CHAPTER 7

SUMMARY AND CONCLUSION
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It has been said in chapter 2 that classical chemical reaction kineties has been mainly concerned with homogeneous reactions and cannot be directly applied to heterogeneous reactions. In heterogeneous systems reactions take place at a phase boundary and the overall process involves several series steps which have relatively simple kinetics. The rate phenomena can be understood for such reactions provided virtual maximum rate of one step is much slower than that for any of the other steps.

A review of existing literature relevent to the present work has been described in Chapter 3, a critical survey of which shows that although various models have been proposed to explain the effect of different factors controlling the rate of decomposition of magnesite but as yet we do not possess any model which can fully account for the rate of its decomposition. So the present investigation was undertaken.

The investigation consisted of a study of the rate of decomposition at different temperatures of small cubes prepared from raw magnesite lumps of different origins. Volume and surface area of the cubes were calculated from the measured values of length of the edge of the cubes.

To study the effect of particle size on the rate of decomposition; particles of four size ranges were prepared from each of the six magnesite samples of different sources followed by sieving, subsequent washing in distilled water and drying at 105° C.

For studying the effects of compaction of loose powder, cylindrical pellets of magnesite of six sources were prepared with agated powder (below 64 micron) pressed in a manually operated hydraulic press at 1350 Kg/cm² pressure for 2 minutes. Similarly cylindrical magnesite pellets of six different sources containing 3 wt% hydrated iron oxide were also prepared.

The rate of weight loss of each of the samples were performed in an automatic Shimadzu DT- 40 thermal Analyser where α-Al₂O₃ has been used as reference substance. The analyser has been provided with an automatic chart recorder for
recording weight of the sample continuously with time at a particular temperature. An arrangement was made to pass purified and dried CO₂ gas through the furnace as and when required from a CO₂ gas cylinder.

All the above weight loss experiments had been carried out in atmospheric air as well as under vacuum (2-3 mm of Hg pressure)

In order to account for the results it was presumed that the decomposition of magnesite occurs at the interface advancing from the surface of the particle or particles to the interior and that its rate was ultimately determined by the rate of forward reaction and the rate of backward reaction, the latter being controlled by the diffusion of CO₂ through the calcined layer and the following equation was developed.

\[ \alpha = - \left( \frac{K_2 \cdot d}{K_3} + \frac{K_1 - K_2 \cdot P_0}{K_3} \right) \]

where

- \( P_0 \) = Pressure of CO₂ at the magnesite surface at temperature \( t \).
- \( d \) = Depth of calcination from the magnesite surface
- \( \alpha \) = Rate of weight loss per unit area i.e. overall rate of decomposition of magnesite.
- \( K_1 \) = Rate of forward reaction per unit area which may be taken as constant.
- \( K_2 \) = Rate constant of backward reaction per unit area.
- \( K_3 \) = Diffusion of CO₂ through the decomposed MgO layer.

Plots of \( \alpha \) versus \( d \) for all the samples of cube, powder, pellet as such and pellet with additive gave straight lines. From the intercept of the straight lines the values of rate constant (\( K_1 \)) were calculated for those samples which were heated under vacuum at different temperatures.

\[ \log_{10} K_1 \] (where \( K_1 \) = rate constant for the forward reaction) were plotted against 1/\( T \) for different temperatures for all the six magnesite cubes. Straight lines were obtained in all the above cases from the slope of which the values of activation energy were calculated. The values of energy of activation in all the above six magnesite cubes were found to be in the range from 24.95 Kcal/mole to 26.05 Kcal/mole. These values are lower than the values reported for pure magnesite by
several scientists. This is possibly due to the fact that products formed during decomposition of magnesite containing minor quantities of \( \text{SiO}_2 \), \( \text{Al}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \) as impurities, consist of \( \text{CaO} \), \( \text{MgO} \) as well as silicates, aluminates, ferrites of calcium and magnesium. The overall heat of reaction is much lower than the heat of decomposition of magnesite as the formation of silicates, aluminates and ferrites of calcium and magnesium are attended with evolution of heat.

