Mathematical Necessities for Thermodynamics

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Credits

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Topic 1

Introduction

To begin with, this isn't a math book. This is a set of notes for the math needed to understand thermodynamics. So the point of view taken is that of thermodynamics, not mathematics. Further, the point of view is *mine*, the rather idiosyncratic author. And, these notes are meant to be used in conjunction with the lectures I give in thermodynamics. You have a text for the chemistry material. You have these notes for the math.

These notes were originally written without research, straight out of my brain. I didn't even have an outline. Succeeding versions had more attention paid to them. This is the second major revision of these notes. Next time they will be better. [1]

My intention is twofold. First, and most obvious, is to cover the material from multivariate calculus that is needed for the usual course in physical chemistry. The material will not be presented with complete mathematical rigor, nor will the order of presentation be that a mathematician might have chosen. I will generally follow the development of the chemistry side of the course, taking up material as it is needed.

The second intention is less obvious. It is to teach you how to *do*mathematics. One part of this is to cover a number of topics that normally do not get much emphasis in regular calculus courses. That is, how to do numerical mathematics: How to do numerical integrations and differentiations, how to find roots of equations, and how to calculate values of strange and unusual functions.

I must stress that the material in these notes can not take the place of class work. Even though I have available some excellent facilities for producing graphs and mathematical symbols and what you see here *should* be relatively professional, it is only a set of notes. You cannot ask questions of a printed page. In class we will stray into related areas, fill out details not present here, and, best of all, in class you can ask questions.

We will begin with a very short review of material you have already learned. I'm doing that just to make sure we all start from the same place. I'll then introduce you to functions of several variables. We'll then be off and running. To make sure that you actually get the ideas I'm presenting, there will be numerous examples and problems scattered throughout this material.[2]

[1] If you've already read through these notes, don't complain. They were worse last time. And a few years before *that*, they didn't exist. Perhaps they will be better next time...

[2] Of course, *I* will find out how you are doing when we give the midterms in the course, but that's *not* the best way for *you* to find out...

Topic 2

Functions of a Single Variable

Let's start by reviewing some absolutely elementary definitions.[1] First is the definition of a **function of a single variable**. In one of those neat things that always seem to crop up in mathematics, there are *two* variables involved in the definition of a function of a single variable.[2] First there is the **independent variable** x. Of course, it doesn't have to be named x. It could be named t, or a, or even sam, although *that* choice might annoy some mathematicians.[3] This variable is called independent because the choice of its value is mostly up to the human using it. I say mostly because there is always a **range** of allowed values for the independent variable. The range could run from $-\infty$ to ∞, or from 1 to 2, or anything else. It is a serious error to pick a value of the independent variable outside of its range.[4] Figure 2.1 is an example of a function defined only over a limited range.

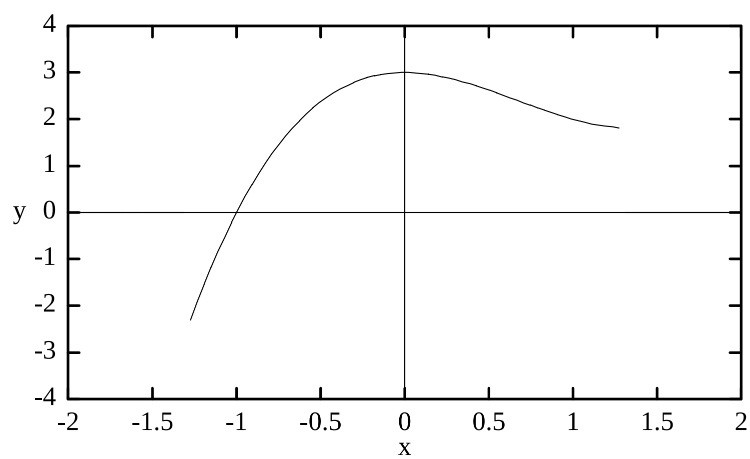

Figure 2.1: A function defined over the range -1.3 to 1.3

The second of the two variables is the **dependent variable** y. Again, it doesn't have to be named

[1]I know. What the teacher thinks is elementary, the student thinks is *awfully* complex.

[2]This isn't *really* correct, but as I've said, this isn't a math text.

[3]Who seem to prefer single letters. This is simply a prejudice, though it is true that sam might be taken to be $s \times a \times m$ with disastrous results...

[4]Who's going to stop you? Nobody. But you will get strange answers or possibly no answers at all, your calculator will be upset with you, and people who try to copy answers from you during exams will think that you are not too bright.

y. This symbol denotes the *value* of a function of a single variable. The relationship between these two variables is denoted in symbols by:

$$y = f(x)\,, \tag{2.1}$$

In which x and y are respectively the independent and dependent variables and the symbol $f()$ denotes a function.

Now $f(x)$ is a **function** of x if, for every valid value of x in its range there is at least one corresponding value of $f(x)$. In other words, we can think of $f(x)$ as a kind of *machine*. Drop a valid value of x into one end of the machine and at least one value of y pops out of the other.

An example of a "function machine" is:

$$y = x^2 + 4\,, \qquad -\infty < x < \infty\,, \tag{2.2}$$

in which $f(x)$ is $x^2 + 4$, and the range of x is $(-\infty < x < \infty)$ If we drop the value $x = 4$ into this "machine", the value 20 pops out the other end. Similarly, dropping $x = -3$ into the machine causes 13 to come out of the other end. In the first instance y ends up with the value 20 and in the second it ends up with the value 13.

Here's another example:

$$\theta = \sin^{-1}(x)\,, \qquad -1 \leq x \leq 1\,. \tag{2.3}$$

Here, the dependent variable is θ instead of y and the range is limited. Now, if we set x equal to zero and drop that value into the "machine" , we get out several different values. A moment's thought will tell you that possible values of θ include 0, π, 2π, etc. Indeed, the general solution is $\theta = n\pi$, for any integer value n, positive or negative.[5]

A function such as equation 2.3 is **multi-valued**. Many such functions exist. But most of the time we are interested in functions that are **single-valued**. That is, functions for which only one value of $f(x)$ pops out when we drop in a value of x. All of the functions considered in these notes will be single-valued unless otherwise indicated.

One last reminder on the use of the terms *independent* and *dependent* variables. *You* can pick any valid value of the independent variable you wish and drop it into the machine. The variable is independent because its value is up to you, the human.[6] Once you drop the independent variable into the machine, you lose control over what pops out. *That* depends on the function. So in $y = f(x)$, y is the *dependent* variable because its value *depends* on the value you have chosen for x. You have no direct choice in the matter.

One should think for a bit before choosing an independent variable in a problem. It may have an impact later. For instance van der Waals equation:

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT\,, \tag{2.4}$$

contains four variables, p, V, T, and n. If we chose p, T, and n as the independent variables the resultant "machine" is:

$$pV^3 - (nbp + nRT)V^2 + n^2 aV - n^3 ab = 0\,, \tag{2.5}$$

which is a cubic equation in V and not so easy to solve.

[5]This example is a good test of what happens if you exceed the range of the independent variable. Put $x = 1.5$ into your calculator and take the inverse sign... See what happens? I warned you, didn't I?

[6]Clearly, I'm making *some* assumptions about the folks reading this...

On the other hand if we chose V, T, and n as the independent variables we get:

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}\,, \tag{2.6}$$

a very nice, very tractable equation.

Problem Set 2.1

1. What are the ranges of the following functions?
   (a) $y = \sin(x)$.
   (b) $y = x^3 - 10$.
   (c) $y = \ln(x)$.
   (d) $y = 4e^x + 3\ln(x^2 + 1)$.
2. Are the following functions single-valued or multiple-valued?
   (a) $y = ax^2 + bx + c\,,\qquad a,\ b,\ \text{and}\ c\ \text{are constants}.$
   (b) $y = \sqrt{x}$.
   (c) $x^2 + y^2 = 4$.

Topic 3

The Derivative of a Function of a Single Variable

With functions of a single variable out of the way, we can now define the **derivatives** of such functions. It is simple.[1] If $x = x_o$ is a point[2] in the range of x, *and* if $f(x)$ is defined in that range, *and* if the limit in equation 3.1 exists, then

$$\lim_{h\to 0} \frac{f(x_o + h) - f(x_o)}{h} = \frac{df(x)}{dx}\,, \tag{3.1}$$

is called the derivative of $f(x)$ with respect to x at the point x_o. At least, that's the technical meaning of $df(x)/dx$. One very good way of thinking about it[3] is to say that $df(x)/dx$ at x_o is the *slope* of the curve $f(x)$ at the point x_o.

Of course, you also know that we sometimes abbreviate the notation of a derivative. We'd write $df(x)/dx$ as df/dx, where it is assumed that we know that x is the independent variable.

Often, in a given problem, one has a choice of what to make the independent variable. This sometimes confuses folks. You are allowed any choice you want. *But*, once you make that choice, you must stick to it all the way through that problem. No changing variables in the middle of a problem! Of course, some choices of independent variable make a problem easier than others. If you want to change to another independent variable, start over!

There are all sorts of rules for finding the derivatives of all sorts of functions. I assume[4] that you've learned a fair number of them in Calculus and I'm not going to repeat them here. They are in your Calculus text.[5]

Problem Set 3.1

1. Just for practice, differentiate the following functions with respect to the independent variable x. Note that ln stand for the natural logarithm.

[1] Since you've already learned it in Calculus.

[2] This notation is confusing. I know that I spent literally *years* getting this sort of thing straight in my own head. The particular point we are talking about is x_o. The notation $x = x_o$ means only that we are setting the independent variable x to the particular value x_o.

[3] And I'm sure most of you *do* think about it this way. Nobody thinks in terms of limits if they can help it.

[4] I'm an optimist.

[5] You *did* keep your Calculus text, didn't you?

(a) $y = e^x$

(b) $y = 4/\ln x$

(c) $y = x^2$

(d) $y = 7e^{x^2}$

2. These are a trifle harder:

   (a) $y = (100 - x^3)^2$

   (b) $y = 1/(2x + 1)^2$

   (c) $y = x^{3/2}(x - 18)^{-1/2}$

   (d) $y = \ln[1/(1 - x)]$

3. And then these:

   (a) $y = \ln[(1 + \cos x)/(1 - \cos x)]^{1/2}$

   (b) $y = \cos^{-1}(1/x^2)$

Topic 4

Functions of Several Variables

It should come as no shock to you that functions of *more* than one variable exist. For example:[1]

$$p = \frac{nRT}{V}\,, \tag{4.1}$$

shows that the value of p depends on n, T, and V. A change in any of these three independent variables will change p.

But again, the right-hand side of equation 4.1 is a machine. Drop in any legal values of n, T, and V and out will pop a value of the dependent variable p.[2]

A function of more than one value is usually written symbolically in a form such as:

$$w = f(x, y, z)\,, \tag{4.2}$$

where w is the dependent variable and x, y, and z are the independent variables.

Now be careful here. If you have an equation such as

$$pV = nRT\,, \tag{4.3}$$

which of the four variables are the independent variables? They can't all be! The answer is that it is your choice. The actual choice is often dictated by the problem to be solved.[3] If, for example, you were given the temperature, number of moles, and pressure and asked to find the volume, then T, n, and p would be the independent variables and V the dependent variable. In some other problem you would make different choices.

Of course, in most problems the choice is obvious. The independent variable is the quantity you are looking for; the other values (the dependent variables) are all given. But in *real* problems the choice is not always so easy. The choice may really be up to you. Some choices may make the problem easy. For example, there is a more complicated equation relating p, V, n, and T which is a *cubic* in V but linear in p. If you have to solve for one of these, pick V.

[1] Sorry to use such an advanced equation, but this *is* an advanced course...

[2] Each of the independent variables has a range. We don't usually state the range of the variables in the ideal gas law because negative values of any of them make no physical sense. Yet we *are* doing math and so it behooves us to pay attention to the fact that the ranges are: $(0 < n, T, V < \infty)$.

[3] Unlike the situation in pure mathematics where the dependent variable is very often the one on the left of the equals sign, we are problem oriented here. *All* of this is aimed at solving problems.

This is a good time to point out that functions of several variables have more complicated graphs than functions of a single variable. For one thing, you need more dimensions to graph them. For a function of two independent variables you need three dimensions. That's OK, we do it in perspective. Figure 4.1 is an example. For more than three we are in trouble. It is fairly easy these days to graph

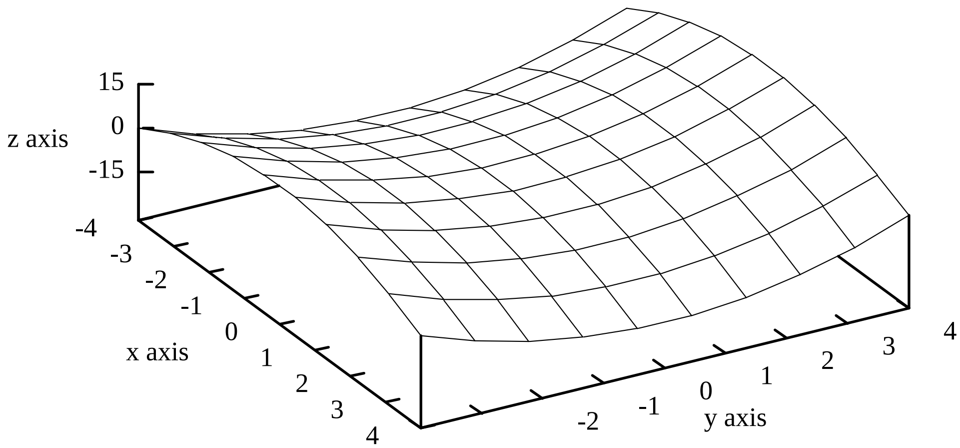

Figure 4.1: A function of two variables drawn in perspective

functions of two variables by computer.[4] Functions of *more* than two variables are a bit harder to produce.[5]

Problem Set 4.1

1. From the way the following equations are written, pick out the independent variables.
   (a) $z = e^{x+y}$.
   (b) $x = y\sin(\theta)$.
   (c) $r = \int_x^y z^2 dz$ .a
2. In the following, pick a set of independent variables and rewrite the equation with the dependent variable on the left
   (a) $(x^2 + y^2 + z^2) = 1$.
   (b) $(p + 0.003n^2/V^2)(V - 0.4n) = nRT$.
   (c) $r^2\sin^2(\theta) + r^2\cos^2(\theta) = 1$.

[4]Figure 4.1 was drawn by *gnuplot* running under Windows. *Gnuplot* is free software and is available for Macs and Linux as well.

[5]It is left to the reader to figure out why.

Topic 5

Derivatives of Functions of Several Variables

Even if one is an expert in the calculus of functions of a single variable, it isn't clear how to handle functions of more than one variable. The trick is this: For both differentiation and integration (which we'll discuss later) we handle only one variable at a time. In other words, we differentiate $f(x, y)$ with respect to x by pretending that y is a constant while we do the differentiation.[1] The basic idea behind this is that the variables are *independent*. Thus we can change one variable without affecting any of the others. So the question of differentiation then becomes "what is the change in $f(x, y)$ when I change x alone?" . As you can see, there then must be *two* different derivatives, one giving the change in $f(x, y)$ with x, and the other giving the change in $f(x, y)$ with y.[2]

Let's look at the notation used. Given a function of two variables:

$$z = f(x, y)\,, \tag{5.1}$$

then the **partial derivative of $f(x, y)$ with respect to x** is defined as[3]

$$\lim_{h \to 0} \frac{f(x_o + h, y_o) - f(x_o, y_o)}{h} = \left(\frac{\partial f(x, y)}{\partial x} \right)_y \tag{5.2}$$

This is the derivative of $f(x, y)$ at the point x_o, y_o with the limit taken in the x-direction. No zig-zag routes. The variable y is held constant at the value y_o throughout the entire process. However, we can't forget that y is a variable too. So the shorthand notation is a bit strange. We use the symbol ∂ instead of d to indicate that this is the derivative of a function of several variables. This symbol is named *partial* and the result of equation 5.2 is called a **partial derivative**. To emphasize the fact that there are other variables being held constant during the process, they are often (but not always) written as subscripts after the closing parenthesis, as on the right-hand side of equation 5.2 However, when no confusion can result, both the parentheses and the subscript are sometimes dropped.

