First Order Derivatives of Thermodynamic Functions under Assumption of no Chemical Changes

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DIFFERENTIALS

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

Table 1. Differentials of thermodynamic parameters

$dE = T \cdot dS - p \cdot dV + \Sigma_i \cdot \mu_i \cdot dn_i$	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 absence of chemical changes
E = internal energy; S = entropy; V = volume; n = number of particles	

[1] M. Hazewinkel, Encyclopaedia of Mathematics: An Updated and Annotated Translation of the Soviet "Mathematical Encyclopaedia." Dordrecht, Netherlands: Reidel, 1988, p. 228.

OBJECTIVES

- Identifying the heat from reversible process $dQ_{rev} = T \cdot dS$ and mechanical work in the form of that from quasi-static processes $dw_{cvs} = -p \cdot dV$, these two thermodynamic quantities (dQ and dw) became total differentials. The condensed collection of the Bridgman's thermodynamic equations [2] was used as starting point in this study. A series of codification schemas were developed and implemented in order to obtain all first order partial derivatives [3] (Table 2).

[2] P.W. Bridgman, A complete collection of thermodynamic formulas, Phys. Rev. 3, 1914, 273-281.

[3] L. Jäntschi, General Chemistry Course, AcademicDirect Publishing House, 2013.

BRIDGMAN'S THERMODYNAMIC EQUATIONS

Table 2. Gradients after pressure (*p*), volume (*V*) and temperature (*T*) of an unknown function (*f*)

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

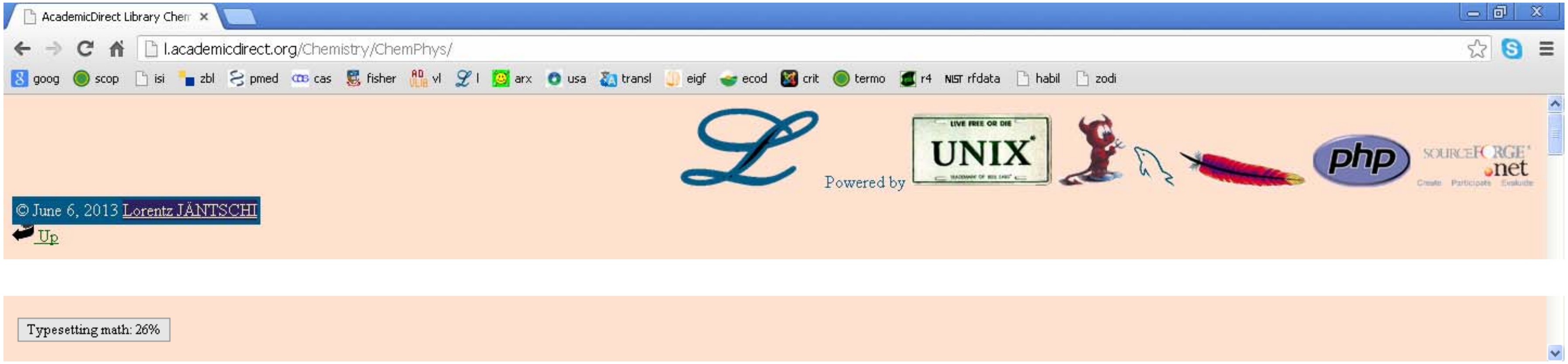
RESULTS

- Inputs: state parameters, process differentials, thermodynamic equations and gradients.

