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MAKING DECOMPOSITION RATE MEASUREMENTS ON SIMPLE INORGANIC CHEMICAL POWDERS BY TGA

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The thermal decompositions of many inorganic materials occur by heterogeneous chemical reactions, i.e., reactions in which two or more phases are involved. Although reactions of this type are common in metallurgical practice, very little information is available about them in text books. Basically, homogeneous and heterogeneous chemical reactions have many features in common. Some of the important points for comparison are shown in Table I.

In the left column of Table I, a typical homogeneous gas phase reaction is shown. By collision with a wall or another molecule, or by other means of energy transfer, the molecule G_1G_2 becomes activated. From this activated state it may lose energy by some process of deactivation and return to its original state, or it may continue in its original path and dissociate to produce the individual particles G_1 and G_2. For this type of system, the amount of reaction can be calculated from the product of the reaction rate constant, the concentration of the reacting species, and the time since the initiation of reaction. In this instance it is convenient to define the reaction rate constant in the units of grams (or moles) of material per litre of gas (or solution) per minute (or second).

In the right column of Table I, three examples of typical heterogeneous reactions are shown. The first, in which one solid decomposes to produce another and a gaseous product, is typical of reactions such as the decomposition of limestone (calcium carbonate) to produce lime (calcium oxide) and carbon dioxide. Many tons of lime are prepared daily by this reaction, for use in the steel and building industries.

The second example, in which a solid reacts with a gas to produce another gas, is typical of the combustion of many solid fuels in air. One interesting modern application of this reaction is a new process being developed by the aluminum industry for the refining of aluminum metal and the recovery of aluminum from scrap alloys. The aluminum reacts with aluminum trichloride gas to produce gaseous aluminum monochloride. When this is cooled, aluminum metal in a very pure state is recovered and aluminum trichloride is regenerated.

The third example, in which a solid reacts with a gas to produce another solid and another gas, may be illustrated by the 600-ton-per-day iron ore plant of the International Nickel Company at Sudbury, Ontario. There, pyrrhotite ore (ferrous sulphide) is roasted in air to produce a magnetite-hematite mixture (Fe_3O_4-Fe_2O_3) and sulphur dioxide. The iron-oxide mixture is an important secondary source of iron for the steel industry.

In each of the foregoing examples of heterogeneous reactions, the reaction mechanism is essentially the same. Reaction takes place at an interface between two phases. The interface is sharply defined and it moves at a constant rate at a constant temperature. To obtain the amount of reaction, it is necessary to multiply the reaction rate constant by the area of the interface and the time since the initiation of reaction. For these heterogeneous reactions, the reaction rate constant can be expressed in the units of grams of material reacting on one square centimetre of interface in one minute. A comparison of the units of the reaction rate constant for the homogeneous and heterogeneous systems shows that the only essential difference is in the concept of expressing the capacity factor of the relationship: in the homogeneous system this is represented by a volume, and in the heterogeneous system by an area. When these similarities and differences of the two systems are appreciated, much of the confusion regarding heterogeneous systems is eliminated. For example, just as no reasonable experimenter would consider measuring a series of reaction rates without knowing the volumes of his solutions, so no reasonable experimenter should consider making rate measurements in heterogeneous systems without knowledge of the interfacial areas involved in his reactions.

The problem of determining interfacial areas can be a very difficult one to resolve because, in addition to their initial determination, means must be found to correlate the observed rate of reaction with a continuously changing interfacial area. This problem can be illustrated by reference to Fig. 1, in which a series of spherical particles are shown. On the top part of the figure, the large spherical particle had the same initial weight as the five small individual particles. After the same period of reaction, during which the rate of migration of the interface into the particle was constant, substantially different amounts of reaction occurred in the single large particle and the five small particles. By visual inspection it is evident that in each of the small particles the reaction is nearing completion, whereas in the large particle it has scarcely more than begun. This example illustrates the fact that even though the reaction rate is identical in both the large and small spheres, the amount of reaction occurring in unit time is very different; it is determined entirely by the area of the reaction interface. One other fundamental feature of this type of reaction is also discernible from the migration of the reaction interfaces in Fig. 1. In each instance the area of the reaction interface decreases progressively as the reaction proceeds. Thus, unless this decrease in interfacial area is taken into account, it would appear from any measurement of the amount of reaction that the rate decreases continuously with the progress of the reaction. Without an appreciation of the decrease in interfacial area it might be reasoned erroneously that the reaction was being progressively impeded by the accumulation of reaction product.

At the bottom of Fig. 1 the pattern of reaction is illustrated for the case when individual particles are piled adjacent to each other. In this instance the reaction interface migrates at its normal rate on the exposed surfaces of the particles. Where the particles touch, and in the spaces between individual particles, very little if any reaction occurs. This type of observation suggested the method by which the reaction rates of powdered materials could be studied. The method is based on compression of the powder into a dense pellet on the assumption that the rate of migration of the interface from the external surface of the pellet will

be uniform, and that changes in its area can be made readily by simple calculations.

The form of the pellet found most convenient to use is shown in Fig. 2. When finely divided powder (approximately in the size range from -200 to +325 mesh) is used, pellet densities approaching 90% of theoretical are obtainable. When such a pellet is decomposed in a stream of non-reactive gas, decomposition is initiated on the surface of the pellet and the reaction interface maintains the same shape and moves from the exterior surface toward the centre of the pellet at a uniform rate. When there is no solid reaction product ($S_1 + G_1 \rightleftharpoons G_2$), the size of the pellet decreases as the reaction proceeds. When there is a solid reaction product and that product is open and porous ($S_1 \rightleftharpoons S_2 + G_1$) or ($S_1 + G_1 \rightleftharpoons S_2 + G_2$), the reactant-product interface maintains the same shape and migrates at a uniform rate toward the centre of the pellet. The interface is sharply defined. When the reactant or product are of a different colour or refractive index, or when a colour difference of one component can be developed chemically, the interface can be observed readily. In the $Fe_2(SO_4)_3$-Fe_2O_3 system, for example (1), the rust colour of hematite can be easily differentiated from the off-white colour of ferric sulphate. Similarly, in the $CaCO_3$-CaO system, the addition of a small amount of a phenolphthalein solution can be used to develop an intense pink colour in the CaO product because of its high degree of alkalinity in water.