[1]No, this didn't seem right to me either when I was learning it. But you will become more comfortable with it as time goes on.

[2]Some of you may wonder what happens if we want to know the change in $f(x, y)$ along, say, some line at a 45° angle between x and y? This can also be computed. Check your local calculus book for details.

[3]With the usual strictures about x and y being within their ranges of definition and other strictures about the limit existing, and so on. I'm ignoring them here as they are the same strictures as those for functions of a single variable.

Here are some examples. If we write

$$p = \frac{nRT}{V} = f(n, T, V)\,, \tag{5.3}$$

then

$$\left(\frac{\partial f(n,T,V)}{\partial V}\right)_{n,T} \tag{5.4}$$

stands for the rate of change of p with V when both T and n are held constant. The result of actually doing the differentiation is

$$\left(\frac{\partial f(n,T,V)}{\partial V}\right)_{n,T} = \left(\frac{\partial}{\partial V}\right)\frac{nRT}{V} = -\frac{nRT}{V^2} = -\frac{p}{V} \tag{5.5}$$

where the last step is the result of using $p = nRT/V$ in the previous expression.

Other examples:

$$z = e^{4x+6y}\,, \qquad \left(\frac{\partial z}{\partial y}\right) = 6e^{4x+6y}\,. \tag{5.6}$$

and

$$z = x^3y + 3x^2y^2 + 6xy^3 + 7\,, \qquad \left(\frac{\partial z}{\partial x}\right) = 3x^2y + 6xy^2 + 6y^3\,. \tag{5.7}$$

One takes **second partial derivatives** in exactly the same way: one holds all other independent variables constant. For example if we now form the *second* derivative of z in equation 5.7 with respect to x, we get

$$\left(\frac{\partial^2 z}{\partial x^2}\right)_y = 6xy + 6y^2\,. \tag{5.8}$$

It is possible to differentiate a second time with respect to a *different* variable. This gives a **second mixed derivative**. Again, if the function in equation 5.8 is differentiated first with respect to x and then the result differentiated with respect to y we get:

$$\left(\frac{\partial^2 z}{\partial x \partial y}\right) = 3x^2 + 12xy + 18y^2\,. \tag{5.9}$$

Check this example carefully to be sure you understand it!

In this last example there were no subscripts to indicate what was being held constant. That's because the notation would get to be too cumbersome. It is always *understood* that all other variables are held constant whenever one differentiates with respect to a particular variable.

Problem Set 5.1

1. Differentiate each of the following functions with respect to y:
   (a) $z = 4y^2 + xy/3$
   (b) $z = y/\ln x$
   (c) $z = \ln(3x + 7y)$
2. Differentiate $p = nRT/V$ with respect to T and then with respect to V

3. The van der Waals equation is:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT\,,$$

   where a and b are constants (different for each different gas) and the other symbols have their usual meanings. Solve this equation for p and then find $\partial p/\partial V$.

4. For van der Waals equation in the problem above, find $\partial p/\partial T$.

5. Again, for van der Waals equation, find $\partial^2 p/\partial V \partial T$.

6. Invent a function of two variables, x and y. Differentiate it first with respect to x and then with respect to y. Now repeat, only this time differentiate it first with respect to y and then with respect to x. Compare the second derivatives.

7. Repeat the last problem for several different functions.

8. Find a function of x and y for which the two mixed second derivatives are different.

Topic 6

The Total Derivative

The very fact that mathematicians created a thing[1] called a partial derivative should warn us that there should be a thing called a *total derivative*.

There is.

For a function of a single variable, say

$$y = f(x)\,, \tag{6.1}$$

it is quite reasonable to ask "what is the change in y when we make some small change in x" Well, if we take a small step along the x-axis, the change in $y$depends on the *slope* of the curve at the point we are standing on. In words:

$$(change\ in\ y) = (slope\ of\ curve) \times (change\ in\ x) \tag{6.2}$$

, or, if we write this out mathematically

$$\Delta y = (slope\ of\ curve)\ \Delta x \tag{6.3}$$

. Now, the slope of the curve is just dy/dx, so what we've really said is:

$$\Delta y \quad = \quad \frac{dy}{dx}\Delta x\,. \tag{6.4}$$

And, if the change in x is sufficiently small[2]. then:

$$dy = \frac{dy}{dx}dx\,, \tag{6.5}$$

which looks strange, but really isn't. Look at it this way: the derivative dy/dx is the slope of the curve and in the derivative we mean dy and dx to be infinitesimal quantities. That is, the ratio dy/dx is the result of a limit process. And the dx that follows the slope is also an infinitesimal quantity, but infinitesimal only in the sense of very small. The same is true of the dy on the left-hand-side of the equation.

Now, if we are dealing with a function of two variables, say

$$z = f(x, y)\,, \tag{6.6}$$

[1]Well, perhaps it isn't a *thing*, but what would *you* call it?
[2]Meaning *infinitesimal*

and we ask: "what is the change in z if we make some small change in x *and* some small change in y simultaneously?" Well, the answer has the same philosophy:

$$\begin{aligned}\Delta z = &(\textit{slope of the curve in the x direction})\Delta x \\ &+(\textit{slope of the curve in the y direction})\Delta y\,,\end{aligned} \tag{6.7}$$

or what is the same thing:

$$\Delta z = \left(\frac{\partial z}{\partial x}\right)_y \Delta x + \left(\frac{\partial z}{\partial y}\right)_x \Delta y\,. \tag{6.8}$$

Now why should this be correct?[3]

The reason is this: we are assuming that the various small changes really are small. In that limit we are not dealing with a curved surface. We are dealing with a portion of the surface so small in area that it can be considered flat.[4] We are standing at one point, and we want to find the change in z in getting to another nearby point on this flat plane. We can walk up first in the x-direction and then in the y, or first in the y-direction and then in the x. But the slope in the x-direction will be the same either way because the plane is *flat*. Similarly the change in the y-direction will be the same either way, for the same reason.

So equation 6.8 is reasonable.[5]

If now the changes in x and y are infinitesimal, then equation 6.8 becomes

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy\,. \tag{6.9}$$

Equation 6.9 is what is called the **total derivative** of a function.

Of course, there can be more than two independent variables. And when there are, one just extends equation 6.9 in an obvious way. For example, given four independent variables v, w, x, and y we'd have

$$dz = \left(\frac{\partial z}{\partial v}\right)_{w,x,y} dv + \left(\frac{\partial z}{\partial w}\right)_{v,x,y} dw + \left(\frac{\partial z}{\partial x}\right)_{w,v,y} dx + \left(\frac{\partial z}{\partial y}\right)_{w,v,x} dy\,, \tag{6.10}$$

and so on.

Any function of several variables has a total derivative. The only conditions are that the function must be differentiable in the ranges of the independent variable. Thus we can take the Ideal Gas law in the form $p = nRT/V$ (with p the dependent variable) and find the total derivative:

$$dp = \left(\frac{\partial p}{\partial V}\right)_{n,T} dV + \left(\frac{\partial p}{\partial T}\right)_{n,V} dT + \left(\frac{\partial p}{\partial n}\right)_{V,T} dn\,. \tag{6.11}$$

Since we know what function of V, T, and n p is, we can find the partial derivatives. The result is:

$$dp = -\frac{nRT}{V^2}dV + \frac{nR}{V}dT + \frac{nT}{V}dn\,. \tag{6.12}$$

[3]This question won't even come up if you are used to taking everything some professor says as being true. This is not a good habit. You should *always* ask yourself "is what was said really reasonable?" If the answer is no, ask questions.

[4]This plane is the plane *tangent* to the surface at the point we are working at. (This information provided for the mathophilic folks in the audience...).

[5]It can even be proven, but, as I've said, this isn't a math book.

This could be simplified by using the Ideal Gas law. For example $nR/V = p/T$ to get:

$$dp = -\frac{p}{V}dV + \frac{p}{T}dT + \frac{p}{n}dn \tag{6.13}$$

But the student is cautioned to be careful. In equation 6.12 the right hand side is a function of *independent variables only*. In equation 6.13 it is a mixture of both independent and dependent variables. Which form one might choose depends on what one wants to do next. If V, T, and n are known and dp is to be evaluated, certainly one must use equation 6.12.

Problem Set 6.1

1. The pressure in a van der Waals gas is given by

   $$p = \frac{nRT}{V - b} - \frac{an^2}{V^2}\,,$$

   where a and b are constants. Find the change in p when small changes are made in T and V. Simplify the results as much as possible.

2. The energy U of a system is a function of its temperature T and its volume V. Write an expression for the total derivative of U as a function of T and V. Can you evaluate the derivatives?

3. It is known that the volume of a material depends on its temperature and pressure. For liquid benzene it is known experimentally that $\partial V/\partial T$ is 12.4×10^{-4} per liter-Kelvin and $\partial V/\partial p$ is 92.1×10^{-6} per liter-atm. Find the change in volume of a liter of benzene when the temperature is raised by 0.01 K and the pressure by 0.01 atm.

Topic 7

Finding Roots of Equations

7.1 Introduction

We're going to shift gears for a while and discuss a purely numeric problem, the finding of roots of equations.

You all know how to solve linear equations. Finding the root of an equation such as $x+4 = 7$ can be done in your head.[1] Quadratics should also provide no terrors. It is tedious to solve quadratics, but with a calculator it is no problem.[2] The problem of finding roots is the problem of solving polynomials of third degree or higher,[3] and of solving transcendental equations. For instance the roots of

$$17x^5 - 3x^4 + 3x^2 + x + 7 = 0\,, \tag{7.1}$$

are not easy to find, nor are the roots of

$$x^2 + \ln x - 7 = 0\,. \tag{7.2}$$

Yet problems such as these come up all the time in "real life" .

In general there are three usable manual ways to solve such problems. They are (1) interval halving, (2) iteration, and (3) Newton-Raphson. There are others, including simply using a computer,[4] but these are adequate for our purposes. I'm going to go over each method[5] and give examples of each. I'd like to use several examples from chemistry[6] but for now I'll focus on one particular and not too nasty example.

No matter what manual method one uses, it *always* pays to have an idea about what is going on.[7] Take equation 7.2 for example. Does it have any real roots at all? The answer, of course, is to graph

[1] If you *can't* solve this in your head, your head is too full of, well,... Make some room in your head. Clean your brain.

[2] Well, that's not quite true. In a later revision of these notes I'll try to show some of the pitfalls and what to do about them.

[3] There are, in fact, formulas for finding the solutions to cubics and quartics using simple algebraic tools such as roots. But they are tedious to use. There are *no* purely algebraic formulas for quintics and higher.

[4] But the *computer* has to use some numeric method, doesn't it!

[5] In boring detail. *All* of these methods have limitations and you have to know what they are. In particular, computers often use these methods, and now you will know why they sometimes fail to find an answer.

[6] And I will, later.

[7] This is known as being clued. The opposite is being clueless.

the function (see Figure 7.1). That's not really what you are going to do.[8]

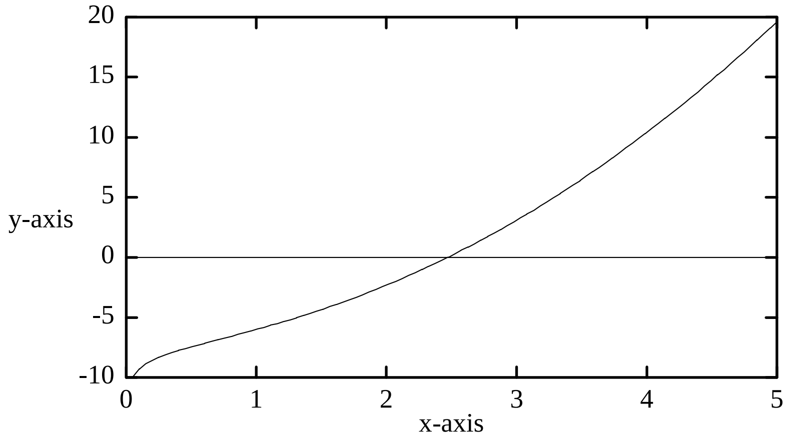

Figure 7.1: A plot of Equation 7.2

What you should do, if you are serious about solving such a problem, is to make a small table. I've constructed one for a few simple values of x:

x	$f(x)$
0.5	-7.44
1.0	-6.00
1.5	-4.34
2.0	-2.31
2.5	0.17
3.0	3.10

Table 7.1: Values from Equation 7.2

The function changes sign somewhere just below $x = 2.5$. So there *is* a root. In fact, the root is $x = 2.469042258$, but I cheated.[9]

7.2 Interval Halving

The first method is **interval halving** This is simply an extension of the table we constructed above. It can be tedious to do by hand, but with a calculator it isn't much trouble.[10] We know there's a root between $x = 2.0$ and $x = 2.5$, so lets look at a value of x about half-way between. If we take $x = 2.30$ we get $f(x) = -0.88$. So now we know there's a root between 2.3 and 2.5. Let's assume we want the root to five significant digits. I'll present my work in another table:

[8]Who carries graph paper around with them? Of course, if you have a graphing calculator you *can* graph it!

[9]I had the program *Derive* solve it for me (on a PC). It used some numeric method. I don't know which one. So I checked it by plugging it back into equation 7.2

[10]In fact, I used a calculator to get the values in these tables.

line	x_{low}	$f(x_{low})$	x_{high}	$f(x_{high})$	new x_{low}	new x_{high}
1	2.0	-2.31	2.5	0.17	2.3	2.5
2	2.3	-0.877	2.5	0.17	2.4	2.5
3	2.4	-0.364	2.5	0.17	2.45	2.5
4	2.45	-0.101	2.5	0.17	2.45	2.47
5	2.45	-0.101	2.47	0.005	2.46	2.47
6	2.46	-0.048	2.47	0.005	2.465	2.47
7	2.465	-0.022	2.47	0.005	2.468	2.47
8	2.468	-0.006	2.47	0.005	2.469	2.47
9	2.469	-0.0002	2.47	0.005	2.4695	2.47
10	2.469	-0.0002	2.4692	0.0008	2.469	2.4691
11	2.469	-0.0002	2.4691	0.0003	2.469	2.46905
12	2.469	-0.0002	2.46905	0.00004		

Table 7.2: Further Values from Equation 7.2

Each line in the table gives the current high and low values for x and $f(x)$ for those values. We want to monitor those $f(x)$ values to keep the sign change between them. The last columns are new high and low values for x. Sometimes one will pick a poor new value for x. You can tell when this happens because both $f(x)$ values will have the same sign. When that happens go back to the original line and pick the *other* x value to change.

The resulting root is $x = 2.4690$ to five significant figures. Note how I kept the "lower" $f(x)$ value negative and the "upper" one positive. Also note that I cheated in a few places, since it was clear that picking a value slightly more or slightly less than half-way would give a quicker result.

What are the defects of this method? It is simple only for simple functions, it requires a certain amount of work, and it only slowly gives more significant figures. We gained about one more significant figure for every three calculations. But the method has a few major advantages too. It is easy to remember how it works and it is self-correcting. If you make a math error in one step, it will become clear very quickly. And it only took 12 tries to get five significant figures. I know that seems like a lot of work, but it isn't really. It only takes a few minutes. And the beautiful thing about it is that it always works.

7.3 Iteration

The second method is one called **iteration**. That isn't really a good name since there are several other schemes called that. But it is simple and we will stick to it. In this method one takes an equation of the form:

$$f(x) = 0\,, \tag{7.3}$$

and converts it to the form

$$x = F(x)\,. \tag{7.4}$$

The idea is to pick a value for x and substitute it into *F(x)*. What pops out on the left-hand side is a new and possibly better value for x. Repeat until you have the number of significant digits you want.