- Output: first order partial derivatives, counting a number of two-hundred and forty equations

- http://l.academicdirect.org/Chemistry/ChemPhys/

RESULTS



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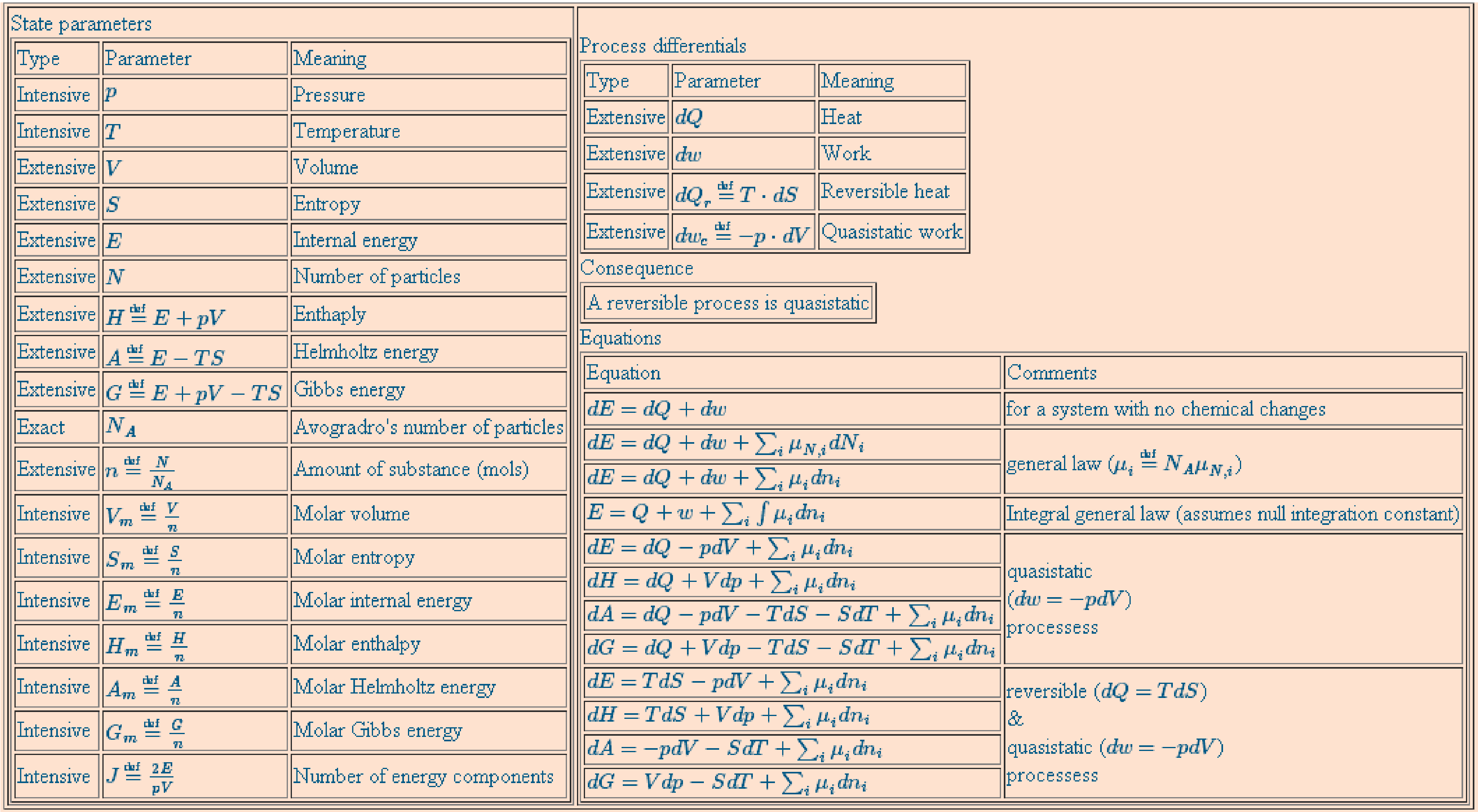
Equations: 240