To express the rate of reaction per unit of interfacial area, it is necessary to normalize the experimentally measured reaction rate. One method of doing this is developed in Fig. 3, which is based on the work of McKewan (2). In this instance the calculation is made for a cylindrical pellet, but the same method can be applied to any particle having reasonably simple geometry. The calculation is based on determining the volume of product formed as a function of a single parameter of the pellet. In this case the radius of the pellet was chosen and the height expressed as a function of the radius and a constant, a, which is characteristic of the pellet shape. From the method suggested in Fig. 3, it is evident that f, the fractional penetration of the radius, is related by a simple cubic equation to the fraction α of the material decomposed. When the values

of f obtained from this equation are multiplied by the original radius of the pellet and its density, the weight loss per unit of interfacial area is obtained. A constant surface roughness factor is assumed and disregarded.

Solution of the cubic equation for many points can be quite time-consuming. Approximate solutions may be obtained from a graph prepared by substituting selected values of f in the equation and solving for α. More exact results may be obtained by reference to Table II in which one thousand computer solutions of the cubic equation for a = 1 are shown for the range of α from 0.001 to 1.000. This table is particularly useful because the relationship when a = 1 (equal height and diameter) applies without alteration to cubes and to spheres. Other shapes, such as plates, discs, rods and bars, can be accommodated by the use of additional constants (3).

In Fig. 4 the relationship has been used to normalize the results from an experiment in which a pellet of calcium carbonate was heated at 800°C in a 50 $cm^3 \cdot min.^{-1}$ stream of dry nitrogen. A typical sigmoid curve is shown against the axis on the left side of the figure. When the results were normalized, the linear relationship plotted against the right side axis was obtained. The linearity of this relationship is in agreement with the concept of linear kinetics; the slope of the line is the rate constant for the reaction at the experimental temperature.

This technique of handling powdered materials has been used at a variety of temperatures to establish the temperature coefficient of the rate of reaction and the effects of partial pressures of carbon dioxide on the reaction rate (3). As might be expected, the technique fails when an attempt is made to use it at pressures below atmospheric. Under these circumstances, sporadic reaction of individual grains of powder occurs throughout the body of the pellet and it becomes impossible to estimate the interfacial area at any specific time during the decomposition.

The techniques of pelletizing and interfacial area normalization can be applied, not only to isothermal experiments, but also to experiments in which rate measurements are made during a linearly programmed heating of a sample (4). Three curves which are typical of the weight loss as a

function of temperatures are shown in Fig. 5. It is evident from the figure that the slower the rate of heating, the lower is the temperature at which the reaction is completed.

The curves in Fig. 5 were obtained for the dissociation of flat circular discs of compressed calcium carbonate. Because the pellet had a radius which was greater than its height by a factor of ten, there was only a minor change in the area of the interface during the reaction, and the shape of the curves can be considered as normalized for interfacial area change. A simplified form of dimensional analysis was used to determine the exact form of the relationship for resolving the data in Fig. 5. The method is as follows:

> When the rate constant is expressed in the units $k = g.cm.^{-2}.min.^{-1}$ and the right side of the equation is multiplied by $degree \cdot degree^{-1}$, a simple rearrangement of the units permits the expression of k as
>
> $$k = (degree \cdot min.^{-1}) \times (g.cm.^{-2}) \times (degree^{-1}).$$
>
> This is the product of a heating rate, a, a loss in weight per unit area, w, and the reciprocal of the absolute temperature. When this relationship is substituted in the Arrhenius equation, the following expressions are obtained:
>
> $$aw/T = Ae^{-E/RT} \quad \text{and}$$
> $$\log (aw/T) = \log A - E/2.303\ RT.$$
>
> This logarithmic expression is the equation of a linear relationship between log (aw/T) and reciprocal temperature. The slope of the relationship is -E/2.303 R, from which the activation energy, E, can be calculated.

In Fig. 6 this relationship has been shown applied to the decomposition of a pellet of calcium carbonate. The relationship is linear from 1.6 to about 88 percent, and from its slope an enthalpy of activation of 48 $kcal.mole^{-1}$ was calculated for the decomposition process. The value determined from isothermal experiments is 41 $kcal.mole^{-1}$ (3), which, within experimental error, is identical with the heat of reaction. Similar comparisons are shown in Table III.

In this type of solid-gas reaction it is impossible to separate the free energy of activation term from the entropy term (6), hence only the enthalpy of activation, $\Delta H^{\ddagger}$, is shown.

It is evident from Table III that, with the exception of copper oxysulphate, the values for the heat of reaction and the isothermally determined enthalpy of activation are identical within the error of experiment. It is also evident - again with the exception of copper oxysulphate - that the enthalpy of activation determined by the linearly programmed temperature experiments is greater than that determined isothermally. The question then arises as to what process or processes are represented by the enthalpy of activation determined from a linearly programmed temperature-increase experiment. At this point sufficient experimental information is not available to be sure of the designation of the slow steps in the reactions represented by these activation energies. There is, however, sufficient information to suggest a mechanism for the process. The suggestion is based on the two-interface-decomposition model of Garner (12). At the reactant-intermediate interface, a gaseous product is expelled to form an amorphous intermediate material which crystallizes at a second sharply defined interface. This is illustrated for calcium carbonate in Fig. 7.

If it is assumed that the process of decomposition is faster than that of crystallization, in an isothermal experiment no appreciable thickness of the amorphous intermediate material would be expected to develop. However, when the decomposition is done using a linearly-programmed heating rate, the two interfaces will separate rapidly and an increasingly thick layer of amorphous material will accumulate as the reaction proceeds. The energy relationships for these processes can be represented as shown in Fig. 8. The right side of the figure represents the endothermic enthalpy of decomposition ($\Delta H^{\ddagger} = 48$ kcal.mole^{-1}) to produce amorphous CaO* from $CaCO_3$. The subsequent step represents the exothermic enthalpy of crystallization ($\Delta H^{\ddagger} = -7$ kcal.mole^{-1}) of the amorphous material. The difference between the two enthalpies should be the heat of reaction, 41 kcal.mole^{-1}. The value of 41 kcal.mole^{-1} is in good agreement with the heat of reaction, and the value of 7 kcal.mole^{-1} is in good agreement with that of 8 kcal.mole^{-1} for the enthalpy of activation of CO_2 addition to CaO as determined in a

linearly programmed experiment (5). In an isothermal experiment, since the amorphous material is not retained, the energy relationship shown by the dotted line in Fig. 8 would be expected.

In the case of cupric oxysulphate, where the enthalpy of activation determined isothermally is identical with that determined by a linear heating programme, it seems reasonable to believe that amorphous copper oxide is the product from both experiments.