To do this with our example let us write equation 7.2 in the form:

$$x = [7 - \ln(x)]^{1/2}\,. \tag{7.5}$$

Now, let us plug the value $x = 2.5$ into the right-hand-side.[11] Grinding through the equation I get $x = 2.466$. Ok, let's use *that* value and do it again. I now get $x = 2.469$. I keep going, and generate Table 7.3 in the process:

x	$f(x)$
2.5	2.466
2.466	2.469
2.469	2.46904
2.46904	2.469042

Table 7.3: An Iterative Method of Solution

The last result is accurate to seven significant figures. Neat, huh? When this method works, it works well.[12] But this method does *not* always work. For instance, how did I arrive at equation 7.5? I might just as easily have picked

$$x = e^{7-x^2}\,, \tag{7.6}$$

as my iteration equation. Start with 2.5 and iterate a few times, just for fun.[13] The values of x don't converge.

That's the problem with the iteration method. It doesn't always converge, and you don't have a clue until you iterate it. Sometimes a simple re-arrangement of the equation (using equation 7.5 instead of equation 7.6 will do the trick, but there is no guarantee.

The technical requirement for an iteration scheme to converge is that

$$|F'(x)| < 1.0\,. \tag{7.7}$$

That is, that the absolute value of the derivative of *F(x)* be less than one. For equation 7.5 we have:

$$\frac{d}{dx}[7 - \ln(x)]^{1/2} = \frac{1}{2x[7 - \ln(x)]^{1/2}}\,, \tag{7.8}$$

which is going to be less than 1 for any value of x around 2.5. On the other hand, for equation 7.6 we have

$$\frac{d}{dx}e^{7-x^2} = -2xe^{7-x^2}\,, \tag{7.9}$$

which isn't going to be less than 1.0 *anywhere* around 2.5.

So the iterative method has the advantage of working well (when it works) and being simple to remember. It has the disadvantage of sometimes not working at all, and it isn't easy to tell when that will happen.[14]

[11] Where did I get the 2.5? From Table 7.1. You simply *have* to have some idea where the root is, or this method will fail.

[12] Indeed, it is the method we now teach Freshmen to use when solving equilibrium constant problems. But we don't tell them that it is anything fancy. Freshmen scare easily.

[13] For the fun-averse crowd, 2.5 gives 2.117 as the next value. And *that* gives 12.407 as the next value. It doesn't take a rocket scientist to figure that *this* ain't goin' anywhere...

[14] The rule of thumb is this: try it. If it converges, fine. If not, try a re-arrangement of the equation. If that converges, fine. If not, you are probably out of luck. There is no point in doing the differentiation in order to see if the method will converge, because, if you do the differentiation, you might as well use the next method, which is harder, because you need to do a differentiation, but more efficient.

7.4 Newton-Raphson

The last method I'm going to discuss is the **Newton-Raphson** technique. An early version of this technique was developed by Sir Isaac Newton, so it isn't exactly new. It uses a simple repetitive formula:

$$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)}\,, \tag{7.10}$$

where *f'(x)* is the derivative of the function *f(x)*. To use this method one *must* compute the derivative of the function. Once that is done, you pick a starting value x_{i} (hopefully close to a root), and use equation 7.10 to get $x_{\mathrm{i+1}}$, the *next*value to use. Repeat. Convergence, if it occurs, is *very* rapid.[15] The derivative of our function $f(x) = x^2 + \ln(x) - 7$ is

$$f'(x) = 2x + \frac{1}{x}\,, \tag{7.11}$$

which isn't too hard. So the equation we want to use is:

$$x_{i+1} = x_i - \frac{x^2 + \ln(x) - 7}{2x + 1/x}\,. \tag{7.12}$$

If we start with $x = 2.5$ we get

$$xi + 1 = 2.5 - \frac{0.1662907}{5.4} = 2.4692054\,, \tag{7.13}$$

which already has four correct figures. Repeating with this new value of x gives 2.4692054 - 0.0008718 / 5.343399432 = 2.4690422, which is as accurate as my calculator will go.

Neat, huh?

The advantage of Newton-Raphson is that *if* you start off near a root, the number of correct digits will double each time through. The disadvantages are that the formula is hard to remember, you need to take a derivative to use it, it is a more complex formula, and, of course, if you are far enough from the root, it won't converge at all.[16]

Problem Set 7.1

1. Find the roots of $\sin(x) - x - \ln(x)$.
2. Find all the real roots of
$$x^5 + 4x^4 - 3x^3 + 2x^2 - x + 1 = 0$$
3. The van der Waals equation is a better description of gas behavior at high densities than the ideal gas equation. For nitrogen the equation (in liter-atm units) is:
$$\left(p + \frac{1.408n^2}{V^2}\right)(V - 0.02370n) = nRT$$
   (a) Use the method of interval-halving to find the volume of one mole of nitrogen at a temperature of 200 K when the pressure is 300 atm.

[15] This method *doubles* the number of significant digits each time you go through it. It is called a **second order method**for this reason.
[16] Again, if you've made a table such as Table 7.1, this last won't happen to you.

(b) Use Newton-Raphson to find *all* the values of the volume for nitrogen under the given conditions. Yes, there are more than one.

4. The equation

$$36x^6 + 36x^5 + 23x^4 - 13x^3 - 12x^2 + x + 1 = 0$$

   has only four real roots. Find them.

5. Use Newton-Raphson to solve Problem 1

6. In Freshman chemistry we often ask students to solve equilibrium constant problems by iteration. Given a 0.1 M solution of acetic acid, find the hydrogen ion concentration. $K_a = 1.0 \times 10^{-5}$ for acetic acid.

Topic 8

Integration

Before I talk about integration, let me say a few words about *antidifferentiation*. Let me introduce it this way: One standard thought in math concerns the *opposite* of any particular action.[1] The "opposite" of addition is subtraction in the sense that if $7 + 2 = 9$, then $9 - 2 = 7$. The "opposite" of taking a logarithm is exponentiation,[2] as in $\ln 5 = 1.609437912$, and $\exp(1.609437912) = 5$. In this sense, the "opposite" of the derivative is the **antiderivative**. It attempts to answer the question: "given a function *f(x)*, what function *F(x)* is there such that *f(x)* is the derivative of *F(x)*?"

As you know, not every *f(x)* has an antiderivative *F(x)*. For example neither

$$f(x) = e^{-x^2}\,, \tag{8.1}$$

nor

$$f(x) = e^{-x} \ln x \tag{8.2}$$

has an antiderivative.

It is very useful to be able to find antiderivatives. But it *is* a bit of an art.[3]

The *definite* integral is a different kind of animal altogether. A definite integral is, basically, a number. It is the answer to the question: "what is the area of a graph between the x-axis and a given function *f(x)*?" Areas lying *below* the x-axis are counted negative, while those lying above it are counted positive.[4] A special notation is used for this sort of definite integral:

$$\int_a^b f(x)dx = A\,, \tag{8.3}$$

means that A is the (numerical) value of the area between the curve *f(x)* and the x-axis from $x = a$ to $x = b$. The a and b are written on the integral sign in the order and position given, and the symbol dx is what tells us that the axis in question is the x axis.

[1] This is more technically called the *inverse* and not the "opposite".

[2] But we have to be a bit careful. Not all "opposites" exist and of those that do, some are multiply-valued. Think of nine being three squared, and ask how many square roots does nine have?

[3] One indispensable tool for finding antiderivatives is a good table of integrals. If you are interested in studying physical chemistry or chemical theory at the graduate level, it is never too early to start equipping yourself with such tables. But sadly these are now becoming rare, being replaced by computer programs such as *Mathematica*, *Maple*, *Derive* and other costly alternatives.

[4] Again, let me remind the reader that this is *not* the definition that a mathematician might love. Nevertheless, it is very useful from a teaching point of view, and that, of course is what is going on here. Hmm. It *is* going on here, isn't it?

A few simple definite integrals can be found using this definition directly. In particular, the definite integral of the function *f(x) = 3* from *x = 2* to *x = 4* is simply the area between the horizontal line three units above the x-axis between 2 and 4. This is a rectangle three units high and two units long. So the area is 6 square units.

But how can areas be found in general? Well, mathematicians don't particularly care. They *are* interested in knowing the conditions under which the area actually can be measured, but they are not really concerned with finding the area as a number.[5]

One standard method of defining a definite integral is illustrated in Figure 8.1.

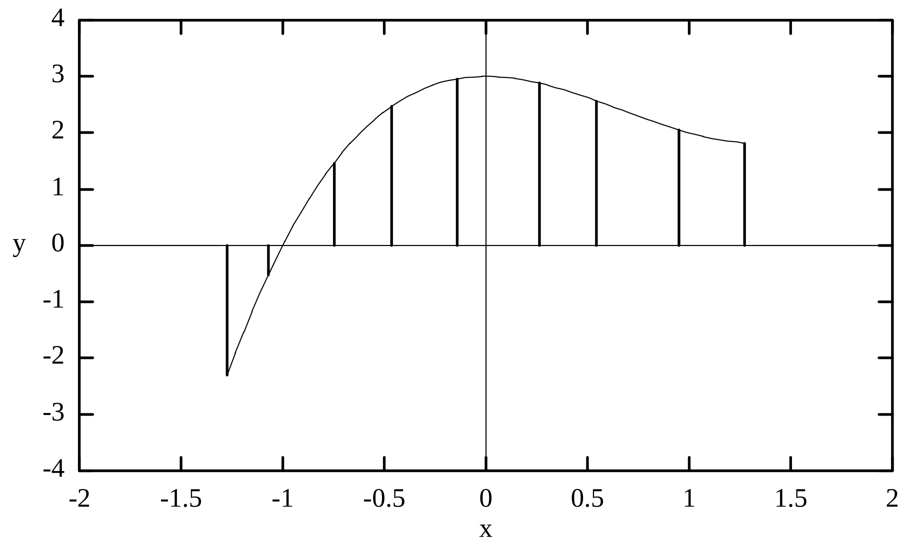

Figure 8.1: The function of Figure 2.1 subdivided

This is the same function that was shown in Figure 2.1. It has been subdivided into strips of varying widths. It is not too hard to estimate the area in each strip; to do so we only have to imagine that the function in each strip can be well-approximated by a straight line. Then each strip becomes a quadrilateral whose area can be computed.[6] After we find the area of each strip, we need only add them up to get the area between the function and the axis. Symbolically:

$$A = \sum_{i=1}^{n} A_i \,, \tag{8.4}$$

where A_{i} is the area of each strip and there are n strips. If we let the width of the ith strip be dx_1 and the average height be x_{i}then we can rewrite equation 8.4 as:

$$A = \sum_{i=1}^{n} f(x_i)dx_i \,. \tag{8.5}$$

Of course, unless the strips are very narrow and there are a very large number of them, A in equation 8.5 is only a poor approximation of the definite integral. But that's the secret. We keep adding

[5]Of course this is a canard on mathematicians. But hey, to some extent they've earned it. Now I suppose I'll be on the mathematicians hit list. That means that they will carefully consider *if* I can have my legs broken, conclude that it is possible, and then not bother actually doing it...

[6]For the regions shown, with vertical sides, the area is just the width of the region times the height in the center of the region. The height in the center is just the average of the heights at each end.

more and more strips, such that the largest strip gets to be (in the limit) vanishingly thin.[7] This now gives us a definition of a **definite integral**:

$$A = \int_a^b f(x)dx = \lim_{\max dx_i \to 0} \sum_n f(x_i)dx_i\,, \tag{8.6}$$

where n is the number of strips,[8] $x_{\rm i}dx_{\rm i}$ is the area of the i'th strip and the symbol max $dx_i \to 0$ means the size of the largest $dx_{\rm i}$ goes to zero. Assuming the limit exists, A is then the definite integral of *f(x)* over the interval from a to b. Generally, if *f(x)* is "reasonably" continuous over the interval, A will exist.[9]

Does this mean that you have to evaluate equation 8.6 by hand to do a definite integral? Not at all. As you already know, there is an interesting theorem in calculus that covers the situation. Very generally, if an antiderivative to *f(x)* can be found, then:

$$A = \int_a^b f(x)dx = F(b) - F(a)\,, \tag{8.7}$$

where *F(x)* is the antiderivative to *f(x)* and *F(a)* and *F(b)* is the antiderivative evaluated at x=a and x=b, respectively.[10] As an example, the antiderivative to *1/x* is ln*(x)*, so

$$\int_1^2 \frac{1}{x}dx = \ln(2) - \ln(1) = 0.69315 - 0 = 0.69315\,. \tag{8.8}$$

An interesting situation occurs when the upper and lower limits are *not* constants, but variables. What happens then? Well, again, as you know, the result is basically the same as equation 8.8. Think of a variable limit as simply delaying your choice of constant until after you've done the integration. Indeed, you *never* have to replace it with a constant. This is, In fact, quite legal. In this case the integral is a function of a *new* variable which represents your choice. Thus,

$$A(y) = \int_a^y f(x)dx = F(y) - F(a)\,. \tag{8.9}$$

where A is now a function of the new variable y. If you wish, the constant a can be replaced by a variable as as well.[11]

It is very common to use the same letter for both the integration variable and the limit variable. This is bad form. But everybody does it, including me. It is just one of those things that seem unpalatable but that you have to get used to.[12] Here's an example:

$$\int_1^x \ln(x)dx\,. \tag{8.10}$$

The two x's in Equation 8.10 are different. The x in the dx and in the ln*(x)* are called *dummy* variables, while the x in the limit is a "real" variable. The result of the integration is:

$$\int_1^x \ln(x)dx = (x\ln(x) - x)\big|_x - (x\ln(x) - x)\big|_1 = x\ln(x) - x - 1\,, \tag{8.11}$$

[7]We specify that the *largest* strip get vanishingly thin because that guarantees that *all* the other strips must be vanishingly thin too.

[8]Which will go to infinity.

[9]I've slurred over a number of difficulties concerning the existence of the limit. Suffice it to say that if *f(x)* contains no more than a finite number of finite discontinuities, the integral will exist. Actually, it will exist even more generally, but lets not get into that. If the details aren't in your Calculus book, get another Calculus book.

[10]I know you all know this already. But we do want to be a *little* complete, don't we?

[11]But not the *same* variable as the upper limit, because then the integral has the value zero, since the *range* of the integral has a zero width.

[12]You know, like beer the first time you tasted it.

where the vertical bar with the subscript x means to evaluate the preceding expression with the independent variable equal to x. If we'd integrated

$$\int_1^x \ln(y)dy\,, \tag{8.12}$$

we'd have gotten *exactly* the same result. Thus we have Gans's Advice: if the integration variable and the integration limits use the same letter, *rewrite* the integration variable wherever it occurs as a different letter. That way you won't get confused.

Problem Set 8.1

Many of the problems below are ones that actually come up in the study of thermodynamics.

1. Find an antiderivative of $f(x) = \exp(ax)$.
2. Find an antiderivative of $f(x) = 1/(a + bx)$.
3. Find an antiderivative of $f(x) = x/(a + bx^2)$.
4. Find the value of
$$\int_1^2 \left(x^2 + 4x - 3 + \frac{2}{x}\right) dx$$
5. Find the value of
$$\int_1^\infty \frac{dx}{x^2}$$
6. When an ideal gas expands at constant temperature from a volume of 1 liter to a volume of 10 liters, the work done by the gas is given by:
$$\int_1^{10} \frac{nRT}{V} dV$$
where $n = 1.5$, $T = 300$, and $R = 0.082056$. The result will be in liter-atm.
7. A general expression for the work done by an ideal gas in expanding from 1 liter to V liters is:
$$w = \int_1^V \frac{nRT}{V} dV$$
Hint: pay attention to which letters stand for variables and which for constants.
8. When an ideal gas expands adiabatically from an initial volume of 1 liter to a final volume of 10 liters, the work done by the gas is given by:
$$\int_a^b \frac{c}{V^\gamma} dV$$
where c and γ are constants. What happens when$\gamma = 1$?
9. The heat needed to heat a mole of a substance from 25° to some higher temperature T at constant pressure is given by:
$$\Delta H = \int_{298}^T C_p dT$$
Write a general expression for the heat ΔH assuming (a) that C_p is constant, and (b) that C_p is given by the expression $a + bT + c/T^2$, where a, b, and c are constants

Topic 9

Numerical Integration

Numerical integration is the evaluation of integrals by numerical methods. There are two general situations where one must resort to this. One is when a function is given only as a table of values. The other is when one needs to integrate a function that does not have an anti-derivative.

