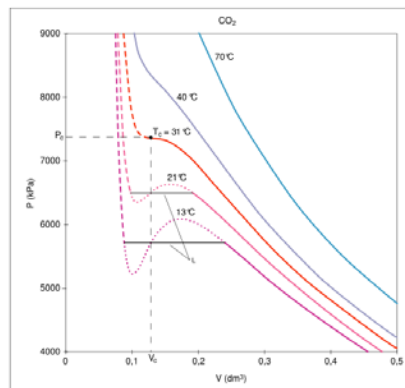


Chemistry BC3252y  
 Problem Session 1  
 Friday, January 23, 2009



1

## Mathematical topics

- Significant figures (see web notes)
- Uncertainty and error
- Approximations
  - successive approximation
- Calculus topics
  - partial derivatives
  - integration and separation of variables

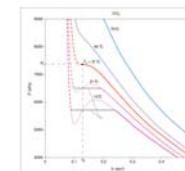
2

## Uncertainty and error

- Uncertainty
  - Governed by rules of probability
  - Not signed:  $\pm$
- Error
  - sometimes used to mean same as uncertainty but sometimes
  - error = (approximate value - true value)
  - % error =  $100 \times \text{error} / (\text{true value})$
  - has a sign: + if approx. value  $>$  true value.

3

## Approximations



Many equations can be solved explicitly:

$$PV = nRT \quad \text{gives} \quad V = nRT/p$$

Some cannot:  $(p + a/V_m^2)(V_m - b) = RT$

$V_m = ?$  Cubic: **no explicit solution**

but for every  $(p, T)$  there is a  $V_m$ .

How do you solve ?

Various methods: graph, guess, calculator or computer solver functions..

4

## Successive Approximation

$$(p + a/V_m^2)(V_m - b) = RT \quad V_m = ?$$

We know that  $a$  and  $b$  are small.

$$\text{Rearrange: } V_m = b + RT/(p + a/V_m^2)$$

$V_m$  is still on both sides,

but is part of a small term on right

Guess 1:  $V_m = RT/p$  (ignore small terms)

Substitute into RHS:

continue until ( $V_m$  in) = ( $V_m$  out)

to the desired number of sig. figs.

5

## Calculus: Partial derivatives

### Single variable calculus

$y = y(x)$ , derivative is  $dy/dx$

$dy/dx$  is the slope of the function  $y(x)$

e.g. if  $y = a + bx + cx^2 + k \ln x$ ,

$$\text{then } dy/dx = b + 2cx + k/x$$

(learn basics; use tables if you forget)

### More variables

$z = z(x, y)$ : what is the slope?

depends on direction!

6

## Calculus: Partial derivatives

$z = z(x, y)$ : what is the slope?

Specify direction: derivative with respect to  $y$  along the direction of constant  $x$

$$\text{slope} = (\partial z / \partial y)_x$$

Mathematically, just treat  $x$  as a constant

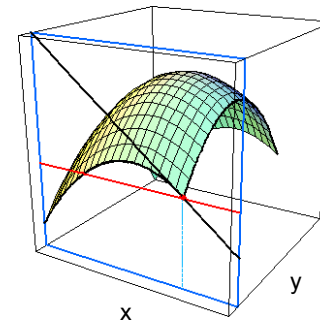
If  $z = axy + by^2$

then  $(\partial z / \partial y)_x = ax + 2by$

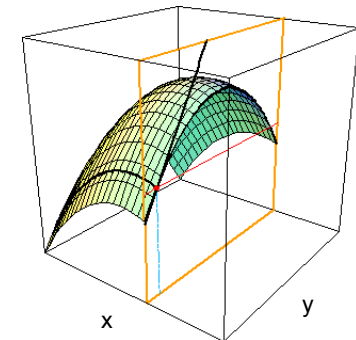
and  $(\partial z / \partial x)_y = ay$  [treating  $y$  as constant]

7

## Calculus: Partial derivatives



$(\partial f / \partial x)_y$



$(\partial f / \partial y)_x$

figures from [www.usd.edu/.../Graphics15/Chapter15\\_3/Pdy.gif](http://www.usd.edu/.../Graphics15/Chapter15_3/Pdy.gif)

8

## Calculus: derivatives to integrals

Suppose we know  $dy/dx$ . What is  $y(x)$ ?

If  $dy/dx = ax$ , then  $dy = ax dx$

Integrate both sides.

LHS:  $\int dy = y$     RHS:  $\int ax dx = \frac{1}{2}ax^2$

definite integral (with explicit limits)

$$y_2 - y_1 = \frac{1}{2}a (x_2^2 - x_1^2)$$

indefinite integral (include a constant)

$$y = \frac{1}{2}ax^2 + C$$

9

## Calculus: Derivatives to integrals

Separate variables before integrating!

Anything involving  $y$  with  $dy$ ,  
anything involving  $x$  with  $dx$ .

Constants can be on either side.

Example:  $dy/dx = axy$

$$dy/y = ax dx \quad \rightarrow \ln y = \frac{1}{2}ax^2 + c$$

$$\rightarrow y = e^{\frac{1}{2}ax^2 + c}$$

**Check:** If  $y = e^{\frac{1}{2}ax^2 + c}$  What is  $dy/dx$ ?

$$dy/dx = (e^{\frac{1}{2}ax^2 + c})(\frac{1}{2}a[2x]) = axy \quad \text{ok!}$$

10

## Calculus: Differential equations

$dy = ax dx$  is a **differential equation**:  
an equation involving differentials.

Differential: infinitesimal quantity

Every term in such equations must  
include a differential:

$$dz = A dx + B dy$$

Thermodynamics full of such equations!

How do we find A and B?

11

## Example: $V/n = V_m = V_m(p, T)$

$$dV_m = A dp + B dT. \quad \text{What is A?}$$

Divide both sides by  $dp$ , at constant T

$$(i.e. dT = 0): \quad A = (\partial V_m / \partial p)_T$$

Curly "d" since there are multiple variables.

A is the slope of  $V_m$  in the  $p$  direction,  
holding T constant.

Likewise  $B = (\partial V_m / \partial T)_p$ . Thus

$$dV_m = (\partial V_m / \partial p)_T dp + (\partial V_m / \partial T)_p dT$$

Such equations exist for all state variables.

12