Sufficient evidence is not yet available to confirm this proposed reaction mechanism, but it is known, from the work of Frost et al. (13), that thick layers of amorphous material may be prepared by the removal of water from some hydrates. In addition, it has been observed for a number of decomposition reactions, that when the reaction product is crystalline the heat of reaction and the enthalpy of activation are identical (12). The final indication of the validity of the hypothesis is that the heat of the amorphous-to-crystalline transition for some hydrates (13) is about 7 to 8 kcal.mole^{-1}, which is within the 3 to 17 kcal.mole^{-1} range shown in the column on the right side of Table III.

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TABLE I

Comparison of Principal Features of Homogeneous and Heterogeneous Reactions

HOMOGENEOUS	HETEROGENEOUS
$G_1G_2 \rightleftarrows G_1 + G_2$	$S_1 \rightleftarrows S_2 + G_1$ $S_1 + G_1 \rightleftarrows G_2$ $S_1 + G_1 \rightleftarrows S_2 + G_2$
$G_1G_2 \rightleftarrows (G_1 \text{--} G_2) \rightarrow G_1 + G_2$	$S_1 \quad S_2 \quad G_1$ $\longleftarrow \mid \longrightarrow G_1 \longrightarrow \mid \longrightarrow$
COLLI-SION ACTIVATED STATE PRODUCTS	REACTION INTERFACE ORIGINAL SURFACE
Amount of reaction = kct	Amount of reaction = kAt
$k = g.litre^{-1}.min.^{-1}$	$k = g.cm.^{-2}.min.^{-1}$

TABLE III

Comparison of Heats of Reaction with Enthalpies of Activation Determined by Isothermal and Linearly Programmed Temperature Experiments

Reaction	ΔH	$\Delta H^{\ddagger}_{iso}$	$\Delta H^{\ddagger}_{lin}$	$\Delta H^{\ddagger}_{lin} - \Delta H^{\ddagger}_{iso}$
$BaCl_2.2H_2O \rightleftarrows BaCl_2.H_2O + H_2O$	16 (7)	16 (8)	19 (8)	3
$BaCl_2.H_2O \rightleftarrows BaCl_2 + H_2O$	18 (7)	18 (8)	26 (8)	8
$CaCO_3 \rightleftarrows CaO + CO_2$	41 (9)	41 (3)	48 (4)	7
$2CuSO_4 \rightleftarrows CuO.CuSO_4 + SO_3$	50 (10)	54 (11)	71 (11)	17
$CuO.CuSO_4 \rightleftarrows 2CuO + SO_3$	49 (10)	67 (11)	68 (11)	-

TABLE 2

Computer Solutions of Cubic Equations for Values of α from 0.001 to 1.000

ALPHA	F	ALPHA	F	ALPHA	F	ALPHA	F
.001	.0003	.051	.0173	.101	.0349	.151	.0531
.002	.0007	.052	.0176	.102	.0352	.152	.0535
.003	.0010	.053	.0180	.103	.0356	.153	.0538
.004	.0013	.054	.0183	.104	.0359	.154	.0542
.005	.0017	.055	.0187	.105	.0363	.155	.0546
.006	.0020	.056	.0190	.106	.0367	.156	.0550
.007	.0023	.057	.0194	.107	.0370	.157	.0553
.008	.0027	.058	.0197	.108	.0374	.158	.0557
.009	.0030	.059	.0201	.109	.0377	.159	.0561
.010	.0033	.060	.0204	.110	.0381	.160	.0565
.011	.0037	.061	.0208	.111	.0385	.161	.0568
.012	.0040	.062	.0211	.112	.0388	.162	.0572
.013	.0044	.063	.0215	.113	.0392	.163	.0576
.014	.0047	.064	.0218	.114	.0395	.164	.0580
.015	.0050	.065	.0222	.115	.0399	.165	.0583
.016	.0054	.066	.0225	.116	.0403	.166	.0587
.017	.0057	.067	.0229	.117	.0406	.167	.0591
.018	.0060	.068	.0232	.118	.0410	.168	.0595
.019	.0064	.069	.0236	.119	.0414	.169	.0598
.020	.0067	.070	.0239	.120	.0417	.170	.0602
.021	.0070	.071	.0243	.121	.0421	.171	.0606
.022	.0074	.072	.0246	.122	.0424	.172	.0610
.023	.0077	.073	.0250	.123	.0428	.173	.0614
.024	.0081	.074	.0253	.124	.0432	.174	.0617
.025	.0084	.075	.0257	.125	.0435	.175	.0621
.026	.0087	.076	.0260	.126	.0439	.176	.0625
.027	.0091	.077	.0264	.127	.0443	.177	.0629
.028	.0094	.078	.0267	.128	.0446	.178	.0632
.029	.0098	.079	.0271	.129	.0450	.179	.0636
.030	.0101	.080	.0274	.130	.0454	.180	.0640
.031	.0104	.081	.0278	.131	.0457	.181	.0644
.032	.0108	.082	.0281	.132	.0461	.182	.0648
.033	.0111	.083	.0285	.133	.0465	.183	.0652
.034	.0115	.084	.0288	.134	.0468	.184	.0655
.035	.0118	.085	.0292	.135	.0472	.185	.0659
.036	.0121	.086	.0295	.136	.0476	.186	.0663
.037	.0125	.087	.0299	.137	.0479	.187	.0667
.038	.0128	.088	.0302	.138	.0483	.188	.0671
.039	.0132	.089	.0306	.139	.0487	.189	.0674
.040	.0135	.090	.0309	.140	.0490	.190	.0678
.041	.0139	.091	.0313	.141	.0494	.191	.0682
.042	.0142	.092	.0317	.142	.0498	.192	.0686
.043	.0145	.093	.0320	.143	.0501	.193	.0690
.044	.0149	.094	.0324	.144	.0505	.194	.0694
.045	.0152	.095	.0327	.145	.0509	.195	.0698
.046	.0156	.096	.0331	.146	.0512	.196	.0701
.047	.0159	.097	.0334	.147	.0516	.197	.0705
.048	.0163	.098	.0338	.148	.0520	.198	.0709
.049	.0166	.099	.0342	.149	.0524	.199	.0713
.050	.0170	.100	.0345	.150	.0527	.200	.0717

TABLE 2 (Continued)