In both cases one uses the numerical value of the integrand at points where it is known. In the first case one is stuck[1] with the points given in the table of numerical values. In the second one can choose the points to suit.

We will discuss these two cases in order. But first a few points must be made. This is *not* a handbook on numerical integration. That is a subject with a long and honorable history,[2] and we can't do justice to it here. What is discussed are methods that can be used on a pocket calculator, even a non-programmable one.[3]

All these methods work in the same general way. In effect they fit a polynomial to the given data and integrate *that* instead of the real function. While this can work well, be warned that no polynomial ever goes vertical, approached a limit asymptotically, or has discontinuities. Since the function you are trying to integrate numerically is usually not a polynomial–if it were it would have an antiderivative. So before you even start you have errors in your answer due to approximating a non-polynomial by one.

9.1 Functions Given as Tables

As an example using a function given as a table let us consider the following problem: how much heat must be added to copper to heat it from 20 K to 100 K given the following data:

[1] Ain't it the truth...

[2] Going back to Newton if not before.

[3] Sure, they can be used on a computer too and indeed will work well there if you pay attention to some of the warnings given later.

T (K)	C_p (J/K)
20	0.489
30	1.716
40	3.813
50	6.291
60	8.706
70	10.993
80	13.026
90	14.743
100	16.141

Table 9.1: Molar Heat Capacity of Copper at Constant Pressure

The formula for this is simple:

$$\Delta H = \int_{20}^{100} C_p dT \,, \tag{9.1}$$

where ΔH is the heat needed per mole and C_{p} is the heat capacity per mole.

9.1.1 The Trapezoidal Rule

The simplest numerical integration technique is known as the **trapezoidal rule**. The method is similar to the definition of a definite integral. One splits the entire integral into a number of strips with the strip boundaries corresponding to the table entries. Then one assumes that the function behaves *linearly* from table entry to table entry.[4] For example, given that $C_{\mathrm{p}} = 1.716$ J/K at 30 K and $C_{\mathrm{p}} = 3.813$ J/K at 40 K, then at 35 K, C_{p} will be half-way between 1.716 and 3.813 or (1.716+3.813)/2 = 2.765 J/K. The area of the strip between 30 K and 40 K is then simply 2.765 J/K $\times$ 10 K or 27.65 J. All we need do then is to add up the contribution for each strip. In our example this would be

$$\Delta H = 10\frac{0.489 + 1.716}{2} + 10\frac{1.716 + 3.813}{2} + 10\frac{3.813}{2} + \cdots + 10\frac{14.743 + 16.141}{2} \,. \tag{9.2}$$

If you look carefully, you will see that each value in the table (except the first and last values) occurs *twice*. Once as the right-hand edge of a strip and once as the left-hand edge of a strip. So the *general formula* for the trapezoidal rule can be written:

$$A = \int_a^b f(x)dx = h\left[\frac{y_0}{2} + y_1 + y_2 + \cdots + y_{n-1} + \frac{y_n}{2}\right] \,, \tag{9.3}$$

where there are n strips,[5] h is the width of each strip,[6] and $y_{\mathrm{i}}$is the i'th table value.[7]

Equation 9.3 is very easy to use. All you have to do is add up all the table entries in Table 9.1, except the first and the last, then add in *half* the first and last entries, multiply the total by h and you are done. Doing just that gives 10 $\times$ (59.288 + 16.63/2) = 676.04 joules as the answer to our problem.

[4]How's *that* for fitting a polynomial to the data!

[5]And hence there must be n+1 table entries. In other words, n is *one less* than the number of table entries.

[6]We've secretly assumed that the strips are all the same width. This is the most convenient way of doing things. But it is not a necessity. When one has a table, one can only use what one has.

[7]Starting the count with 0, not 1.

The trapezoidal rule is not exact. There is an error due to the fact that we are approximating. The error in each step is

$$\epsilon = h^3 \frac{1}{12} \frac{d^2 f(x)}{dx^2} , \tag{9.4}$$

where the second derivative is evaluated at some point inside the strip for the *real* function being integrated[8] and h is the width of the strip. The total error is the sum of all the errors. Since there are $(b-a)/h$ strips the total error ϵ_T is then

$$\epsilon_T = \frac{b-a}{h} \epsilon = h^2 (b-a) \frac{1}{12} \frac{d^2 f(x)}{dx^2} , \tag{9.5}$$

where the second derivative can be conservatively taken as the largest absolute value the second derivative takes in the range from a to b. The total error is considerably larger than the error for one strip in equation 9.4.

Because of the exponent on h, the trapezoidal rule is often referred to as a *second order method*.

9.1.2 Simpson's Rule

A slightly better method of numerical integration[9] is known as **Simpson's rule**. Simpson's rule basically takes two strips at a time and fits that data to a *parabola* that goes exactly through those three table values at the three points in the two strips.[10] This results in the following formula for one strip:

$$A = \frac{h}{3} \left[y_0 + 4y_1 + y_2 \right] . \tag{9.6}$$

Repeated application of this means that, except for the first and last entries (again!) we end up with each end point counted twice. Thus for the entire range:

$$A = \int_a^b f(x) dx = \frac{h}{3} \left[y_0 + 4(y_1 + y_3 + \cdots + y_{n-1}) + 2(y_2 + y_4 + ... + y_{n-2}) + y_n \right] , \tag{9.7}$$

where the symbols have the same meaning as in equation 9.3. To use equation 9.7you must have an *odd* number of table values and, as was not true above, they must be evenly spaced.[11] This formula is not much harder to use than the trapezoidal rule, except now you add every other table entry separately. In the case of our example we would have:

$$A = \frac{10}{3} \left[0.489 + 4(1.716 + 6.291 + \cdots + 14.743) + 2(3.813 + \cdots + 13.026) + 16.141 \right] , \tag{9.8}$$

which gives 675.65 J/K as a result. This isn't quite the same as the value we got from the trapezoidal rule but it differs from it only by 0.39 or about 0.06%

Simpson's rule is more accurate than the trapezoidal rule. It has an individual step error given by:

$$\epsilon = \frac{1}{90} h^5 \frac{d^4 f(x)}{dx^4} \tag{9.9}$$

[8] And, of course, not knowing the *real* function, one can't evaluate it, only estimate it from all the data.

[9] In the sense of less built-in error

[10] You will recall that the trapezoidal rule assumed that the two table values involved in a single strip were fit by a straight line.

[11] This isn't quite true. The values occur in triples and the two strips in each triple of values must be evenly spaced. But different triples can have different spacing inside.

with the derivative being evaluated at some point in the interval. For the total range, the number of "strips" is $(b-a)/2h$, and so the total error is:

$$\epsilon_T = \frac{b-a}{2h}\epsilon = \frac{1}{180}h^4(b-a)\frac{d^4f(x)}{dx^4} \tag{9.10}$$

Thus Simpson's rule is sometimes referred to as a *fourth order* method. The error terms don't usually mean much if one is dealing with a table because what you've got is what you've got. But it does show one thing: if the data in the table really comes from a cubic equation or one of lesser order, the derivative is zero and the method is exact. But then, if you knew that you could easily find the cubic and simply integrate *that* instead.

9.2 Functions that Have No Antiderivative

The major difference between integrating functions that have no antiderivative (and hence no indefinite integral) and those functions given only in tabular form is this: one can evaluate such functions at any point one desires. A number of very fancy and formerly heavily used integration schemes (many associated with the name Gauss) are based on this. They require picking special points in the range to be integrated. These methods are highly accurate and were very popular when things were done by hand.

But they provided no easy estimate of error. Sure, there was a theoretical error associated with them, just as there is with the trapezoidal and Simpson's rules, but that was only infrequently useful.

With the advent of computers the standard way of checking an integral was to simply use more and more points until the value of the integral did not change by much. The user could set the acceptable error to whatever value he or she liked.

Believe it or not, most modern integration routines today use something very simple, such as Simpson's rule or, even more often, the trapezoidal rule. And the technique can also be used on a programmable calculator or even by hand.[12]

The basic idea is as I've said. Use say n points in the trapezoidal rule and get an answer, A_1. Then use an additional n points and get an answer A_2. Repeat until the difference between successive answers is small enough.[13]

To see how this works let's take a concrete example. We'll do the integral:

$$A = \int_0^{1.28} \tan(x)dx \tag{9.11}$$

Here's what the function looks like: which looks nice enough, but as x increases toward $\pi/2$, $\tan x$ heads for infinity. Of course 1.28 radians isn't quite $pi/2 = 1.5707963$ radian, but it is hard to approximate this curve by a polynomial. So let's see.

[12] A perfectly good way to use the trapezoidal rule in this manner is by using a spreadsheet. These are often supplied with computers using Microsoft, Apple, or Linux machines.

[13] But be warned. If one keeps subdividing the integration range eventually round-off error will start to predominate. If that happens you have gone too far...

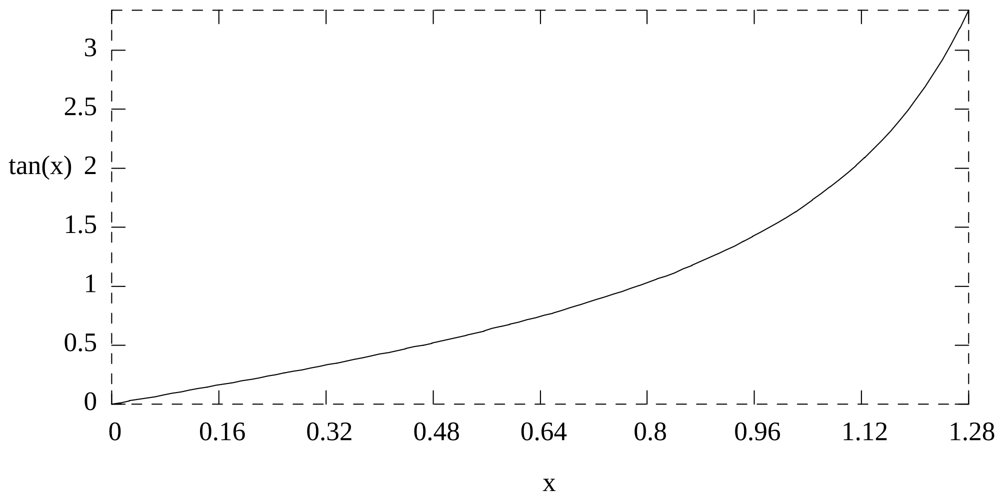

Figure 9.1: The Tangent from 0 to 1.28 Radians

n	θ	$\tan\theta$	1.28	0.64	0.32	0.16	0.08
0	0.00	0.00000	0.00000				
1	0.08	0.08017					0.08017
2	0.16	0.16138				0.16138	
3	0.24	0.24472					0.24472
4	0.32	0.33139			0.33139		
5	0.40	0.42279					0.42279
6	0.48	0.52061				0.52061	
7	0.56	0.62695					0.62695
8	0.64	0.74454		0.74454			
9	0.72	0.87707					0.87707
10	0.80	1.02964				1.02964	
11	0.88	1.20966					1.20966
12	0.96	1.42836			1.42836		
13	1.04	1.70362					1.70362
14	1.12	2.06596				2.06596	
15	1.20	2.57215					2.57215
16	1.28	3.34135	3.34135				

Table 9.2: Values for the Integration of equation 9.11

Table 9.2 is the result of a computation I did. I started with the two end-points, 0 radians and 1.28 radians. The distance between them, h, was 1.28. Their sum, divided by two since they are the endpoints, and multiplied by h gave an estimate for the integral of 2.13846, which is probably not very good. If we look at the graph, Figure 9.1 we see that a line between the end-points always lies *above* the curve. So the integral is certainly less than 2.13846. Of course, I didn't expect this to be a very good estimate.

This data is in the column headed "1.28" in Table 9.2.

Next I added a data point in the middle, at 0.64 radians. That's in the column headed "0.64" . To get the new estimate all I had to do was add this to half the sum of the first column and multiply by

0.64. The half, of course, comes from the first column being the end-points. The result is 1.54574, which is certainly better. I then added a third column, headed "0.32" and added that to the sum of the other columns[14] and multiplied that sum by 0.32. The result now is 1.33599, surely a better value but still too far from the previous estimate. So we do this again in the column headed "0.16" and get 1.27241. We seem to be converging toward an answer, but very slowly.[15] The final answer is likely 1.2 something, but what?

So we do it once more with h = 0.08 and now get an estimate of 1.25517. This actually differs from the best answer by only 0.006 so one more shot ought to do it.

I've summarized this processing:

$h =$	1.28	0.64	0.32	0.16	0.08
column sum =	3.34135	0.74454	1.75975	3.77758	7.73713
estimate =	2.13846	1.54574	1.33599	1.27241	1.25517

Table 9.3: Tabulated Results from Table 9.2

Now, I've not gone through all this tedium for nothing. And if you've followed along you will be rewarded too. I've got two surprises. The first isn't much of a surprise. The integral, equation 9.11 can be done. It is, in fact

$$A = \int \tan(x)dx = -\ln\cos(x) \tag{9.12}$$

or, in our case

$$A = \int_0^{1.28} \tan(x)dx = -\ln\cos(1.28) = 1.2492659 \tag{9.13}$$

to 7 decimal places. Compare this to the values in Table 9.2 and see that we've not done too well, having an error of 0.006.

The third surprise is that we can do better with very little extra work. How? If we plotted our answers we could *extrapolate* them to an h of zero[16] and get a better answer. Turns out that a fellow named Romberg worked out a way to do this back in 1955. One makes a table[17] Here's how it starts:

0
2.13846
1.54574
1.33599
1.27241
1.25517

Table 9.4: Start of the Romberg Extrapolation

which you will recognize as the results we got from our attempts to get a good answer. We now fill in a column just to the left of this one using the following formula:

$$c = \frac{4^k b - a}{4^k - 1} \tag{9.14}$$

[14]Remembering always to take *half* of the first column.
[15]Remember, in spite of its apparent smoothness, this is not an easy function to numerically integrate.
[16]In the sense of an infinitesimally small h.
[17]NO! NOT ANOTHER TABLE!!!! <groan> .

where c is the new table entry, b is the already existing table entry just to its left, and a is the already existing table entry just above b. The value of k is the number at the head of the column, which is now 1 as can be seen in Table 9.2

0	1
2.13846	
1.54574	1.34817
1.33599	1.26607
1.27241	1.25121
1.25517	1.24943

Table 9.5: Second Step of the Romberg Extrapolation

The value at the bottom of the new column is a *better* estimate of the integral. In fact it is off by only 0.0002, which is more than 10 times better than our best answer, 1.25517. But we are not done. We can do this extrapolation again to fill in column 2. And even that isn't the end of it, we can go until we run out of values. I've done this in Table 9.2

0	1	2	3	4
2.13846				
1.54574	1.34817			
1.33599	1.26607	1.26060		
1.27241	1.25121	1.25022	1.25006	
1.25517	1.24943	1.24931	1.24930	1.24929

Table 9.6: The Full Romberg Extrapolation

I remind you that the best answer is 1.2492659. So the Romberg extrapolation has given us that answer with an error of 0.00002 (or, as is said, two in the last decimal place) with only 16 evaluations of the function to be integrated across a very large range.

This is a very powerful technique. It can easily be done with pencil and paper and one can do the extrapolation as one goes along. The answers get better as you go down in a column and to the right across a row.

