University of Washington
Department of Chemistry
Chemistry 452
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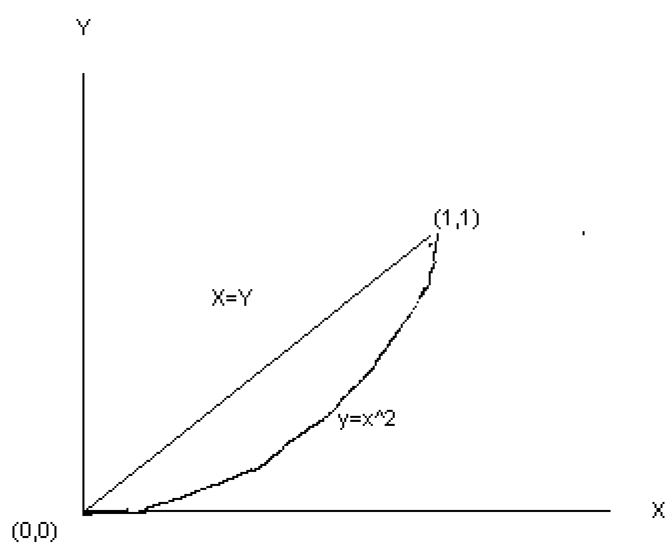
Math Tutorial 2. 6/27/01

A. Integrals involving Exact and Inexact Differentials

- Small changes in state functions like E and H may be represented as exact differentials. On the other hand, quantities like heat and work are inexact differentials…a fact that we will demonstrate shortly. In thermodynamics inexact differentials are indicated by a back slash \ through the stem of the d.
- An interesting and very useful property of differentials is their behavior upon integration. Given a differential $M\left(x,y\right)dx+N\left(x,y\right)dy$, we ask how this may be integrated in the x-y plane? Let's consider a function $F=x^2y+constant$. Then the exact differential of F is $dF=2xydx+x^2dy$. Suppose we want to integrate this differential from $(x_1,y_1)=(0,0)$ to $(x_2,y_2)=(1,1)$. To obtain a numerical answer, we have to assume a functional relationship between x and y. Suppose we assume that x=y. Then the differential may be written as $dF=2xydx+x^2dy=2x^2dx+y^2dy$. On the other hand if we assume $y=x^2$, the differential is written as $dF=2xydx+x^2dy=2x^3dx+ydy$.
- An integration of a differential that assumes a particular functional relationship between x and y is called a path integral. The reason for its name is clear if you write out the graph of the two relationships x=y and $x^2=y$ in the x-y plane…



- A path integral is the integration of a differential along a certain path in the x-y plane. This can be generalized to three dimensions and higher.
- Example: Complete the integral of the differential $dF = 2xydx + x^2dy$ between (0,0) and (1,1) for the paths x=y and y=x^2.

Solution:

$$\Delta F = \int_0^1 2xydx + \int_0^1 x^2dy$$

and for x=y…

$$\Delta F = \int_0^1 2xydx + \int_0^1 x^2dy = \int_0^1 2x^2dx + \int_0^1 y^2dy$$

$$= \frac{2x^3}{3}\bigg|_0^1 + \frac{y^3}{3}\bigg|_0^1 = \frac{2}{3} + \frac{1}{3} = 1$$

And for y=x^2…

$$\Delta F = \int_0^1 2xydx + \int_0^1 x^2dy = \int_0^1 2x^3dx + \int_0^1 ydy$$

$$= \frac{2x^4}{4}\bigg|_0^1 + \frac{y^2}{2}\bigg|_0^1 = \frac{1}{2} + \frac{1}{2} = 1$$

Conclusion: the integral of an exact differential does not appear to be dependent upon the details of the path. In fact this is a important property of state functions…their changes are path independent and only depend upon the initial and the final states.

- Example: Now consider the inexact differential $xydx + xydy$. That this differential is inexact can be demonstrated using Euler's criterion. Calculate the same two path integrals…

Solution:

For x=y…

$$\Delta F = \int_0^1 xydx + \int_0^1 xydy = \int_0^1 x^2dx + \int_0^1 y^2dy$$

$$= \frac{1}{3} + \frac{1}{3} = \frac{2}{3}$$

For y=x^2…

$$\Delta F = \int_0^1 xydx + \int_0^1 xydy = \int_0^1 x^3dx + \int_0^1 y^{3/2}dy$$

$$= \frac{x^4}{4}\bigg|_0^1 + \frac{2y^{5/2}}{5}\bigg|_0^1 = \frac{1}{4} + \frac{2}{5} = \frac{5}{20} + \frac{8}{20} = \frac{13}{20}$$

Note that for path integrals of inexact differentials are dependent upon the details of the path. Small changes in heat and work are inexact differentials.