Computer Solutions of Cubic Equations for Values of α from 0.001 to 1.000

ALPHA	F	ALPHA	F	ALPHA	F	ALPHA	F
.201	.0721	.251	.0918	.301	.1125	.351	.1342
.202	.0725	.252	.0922	.302	.1129	.352	.1347
.203	.0728	.253	.0927	.303	.1134	.353	.1351
.204	.0732	.254	.0931	.304	.1138	.354	.1355
.205	.0736	.255	.0935	.305	.1142	.355	.1360
.206	.0740	.256	.0939	.306	.1146	.356	.1364
.207	.0744	.257	.0943	.307	.1151	.357	.1369
.208	.0748	.258	.0947	.308	.1155	.358	.1373
.209	.0752	.259	.0951	.309	.1159	.359	.1378
.210	.0756	.260	.0955	.310	.1163	.360	.1382
.211	.0760	.261	.0959	.311	.1168	.361	.1387
.212	.0763	.262	.0963	.312	.1172	.362	.1391
.213	.0767	.263	.0967	.313	.1176	.363	.1396
.214	.0771	.264	.0971	.314	.1181	.364	.1400
.215	.0775	.265	.0975	.315	.1185	.365	.1405
.216	.0779	.266	.0979	.316	.1189	.366	.1409
.217	.0783	.267	.0984	.317	.1193	.367	.1414
.218	.0787	.268	.0988	.318	.1198	.368	.1418
.219	.0791	.269	.0992	.319	.1202	.369	.1423
.220	.0795	.270	.0996	.320	.1206	.370	.1427
.221	.0799	.271	.1000	.321	.1211	.371	.1432
.222	.0803	.272	.1004	.322	.1215	.372	.1436
.223	.0807	.273	.1008	.323	.1219	.373	.1441
.224	.0811	.274	.1012	.324	.1224	.374	.1446
.225	.0815	.275	.1016	.325	.1228	.375	.1450
.226	.0819	.276	.1021	.326	.1232	.376	.1455
.227	.0822	.277	.1025	.327	.1237	.377	.1459
.228	.0826	.278	.1029	.328	.1241	.378	.1464
.229	.0830	.279	.1033	.329	.1245	.379	.1468
.230	.0834	.280	.1037	.330	.1250	.380	.1473
.231	.0838	.281	.1041	.331	.1254	.381	.1478
.232	.0842	.282	.1045	.332	.1258	.382	.1482
.233	.0846	.283	.1050	.333	.1263	.383	.1487
.234	.0850	.284	.1054	.334	.1267	.384	.1491
.235	.0854	.285	.1058	.335	.1271	.385	.1496
.236	.0858	.286	.1062	.336	.1276	.386	.1501
.237	.0862	.287	.1066	.337	.1280	.387	.1505
.238	.0866	.288	.1071	.338	.1285	.388	.1510
.239	.0870	.289	.1075	.339	.1289	.389	.1514
.240	.0874	.290	.1079	.340	.1293	.390	.1519
.241	.0878	.291	.1083	.341	.1298	.391	.1524
.242	.0882	.292	.1087	.342	.1302	.392	.1528
.243	.0886	.293	.1091	.343	.1307	.393	.1533
.244	.0890	.294	.1096	.344	.1311	.394	.1538
.245	.0894	.295	.1100	.345	.1315	.395	.1542
.246	.0898	.296	.1104	.346	.1320	.396	.1547
.247	.0902	.297	.1108	.347	.1324	.397	.1552
.248	.0906	.298	.1113	.348	.1329	.398	.1556
.249	.0910	.299	.1117	.349	.1333	.399	.1561
.250	.0914	.300	.1121	.350	.1338	.400	.1566

TABLE 2 (Continued)

Computer Solutions of Cubic Equations for Values of α from 0.001 to 1.000

ALPHA	F	ALPHA	F	ALPHA	F	ALPHA	F
.401	.1570	.451	.1812	.501	.2068	.551	.2343
.402	.1575	.452	.1817	.502	.2074	.552	.2348
.403	.1580	.453	.1822	.503	.2079	.553	.2354
.404	.1584	.454	.1827	.504	.2084	.554	.2360
.405	.1589	.455	.1832	.505	.2090	.555	.2365
.406	.1594	.456	.1837	.506	.2095	.556	.2371
.407	.1599	.457	.1842	.507	.2100	.557	.2377
.408	.1603	.458	.1847	.508	.2106	.558	.2383
.409	.1608	.459	.1852	.509	.2111	.559	.2388
.410	.1613	.460	.1857	.510	.2116	.560	.2394
.411	.1618	.461	.1862	.511	.2122	.561	.2400
.412	.1622	.462	.1867	.512	.2127	.562	.2406
.413	.1627	.463	.1872	.513	.2132	.563	.2411
.414	.1632	.464	.1877	.514	.2138	.564	.2417
.415	.1637	.465	.1882	.515	.2143	.565	.2423
.416	.1641	.466	.1887	.516	.2149	.566	.2429
.417	.1646	.467	.1892	.517	.2154	.567	.2435
.418	.1651	.468	.1897	.518	.2159	.568	.2440
.419	.1656	.469	.1902	.519	.2165	.569	.2446
.420	.1660	.470	.1907	.520	.2170	.570	.2452
.421	.1665	.471	.1912	.521	.2176	.571	.2458
.422	.1670	.472	.1918	.522	.2181	.572	.2464
.423	.1675	.473	.1923	.523	.2187	.573	.2470
.424	.1680	.474	.1928	.524	.2192	.574	.2476
.425	.1684	.475	.1933	.525	.2198	.575	.2482
.426	.1689	.476	.1938	.526	.2203	.576	.2487
.427	.1694	.477	.1943	.527	.2209	.577	.2493
.428	.1699	.478	.1948	.528	.2214	.578	.2499
.429	.1704	.479	.1953	.529	.2220	.579	.2505
.430	.1709	.480	.1959	.530	.2225	.580	.2511
.431	.1714	.481	.1964	.531	.2231	.581	.2517
.432	.1718	.482	.1969	.532	.2236	.582	.2523
.433	.1723	.483	.1974	.533	.2242	.583	.2529
.434	.1728	.484	.1979	.534	.2247	.584	.2535
.435	.1733	.485	.1984	.535	.2253	.585	.2541
.436	.1738	.486	.1990	.536	.2258	.586	.2547
.437	.1743	.487	.1995	.537	.2264	.587	.2553
.438	.1748	.488	.2000	.538	.2269	.588	.2559
.439	.1753	.489	.2005	.539	.2275	.589	.2565
.440	.1757	.490	.2010	.540	.2281	.590	.2571
.441	.1762	.491	.2016	.541	.2286	.591	.2577
.442	.1767	.492	.2021	.542	.2292	.592	.2583
.443	.1772	.493	.2026	.543	.2297	.593	.2589
.444	.1777	.494	.2031	.544	.2303	.594	.2595
.445	.1782	.495	.2037	.545	.2309	.595	.2601
.446	.1787	.496	.2042	.546	.2314	.596	.2607
.447	.1792	.497	.2047	.547	.2320	.597	.2614
.448	.1797	.498	.2052	.548	.2326	.598	.2620
.449	.1802	.499	.2058	.549	.2331	.599	.2626
.450	.1807	.500	.2063	.550	.2337	.600	.2632