Problem Set 9.1

Integrate the following numerically. The answers are given so that you can check your work.

1.
$$\int_0^1 x\ln(1+x)dx = 1/4$$

2.
$$\int_0^{2\pi} \frac{dx}{1+(1/2)\cos(x)} = \frac{2\pi}{\sqrt{3/4}}$$

3.
$$\int_0^1 x^4(1-x)^3 dx = \frac{1}{60}$$

Topic 10

Multiple Integrals

Just as there are derivatives of functions of multiple variables, there are integrals of functions of multiple variables. But, while differentiation was (relatively) simple,[1] integration is more complex. This is because there are a number of *different* kinds of multiple integrals. In single-variable calculus, an integral was essentially an area under a curve. When dealing with a function of two variables, an integral *might* be a volume inside a surface, or it might be an area under a line that moves in three dimensions.[2] In this section I will talk about the first kind of integral, the volume under a certain surface.

The *definition* of this kind of **multiple integral** can get complex. I'm not going to go into detail. Suffice it to say that it can be defined in a manner analogous to a "single" integral. In particular, let me deal with a function of two variables, x, and y, i.e:

$$z = f(x, y)\,, \tag{10.1}$$

where $f(x, y)$ is a two-dimensional surface in three-dimensional space. Now imagine that under this surface are a very large number of columns reaching all the way down to the x, y plane.[3] These columns, we will imagine, fill up the entire volume under the surface. The integral has a boundary, which may indeed be at infinity, but in general will be some closed region in the x, y plane. The columns are all inside this region.

What we need to do next is simple. The bases of the columns are very small, so small that they can be treated as rectangles of sides Δx and Δy. And again, the columns are assumed to be small enough that the surface is a plane with an average height of $f(x, y)$. Then the volume of one of these columns is

$$\Delta V = f(x, y)\Delta A = f(x, y)\Delta x \Delta y\,, \tag{10.2}$$

where ΔV is the volume and ΔA is the area of the base of the column such that $\Delta A = \Delta x \Delta y$. One intuitive way to define the integral over $f(x, y)$ then is:

$$I = \lim_{\text{all } \Delta A_i \to 0} \sum_i f(x_i, y_i)\Delta A_i\,, \tag{10.3}$$

[1] There I go again. Who says any of this is simple?

[2] I *know* that sounds confusing, but it turns out to be important in thermodynamics. We will take up the subject soon.

[3] Or up to it, if the surface is below the x, y plane.

where each column is numbered i. Equation 10.3 simply says that the integral is the sum of the volumes of all of the columns as the number of columns goes to infinity and the area of the bases of *all* the columns goes to zero.[4] In that limit, $\Delta x \to dx$, $\Delta y \to dy$ and the sum becomes an integral:

$$I = \int_A f(x,y)dxdy\,, \tag{10.4}$$

where A is the area in the x, y plane over which the integral is taken. There are the usual bunch of limitations on this. The limit must exist, x and y must lie within their ranges, etc. In general as long as $f(x,y)$ is continuous there will be no trouble.[5]

Now all of this is neat, but how do we actually *do* a multiple integral? Again, I'm going to skip the proof, but a multiple integral can be evaluated as an **iterated integral**. That is:

$$I = \int_A f(x,y)dxdy = \int_a^b \int_c^d f(x,y)dxdy\,. \tag{10.5}$$

The thing on the right is the *iterated integral.* It is evaluated by first pretending that y is a constant and just doing the integral on x. The result will, of course, be a function of y, but *not* of x. Then, integrate on y. The result will be a constant, the value of the integral.[6] Thus the iterated integral is two successive single integrals.

This extends easily to integrals with more variables. An integral over $f(x,y,z)$ becomes a *triply* iterated integral, and so on.[7]

There's one other not too minor point. Which set of limits goes with which integration? Gans's very own definition is the *nested* definition. In equation 10.5 the limits c and d go with the x integration while a and b go with the y integration.

Here's an example of integration. Let's evaluate

$$I = \int_1^2 \int_3^4 x^2 y dxdy = \int_1^2 \left[\int_3^4 x^2 y dx\right] dy \tag{10.6}$$

Now we do the inner integral first, pretending y is a constant. It is:

$$g(y) = \int_3^4 x^2 y dx = \frac{1}{3}x^3 y\Big|_3^4 = \frac{1}{3}\left(4^3 y - 3^3 y\right) = \frac{55y}{3}\,. \tag{10.7}$$

We now do the second integral,

$$I = \int_1^2 g(y)dy = \int_1^2 \frac{55y}{3}dy = \frac{55}{3}\frac{1}{2}y^2\Big|_1^2 = \frac{55}{2}\,. \tag{10.8}$$

In the example above, the region of integration was a rectangle running from $x = 3$, $y = 1$ to the diagonally opposite corner at $x = 4$,$y = 2$. Things can be more complex than this. The limits can

[4]The reason for all this obfuscation is to avoid the pathological cases in which one or two of the columns remain finite while all the others have base areas that go to zero.

[5]In fact, even this can be relaxed somewhat and $f(x,y)$ can indeed even go to infinity at a few points *provided* that the area under the surface remains finite. Again, if you wish more information, consult your local Calculus book.

[6]Of course, the naming of the letters is arbitrary. And you certainly may integrate on y first and then x, if that is easier.

[7]In fact, the word "iterated" is often left out and the thing is just called a *double integral* or a *triple integral.* This is unfortunate, since there is, in fact, a technical difference between the *integral* and an *iterated integral.* But that difference will never worry us in this course.

be equations as well. Here's an example of that.

$$I = \int_0^1 \int_0^{y^2} x^2 y dx dy \,. \tag{10.9}$$

We evaluate the inner integral first:

$$g(y) = \int_0^{y^2} x^2 y dx dy = \frac{1}{3} x^3 y \Big|_0^{y^2} = \frac{1}{3} y^7 \,. \tag{10.10}$$

Check that out to make sure you understand it.[8] Now we do the outer integral:

$$I = \int_1^0 g(y) dy = \frac{1}{3} \int_0^1 y^7 dy = \frac{1}{24} y^8 \Big|_0^1 = \frac{1}{24} \,. \tag{10.11}$$

So iterated integrals are really just special cases of "ordinary" one-dimensional integrals. All one needs is patience. Do the integrals one at a time and all will be well.

Problem Set 10.1

Evaluate the following integrals:

1. $\int_0^1 \int_0^1 xy dx dy$
2. $\int_0^1 \int_0^{1-y^2} \left[(x-1)^2 + y^2\right] dx dy$
3. $\int_0^a \int_{a-x}^{\sqrt{a^2-x^2}} y dy dx$
4. $\int_{-1}^2 \int_{x+2}^x dy dx$
5. $\int_a^b \int_{x^2}^7 y dx dy$

---

[8]The term x^3 becomes y^6 when y^2 is substituted for x. The "other" y makes it y^7.

Topic 11

Line Integrals and Path Independence

Now we get to deal with something a bit more esoteric,[1] and quite important in thermodynamics. We get to talk about integrals that are the areas under a line in three (or more) dimensional space. These are called, strangely enough, **line integrals**. Figure 11.1 shows an example of a curve in space, its "shadow" on the x, y plane, and the area between the curve and its shadow.

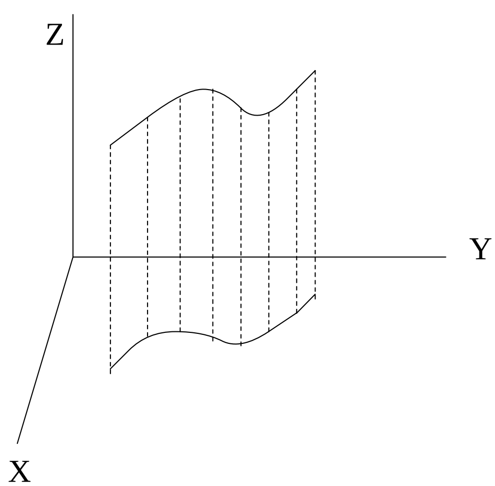

Figure 11.1: A Line Integral

Line integrals are written in a strange notation:

$$\int_C [f(x,y)dx + g(x,y)dy] \ , \tag{11.1}$$

where C indicates that the integral is along a *contour* or line, and $f(x,y)$ and $g(x,y)$ are functions of the independent variables x and y. If there were three independent variables, equation 11.1 would

[1] Lucky us...

have three terms.[2]

Doing integrals of the form of equation 11.1 isn't really hard. In fact, it is often so easy that folks feel that they are doing something wrong. They aren't.[3]

To begin with, you *cannot* do a line integral unless you know the line or path along which the integral is to be done. A glance at Figure 11.1 will demonstrate that need. So in addition to the integral itself you also *must* have an equation, the equation of the line under which the integral will be taken.[4] This equation is known as the *path*. The path is what makes line integrals easy. Line integrals only *look* like they depend on two variables. They really don't. They depend only on one. The *path* provides a relationship between the two variables, so they aren't both independent. The line us usually specified either by an equation, or sometimes by a set of equations. For instance let us evaluate the line integral

$$I = \int_C \left[xydx + x^2ydy\right], \tag{11.2}$$

along the line[5] $x = 2y$ from the point (2,1) to the point (4,2). We now know a starting point, an ending point, and the path connecting them.[6] The equation tells us that at every point at which we evaluate equation 11.2, x will be equal to $2y$. So I can replace x everywhere it occurs by $2y$, or, correspondingly y by $x/2$. Either way, I'm left with only *one* variable.

In fact, although I've not said it so far, integrals such as equation 11.1 or equation 11.2 can be broken into two parts:

$$I = \int_C xydx + \int_C x^2ydy\,. \tag{11.3}$$

And we can do different substitutions in each part. Let us remove the y in the first integral by replacing it with $x/2$. Then that integral depends only on x. Too, we can get rid of the $xsup2$ in the second integral by replacing x with $2y$. Then that integral will depend only on y:

$$I = \int_2^4 \frac{x^2}{2}dx + \int_1^2 4y^3dy\,. \tag{11.4}$$

That's it! We are now left with two plain ordinary integrals to do.[7] They evaluate simply to 6 + 252 or 258.

It sometimes happens that one of the two terms in a line integral is missing. That doesn't matter, it is still a line integral. For instance

$$I = \int_C ydx\,, \tag{11.5}$$

on the line $y = e^x$ from (0,1) to (1,e) is evaluated just as the example above, but we've got only one term. So equation 11.5 becomes (making the obvious substitution)

$$I = \int_0^1 e^x dx = e^x\big|_0^1 = e - 1\,. \tag{11.6}$$

[2]This would also be a bit more complex. We would be talking a more complex geometry, but the method of integration would be the same. For now we will stick to two independent variables.

[3]At least not usually.

[4]You should interpret the word "equation" here loosely. The "equation" can be a verbal description which *you* will have to reduce to mathematics.

[5]Let me remind you that the C in the integral 11.2 simply means *contour*, or line. It's a quick way to show that we are dealing with a line integral and not the more ordinary sort of integral such as a double integral.

[6]One thing that you must **always** do is to check that the starting and ending points actually lie on the given line. You'd be surprised how often an error has been made and they don't!

[7]You will have seen that in equation 11.4 I've put in the starting and ending points of the path as limits on the integrals, because they *are* the limits on the integrals.

Another point. Sometimes it is necessary to change the integration variable. This is done in the usual way. If, for instance, we were integrating

$$I = \int_C x dy\,, \tag{11.7}$$

on the line $x^2 = y$ from (0,0) to (1,1), we *could* get rid of the x by substitution, but we'd have to integrate $y^{1/2}dy$. Instead we could simply change dy to $2xdx$ and integrate on x instead, giving $I = 2/3$ as the answer.[8]

I know that your heads hurt at this point. You signed up for a course in physical chemistry and I'm ruining your brain with Simpson's Rule and line integrals. What has *any* of this to do with thermodynamics? Well, many of the integrations we do in thermodynamics are in fact line integrals. To illustrate I'll work out a few examples from thermodynamics.

For instance: One mole of an ideal gas is expanded adiabatically against a constant external pressure of 1 atm from an initial volume of 10 liters to a final volume of 100 liters. How much work is done? Think about this. Is it a line integral? We have a path, it is $p = 1$. The path starts at $p = 1$ and $V = 10$ and ends at $p = 1$ and $V = 100$. The equation to be integrated is:

$$dw = -pdV\,. \tag{11.8}$$

What are the variables? Clearly p and V. The line integral is really

$$w = \int_C [-pdV + 0dp]\,. \tag{11.9}$$

It is easy enough to solve this; we need to eliminate either p or V, and p is the easiest, since it is simply 1. Thus we have:

$$w = \int_{10}^{100} dV\,, \tag{11.10}$$

which gives 90 liter-atm for the work.

Here's another: Find the work done by an ideal gas when it starts at $p = 1$ atm, $T = 300$ K, is reversibly heated at constant pressure to a temperature of 400 K, and is then reversibly expanded isothermally to a final pressure of 0.1 atm. Can we do this problem? Hmm. The equation to be integrated is, as usual

$$dw = -pdV\,, \tag{11.11}$$

and we have to get rid of p again. But the path isn't a simple formula! What do we do?[9] The given path is in two segments. The first segment is $p = 1$, the second is $T = 400$. So we can break the problem into two parts, one involving a change in T, the other a change in p. But we don't know the starting and ending points![10] The gas is ideal, so the initial conditions correspond to a volume of $V = 300R$. At the end of the constant pressure expansion we will have $V = 400R$. And the final state is $V = 4000R$.[11] So the first segment integral is:

$$w_1 = \int_{300R}^{400R} 1dV = 100R\,, \tag{11.12}$$

[8] Don't take my word for it, work it out!

[9] Well, we could crunch up our eyes real tight and bang our fists on the table real hard, or we could pull our hair, but that hurts. Or we could think about it. Nah! That's much too hard! Lets just keep reading 'cause Gans will give us the answer without our having to strain a single brain cell...

[10] More trouble. If you think it is easy sitting here trying to do all these computations while attempting to write readable English at the same time, well, YOU write out the class notes...

[11] Try working these out. They are just applications of the ideal gas law.

and the second segment is:

$$w_2 = \int_{400R}^{4000R} pdV\,. \tag{11.13}$$

Now what do we do? We've got to convert the p to something we can use! We can't integrate it the way it stands.[12] But we do know that the process is isothermal! Along an isothermal path $p = nRT/V = 400R/V$. So we have

$$w_2 = \int_{400R}^{4000R} \frac{400R}{V} dV = 400R \ln 10\,. \tag{11.14}$$

And the final value of the work is $w = 100R + 400R \ln 10$.

This is a good spot to say again: line integrals depend not only on the integral, but on the path (line) taken between the starting and ending points.

After having said that, *some* line integrals are *independent* of the path. More exactly, they give the same value for *any* path. They depend only on the starting and ending points. For instance

$$I = \int_C 2xydx + (x^2+1)dy\,. \tag{11.15}$$

from (1,0) to (2,1) along the line $x = y+1$. This is easy to evaluate using $x = y+1$ and $y = x-1$:

$$I = \int_1^2 [2x(x-1)]\,dx + \left[(y+1)^2+1\right] dy\,, \tag{11.16}$$

Evaluation of the integrals isn't too hard,

$$I = \int_1^2 (2x^2-2x)dx + \int_0^1 (y^2+2y+2)dy\,. \tag{11.17}$$

Doing the integrals yields

$$I = \left[\frac{2}{3x^3} - x^2\right]_1^2 + \left[\frac{1}{3y^3} + y^2 + 2y\right]_0^1 = 5\,. \tag{11.18}$$

You should work out that example in detail to make sure that you understand it. If you do, then you can go on to the next example, which is the *same* integral between the same two points, this time done along the line $x = y^2+1$. The integral to be evaluated is equation 11.15, only now we have a *different* path equation. Looking at the first integral in equation 11.15, you should be able to see a problem. If we use the path to get rid of the y term, we'll be replacing y with $(x-1)^{1/2}$. I don't know about you, but I don't like to integrate square roots.[13] But there is a way out. We can convert the first integral in equation 11.15 to an integral over y by doing a *change of variable.* Then we'll get rid of the x easily. For dx we only need note that if $x = y^2+1$, then $dx = 2ydy$. With this in mind equation 11.15 becomes:

$$I = \int_0^1 2(y^2+1)y \times 2ydy + \int_0^1 (y^2+2)dy\,, \tag{11.19}$$

where I've not forgotten to change the integration limits on the first integral.[14] This slightly messy beast becomes

$$I = \int_0^1 4(y^4+y^2)dy + \int_0^1 (y^2+2)dy = 4\left[\frac{1}{5}y^5 + \frac{1}{3}y^3\right]_0^1 + \left[\frac{1}{3}y^3 + 2y\right]_0^1, \tag{11.20}$$

[12] This is an important point. We do *not* know, from equation 11.13 alone, how p varies with V.

