## Paragraph HW 04

## The chain rule and physical chemistry/thermodynamics Math 112, Spring 2006

Consider a function  $F: \mathbb{R}^3 \to \mathbb{R}$ , i.e., a function F(x,y,z). We say that the equation F(x,y,z)=0 determines z implicitly as a function of x and y in the neighborhood  $U\subseteq \mathbb{R}^2$  if, for all  $(x,y)\in U$ , there is exactly one z such that F(x,y,z)=0. In other words, we can (locally) "solve" for z in terms of x and y; in fact, for many F(x,y,z)=0, we can solve for each of x, y, and z in terms of the other two, and therefore think of each quantity as a function of the other two. For example, consider the Ideal Gas Law, which says that PV=nRT, or

$$F(P, V, T) = \frac{PV}{nRT} - 1 = 0,$$

where the constant n is the number of moles (amount) of gas present, the constant R is the "universal gas constant," and the pressure P, volume V, and temperature T can change. When the Ideal Gas Law holds, we can think of each of P, V, and T as a function of the other two variables.

In this homework, we look at the derivatives of implicit functions and the (sometimes strange) formulas that result.

1. Let F(x,y,z) and g(x,y) be functions such that

$$H(x,y) = F(x,y,g(x,y)) = 0$$

for all  $(x,y) \in U \subset \mathbb{R}^2$ . In other words, suppose that the equation F(x,y,z) = 0 determines z as an implicit function z = g(x,y). We may therefore define  $\left(\frac{\partial z}{\partial x}\right)_y$ , the partial derivative of z with respect to x, holding y constant, and  $\left(\frac{\partial z}{\partial y}\right)_x$ , the partial derivative of z with respect to y, holding x constant, by

$$\left(\frac{\partial z}{\partial x}\right)_{y} = \frac{\partial g}{\partial x}, \qquad \left(\frac{\partial z}{\partial y}\right)_{x} = \frac{\partial g}{\partial y}.$$

- (a) Find a function  $G: \mathbb{R}^2 \to \mathbb{R}^3$  such that  $H = F \circ G$ .
- (b) Note that H(x,y) is identically 0, which means that  $\frac{\partial H}{\partial x} = \frac{\partial H}{\partial y} = 0$ . Apply the chain rule to the composition  $F \circ G$  to find formulas for  $\left(\frac{\partial z}{\partial x}\right)_y$  and  $\left(\frac{\partial z}{\partial y}\right)_x$  in terms of  $\frac{\partial F}{\partial x}$ ,  $\frac{\partial F}{\partial y}$ , and  $\frac{\partial F}{\partial z}$ . Check your answers with F(x,y,z) = xyz 1,  $g(x,y) = \frac{1}{xy}$ .
- (c) If F(x,y,z)=0 determines y as a function of x and z, what are the analogous formulas for  $\left(\frac{\partial y}{\partial x}\right)_z$  and  $\left(\frac{\partial y}{\partial z}\right)_x$  in terms of  $\frac{\partial F}{\partial x}$ ,  $\frac{\partial F}{\partial y}$ , and  $\frac{\partial F}{\partial z}$ ? How about  $\left(\frac{\partial x}{\partial y}\right)_z$  and  $\left(\frac{\partial x}{\partial z}\right)_y$ ? (You do not need to do any new calculations; just permute x, y, and z.)

(d) Now assume that the equation F(x, y, z) = 0 determines each of x, y, z as an implicit function of the other two. Explain why

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

and

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y.$$

2. In the mid-19th century, the British scientist James Prescott Joule performed an experiment to determine if the "internal energy" U of a gas (you do not need to know what that means) changes as its volume V changes and its temperature T remains constant. In this experiment, Joule held a gas in a state in which its volume would expand, but its internal energy would not change. He then determined, up to the accuracy of his instruments, that the gas he was examining, while expanding in volume and staying constant in internal energy, underwent no change in temperature. In other words, he measured that  $\left(\frac{\partial T}{\partial V}\right)_U = 0$ .

Joule then concluded that the internal energy of the gas would not change as its volume changes and its temperature remains constant, or in other words, that  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ . Assuming that the temperature, internal energy, and volume of a gas always satisfy a fixed equation F(T, U, V) = 0 that determines each quantity as an implicit function of the other two, carefully **JUSTIFY** (explain) Joule's conclusion.

Note: Remarkably, in the last problem, it **does not matter** what the physical law F(T, U, V) = 0 says; it only matters that there is **some** physical law of that type.