

Data Reduction & the Propagation of Errors :- Many values that are obtained by measurement in physical chemistry laboratory are used along with other values to calculate some quantity that is not directly measured. Such a calculation is called data reduction. An experimental error in a measured quantity will affect the accuracy of any quantity that is calculated from it. This is called propagation of errors.

Errors Propagation in Data Reduction Using Mathematical Formulas -

The Dumas method for determining the molar mass of a volatile liquid one uses the formula:

$$M = \frac{wRT}{PV} \quad \text{--- (1)}$$

where  $M$  is the molar mass,  $w$  is the mass of sample of substance contained in volume  $V$  at pressure  $P$  & temperature  $T$  &  $R$  is the Ideal Gas constant. We may assume eqn. (1) being an example of general formula:

$$y = y(x_1, x_2, x_3, \dots, x_n) \quad \text{--- (2)}$$

Let us assume that we have a 95% confidence interval for each of the independent variable  $x_1, x_2, \dots$  such that

$$x_i = \bar{x}_i \pm \epsilon_i \quad (i=1, 2, \dots, n) \quad \text{--- (3)}$$

Our problem is to take uncertainties in  $x_1, x_2, \dots, x_n$  & calculate the uncertainty in  $y$ , the dependent variable. This is called propagation of error. If the errors are not too large, we can take an approach based on differential calculus. The fundamental eqn. of differential calculus is:

$$dy = \left(\frac{\partial y}{\partial x_1}\right) dx_1 + \left(\frac{\partial y}{\partial x_2}\right) dx_2 + \left(\frac{\partial y}{\partial x_3}\right) dx_3 + \dots + \left(\frac{\partial y}{\partial x_n}\right) dx_n \quad \text{--- (4)}$$

This eqn. gives an infinitesimal change in dependent variable due to arbitrary infinitesimal changes in the independent variables  $x_1, x_2, x_3, \dots, x_n$ .

If finite changes  $\Delta x_1, \Delta x_2$  & so on, are made in the independent variables, we could write an approximation

$$\Delta y \approx \left(\frac{\partial y}{\partial x_1}\right) \Delta x_1 + \left(\frac{\partial y}{\partial x_2}\right) \Delta x_2 + \dots + \left(\frac{\partial y}{\partial x_n}\right) \Delta x_n \quad \text{--- (5)}$$

If we had some known errors in  $x_1, x_2$  & so on, we could use eqn. (5) to calculate known error in  $y$ . Since all we have is probable errors in the independent variables & do not know whether the actual errors are positive or negative,

The cautious way to proceed would be to assume that the worst might happen & that all the errors would add: (2)

$$\epsilon_y \approx \left| \left( \frac{\partial y}{\partial x_1} \right) \epsilon_1 \right| + \left| \left( \frac{\partial y}{\partial x_2} \right) \epsilon_2 \right| + \dots + \left| \left( \frac{\partial y}{\partial x_n} \right) \epsilon_n \right| \quad (6)$$

where  $\epsilon_1, \epsilon_2, \dots, \epsilon_n$  represent the expected errors in the  $n$  independent variables &  $\epsilon_y$  represents the expected error in  $y$ . [First estimate]

This eqn. overestimates the error in  $y$  because there is some probability that the errors in the  $x$  values will cancel instead of adding. An eqn. that incorporates the statistical probability of error cancellation is:

$$\epsilon_y = \left[ \left( \frac{\partial y}{\partial x_1} \right)^2 \epsilon_1^2 + \left( \frac{\partial y}{\partial x_2} \right)^2 \epsilon_2^2 + \dots + \left( \frac{\partial y}{\partial x_n} \right)^2 \epsilon_n^2 \right]^{1/2}$$

This will be our working eqn. for the propagation of errors through formulas. Since it is based on a differential formula, it becomes more nearly exact if errors are small. [Final formula]

Num. - a) Find the expression for the propagation of errors for Dumas molecular mass determination.

b) Apply this expression to the following set of data for n-hexane

$$T = 373.15 \pm 0.25 \text{ K}, \quad V = 206.34 \pm 0.15 \text{ ml}$$

$$P = 760 \pm 0.2 \text{ torr}, \quad w = 0.585 \pm 0.005 \text{ g}$$

Sol: a) the required eqn. is

$$\epsilon_M \approx \left[ \left( \frac{\partial M}{\partial w} \right)^2 \epsilon_w^2 + \left( \frac{\partial M}{\partial V} \right)^2 \epsilon_V^2 + \left( \frac{\partial M}{\partial T} \right)^2 \epsilon_T^2 + \left( \frac{\partial M}{\partial P} \right)^2 \epsilon_P^2 \right]^{1/2}$$

$$\epsilon_M \approx \left[ \left( \frac{RT}{P} \right)^2 \epsilon_w^2 + \left( \frac{wR}{P} \right)^2 \epsilon_V^2 + \left( \frac{wRT}{P^2} \right)^2 \epsilon_P^2 + \left( \frac{wRT}{P} \right)^2 \epsilon_T^2 \right]^{1/2}$$