[13] Among other reasons, one often gets *two* answers, corresponding to the positive and negative square roots.

[14] Because we are now integrating over y, not x.

which, believe it or not, evaluates to 5.

Although it is quite clear that I've beaten this subject to death,[15] There's one more example you need to see.[16] Let's do the same integral, equation 11.15, between the same starting and ending points, but this time along a path that is *continuous*[17] but which has a sharp angle in it. Let us integrate from the point (1,0) out along the x-axis until we come to $x = 2$, keeping y constant at 0 along the way. Now we'll take a right-turn and keep x constant at 2 while we integrate from $y = 0$ to $y = 1$.[18] So how do you do the integral for a path where there *isn't* an equation?

Ah, it is true that there is not a single equation for the path, there are *two*! The first is $y = 0$ while x goes from 1 to 2, and the second is $x = 2$ while y goes from 0 to 1. We can break equation 11.15 into *two* integrals:

$$I = \int_{(1,0)}^{(2,0)} 2xydx + (x^2 + 1)dy + \int_{(2,0)}^{(2,1)} 2xydx + (x^2 + 1)dy\,. \tag{11.21}$$

These are now, in fact, easier than the others![19] Why? Because in the first integral y is 0. When we substitute that value the first integral is:

$$I_1 = \int_{(1,0)}^{(2,0)} \left[0dx + (x^2 + 1)dy\right]\ , \tag{11.22}$$

which is *zero*! The first part is clearly zero, and the second part is zero because y doesn't change.[20] So I_1 is zero.

Now for the second leg of this path. Now we have

$$I_2 = \int_{(2,0)}^{(2,1)} 4ydx + (2^2 + 1)dy\,, \tag{11.23}$$

where now I've substituted 2 for x. Again the first part of this is zero since x is constant. The only thing left is the evaluation of the very complex integral

$$\int_0^1 5dy\,, \tag{11.24}$$

which, I think you will agree, again gives 5.

So, when all the fuss died down, in the broken path example, we had to do *four* integrals, three of which were obviously zero and the fourth was the complicated integral 11.24. Not bad, eh?

But the more important point[21] is that in all three examples, each using a different path, the integral had the *same* value! The value of this integral is *independent* of the path. It depends only on the starting and ending points.[22] I haven't really proven that this integral is independent of path. This

[15] I can telepathically feel this paper shake in fear as you read this.
[16] Because the path in this example is typical of the kinds of paths one finds in thermodynamics.
[17] The path, as far as this course is concerned, must *always* be continuous.
[18] I *told* you it was a weird path.
[19] We teachers always say that, don't we?
[20] Technically, in the second part x will be changed to its equivalent in y as given by the path. The resulting integral will have only y's in it. Now the upper and lower limits on the y integral are the same, 0, so the integral is zero. Most folks prefer to simply remember that if y is constant, dy is zero and so is the integral.
[21] You did remember the subject, didn't you? Hmmm, I thought not.
[22] Just like a thermodynamic state function!!! Boy, are you surprised!!!

is just an example. You are at liberty to try your own path.[23] But such things exist and can be proven to exist. Indeed, I will let you in on a secret. Look at the function:

$$F(x, y) = x^2y + y\,, \tag{11.25}$$

and at its total derivative:

$$dF = 2xydx + (x^2 + 1)dy\,. \tag{11.26}$$

Look familiar? The thing we've been integrating is the total differential of $x^2y + y$. We could have done the entire thing this way:

$$I = \int_{(1,0)}^{(2,1)} 2xydx + (x^2 + 1)dy = \int_{(1,0)}^{(2,1)} d(x^2y + y) = \left[x^2y + y\right]_{(1,0)}^{(2,1)} = 5\,, \tag{11.27}$$

where the integral is evaluated by using 1 and 2 for the lower and upper limits on x and 0 and 1 for the same on y. Note that there is no need for a path. We have an antiderivative for this integral.

But remember, not all functions that *look* like total derivatives *are* total derivatives. There is no guarantee that any old line integral you think up will actually be the derivative of anything in particular. Those integrals depend on path. The ones that are total derivatives[24] do *not* depend on the path. Their value is always the same.

So we have something entirely new. There are two kinds of line integrals. Those that are independent of path and those that are not. Corresponding to them we have two kinds of differentials, those that are total differentials of some function and those that are not. The former have line integrals that are independent of path. The latter do not. In fact, the differentials that are total derivatives of some function are known as **exact differentials**. The others are known as **inexact differentials**.

I think you all will see that there is a direct connection between exact differentials and thermodynamics. Thermodynamic state functions are *exact differentials*. In fact, the First Law of Thermodynamics could be stated:

The internal energy is an exact differential

Thus the change in internal energy between two states is automatically *independent of path*. Further, if the initial and final states are the same, the change in internal energy *must* be zero, a statement better known as the *Law of Conservation of Energy*.

Problem Set 11.1

1. Find the value of
$$\int_{(0,0)}^{(1,3)} \left[x^2dx + (x^2\ -\ y^2)dy\right]\,,$$
along the lines (a) $y = 3x^2$ and (b) $y = 3x$.

2. Find the value of
$$\int_{(0,0)}^{(1,1)} \left[\sqrt{y}dx + (x - y)dy\right]\,,$$
along the following curves: (a) $x = y$, (b) $x = y^2$, and (c) $x = y^3$.

[23] If you really want to suffer and have serious academic sins to atone for, try this path: $x = -2.17534265\cos(y) + 3.17534265$. Enjoy. The answer is 5.

[24] And so have antiderivatives.

3. The volume of an ideal gas can be regarded as a function of p and T for a fixed number of moles. The total derivative of $V(p,T)$ is

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \,,$$

where the partial derivatives are easy to evaluate using the ideal gas law. Integrate this expression along the line $p = T/300$ from $p = 1$, $T = 300$ to $p = 10$, $T = 3000$.

Topic 12

Exact and Inexact Differentials

In a previous section we saw that certain line integrals were *independent* of the path of integration, while most line integrals are not. Indeed, we saw that the line integral from a to ba

$$I = \int_C \left[f(x,y)dx + g(x,y)dy \right] , \tag{12.1}$$

is independent of path if there is a function $F(x,y)$ such that

$$dF(x,y) = f(x,y)dxg(x,y)dy \, . \tag{12.2}$$

In other words, *the integral is independent of path if the integrand is the total derivative of some function*. That statement needs thinking about. If the integrand in equation 12.1 *is* the total differential of some function, then it can be written:

$$I = \int_C dF(x,y) \, , \tag{12.3}$$

which integrates instantly into

$$I = F(x,y)\Big|_a^b \, , \tag{12.4}$$

which, of course, depends only on the endpoints a and b of the path. Differentials whose line integrals are independent of path are called **exact differentials**.

But, if the integrand in equation 12.1 is *not* the total differential of any function,[1] then the simplification in equations 12.3 and 12.4 are not possible. And then to do the integral one must know the path. Such differentials are called **inexact differentials**.

The obvious question is "how do I tell if a given integrand is a total derivative or not?"[2] One possibility is to simply try different functions until you either (a) find the parent function or (b) get very discouranged.[3] A better way is to have a theory.[4]

[1] Which, of course, is the common case. If you pick two functions of $f(x,y)$ and $g(x,y)$ at random, the odds on their being part of a total derivative are clearly very small.

[2] Hey, if you don't ask questions, you'll never get *any* answers!

[3] Sincere practitioners of life will have already discovered that guessing is a bad way to go about things. Knowledge gives one an edge, and that's why you are studying this material!

[4] It also helps if the theory is correct...

Let us take the total differential of a function $F(x, y)$. This gives[5]

$$dF(x,y) = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy\,. \tag{12.5}$$

Now it is a curious fact[6] that mixed second partial derivatives of a function, under very general conditions, are equal. In symbols that means:

$$\left(\frac{\partial^2 F}{\partial y \partial x}\right) = \left(\frac{\partial^2 F}{\partial x \partial y}\right)\,. \tag{12.6}$$

Or, in words, the order in which you differentiate F with respect to x and y isn't important. Here's an example: Let the function be

$$F(x,y) = y^2 \ln(x) + \sin(xy)e6{-}x\,, \tag{12.7}$$

then the two first partial derivatives are:

$$\left(\frac{\partial F}{\partial x}\right) = \frac{y^2}{x} + y\cos(xy)e^{-x} - \sin(xy)e^{-x}\,, \tag{12.8}$$

$$\left(\frac{\partial F}{\partial y}\right) = 2y\ln(x) + y\cos(xy)e^{-x}\,. \tag{12.9}$$

Differentiating equation 12.8 with respect to y

$$\left(\frac{\partial^2 F}{\partial y \partial x}\right) = \frac{2y}{x} + \cos(xy)e^{-x} - xy\sin(xy)e^{-x} - x\sin(xy)e^{-x}\,, \tag{12.10}$$

and equation 12.9 with respect to x

$$\left(\frac{\partial^2 F}{\partial x \partial y}\right) = \frac{2y}{x} - \cos(xy)e{-}x - xy\sin(xy)e{-}x - x\cos(xy)e^{-x}\,, \tag{12.11}$$

which is identical to equation 12.10.

Now our problem is solved. *If* the integrand in equation 12.1 is the total differential of some function $F(x, y)$, *then* it must be true that

$$f(x,y) = \left(\frac{\partial F}{\partial x}\right)\,, \tag{12.12}$$

and

$$g(x,y) = \left(\frac{\partial F}{\partial y}\right)\,. \tag{12.13}$$

And *if* these things are true, then the second mixed derivatives of $F(x, y)$ must be equal. The second mixed derivatives are $\partial f(x, y)/\partial y$ and $\partial g(x, y)/\partial x$. So what we have found is that *if*, in a line integral such as equation 12.1,

$$\left(\frac{\partial f(x,y)}{\partial y}\right) = \left(\frac{\partial g(x,y)}{\partial x}\right)\,, \tag{12.14}$$

then that line integral is independent of path.

[5]You will note that these are *formal* operations. We are not actually differentiating anything, just manipulating symbols.

[6]Which means that I'm not going to prove it.

What happens when there are more than two indepedent variables? The result is essentially the same. The mixed second derivatives of any function will be equal in pairs. For instance, the function $F(x, y, z)$ has the following equal mixed second derivatives

$$\left(\frac{\partial^2 F}{\partial x \partial y}\right) = \left(\frac{\partial^2 F}{\partial y \partial x}\right) \quad \left(\frac{\partial^2 F}{\partial x \partial z}\right) = \left(\frac{\partial^2 F}{\partial z \partial x}\right) \quad \left(\frac{\partial^2 F}{\partial y \partial z}\right) = \left(\frac{\partial^2 F}{\partial z \partial y}\right) . \tag{12.15}$$

For a three-variable line integral to be exact, all three equalities must hold.

Problem Set 12.1

Which of the following differentials are exact?

1. $ydx + xdy$
2. $y^2dx + x^2dy$
3. $[(x^2 + y^2)dx + 2xydy]$
4. $yzdx + xzdy + xydz$
5. $[nR/(V - b)]dT - [RT/(V - b)^2 - a/(V^3)]dV$

Topic 13

Exact Differentials and Thermodynamics

One way of stating the First Law of Thermodynamics is to say that the internal energy change dU is an exact differential. Put another way, the change in internal energy ΔU in going from one state to another is independent of path.

On the other hand, simple accounting tells us that

$$dU = dq + dw \,. \tag{13.1}$$

But it is easy to show that dw is *not* independent of path. For example, take the case of an ideal gas[1] confined to a cylinder and held in place by the usual frictionless, massless piston.[2] If a mass m is placed on top of the piston and if the pressure in the gas is sufficient to isothermally lift the mass through a height h, then the work done by the gas is

$$w = -mgh \,, \tag{13.2}$$

where g is the accelleration due gravity.[3] On the other hand, if *no* weight is placed on the cylinder, then no work at all is done. But the ideal gas in the cylinder goes from the same initial state to the same final state. So w *does* depend on the path (weight lifted).[4]

Now since we can write equation 13.1 as

$$dw = dU - dq \,, \tag{13.3}$$

and remembering that dU is exact, the only way dw can be inexact is if dq is inexact as well.

So, by a relatively simple application of the ideas we've previously developed, we have arrived at a conclusion regarding the heat of a process. The heat depends on the path. That's why ΔH was invented. ΔH is exact. It is defined as

$$H = U + pV \,. \tag{13.4}$$

[1]All requests for ideal gases should be passed to the Department of Chemistry stockroom...

[2]Such an apparatus can be requested at the Department of Physics stockroom...

[3]We are using the usual thermodynamic sign convention here.

[4]Here we see an interesting difference between the physical sciences and pure math. What we've done is demonstrated that what we think of as work does depend on the path. Therefore, any mathematical description of work must also depend on the path. For a pure mathematician we'd have to show *mathematically* that the work is an inexact differential.

Both p and V are exact as we can tell from experience. For instance increasing the volume of a system by one liter increases the volume by one liter, regardless of how we do it. A similar argument can be given for the pressure. Thus, with the entire right-hand side of equation 13.5 exact, H must be exact as well. And since, at constant pressure[5]

$$\Delta H = q \,, \tag{13.5}$$

then, at constant pressure the heat of a process *is* independent of path. What this really means is that if the process were done totally at constant pressure, ΔH would have a certain q. But since ΔH is independent of path and depends only on the end points, as long as we both start and end at the same pressure, the value of ΔH will be unchanged. The actual heat q would likely be different on each path, but no matter, we know what that heat would be if the process were done at constant pressure.

We can use the tools we've developed to do more. For an example let us consider the rather boring question:[6] does C_V vary with volume? Huh? I hear you say. $CsubV$ is the heat capacity at constant volume. How can something at constant volume vary with volume? Well, read on. .PP There is a famous apartment house[7] in Manhattan called Thermo House. The apartments in Thermo House are interesting. All the apartments on the first floor are *exactly* the same size. And all of the apartments on the second floor are *exactly* the same size. Indeed, all of the apartments on any given floor are *exactly*R the same size as all the other apartments on that floor. But, the apartments on the first floor are a *different* size than the apartments on the second floor. In fact, no two floors in Thermo House have the same sized apartments!

Now do you see why C_V can vary with volume? In Thermo House while all the apartments on a given floor have the same volume (size), the size differs with floor. When a system has a volume of 20.0 liters, C_V, per mole, might be 12.56 joules/mol-K. And at a volume of 21.0 liters, C_V per mole might be 12.58 joules/mol-K.

So it is legitimate to ask how $CsubV$ varies with volume. But how to calculate this?

Well, we can start with U as a function of T and V. In those terms we get:

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T \,, \tag{13.6}$$

and we know that the mixed second derivatives must be equal. So we know that

$$\left(\frac{\partial C_V}{\partial V}\right) = \left(\frac{\partial \pi_T}{\partial T}\right)_V \,, \tag{13.7}$$

where I have written π_T for $(\partial U/\partial V)_T$. So all we have to do is evaluate the right-hand side of equation 13.7 to answer our question.