RESULTS



State parameters

Type	Parameter	Meaning
Intensive	p	Pressure
Intensive	T	Temperature
Extensive	V	Volume
Extensive	S	Entropy
Extensive	E	Internal energy
Extensive	N	Number of particles
Extensive	$H \overset{\text{def}}{=} E + pV$	Enthaply
Extensive	$A \overset{\text{def}}{=} E - TS$	Helmholtz energy
Extensive	$G \overset{\text{def}}{=} E + pV - TS$	Gibbs energy
Exact	N_A	Avogradro's number of particles
Extensive	$n \overset{\text{def}}{=} \frac{N}{N_A}$	Amount of substance (mols)
Intensive	$V_m \overset{\text{def}}{=} \frac{V}{n}$	Molar volume
Intensive	$S_m \overset{\text{def}}{=} \frac{S}{n}$	Molar entropy
Intensive	$E_m \overset{\text{def}}{=} \frac{E}{n}$	Molar internal energy
Intensive	$H_m \overset{\text{def}}{=} \frac{H}{n}$	Molar enthalpy
Intensive	$A_m \overset{\text{def}}{=} \frac{A}{n}$	Molar Helmholtz energy
Intensive	$G_m \overset{\text{def}}{=} \frac{G}{n}$	Molar Gibbs energy
Intensive	$J \overset{\text{def}}{=} \frac{2E}{pV}$	Number of energy components

Process differentials

Type	Parameter	Meaning
Extensive	dQ	Heat
Extensive	dw	Work
Extensive	$dQ_r \overset{\text{def}}{=} T \cdot dS$	Reversible heat
Extensive	$dw_c \overset{\text{def}}{=} -p \cdot dV$	Quasistatic work

Consequence

A reversible process is quasistatic

Equations

Equation	Comments
$dE = dQ + dw$	for a system with no chemical changes
$dE = dQ + dw + \sum_i \mu_{N,i} dN_i$	general law ($\mu_i \overset{\text{def}}{=} N_A \mu_{N,i}$)
$dE = dQ + dw + \sum_i \mu_i dn_i$	
$E = Q + w + \sum_i \int \mu_i dn_i$	Integral general law (assumes null integration constant)
$dE = dQ - pdV + \sum_i \mu_i dn_i$	quasistatic ($dw = -pdV$) processess
$dH = dQ + Vdp + \sum_i \mu_i dn_i$	
$dA = dQ - pdV - TdS - SdT + \sum_i \mu_i dn_i$	
$dG = dQ + Vdp - TdS - SdT + \sum_i \mu_i dn_i$	
$dE = TdS - pdV + \sum_i \mu_i dn_i$	reversible ($dQ = TdS$) & quasistatic ($dw = -pdV$) processess
$dH = TdS + Vdp + \sum_i \mu_i dn_i$	
$dA = -pdV - SdT + \sum_i \mu_i dn_i$	
$dG = Vdp - SdT + \sum_i \mu_i dn_i$	

