

CHEM 3410: Physical Chemistry I — Fall 2009

**Homework 1 — Model Solutions**

1. (a) This derivative involves the sum of some polynomials and a trig function:

$$\frac{dy}{dx} = 20x^3 - 6x + \cos x$$

- (b) This function is a little more challenging and involves using the chain rule for both parts and the product rule for the second term. The first term:

$$\frac{d}{dx} (e^{4x^2}) = e^{4x^2} \times 8x$$

In words, I took the derivative of  $e$  to the anything which is  $e$  to the anything and multiplied by the derivative of “anything” (which in the case is  $4x^2$ ) giving  $8x$ .

For the second term you need to use the product rule: “first function times the derivative of the second plus the second times the derivative of the first”:

$$\frac{d}{dx} (5x^2 \cos(6x)) = 5x^2(-6 \sin(6x)) + \cos(6x)10x = -30x^2 \sin(6x) + 10x \cos(6x)$$

Giving a final answer of:

$$8xe^{4x^2} - 30x^2 \sin(6x) + 10x \cos(6x)$$

2. (a) Remembering to treat  $w$ ,  $y$  and  $z$  as constants in the partial derivative, we get:

$$\left(\frac{\partial F}{\partial x}\right)_{w,y,z} = 3y^2 - \frac{y^2 z^3}{w}$$

- (b) Now taking the derivative with respect to  $w$  holding the other variables constant:

$$\left(\frac{\partial F}{\partial w}\right)_{x,y,z} = \frac{3w^2 z^3}{32y} + \frac{xy^2 z^3}{w^2}$$

- (c) Using our answer from part (a) and now taking the derivative with respect to  $z$  holding  $w$ ,  $x$  and  $y$  constant:

$$\left[\frac{\partial}{\partial z} \left(\frac{\partial F}{\partial x}\right)_{w,y,z}\right]_{w,x,y} = \left[\frac{\partial}{\partial z} \left(3y^2 - \frac{y^2 z^3}{w}\right)\right]_{w,x,y} = -\frac{3y^2 z^2}{w}$$

- (d) First we need to take the derivative of the function  $F$  with respect to  $z$  and then with respect to  $x$ . (The reverse order of derivatives from the previous part.)

$$\left(\frac{\partial F}{\partial z}\right)_{w,x,y} = \frac{3w^3 z^2}{32y} - \frac{3xy^2 z^2}{w}$$

Now with respect to  $x$ :

$$\left[\frac{\partial}{\partial x} \left(\frac{\partial F}{\partial z}\right)_{w,x,y}\right]_{w,y,z} = \left[\frac{\partial}{\partial x} \left(\frac{3w^3 z^2}{32y} - \frac{3xy^2 z^2}{w}\right)\right]_{w,y,z} = -\frac{3y^2 z^2}{w}$$

The solutions for (c) and (d) are equivalent, meaning the solution is independent of the order in which the partial derivatives are performed. This is another property of an exact differential that we will take advantage of shortly.

3. For an ideal gas we have:

$$P = \frac{nRT}{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

Using the relationship given in the problem and substituting in for  $\left(\frac{\partial P}{\partial T}\right)_V$  we get:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{nR}{V}\right) - P$$

But  $P = \frac{nRT}{V}$ , leaving us with:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - \frac{nRT}{V} = 0$$

So under isothermal conditions, the internal energy of an ideal gas does not vary with volume. This is a very useful tidbit we will also use frequently.