How do we evaluate the right-hand side of equation 13.7. It can be done experimentally, but for us it will be more interesting to use various equations of state. To do that we must know π_T in more useful terms. It can be shown[8] that

$$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \,, \tag{13.8}$$

[5]And don't forget this limitation!
[6]Hey, I'm being realistic.
[7]Famous mostly because of the following example.
[8]By using the equality of second mixed derivatives on a thermodynamic function you don't know about yet.

which is just what we want. For instance, using equation 13.8 it is simple to show that $\pi subT$ is zero for an ideal gas. Then, for an idea gas we have

$$dU = C_V dT + 0dV\,, \tag{13.9}$$

and since any derivative of 0 is 0, we have shown that

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0\,. \tag{13.10}$$

or, that C_V is independent of volume for an ideal gas.

The Berthelot equation of state for gases is:

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{TV^2}\,. \tag{13.11}$$

From this we can discover[9] that

$$\pi_T = \frac{2a}{TV^2}\,, \tag{13.12}$$

and then, after differentiating this with respect to Ta

$$\left(\frac{\partial C_V}{\partial V}\right)_T = -\frac{2a}{T^2V^2}\,. \tag{13.13}$$

In this case you see that $CsubV$ *does* change with volume (albeit very slowly since the right-hand side is *almost* zero).

Of course, we've only scratched the surface of this subject here. But I hope that you've seen enough to understand that exact differentials are one of the fundamental mathematical bases for thermodynamics.

Problem Set 13.1

1. How does C_V for a van der Waals gas depend on volume?
2. Once you know that a given differential is independent of path (i.e., is exact) there are several ways to evaluate integrals involving that differential. For instance, given one mole of chlorine initially at 400.0 K and a volume of 20.0 liters, by how much does the internal energy change if we change the state of the gas to 650.0 K and a volume of 30.0 liters. Assume that chlorine is a van der Waals gas with $a = 6.579$liter^{2}atm/mol and $b = 0.05622$ liter/mol. $CsubV$ for chlorine is 37.03 + 0.00067 T - 2.85 × $10^5/T^2$.

[9] Work it out! Don't go lazy on me now!

Topic 14

Euler's Theorem

There are many Euler's theorems,[1] but only one beloved of students of thermodynamics. Before we can discuss the actual theorem and its use in thermodynamics we need some terminology unfamiliar to most chemists.

Let's look at a function of m variables

$$z = f(x_1, x_2, \ldots, x_m)\,, \tag{14.1}$$

and remember that $f(...)$ stands for a formula involving the m x's. Now let's play a game. Everywhere an x occurs we'll replace it with λx. We now have[2]

$$z = f(\lambda x_1, \lambda x_2, \ldots, \lambda x_m)\,. \tag{14.2}$$

If we can factor λ to some power (say n) out of the resulting formula we then say that the function $f(...)$ is *homogeneous* of degree n.

Here's an example: Consider the function of three variables

$$w = xyz + \frac{x^2y^2}{z}\,. \tag{14.3}$$

Now we replace each x, y, and z with λx, λy, and λz. We get:

$$w = (\lambda x)(\lambda y)(\lambda z) + \frac{(\lambda x)^2(\lambda y)^2}{(\lambda z)}\,. \tag{14.4}$$

[1]Leonhard Euler (pronounced "oiler") lived from 1707 to 1783. He was the son of a clergyman who showed an early aptitude for mathematics. He was sent to the University of Basel where he became the pupil of John Bernoulli, one of the famous Bernoulli brothers. In 1727 (the year Newton died) Euler set off for St. Petersburg where the Bernoullis had settled. In 1733 he took the Chair of Natural Philosophy there, later moving to Berlin at the invitation of Frederick the Great (yes, in those days rulers worried about mathematicians) and lived there until 1766, when he returned to St. Petersburg where he died in 1783. He became blind in his later years, working mathematics in his head and dictating the results to his pupils. His output was prodigious. Hundreds of his theorems and countless lesser results are still quoted in the literature. Perhaps Euler's relation $e^{ipi} + 1 = 0$, one of the most beautiful relationships in mathematics, is known to you.

[2]Note that λ is an *arbitrary* parameter. The best way to think about arbitrary parameters is to think of them as variables standing for some quantity to be specified later. For instance λ could later be 1 or 2 or whatever. If it is 1, it will effectively disappear and we are left with the original formula. Keep that in mind because that is exactly what we will do later.

We can indeed factor λ^3 out of each of these terms giving

$$w = \lambda^3 \left(xyz + \frac{x^2y^2}{z} \right) . \tag{14.5}$$

Thus, according to our definition, the function in equation 14.3 is homogeneous of degree 3.

A function can even be homogeous of degree *zero*, for example

$$w = \frac{x}{y} . \tag{14.6}$$

And, of course, most functions aren't homogeneous at all, such as

$$w = x + y^2 - 7 , \tag{14.7}$$

since, when you replace x and y with λx and λy all you get is

$$w = \lambda x + \lambda^2 y^2 - 7 , \tag{14.8}$$

which doesn't factor at all.[3]

Just to have it written down clearly, let me define **homogeniety** more mathematically:

DEFINITION 14.1 *A function of* $\boldsymbol{m}$ *variables* $x_1, x_2, \ldots, x_m$ *is called **homogeneous of degree*** $\boldsymbol{n}$ *if and only if*

$$f(\lambda x_1, \lambda x_2, \ldots, \lambda x_m) = \lambda^n f(x_1, x_2, \ldots, x_m) . \tag{14.9}$$

With that settled here's our Euler's theorem:

THEOREM 14.1 *If* $f(x_1, x_2, \ldots, x_m)$ *with continuous partial derivatives, is homogeneous of degree* n*, then*

$$x_1 \left(\frac{\partial f}{\partial x_1} \right) + x_2 \left(\frac{\partial f}{\partial x_2} \right) + \ldots + x_m \left(\frac{\partial f}{\partial x_m} \right) = n f(x_1, x_2, \ldots, x_m) . \tag{14.10}$$

The proof is easy enough. I normally don't burden you with proofs, but this one is actually beautiful.[4] Look at equation 14.10. There is nothing at all obvious about it. It *does* look almost familiar. If the left-hand side had dx's instead of x's it would equal df, the total derivative. But it *doesn't* have dx's and it isn't equal to a total derivative, it's equal to the original function!

So how does one prove such a thing? Well, the clue is that it applies to homogeneous functions. So we will use equation 14.9 in a slightly modified form.

Let's introduce a set of new variables:[5] x'_1, x'_2, etc., where $x'_1 = \lambda x_1$, and so on. Then we can write equation 14.9 as:

$$f(x'_1, x'_2, \ldots, x'_m) = \lambda^n f(x_1, x_2, \ldots, x_m) , \tag{14.11}$$

To prove the theorem, all we have to do is differentiate equation 14.11 with repect to λ and that's about it.[6]

$$\left(\frac{\partial f}{\partial x'_1} \right) \left(\frac{\partial x'_1}{\partial \lambda} \right) + \left(\frac{\partial f}{\partial x'_2} \right) \left(\frac{\partial x'_2}{\partial \lambda} \right) + \ldots + \left(\frac{\partial f}{\partial x'_m} \right) \left(\frac{\partial x'_m}{\partial \lambda} \right) = n\lambda^{n-1} f(x_1, x_2, \ldots, x_m) , \tag{14.12}$$

[3] Of course, *most* functions aren't homogeneous at all. But then, we aren't interested in those in this section.

[4] Yes, I know, mathematicians and thermodynamicists have weird notions of what the word *beautiful* means.

[5] You will see why later. Treat this as a mystery story and try to figure out how I'm going to do this.

[6] Whoa!, I hear you say. You can't do that! To which I reply, "why not?" This is an old and very worthwhile trick in mathematics. As long as I set λ equal to 1 in any final formula, this is perfectly OK.

where I have used the chain rule to differentiate the $x\prime$ with respect to λ. Two more simple steps and we are done. First, $\partial x_i'/\partial\lambda$ is simply x_i since $x_i' = \lambda x_i$. This gives:

$$\left(\frac{\partial f}{\partial x_1\prime}\right) x_1 + \left(\frac{\partial f}{\partial x_2\prime}\right) x_2 + \ldots + \left(\frac{\partial f}{\partial x_m\prime}\right) x_m = n\lambda^{n-1} f(x_1, x_2, \ldots, x_m)\,, \tag{14.13}$$

Now we have only to set λ equal to 1. This converts all remaning x_i' to x_i:

$$\left(\frac{\partial f}{\partial x_1}\right) x_1 + \left(\frac{\partial f}{\partial x_2}\right) x_2 + \ldots + \left(\frac{\partial f}{\partial x_m}\right) x_m = n f(x_1, x_2, \ldots, x_m)\,, \tag{14.14}$$

which is what we set out to prove.[7]

Problem Set 14.1

Which, if any, of the following functions are homogeneous, and, if they are, what is their order?

1. $f(x, y) = \sqrt{y^2 - x^2}\,\sin^{-1}(y/x)$
2. $f(x, y, z) = \sqrt{z/(x^2 + y^2}$
3. $f(x, y) = e^{x/y}$
4. $f(x, y) = x^2 + 2x + y^2$

---

[7]It leaves open, of course, the question "why do we care?" Ah, I do have my moments of mystery. *That* question will be answered in the next section.

Topic 15

Euler's Theorem and Thermodynamics

OK, enough. The utility of Euler's Theorem in thermodynamics is that the functions of thermodynamics are homogeneous functions of the extensive properties of a system. Indeed, any **extensive property** is a first degree homogeneous function of the other extensive properties of a system, while an **intensive property** is a zeroth degree homogeneous function of the extensive properties of a system.

To see how this works, the pressure of a van der Waals gas is given by:

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}\,, \tag{15.1}$$

where V and n are the extensive variables. If we substitute λV for V and λn for n, it is easy to see that the λ's cancel out. In other words, p is a homogeneous function of degree zero. Now this example doesn't prove that for all formulas for p, but it will always work out that way.

We can use this idea to decide which new thermodynamic functions are extensive and which are not. For example, what about the enthalpy H? It is defined by:

$$H = U + pV\,, \tag{15.2}$$

and, if we agree that U and V are extensive (p is intensive) it's clear that H is also extensive.[1]

The thermodynamics of single-component systems are fairly simple.[2] The thermodynamics of multiple-component systems are more comples.[3] Yet multiple-component systems are what chemistry is all about.[4] As an example, I'm going to look at the properties of the volume of a solution. To make it simple, it will be a *binary* solution. As independent variables I'll take the pressure, temperature, and the number of moles of each component. Then

$$V = V(p, T, n_1, n_2)\,. \tag{15.3}$$

[1] To see this more clearly, just multiply U and V by λU and λV and factor out the λ. What you get is $H = \lambda(U + pV)$, proving that H is homogeneous of degree 1.

[2] Sure, easy for *me* to say, right?

[3] See, we save this bit of news until it is too late to drop the course!

[4] Chemical reactions naturally involve more than one component...

The total differential of this volume is

$$dV = \left(\frac{\partial V}{\partial p}\right) dp + \left(\frac{\partial V}{\partial T}\right) dT + \left(\frac{\partial V}{\partial n_1}\right) dn_1 + \left(\frac{\partial V}{\partial n_2}\right) dn_2 \,. \tag{15.4}$$

The terms $\partial V/\partial n_1$ and $\partial V/\partial n_2$ occur so often they are given special names. They are each called the **partial molar volume** and given a special symbol. The symbol is a V with a subscript to indicate which derivative they represent. For the i'th component

$$\left(\frac{\partial V}{\partial n_i}\right) = V_i \,. \tag{15.5}$$

Be careful with this notation. If you miss the subscript you will think that the total volume is being used.[5] I'm going to be concerned with the variation of volume with composition. So I'm going to hold T and p constant from now on, so we can drop any variation in them. With this equation 15.4 becomes

$$dV = V_1 dn_1 + V_2 dn_2 \,, \tag{15.6}$$

which *looks* simple (but isn't).

Now let's look at this from the standpoint of Euler's Theorem. From that point of view (remembering that V is first degree homogeneous in the n's). According to Euler's theorem what we should do is this:

1. Write down the function involved (V) multiplied by the degree of homogeneity. So we have $1\,V$.
2. Now write an equals sign, giving us $1V =$.
3. And now write down each independent *extensive* variable multiplied by the derivative of the function with respect to that variable. These are terms like $n_1 \partial V/\partial n_1$. And there is one of them for *each* independent extensive variable.

The result is

$$V = n_1 V_1 + n_2 V_2 \,. \tag{15.7}$$

Don't take my word for it. Go back to Euler's Theorem and put in V for f and n for x.

Now let's form the derivative of equation 15.7

$$dV = n_1 dV_1 + n_2 dV_2 + V_1 dn_1 + V_2 dn_2 \,, \tag{15.8}$$

and compare that with equation 15.6. Indeed, let us subtract equation 15.6 from equation 15.8. We get:

$$n_1 dV_1 + n_2 dV_2 = 0 \,. \tag{15.9}$$

This is a completely non-obvious result of Euler's Theorem. It can (and will) be used to determine the change in one partial molar volume from a given change in the other.

But this is not all.[6] The partial molar volume is itself an intensive property. That is, it is a homogeneous function of degree zero in the numbers of moles that make up the system. We can see this if we recall equation 14.9

$$f(\lambda x_1, \lambda x_2, \ldots, \lambda x_m) = \lambda^n f(x_1, x_2, \ldots, x_m) \,.$$

[5] In some of the literature a bar above the letter is used as well as a subscript, $\bar{V}_i$. But this is no longer popular except with students who miss the subscript.

[6] It gets worse. It *always* gets worse.

and differentiate it with respect to, say, x_1, we get

$$\left(\frac{\partial\partial f(\lambda x_1, \lambda x_2, \ldots, \lambda x_m)}{\partial x_1}\right) = \lambda^n \left(\frac{\partial f}{\partial x_1}\right), \tag{15.10}$$

and, if we now divide through by λ we get:

$$\left(\frac{\partial f(\lambda x_1, \lambda x_2, \ldots, \lambda x_m)}{\partial \lambda x_1}\right) = \lambda^{n-1} \left(\frac{\partial f}{\partial x_1}\right) \tag{15.11}$$

But equation 15.11 is exactly what must be true of $\partial f/\partial xsub1$ if *that* quantity is to be homogeneous of degree $n-1$. Now since the volume is homogeneous of degree 1, then $\partial V/\partial n_1 = V_1$ must be homgeneous of degree 0.

Now we[7] can apply this to partial molar volumes. For example, if we apply Euler's Theorem to V_1 we get:

$$0 = n_1 \left(\frac{\partial V_1}{\partial n_1}\right) + n_2 \left(\frac{\partial V_1}{\partial n_2}\right). \tag{15.12}$$

Let's make sure we[8] know where this comes from. If we[9] go back to the recipe given above, we first write down the function (here V_1) times the degree of homogeniety. Since the degree of homogeniety is *zero*, we write down zero. We then write down an equals sign. Now we write down each of the independent variables (here n_1 and n_2) and follow them each with the differential of the function with respect tot that independent variable (here $\partial V_1/\partial n_1$, and $\partial V_1/\partial n_2$).

Now look at equation 15.12 for a while. Pay attention to the fact that it is V_1 that is always being differentiated.[10] And pay attention to the fact that the derivatives in equation 15.12 are the *second* derivatives of the volume, because

$$\left(\frac{\partial V_1}{\partial n_2}\right) = \left(\frac{\partial^2 V}{\partial n_1 \partial n_2}\right) = \left(\frac{\partial V_2}{\partial n_1}\right). \tag{15.13}$$

So we can conclude that

$$n_1 \left(\frac{\partial V_1}{\partial n_1}\right) + n_2 \left(\frac{\partial V_2}{\partial n_1}\right) = 0\,. \tag{15.14}$$

This equation is often used, though most often when it is divided through by the total number of moles. Doing that we get:

$$X_1 \left(\frac{\partial V_1}{\partial n_1}\right) + X_2 \left(\frac{\partial V_2}{\partial n_1}\right) = 0\,, \tag{15.15}$$

where the X's are *mole fractions*. This is a major result. It is often called the **Gibbs-Duhem Equation**, although, strictly speaking, that's only if we are talking about the Gibbs free energy.