TABLE 2 (Continued)

Computer Solutions of Cubic Equations for Values of α from 0.001 to 1.000

ALPHA	F	ALPHA	F	ALPHA	F	ALPHA	F
.601	.2638	.651	.2959	.701	.3313	.751	.3709
.602	.2644	.652	.2966	.702	.3321	.752	.3717
.603	.2650	.653	.2973	.703	.3328	.753	.3726
.604	.2657	.654	.2980	.704	.3336	.754	.3734
.605	.2663	.655	.2986	.705	.3343	.755	.3743
.606	.2669	.656	.2993	.706	.3351	.756	.3751
.607	.2675	.657	.3000	.707	.3358	.757	.3760
.608	.2681	.658	.3007	.708	.3366	.758	.3768
.609	.2688	.659	.3014	.709	.3373	.759	.3777
.610	.2694	.660	.3020	.710	.3381	.760	.3786
.611	.2700	.661	.3027	.711	.3389	.761	.3794
.612	.2706	.662	.3034	.712	.3396	.762	.3803
.613	.2713	.663	.3041	.713	.3404	.763	.3812
.614	.2719	.664	.3048	.714	.3411	.764	.3820
.615	.2725	.665	.3055	.715	.3419	.765	.3829
.616	.2732	.666	.3062	.716	.3427	.766	.3838
.617	.2738	.667	.3069	.717	.3435	.767	.3847
.618	.2744	.668	.3076	.718	.3442	.768	.3855
.619	.2750	.669	.3083	.719	.3450	.769	.3864
.620	.2757	.670	.3090	.720	.3458	.770	.3873
.621	.2763	.671	.3097	.721	.3466	.771	.3882
.622	.2770	.672	.3104	.722	.3473	.772	.3891
.623	.2776	.673	.3111	.723	.3481	.773	.3900
.624	.2782	.674	.3118	.724	.3489	.774	.3909
.625	.2789	.675	.3125	.725	.3497	.775	.3918
.626	.2795	.676	.3132	.726	.3505	.776	.3927
.627	.2802	.677	.3139	.727	.3513	.777	.3936
.628	.2808	.678	.3146	.728	.3521	.778	.3945
.629	.2814	.679	.3153	.729	.3529	.779	.3954
.630	.2821	.680	.3160	.730	.3537	.780	.3963
.631	.2827	.681	.3167	.731	.3545	.781	.3972
.632	.2834	.682	.3174	.732	.3553	.782	.3982
.633	.2840	.683	.3182	.733	.3561	.783	.3991
.634	.2847	.684	.3189	.734	.3569	.784	.4000
.635	.2853	.685	.3196	.735	.3577	.785	.4009
.636	.2860	.686	.3203	.736	.3585	.786	.4019
.637	.2867	.687	.3210	.737	.3593	.787	.4028
.638	.2873	.688	.3218	.738	.3601	.788	.4037
.639	.2880	.689	.3225	.739	.3609	.789	.4047
.640	.2886	.690	.3232	.740	.3617	.790	.4056
.641	.2893	.691	.3239	.741	.3626	.791	.4066
.642	.2899	.692	.3247	.742	.3634	.792	.4075
.643	.2906	.693	.3254	.743	.3642	.793	.4085
.644	.2913	.694	.3261	.744	.3650	.794	.4094
.645	.2919	.695	.3269	.745	.3659	.795	.4104
.646	.2926	.696	.3276	.746	.3667	.796	.4113
.647	.2933	.697	.3283	.747	.3675	.797	.4123
.648	.2939	.698	.3291	.748	.3684	.798	.4133
.649	.2946	.699	.3298	.749	.3692	.799	.4142
.650	.2953	.700	.3306	.750	.3700	.000	.4152

TABLE 2 (Continued)

Computer Solutions of Cubic Equations for Values of α from 0.001 to 1.000

ALPHA	F	ALPHA	F	ALPHA	F	ALPHA	F
.801	.4162	.851	.4699	.901	.5374	.951	.6341
.802	.4172	.852	.4710	.902	.5390	.952	.6366
.803	.4181	.853	.4722	.903	.5405	.953	.6391
.804	.4191	.854	.4734	.904	.5421	.954	.6417
.805	.4201	.855	.4746	.905	.5437	.955	.6443
.806	.4211	.856	.4759	.906	.5453	.956	.6470
.807	.4221	.857	.4771	.907	.5469	.957	.6497
.808	.4231	.858	.4783	.908	.5486	.958	.6524
.809	.4241	.859	.4795	.909	.5502	.959	.6552
.810	.4251	.860	.4808	.910	.5519	.960	.6580
.811	.4261	.861	.4820	.911	.5535	.961	.6609
.812	.4271	.862	.4832	.912	.5552	.962	.6638
.813	.4282	.863	.4845	.913	.5569	.963	.6668
.814	.4292	.864	.4857	.914	.5586	.964	.6698
.815	.4302	.865	.4870	.915	.5603	.965	.6729
.816	.4312	.866	.4883	.916	.5620	.966	.6760
.817	.4323	.867	.4896	.917	.5638	.967	.6792
.818	.4333	.868	.4908	.918	.5656	.968	.6825
.819	.4343	.869	.4921	.919	.5673	.969	.6859
.820	.4354	.870	.4934	.920	.5691	.970	.6893
.821	.4364	.871	.4947	.921	.5709	.971	.6928
.822	.4375	.872	.4960	.922	.5727	.972	.6963
.823	.4385	.873	.4973	.923	.5746	.973	.7000
.824	.4396	.874	.4987	.924	.5764	.974	.7038
.825	.4407	.875	.5000	.925	.5783	.975	.7076
.826	.4417	.876	.5013	.926	.5802	.976	.7116
.827	.4428	.877	.5027	.927	.5821	.977	.7156
.828	.4439	.878	.5040	.928	.5840	.978	.7198
.829	.4450	.879	.5054	.929	.5859	.979	.7241
.830	.4460	.880	.5068	.930	.5879	.980	.7286
.831	.4471	.881	.5081	.931	.5898	.981	.7332
.832	.4482	.882	.5095	.932	.5918	.982	.7379
.833	.4493	.883	.5109	.933	.5938	.983	.7429
.834	.4504	.884	.5123	.934	.5959	.984	.7480
.835	.4515	.885	.5137	.935	.5979	.985	.7534
.836	.4526	.886	.5151	.936	.6000	.986	.7590
.837	.4537	.887	.5165	.937	.6021	.987	.7649
.838	.4549	.888	.5180	.938	.6042	.988	.7711
.839	.4560	.889	.5194	.939	.6064	.989	.7776
.840	.4571	.890	.5209	.940	.6085	.990	.7846
.841	.4582	.891	.5223	.941	.6107	.991	.7920
.842	.4594	.892	.5238	.942	.6129	.992	.8000
.843	.4605	.893	.5253	.943	.6151	.993	.8087
.844	.4617	.894	.5267	.944	.6174	.994	.8183
.845	.4628	.895	.5282	.945	.6197	.995	.8290
.846	.4640	.896	.5297	.946	.6220	.996	.8413
.847	.4652	.897	.5312	.947	.6244	.997	.8558
.848	.4663	.898	.5328	.948	.6267	.998	.8740
.849	.4675	.899	.5343	.949	.6292	.999	.9000
.850	.4687	.900	.5358	.950	.6316	1.000	1.0000