\( \alpha \) versus \( d \) for magnesite cubes heated in air were plotted. Intercept of the straight lines gave the values of \( (K_1 - K_2 P_0) \). The results show as expected, that the experimental values of \( (K_1 - K_2 P_0) \) are significantly less than those of \( K_1 \) which indicates that the proposed model is valid for the decomposition of magnesite.

From the plots of \( \alpha \) versus \( d \) for all the the four size fractions of magnesite powder heated under vacuum, the values of \( K_1 \) were obtained.

A comparison of the values of rate constant \( (K_1) \) of magnesite for powders and cubes shows that the values of \( K_1 \) is higher for cubes at all temperatures. It so happens because of the diffusibility of \( \text{CO}_2 \) being higher in case of cubes. For powders the rate constant \( (K_1) \) also decreases with decrease in particle size vis-a-vis pore opening. Both the above two phenomena indicate that the diffusibility of \( \text{CO}_2 \) is the rate controlling factor as cited in the proposed model.

As was done for magnesite cubes, \( \log_{10} K_1 \) were plotted against \( 1/T \) for powders under vacuum and from the straight lines, energy of activation was calculated. It has been observed that the energy of activation for powder, as expected, are lower than those for magnesite cubes. Besides above it is also seen that energy of activation of a particular magnesite powder increases with decrease in particle size. It has been noted from the results that rate constant \( (K_1) \) decreases with diminishing particle size.

In general it is concluded for a heterogeneous reaction that with decrease in particle size of reacting powders, the energy of activation decreases. But from the results it has been observed that energy of activation increases with decrease in particle size which is possibly due to the role of diffusibility of \( \text{CO}_2 \) from decomposing interface.
The values of intercepts i.e. \((K_1 - K_2 P_0)\) obtained from plots of \(\alpha\) versus \(d\) for magnesite powders of four size fractions at different temperatures in atmospheric air are much lower than those for magnesite cubes. This means that the values of \(P_0\) for powders are much higher than for cubes. This is what is expected as the diffusibility of CO\(_2\) through the pores between the particles becomes less. It is also observed that finer the particles less is the value of \((K_1 - K_2 P_0)\) indicating increase in the value of \(P_0\) with decrease in particle size.

Values of \(K_1\) for magnesite pellets were obtained from the intercepts of the straight lines obtained by plotting \(\alpha\) versus \(d\) values for pellets heated in vacuum at different temperatures. Energy of activation was also calculated from the slope of the straight lines obtained from the plots of \(\log_{10} K_1\) versus \(1/T\).

\(\alpha\) versus \(d\) values were plotted for magnesite pellets heated in air and the intercept of the straight lines gave the values of \((K_1 - K_2 P_0)\). The results show, as expected, as per the proposed model that the values of \((K_1 - K_2 P_0)\) for magnesite pellets are significantly less than the values of \(K_1\).

\(\alpha\) versus \(d\) plots were done in case of magnesite pellets with 3 wt% hydrated iron oxide additive in vacuum at different temperatures and values of \(K_1\) were obtained from the intercept of the straight lines. Activation energy for decomposition of magnesite pellets were determined from the slopes of straight lines obtained from the plot of \(\log_{10} K_1\) versus \(1/T\).

Plots of \(\alpha\) versus \(d\) were carried out for magnesite pellets containing 3 wt% hydrated iron oxide additive heated in air at different temperature. Intercepts of the straight lines gave values of \((K_1 - K_2 P_0)\). The results show, as expected, as per the proposed model that the values of \((K_1 - K_2 P_0)\) for magnesite pellets with additive are significantly less than those of \(K_1\).

It is noted from the results that energy of activation of all the pellets containing 3 wt% hydrated iron oxide additive are less than those of corresponding pellets without additive and also less from the values of energy of activation of magnesite cubes. This is possibly due to the fact that various exothermic reactions take place due to formation of \(\text{Fe}_2\text{O}_3\) or \(2\text{CaO}\cdot\text{Fe}_2\text{O}_3\) or \(2\text{CaO}\cdot\text{MgO}\cdot\text{Fe}_2\text{O}_3\) leading to evolution of heat and ultimately reducing the energy of activation.