Chemistry 20262 — Spring 2018
Professor J. Daniel Gezelter — Due Fri. 2/9/2018

Problem Set 3
(Derivatives, Chain rules, Differentials, Taylor Series)

1. Use the chain rule to evaluate $\frac{du}{dt}$ if $u(x,y) = ye^{-x^2}$ where $x(t) = t^2$ and $y(t) = t^4$.

2. Use the chain rule to evaluate $\frac{du}{dt}$ if $u(x,y,z) = x^2 + ze^y$ where $x(t) = t$, $y(t) = t^2$ and $z(t) = t^3$.

3. If $u = u(x,y)$ and $x = r\cos\theta$ and $y = r\sin\theta$, then show that

$$\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial y}\right)^2 = \left(\frac{\partial u}{\partial r}\right)^2 + \frac{1}{r^2}\left(\frac{\partial u}{\partial \theta}\right)^2$$

   Use some caution here. This problem is asking about the *squares* of the first derivatives and not the second derivatives. This is a crucial distinction. Note that in general:

$$\left(\frac{\partial u}{\partial x}\right)^2 \neq \left(\frac{\partial^2 u}{\partial x^2}\right)$$

4. Determine the total differential of

   a) $f(x,y) = x^2 \sin y$

   b) $g(u,v) = (u^3 + v)e^v$

5. Determine dP if we have one mole of a gas that obeys the van der Waals equation of state:

$$P(V,T) = \frac{RT}{V-b} - \frac{a}{V^2}$$

6. Given that $df = 2x\sin y\,dx + (x^2\cos y + e^y)dy$ is an exact differential, determine $f(x,y)$ to within an additive constant.

7. Use the Taylor expansion of e^x about $x = 0$ to determine the value of e to four decimal places.

8. The Morse oscillator model provides a reasonably realistic description of the vibrations of a diatomic molecule. The Morse potential energy function,

$$V(r) = D_e\left(1 - e^{-\alpha(r-r_0)}\right)^2$$

   where r_0 is the equilibrium bond length, D_e is the dissociation energy of the molecule and α is a constant.

(a) Plot $V(r)$ for carbon monoxide on a graph where the horizontal axis is the bond length in Angstroms (1 Å= 10^{-10} m), and the vertical axis is the potential energy in kJ / mol. You may use a value of 3.22 Å^{-1} for α, but you will need to do some research to find the other constants.

(b) Taylor expand $V(r)$ about $r = r_0$ to quadratic order.

(c) In the *harmonic* model for bonding, $V(r) = \frac{1}{2}k(r - r_0)^2$, the quantity k is called the force constant. What is the effective force constant of the Morse oscillator in terms of D_e and α? You'll need your results from part (b) to do this.

(d) Plot the Taylor expansion to quadratic order along with the Morse function. Use the effective force constant you found in part (c).