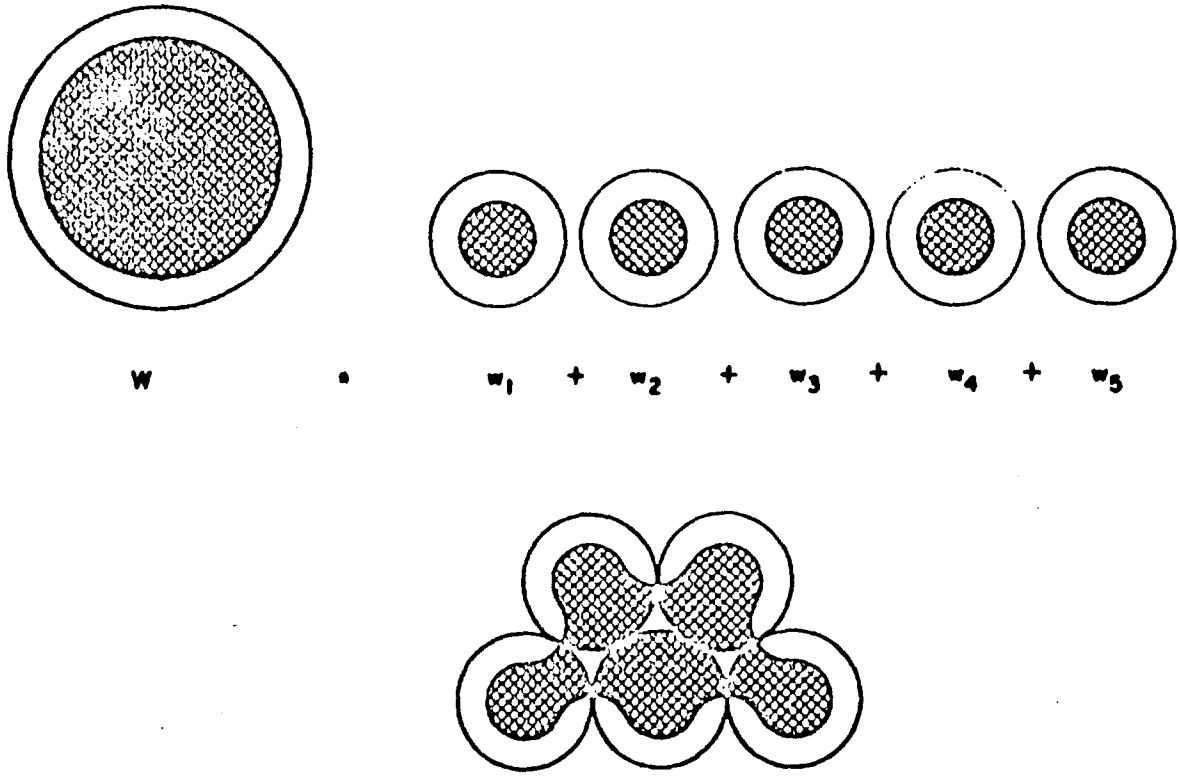


FIGURE 1 - Solid spherical particles of decomposing material

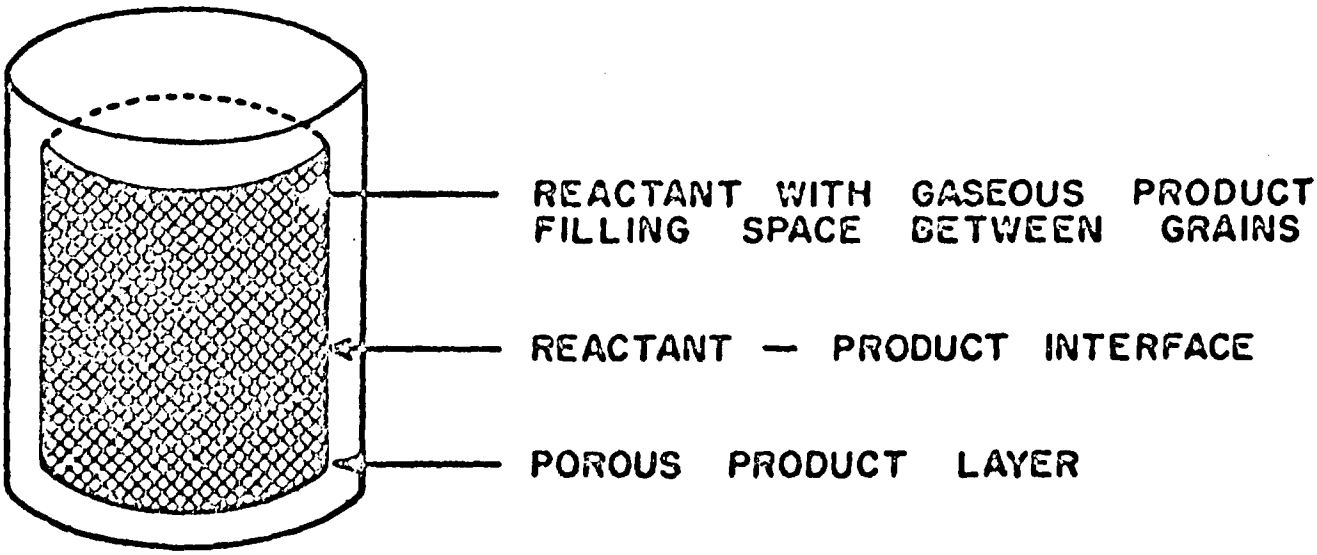
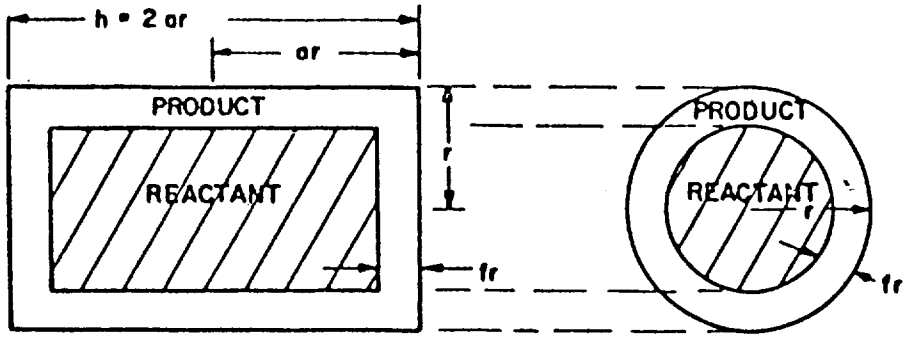


