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EFFECT OF ALKALINE EARTH METAL DOPANTS ON THE THERMAL DECOMPOSITION OF THE $CaCO_3$–SiO_2 SYSTEM.
PART I

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ABSTRACT

Mixtures of calcium carbonate and silica in a 2 : 1 molar ratio containing varying amounts of MgO, $SrCO_3$ and $BaCO_3$ as dopants were separately subjected to thermal analysis. The decomposition behaviour of these systems is reported here on the basis of TG, DTG and DTA investigations. Activation energies (E_a) and enthalpies (ΔH) for the decomposition reactions have been calculated and the variations in these parameters have been discussed. It was observed that the application of a first-order kinetic equation provides an adequate quantitative description of the DTA curves and E_a values, calculated from the thermal data.

INTRODUCTION

Dicalcium silicate is an important mineral constituent of Ordinary Portland Cement, resulting from the reaction of calcium carbonate derived from limestone and silica from alumino silicate and quartz. The process is highly energy intensive and efforts are being made to bring about the reaction at a lower temperature and with relative ease. The major endothermic reaction is the thermal decomposition of calcium carbonate which is crucial to the energy balance in the formation of dicalcium silicate.

Investigations have been reported on the role of activators in lowering the decomposition temperature and improving the rate of reaction.

The thermal decomposition of pure calcium carbonate and the effect of various dopants on its decomposition behaviour have been studied [1–3]. Some work has also been reported on the thermal decomposition of naturally occurring limestone containing different amounts of impurities such as SiO_2, Fe_2O_3, Al_2O_3, etc. [4,5]. The literature reveals that systematic thermal studies of calcium carbonate in the presence of silica in a 2 : 1 molar ratio have not been carried out. Here, we report part of a study on the formation of dicalcium silicate using pure calcium carbonate and silica in a 2 : 1 molar ratio in the presence of dopants.

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Since decomposition precedes the formation of dicalcium silicate, the effect of various alkaline earth dopants (MgO, $SrCO_3$, $BaCO_3$) on the kinetics of decomposition of $CaCO_3$ in the $CaCO_3$–SiO_2 system has been studied.

EXPERIMENTAL

Samples of calcium carbonate (SM, GR) and quartz powder (Fluka, purity > 99.5%) in a 2 : 1 molar ratio along with varying amounts of MgO, $SrCO_3$ and $BaCO_3$ (BDH Analar) as dopants were separately ground to a fine powder and homogenised in a pot mill. The resulting mixture, after thorough mixing with distilled water, was changed into a slurry and shaped into nodules of ~ 10 mm size. These nodules were dried at 100 ± 5°C in a hot-air oven, pulverised to pass through a 100-μm sieve and then used for the experimental work.

The thermal measurements were carried out on a Mettler thermal analyzer (TA-1) system which simultaneously records DTA, DTG and TG curves. The samples (60 mg) were heated at a rate of 8°C $\min^{-1}$ in a platinum crucible to a temperature of around 1200°C. α-Alumina was used as reference material, which had been previously burnt at 1500°C for 30 min. All the operations were, as far as possible, performed under identical conditions. The calcium carbonate decomposition peak was used to calculate the enthalpy in the present case. Duplicate runs were made to check for reproducibility. The following data were computed from the thermal curves.

(i) Peak temperature of decomposition of calcium carbonate from the DTA curve.

(ii) Activation energies from the DTA and DTG curves [6,7].

(iii) Enthalpies (ΔH) from the DTA curve [8].

(iv) Shape index from the DTA curve [9].

RESULTS AND DISCUSSION

A broad exotherm in the DTA curve was observed for all samples in the region 100–200°C, which could be due to heat capacity changes since no features are observed in the DTG curve. A distinct endotherm at 370°C was observed, due to the dehydration of magnesium hydroxide (Fig. 1). This feature is not observed in the case of $SrCO_3$ and $BaCO_3$ since they are in the carbonate form and decompose at higher temperatures, close to that of calcium carbonate. The endothermic peak at 575°C may be attributed to an α–β-quartz transformation, which is not influenced by the presence or concentration of the dopants studied. The threshold decomposition temperature of calcium carbonate as indicated by the DTA and DTG curves, shape