Substituting the numerical values

$$M = \frac{(0.585 \text{ g}) (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) (373.15 \text{ K})}{(1.00 \text{ atm}) (206.34 \text{ L})} = \frac{17.92}{0.206} = 86.81 \text{ g mol}^{-1}$$

Now fractional error for  $T = \frac{0.25}{373.15} = 6.7 \times 10^{-4}$  (3)

fractional error for  $V = \frac{0.15}{206.34} = 7.3 \times 10^{-4}$

fractional error for  $P = \frac{0.2}{760} = 2.6 \times 10^{-4}$

fractional error for  $w = \frac{0.005}{0.585} = 85.5 \times 10^{-4}$

$$\therefore \text{total fractional uncertainty} = \sqrt{(6.7 \times 10^{-4})^2 + (7.3 \times 10^{-4})^2 + (2.6 \times 10^{-4})^2 + (85.5 \times 10^{-4})^2}$$

$$= \sqrt{44.89 + 53.29 + 6.76 + 7310.25} \times 10^{-4}$$

$$= \sqrt{7415.19} \times 10^{-4} = 86.11 \times 10^{-4}$$

$\therefore$  absolute uncertainty in  $M = 86.81 \times 86.11 \times 10^{-4} \text{ g mol}^{-1}$   
 $= 0.7475 \text{ g mol}^{-1}$

$\therefore M = 86.81 \pm 0.75 \text{ g mol}^{-1}$

### Experimental Errors in Methods

Graphical & Numerical Data Reduction:- There are a number of function relationships in physical chemistry that require data reduction that is more involved than substituting values into a formula. For example, thermodynamic relations imply that eqbm pressure of a two phase system containing one substance is a function of temperature. If one cooks the temperature & measure the pressure, we write-

$$P = P(T)$$

Num. - The following data was obtained by a student for vapour pressures of ethanol, which is pressure observed when liquid & vapour are at eqbm. Errors estimates are included in the table

$t/^\circ\text{C}$	$T/\text{K}$	vapour pressure (torr)	Expected error (torr)
25.00	298.15	55.9	3.0
30.00	303.15	70.0	3.0
35.00	308.15	93.8	4.2
40.00	313.15	117.5	5.5
45.00	318.15	154.1	6.0
50.00	323.15	190.7	7.6
55.00	328.15	241.9	8.0
60.00	333.15	304.5	8.8
65.00	338.15	377.9	9.5

The Clapeyron eqn. for any phase transition is

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m}$$

where  $P$  is the pressure,  $\Delta H_m$  is molar enthalpy change of phase transition,  $T$  is the absolute temperature &  $\Delta V_m$  is the molar volume change of phase transition.

Find the value of  $\frac{dP}{dT}$  at  $40^\circ\text{C}$  & find the value of  $\Delta H_m$ .

Ans - from graph  $\frac{dP}{dT}$  at  $40^\circ\text{C} = 4.55 \text{ bar K}^{-1}$  [Plot the graph]

The enthalpy change of vaporization was calculated using the approximation:

$$\Delta V_m = V_m(\text{gas}) - V_m(\text{liquid}) \approx V_m(\text{gas}) = \frac{RT}{P}$$

$$\begin{aligned} \therefore \Delta H_m &= T V_m \frac{dP}{dT} = \frac{RT^2}{P} \frac{dP}{dT} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (313.15 \text{ K})^2 (4.55 \text{ bar K}^{-1})}{117.5 \text{ bar}} \\ &= 31571.00 \text{ J mol}^{-1} = 31.57 \text{ kJ mol}^{-1} \end{aligned}$$

Linearization:- In some cases, a variable obeys a mathematical relation that can be linearized. This means finding new variables such that the curve in a graph of our data is expected to be a line instead of some other curve. In our vapour pressure example, these variables are found by manipulation of the Clapeyron eqn. We assume that the volume of liquid is negligible compared to that of gas, & that of the gas is ideal.

$$\Delta V_m = V_m(\text{gas}) - V_m(\text{liquid}) \approx V_m(\text{gas}) = \frac{RT}{P} \quad \text{--- (1)}$$

We also assume that  $\Delta H_m$  is equal to a constant. ~~After~~  
Now the Clapeyron eqn. becomes:

$$\frac{dP}{dT} = \frac{\Delta H_m}{T} \frac{P}{RT} \quad \text{or} \quad \frac{dP}{P} = \frac{\Delta H_m}{R} \frac{dT}{T^2}$$

Integrating we get

$$\ln P = - \frac{\Delta H_m}{RT} + C$$

where  $C$  is constant of integration

The above eqn is called Clausius - Clapeyron eqn.

This eqn. represents a linear function if we use  $1/T$  as independent variable &  $\ln P$  as dependent variable. This is similar to  $y = mx + c$ . The slope of the eqn. of straight line & slope  $m = - \frac{\Delta H_m}{R}$