FIGURE 2 - Partly decomposed pellet of compressed powder



$$\alpha = \text{FRACTION DECOMPOSED} = \frac{\text{ORIGINAL VOLUME} - \text{UNREACTED VOLUME}}{\text{ORIGINAL VOLUME}} = \frac{V_0 - V}{V_0}$$

$$\text{but } V_0 = (2ar)(\pi r^2) = 2a\pi r^3$$

$$V = 2(ar - fr)\pi(r - fr)^2 = 2\pi r^3(a-f)(1-f)^2$$

$$\alpha = \frac{V_0 - V}{V} = \frac{2a\pi r^3 - 2\pi r^3(a-f)(1-f)^2}{2a\pi r^3}$$

$$\alpha = 1 - \left(\frac{a-f}{a}\right)(1-f)^2 \quad \text{when } a = 1,\ \alpha = 1-(1-f)^3 \text{ or } f = 1-(1-\alpha)^{\frac{1}{3}}$$

FIGURE 3 - Development of equation for normalizing interfacial area changes during decomposition

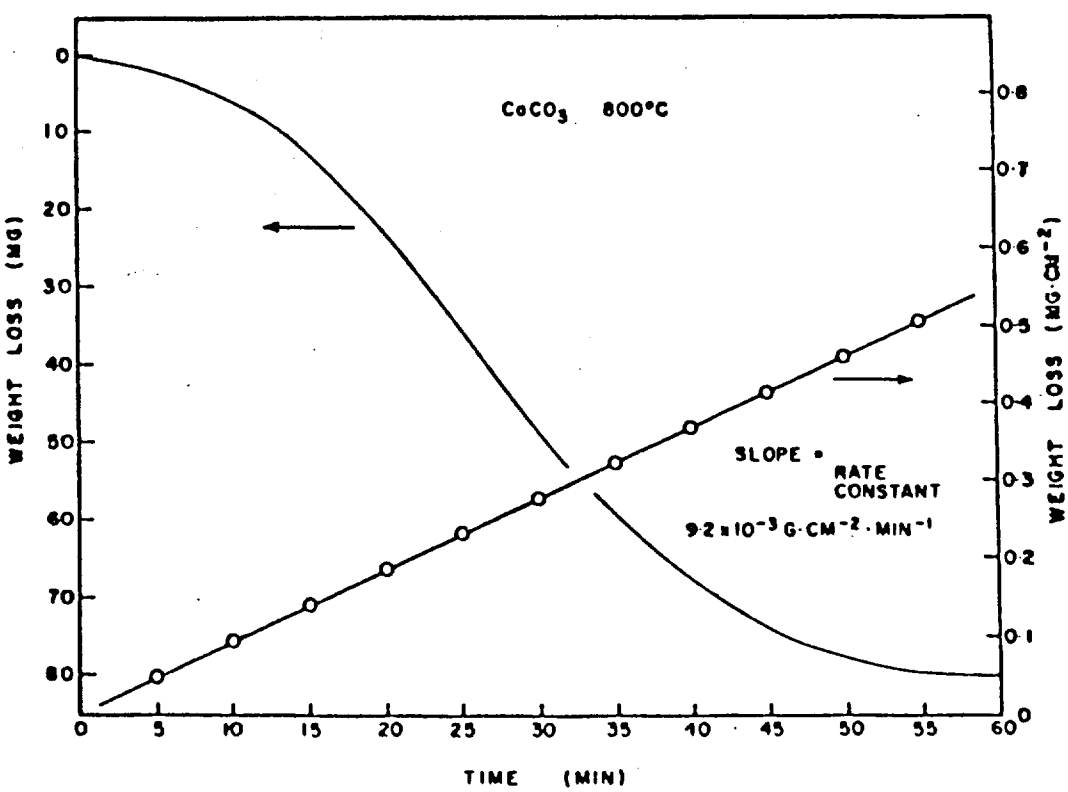


FIGURE 4 - Original and normalized results for the decomposition of calcium carbonate at 800°C in 50 $cm^2 \cdot min^{-1}$ of nitrogen

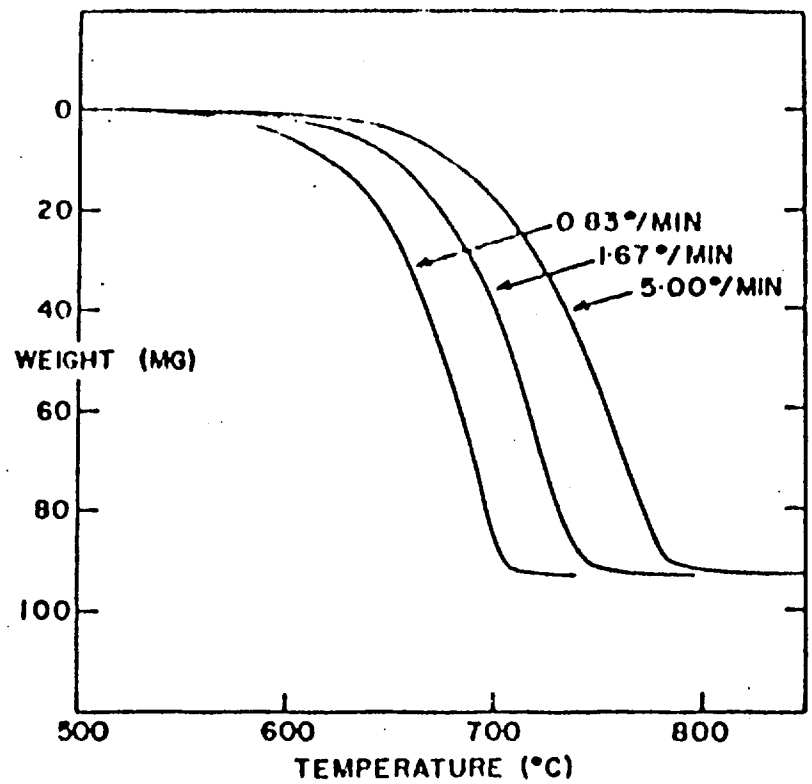


FIGURE 5 - Automatic recording of weight loss versus temperature for the heating of calcium carbonate at 0.83°C·min^{-1}, 1.67°C·min^{-1} and 5.00°C·min^{-1}