Yes, what is true here about the partial molar volume is true of *every other partial molar quantity*, in particular the Gibbs free energy. In that case the equation is, in general:

$$X_1 \left(\frac{\partial \mu_1}{\partial n_1}\right) + X_2 \left(\frac{\partial \mu_2}{\partial n_1}\right) = 0\,, \tag{15.16}$$

[7] I *hope* you are still here, dear reader... Because if you aren't, I've made a real mess of explaining this, haven't I?

[8] Of course, the word *we*is a euphemism for *you*...

[9] See the previous footnote.

[10] Of course, we could have written a similar equation for V_2 or any other V_i if there were more components in the solution.

where μ_i is the partial molar Gibbs free energy with respect to the i'th compoent, or in more long winded symbols:

$$\left(\frac{\partial G}{\partial n_i}\right) = \mu_i\,. \tag{15.17}$$

Problem Set 15.1

1. Write the equivalent of the Gibbs-Duhem equation for the Helmholtz free energy.
2. The molar volume of pure methanol is 40 cc/mole. Also, the volume of a solution containing 1000 g of water and n moles of methanol is given by:

   $$V = 1000 + 35n + 0.5n^2$$

   Calculate the partial molar volume for methanol when the molality of the solution is 0 and also when the molality is 1.
3. The volume of aqueous sodium chloride solutions at 25°C is given by:

   $$V = 1001.38 + 16.6253m + 1.7738m^{3/2} + 0.1194m^2$$

   where m is the molality of the solution. Find V_{NaCl} (the partial molar volume of NaCl). Then use the "Gibbs-Duhem" equation to find $V_{\mathrm{H_2O}}$. The volumes are given in milliliters. Hint: assuming 1000 g of water, the answer is

   $$V_{\mathrm{H_2O}} = 18.08 - 0.015977m^{3/2} - 0.002151m^2$$

Topic 16

Least Squares

Physical chemistry is a strange mixture of abstract mathematics and practical problems. Of the two, the practical problems are likely the hardest.[1]

One typical example is making theory and practice work together. As the saying goes, in theory the two are the same. In practice, they are not. For example, let's say that you have a theoretical equation and some experimental data. Theory says that the data (here cleverly called x and y) is supposed to fit a straight line of the form:

$$y' = mx + b\,, \tag{16.1}$$

where x is the independent variable (i.e. the one you control) and y' is the resultant *correct* data point.

Unfortunately, you didn't get y' when you took your data. You actually got y, which is the correct value with some experimental error included.[2] In other words if you took data at various points y_i what you have is:

$$y_i = y_i' + \epsilon_i = mx_i + b + \epsilon_i\,, \tag{16.2}$$

where ϵ_i is the error included at each data point y_i.

Now what you've been asked to do[3] is some kind of magic on your data and find out what values of m and b will give a calculated value of y closest to the real value *yprime* for any value of y you choose. In other words, what are the *best* values of m and b to use?

The first thing to do is to find out if this is a reasonable request. The way to do that is to graph the data. Does it look like a straight line would go anywhere near the data points? Or does the data look like a a circle? If the data doesn't look anything like a straight line, don't bother even trying to find m and b. I've done that with some data in Figure 16.1 The data *looks* roughly straight. There's that second point from the left that looks a bit low, or is it that the first and third points are too high? Guessing is fun, but it won't get us anywhere... What we have to do is to find some impartial way of doing this.

Now most all of you have heard that what you need to do is called *least squares*. You can grub around in some book and find some least squares equations, plug your data into the equations and

[1] Life's like that, isn't it?

[2] You don't have experimental error? Your experiments are perfect each time? Wow! Can I have your autograph?

[3] Hey, nobody does this for the fun of it...

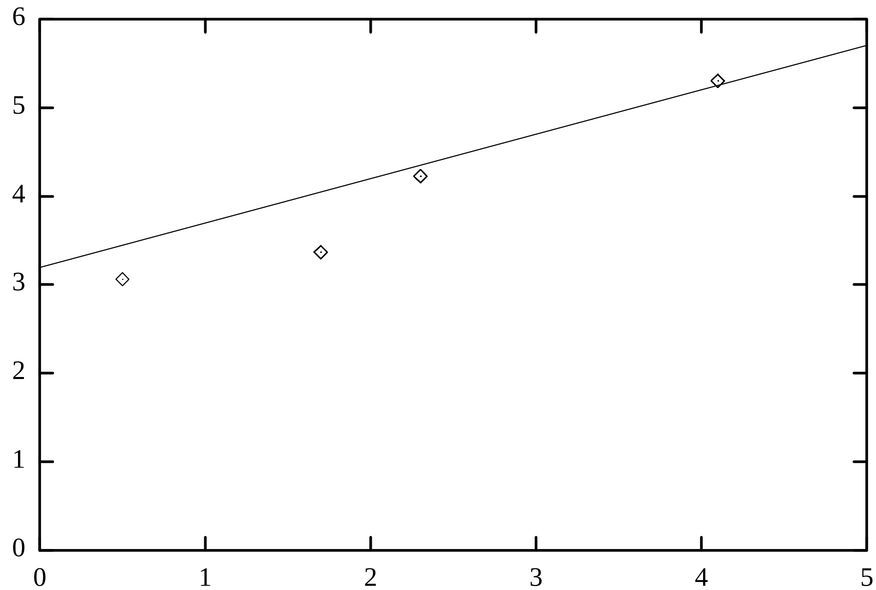

Figure 16.1: Data and a Random Line

come up with values of m and b. You'll have no idea where those equations come from or what assumptions have gone into them. Nor are you likely to care very much, after all, the job will be done.[4] However, it is a good thing to know that somewhere in your vast collection of college notes, texts, and other impedimentia you actually have the answer to that question. That's what this section is all about. Cherish it.

Let's have some data carefully made up for this example.[5]

x	y
0.5	3.064
1.7	3.369
2.3	4.225
4.1	5.304

Table 16.1: Some Arbitrary Data

This is the data plotted in Figure 16.1. Carefully hidden in those y values are the "true" values $y_i prime$ and the errors ϵ_i. In Figure 16.1 I've drawn an arbitrary straight line. Is that the line that the data should fit? Take a moment and think about it.

Ok, time's up. The line isn't really too good. It seems to be a bit too high. The right two points are quite close to the line, but the other two are 'way off. What we'd like is to somehow "split the difference" and try to find a line that lies as close as possible to all the points, even if it means lying a little further from some of them.

If we think about it for a moment it is the errors that keep the line from going through the points.

[4]This is reality. Do you want me to pretend that you lie awake at night tossing and turning wondering where the least square equations come from?

[5]Actually, it wasn't even *that* carefully made up...

So what we want really is a line that makes the total of the errors (the differences between the line and the points) as small as possible. Or, we'd like to make the *average error* as near zero as we can.

Let's denote the total error by E. Then, if we add up the equations 16.2 for each of the points, we get:

$$\sum_i y_i = m \sum_i x_i + \sum_i b + \sum_i \epsilon_i \,. \tag{16.3}$$

We can simplify this slightly. The last sum is just E, the total error. The next to the last term is b added four times since we have four data points, or nb (where n is the number of data points). Rearranging a bit we have

$$E = \sum_i y_i - m \sum_i x_i - nb \,. \tag{16.4}$$

For our data $\sum_i x_i = 8.6$ and $\sum_i y_i = 15.962$, so our equation is:

$$E = 15.962 - 8.6m - 4b \,. \tag{16.5}$$

Now we want E to be as small as possible. Can we make E equal zero? Sure, $m = 1$, $b = 1.8405$ will do it. So will $m = -1$ and $b = 6.1405$. In fact, there are an infinite number of pairs of m and b that will make E zero.

What's happened here? It is easy to see graphically. All we are doing is putting a line down so that no matter how far some points lie *above* the line, others lie equally far *below* the line. Then the positive and negative errors balance out. And there are lots of ways to do this.[6] So this approach won't work.

What went wrong? We slipped. What we really wanted was not to have a big error at one point balanced by an equally big error at another point, but having the opposite sign. We wanted to get rid of big errors in favor of small errors. We need to redo this in such a way that the errors always have the same sign and then make their sum as small as possible. That will do it.[7] So what we need is to work with is something like the absolute values of the errors. But that's a real problem. Absolute values are not friendly. Taking their derivaties is a pain. Even dealing with them algebraically is a pain.

So what shall we do? We'll cheat.[8] What we'll do is use the *sqare* of the error, not the error alone. The squared error is always positive; dealing with squares isn't hard, and in fact we can pull the whole thing off rather nicely.

So we start by going back to equation 16.2 and solving it for ϵ_i:

$$\epsilon_i = y_i - mx_i - b \,. \tag{16.6}$$

The squared error at each point is:

$$, \epsilon_i^2 = \big(y_i - mx_i - b\big)^2 \tag{16.7}$$

and, adding all these errors up to get the total squared error (which I'll call E^2) we get:

$$\sum_i \epsilon_i^2 = \sum_i (y_i - mx_i - b)^2 \,. \tag{16.8}$$

[6] Don't take my word for it. Draw a few in and see for yourself.

[7] So will a large number of other schemes such as making the sum of the distances of the points from the best line as small as possible. But those distances are hard to work with mathematically. So when we choose a method we are not only looking for a reasonable one, we are also looking for one with nice mathematical properties.

[8] Boy, are you surprised! Statisticians cheat, physical chemists cheat, but if you cheat we get you. Yes, life's like that. Besides, I'm not talking about *that* kind of cheating.

Looking at it this way gives us a better feeling.[9] We see right away that we can never make E^2 zero, unless there are no errors at all.[10] So all we can do is to make E^2 as small as possible. What does that really mean? Math-wise it means that the m and b we end up with should make E^2 a minimum. And *that* means that if we vary m or b even slightly, we should get a worse line and a larger E^2. This should start ringing bells in your head.[11] We want to find the derivative of E^2 with respect to m and again with respect to b, and set each of them to zero and then solve the resulting pair of equations for m and b. Those values will then be the best values. In math-speak we want

$$\left(\frac{\partial E^2}{\partial m}\right)_b = 0\,, \qquad \left(\frac{\partial E^2}{\partial b}\right)_m = 0\,. \tag{16.9}$$

Actually doing the differentiation of equation 16.8 is a bother, so I'm going to work it out in some detail. The derivatives are:

$$\begin{aligned} \left(\frac{\partial E^2}{\partial m}\right)_b &= -2\sum_i (y_i - mx_i - b)x_i\,, \\ \left(\frac{\partial E^2}{\partial b}\right)_m &= -2\sum_i (y_i - mx_i - b)\,. \end{aligned} \tag{16.10}$$

Writing equations 16.10 in more detail and equating them to zero:

$$\begin{aligned} \left(\frac{\partial E^2}{\partial m}\right)_b &= -2\sum_i x_i y_i + m\sum_i x_i^2 + b\sum_i x_i = 0\,, \\ \left(\frac{\partial E^2}{\partial b}\right)_m &= -2\sum_i y_i + m\sum_i x_i + nb = 0\,. \end{aligned} \tag{16.11}$$

We have two equations from which to find m and b. Doing a very slight rearrangement, the equations are:

$$\begin{aligned} m\sum_i x_i^2 + b\sum_i x^i &= \sum_i x_i y_i\,, \\ m\sum_i x_i + nb &= \sum_i y_i\,. \end{aligned} \tag{16.12}$$

Which aren't too hard to solve *if* one is systematic about it. The right thing to do is to compute each of:

$$\sum_i x_i\,, \qquad \sum_i x_i^2\,, \qquad \sum_i y_i\,, \quad \text{and} \qquad \sum_i x_i y_i\,, \tag{16.13}$$

once and get it over with. The solution to the pair of equations 16.12 involves first computing Δ:

$$\Delta = n\sum_i x_i^2 - \left(\sum_i x_i\right)^2\,, \tag{16.14}$$

and then:

$$m = \frac{1}{\Delta}\left[n\sum_i x_i y_i - \left(\sum_i x_i\right)\left(\sum_i y_i\right)\right]\,, \tag{16.15}$$

[9] Well, it gives *me* a better feeling!

[10] But we've seen the data plotted, so we know we have errors.

[11] Do you hear bells often? Do they play tunes? Do you need help?

and

$$b = \frac{1}{\Delta}\left[\left(\sum_i x_i^2\right)\left(\sum_i y_i\right) - \left(\sum_i x_i y_i\right)\left(\sum_i x_i\right)\right]. \tag{16.16}$$

For our data[12] we have

$$\sum_i x_i = 8.6, \quad \sum_i x_i^2 = 25.24, \quad \sum_i y_i = 15.962, \text{ and } \quad \sum_i x_i y_i = 38.7232\,. \tag{16.17}$$

You are hereby warned **not** to round off any numbers. Carry everything to your full calculator accuracy. The reason is this: the computed results involve subtractions of numbers that easily can be almost the same size. When you subtract in that case you will lose many significant digits. If you've rounded off, your answer may well have been rounded away.

Now, plugging in we find $\Delta = 27.00$. Then $m = 0.652$ and $b = 2.587$. I've repeated Figure 16.1 with this line drawn in: Looks much better, doesn't it? In fact, the data, when measured against

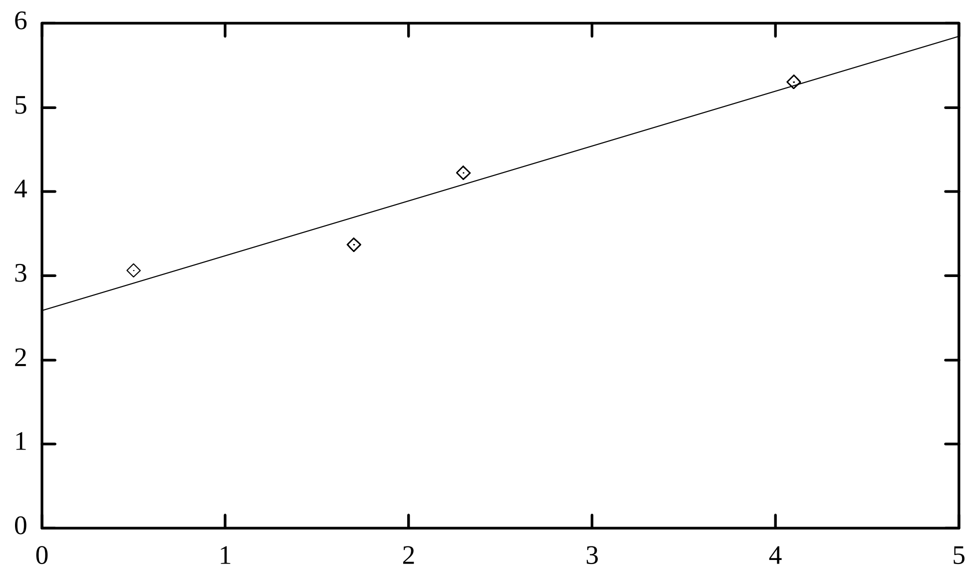

Figure 16.2: Data and the Best Straight Line through It.

the line, doesn't even look that bad. That second point on the left though...

[12] Thought I'd forgotten, right?

Problem Set 16.1

Here's some real heat capacity data for carbon dioxide at 1.000 atm. Find an equation of the form $C_p = a + bT$ for this data by determining a and b by least squares.

T (K)	C_p (J/mole-K)
260.00	35.871
280.00	36.687
300.00	37.519
320.00	38.345
340.00	39.153
360.00	39.936
380.00	40.693
400.00	41.421

Table 16.2: Heat Capacity in J/mol-K for Carbon Dioxide[13]

[13] Data from NIST (*http://webbook.nist.gove/chemistry/fluid/*)