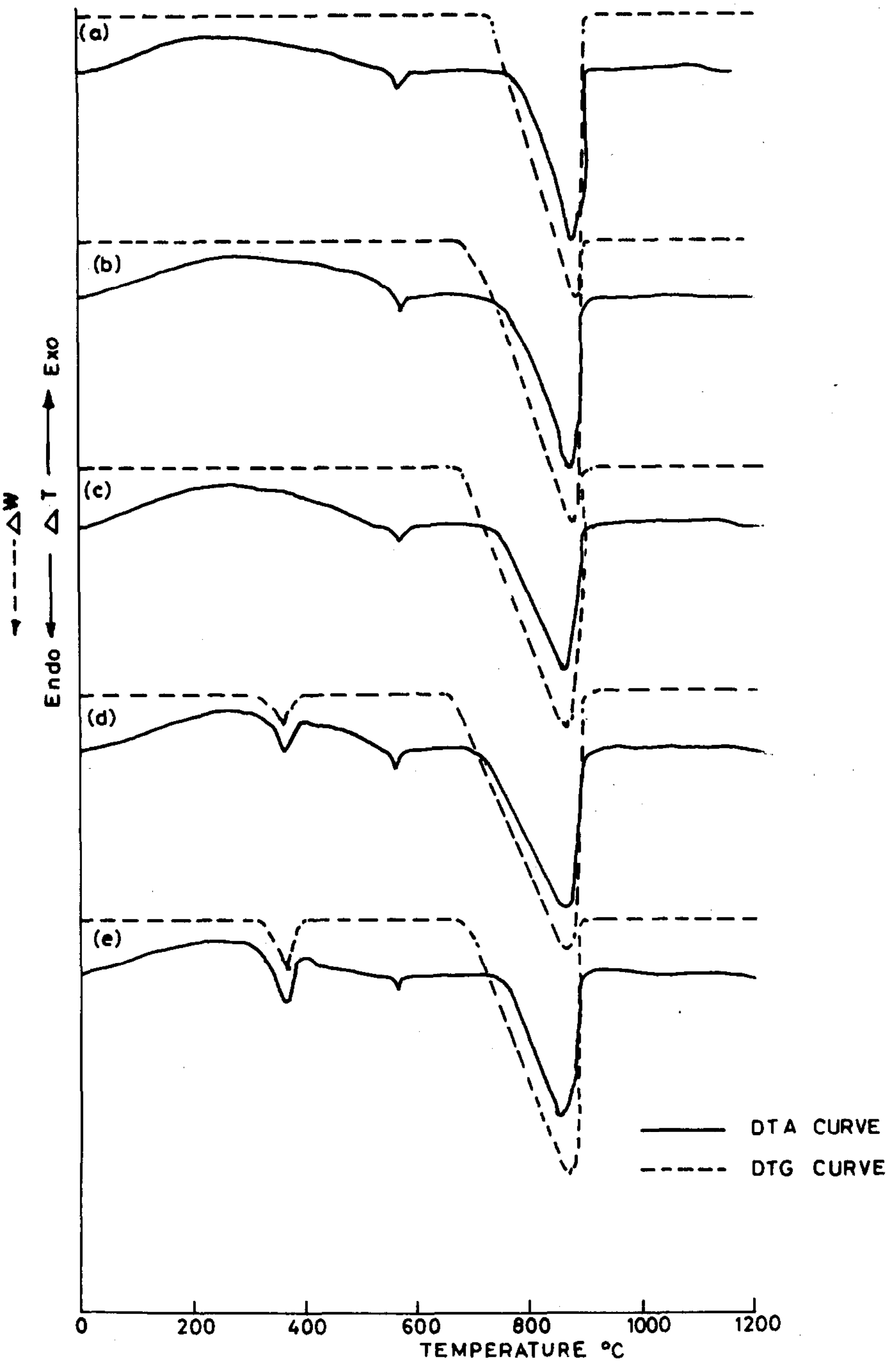


Fig. 1. Thermal curves of (a) 2 $CaCO_3:SiO_2$, (b) 2 $CaCO_3:SiO_2$ + 0.1% MgO, (c) 2 $CaCO_3:SiO_2$ + 0.5% MgO, (d) 2 $CaCO_3:SiO_2$ + 1% MgO, (e) 2 $CaCO_3:SiO_2$ + 5% MgO.