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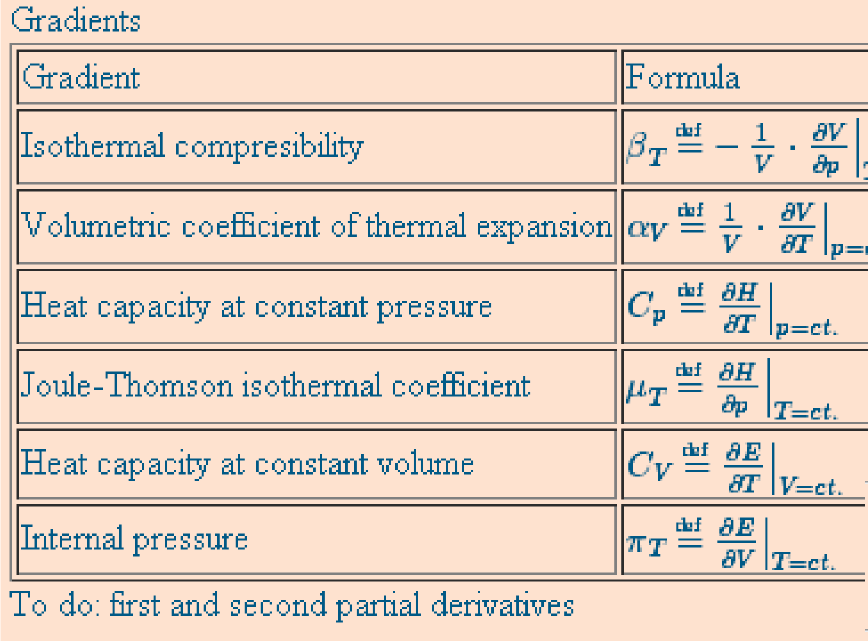
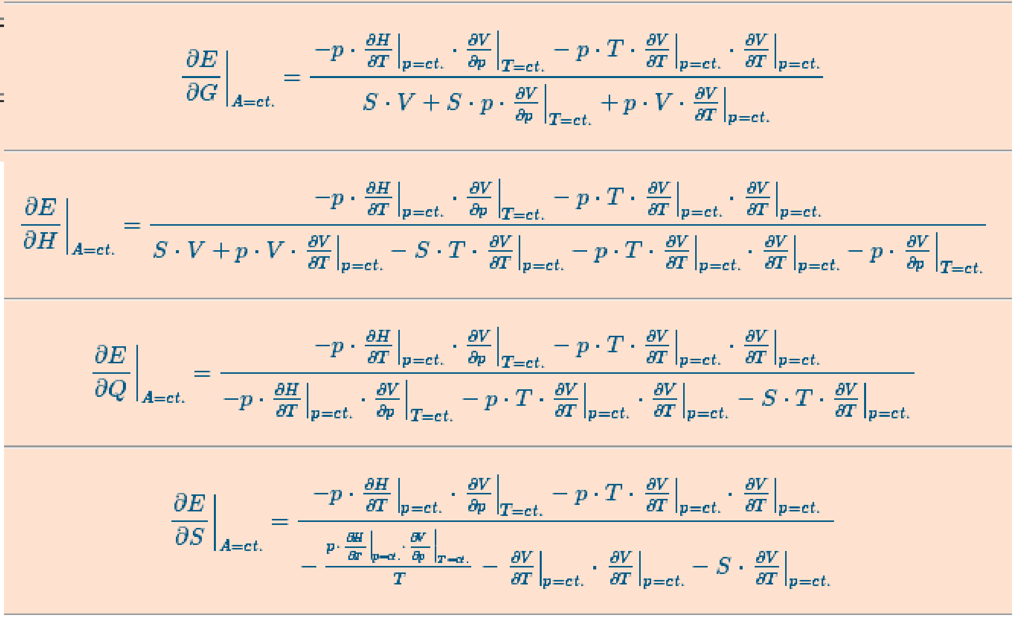
RESULTS



Gradients

Gradient	Formula
Isothermal compresibility	$\beta_T \overset{\text{def}}{=} -\frac{1}{V} \cdot \frac{\partial V}{\partial p}\Big\|_{T=ct.}$
Volumetric coefficient of thermal expansion	$\alpha_V \overset{\text{def}}{=} \frac{1}{V} \cdot \frac{\partial V}{\partial T}\Big\|_{p=ct.}$
Heat capacity at constant pressure	$C_p \overset{\text{def}}{=} \frac{\partial H}{\partial T}\Big\|_{p=ct.}$
Joule-Thomson isothermal coefficient	$\mu_T \overset{\text{def}}{=} \frac{\partial H}{\partial p}\Big\|_{T=ct.}$
Heat capacity at constant volume	$C_V \overset{\text{def}}{=} \frac{\partial E}{\partial T}\Big\|_{V=ct.}$
Internal pressure	$\pi_T \overset{\text{def}}{=} \frac{\partial E}{\partial V}\Big\|_{T=ct.}$

To do: first and second partial derivatives



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

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

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

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

FUTHER WORK

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

Thank you for your attention!

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