Comments on Mathematical Techniques for Chemistry 163B

Our text (*E&R$_{4th}$: ME2, pp 17-28; ME3, pp.63-68*)*[Appendix B.2.1-B.2.3]$_{3rd}$* contains detailed information on the aspects of differential and integral calculus relevant to our study of thermodynamics. We will review these techniques in the context of class derivations and homework problems, rather than just as abstract mathematical exercises. However it is useful to categorize them below. In your first discussion section the TAs will also comment on the techniques.

1. Partial derivatives:
   a. Know physical meaning of partial derivatives
   b. Know how to evaluate them mechanically
   c. Know chain rule

2. You should have "at hand" the derivatives and integrals of functions like:
   x^n , x^{-n}, ln (x), e^{ax}, sin ax, cos ax [*"at hand" ≡ in your accessible neurons*]

3. Differential expressions (E&R$_{4th}$ 2.8; pp 39-41, 63)*[pp 28, 45-49]$_{3rd}$*

   a. $đ\psi$ is **inexact** differential if $\int_{initial}^{final} đ\psi$ depends on the path from initial $\rightarrow$ final
   This implies there is no "underlying" well behaved, function ψ that changes like $đ\psi$

   b. $d\psi$ is **exact** differential if $\int_{initial}^{final} d\psi$ does not depend on the path from initial $\rightarrow$ final

4. Implications that arise from $d\psi$ being an **exact** differential:

   a. There is a well behaved function ψ whose change is described by $d\psi$
   b. $d\psi\,(V,T) = \left(\frac{\partial \psi}{\partial V}\right)_T dV + \left(\frac{\partial \psi}{\partial T}\right)_V dT$
   or in more general notation
   $d\psi\,(x, y, z) = \left(\frac{\partial \psi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} dz$
   c. $\oint d\psi = 0$ (integral for any cyclic path; i.e. the initial and final states are identical)
   d. $\int_{initial}^{final} d\psi = \psi(final) - \psi(initial)$

5. Suppose we know that a differential is of the form and is an **exact** differential:
$d\,\psi\,(x, y) = M\,dx + N\,dy$ (where M and N are some functions or variables)

example (1st and 2nd Laws of Thermodynamics give dG as exact differential)
$d\,G\,(T,P) = -S\,dT + V\,dP$ (G and S are free energy and entropy)

THEN WE HAVE THE FOLLOWING USEFUL RELATIONSHIPS:

a.
$$\left(\frac{\partial \psi}{\partial x}\right)_y = M \quad \text{and} \quad \left(\frac{\partial \psi}{\partial y}\right)_x = N$$
or
$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

b. and since, for well behaved functions, “mixed” second partial derivatives are equal (i.e. the order of differentiation does not matter)

$$\left(\frac{\partial^2 \psi}{\partial y \partial x}\right)_{x,y} = \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 \psi}{\partial x \partial y}\right)_{y,x}$$
or
$$\left(\frac{\partial (-S)}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad \text{which is same as} \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

this is an example of the Maxwell-Euler relationships that we will use often

6. **Using differentials to get derivatives** by “dividing through by dx”. This is justified by taking limits of finite δ’s as $\delta \to 0$.

$$dU = đq - PdV$$
divide by dT with P const

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{đq}{dT}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P$$
$$\left(\frac{\partial U}{\partial T}\right)_P = C_P - P\left(\frac{\partial V}{\partial T}\right)_P$$
since $C_P \equiv \left(\frac{đq}{dT}\right)_P$

or

$$dG = -SdT + VdP$$
divide by dV with P const

$$\left(\frac{\partial G}{\partial V}\right)_P = -S\left(\frac{\partial T}{\partial V}\right)_P + V\left(\frac{\partial P}{\partial V}\right)_P$$
$$\left(\frac{\partial G}{\partial V}\right)_P = -S\left(\frac{\partial T}{\partial V}\right)_P$$
why does 2nd term drop out ?