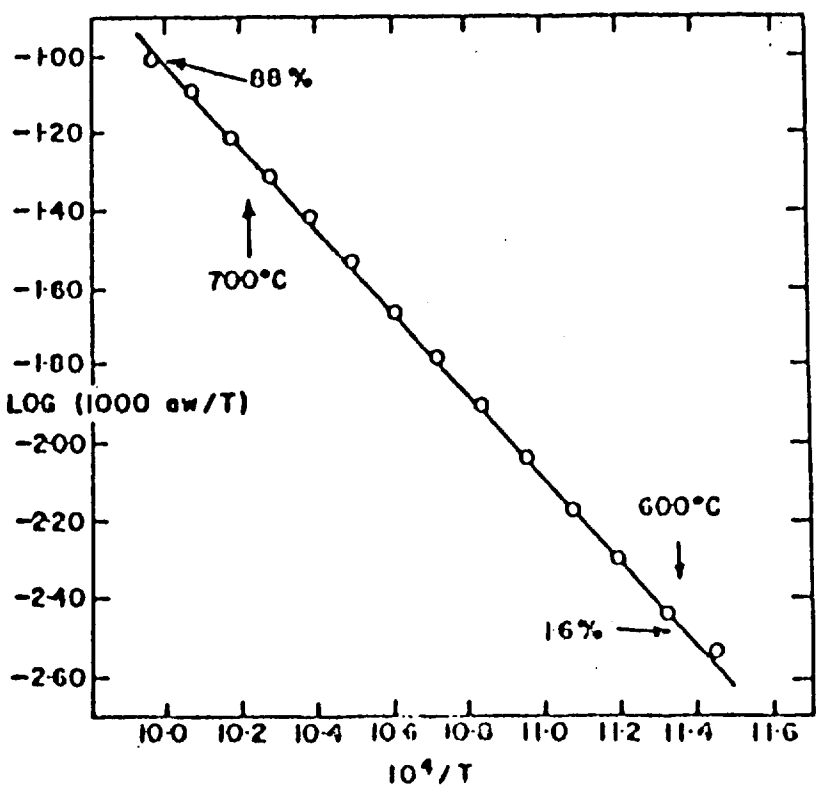


FIGURE 6 - Relationship for determining enthalpy of activation from a linearly programmed temperature-increasing experiment.

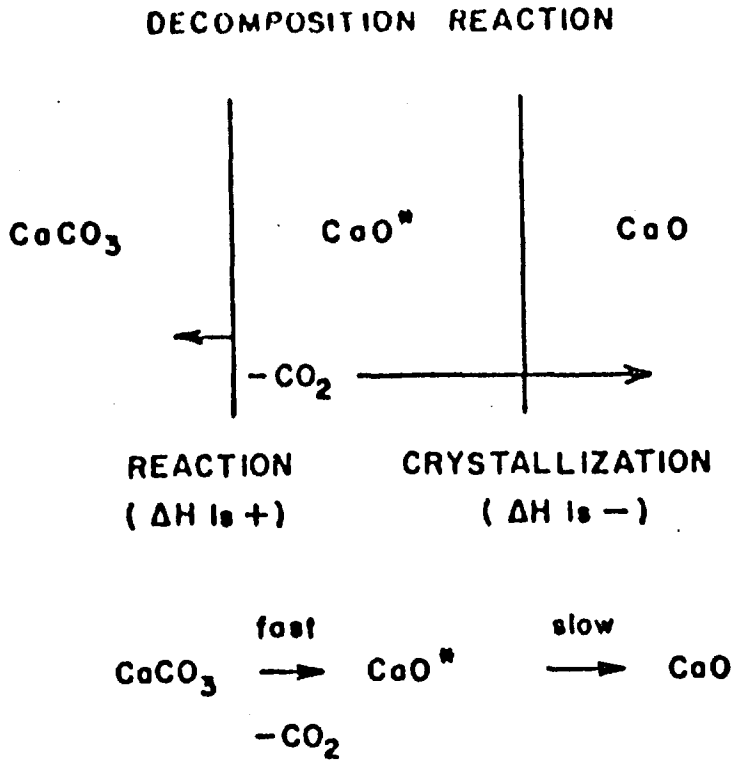


FIGURE 7 - Two interface model of decomposition process

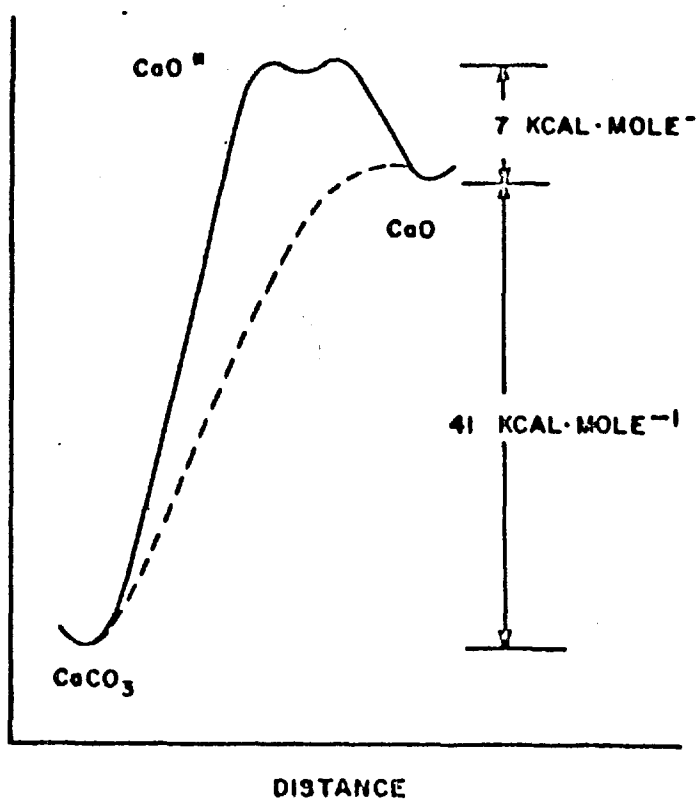


FIGURE 8 - Energy relationship for the formation of amorphous and crystalline calcium oxide from calcium carbonate