of the page.

4.3. Applicability

Understanding thermodynamic quantities represents fundamental information for any undergraduate student in order to form their thinking and understanding of processes. If students understand basic processes they will become good workers in their future fields. Research on the thermodynamic quantities had been conducted for the dissociation equilibrium of active biological compounds: glycerol 2-phosphoric acid [14], phosphoric acid, glucose 1-phosphoric acid and glycerol 2-phosphoric acid [15], glucose 1-phosphoric acid [16], 2-aminoethanol 1-phosphoric acid [17], glycerol 1-phosphate [18], arginine [19], etc.

Several authors used thermodynamic parameters as functions to investigate folding of biomolecules [20–22]. Nakakido et al. use thermodynamic quantities to investigate the mechanism of arginine hydrochloride on proteins [23]. Wang et al. showed that the

Thermodynamic state parameters:

- ▶ Pressure (p);
- ▶ Temperature (T);
- ▶ Volume (V);
- ▶ Entropy (S);
- ▶ Internal energy (E);
- ▶ Number of particle (N);
- ▶ Enthalpy (H);
- ▶ Helmholtz energy (A);
- ▶ Gibbs energy (G);
- ▶ Avogadro's number of particles (N_A);
- ▶ Amount of substance expressed in mols (n);
- ▶ Molar volume (V_m);
- ▶ Molar entropy (S_m);
- ▶ Molar internal energy (E_m);
- ▶ Molar enthalpy (H_m);
- ▶ Molar Helmholtz energy (A_m);
- ▶ Molar Gibbs energy (G_m);
- ▶ Number of energy components (J)

Process differentials:

- ▶ Heat (dQ);
- ▶ Work (dw);
- ▶ Reversible heat (dQ_r);
- ▶ Quasistatic work (dw_c);

Equations:

- ▶ $dE=dQ+dw$;
- ▶ $dE=dQ+dw+\sum_i \mu_{N,i} dN_i$;
- ▶ $dE=dQ+dw+\sum_i \mu_i dn_i$;
- ▶ $E=Q+w+\sum_i \int \mu_i dn_i$;
- ▶ $dE=dQ-pdV+\sum_i \mu_i dn_i$;
- ▶ $dH=dQ+Vdp+\sum_i \mu_i dn_i$;
- ▶ $dA=dQ-pdV-Tds-SdT+\sum_i \mu_i dn_i$;
- ▶ $dG=dQ+Vdp-Tds-SdT+\sum_i \mu_i dn_i$;
- ▶ $dE=Tds-pdV+\sum_i \mu_i dn_i$;
- ▶ $dH=Tds+Vdp+\sum_i \mu_i dn_i$;
- ▶ $dA=-pdV-SdT+\sum_i \mu_i dn_i$;
- ▶ $dG=Vdp-SdT+\sum_i \mu_i dn_i$;

Gradients:

- ▶ Isothermal compressibility (β_T);
- ▶ Volumetric coefficient of thermal expansion (α_V);
- ▶ Heat capacity at constant pressure (C_p);
- ▶ Joule-Thomson isothermal coefficient (μ_T);
- ▶ Heat capacity at constant volume (C_V);
- ▶ Internal pressure (π_T);

Fig. 1. Web portal architecture and design: input.

entropy of a system accurately predicts the thermodynamics of protein folding [24].

Thermodynamic descriptions have been used besides kinetic descriptors to analyze the collective behavior of RNA replicators [25]. Furthermore, databases of thermodynamic properties for several biochemical reactions had been created since these parameters are needed in analysis of biochemical systems: reactions of glycolysis and the tricarboxylic acid

cycle [26], reactions catalyzed by PABA (4-aminobenzoate) syntheses [27], protein–nucleic acid interactions (ProNIT [28]), protein–protein interactions (PINT [29]), proteins and mutants (ProTherm [30,31]), protein–ligand interactions [32], etc.

Material science is another field of research where thermodynamic parameters found their usefulness: nanoscience and nanoparticles [33–35], two-band superconductivity [36], steel

$$\frac{\partial E}{\partial G} \Big|_{A=ct.} = \frac{-p \cdot \frac{\partial H}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial p} \Big|_{T=ct.} - p \cdot T \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.}}{S \cdot V + S \cdot p \cdot \frac{\partial V}{\partial p} \Big|_{T=ct.} + p \cdot V \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.}}$$

$$\frac{\partial E}{\partial H} \Big|_{A=ct.} = \frac{-p \cdot \frac{\partial H}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial p} \Big|_{T=ct.} - p \cdot T \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.}}{S \cdot V + p \cdot V \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} - S \cdot T \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} - p \cdot T \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} - p \cdot \frac{\partial V}{\partial p} \Big|_{T=ct.}}$$

$$\frac{\partial E}{\partial Q} \Big|_{A=ct.} = \frac{-p \cdot \frac{\partial H}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial p} \Big|_{T=ct.} - p \cdot T \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.}}{-p \cdot \frac{\partial H}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial p} \Big|_{T=ct.} - p \cdot T \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} - S \cdot T \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.}}$$

$$\frac{\partial E}{\partial S} \Big|_{A=ct.} = \frac{-p \cdot \frac{\partial H}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial p} \Big|_{T=ct.} - p \cdot T \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.}}{-\frac{p \cdot \frac{\partial H}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial p} \Big|_{T=ct.}}{T} - \frac{\partial V}{\partial T} \Big|_{p=ct.} \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.} - S \cdot \frac{\partial V}{\partial T} \Big|_{p=ct.}}$$

Fig. 2. Web portal architecture and design: output snapshot (first partial derivatives).

refining [37], pulp suspensions in paper-making process [38], alloys [39–41], and so on. Thermodynamic parameters also found their usefulness in computer science and mathematics [42,43], astronomy and astrophysics [44], physics and chemistry [45–48], etc.

Our open free available application is just the first step toward thermodynamic parameters. Our further plans include simplification of the equations as well as generating of the second order derivatives. Furthermore, translation of our implementation also with regard to irreversible thermodynamics is under implementation in our lab as well as improvement of its speed.

5. Conclusion and future improvements

The fundamental thermodynamic quantities based on the relations given by Bridgman's had been successfully implemented as a web-page independently from other programs. The users have access to a total number of two hundred and forty first order partial derivatives relating the fundamental thermodynamic quantities. The program is free and its speed is directly dependent on data transfer rate, processing speed of the client and processing speed of the server. Some aspects are under consideration regarding the implemented algorithm: to increase its speed; to obtain the enthalpies of formation and standard Gibbs energies of formation included by the algorithm; to transform the program into an interactive program which allow selection of the function, variables and constants before generation of first order derivatives of thermodynamic functions.

The developed application is useful for training students in using thermodynamic quantities as well as for researchers in the field of applied chemistry providing in full the first order derivatives of thermodynamic parameters.

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