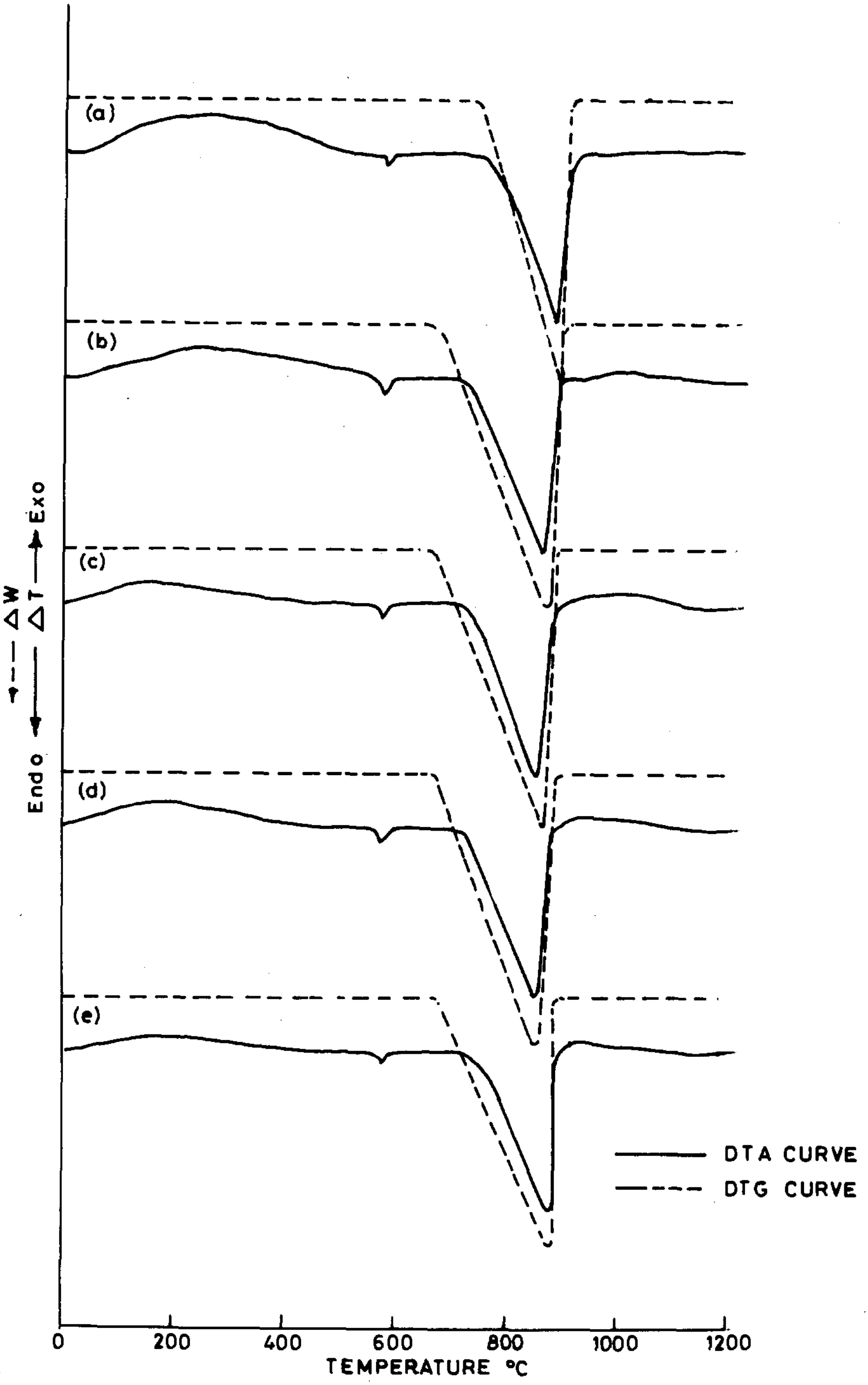


Fig. 2. Thermal curves of (a) 2 $CaCO_3:SiO_2$, (b) 2 $CaCO_3:SiO_2$ +0.1% $SrCO_3$, (c) 2 $CaCO_3:SiO_2$ +0.5% $SrCO_3$, (d) 2 $CaCO_3:SiO_2$ +1% $SrCO_3$, (e) 2 $CaCO_3:SiO_2$ +5% $SrCO_3$.

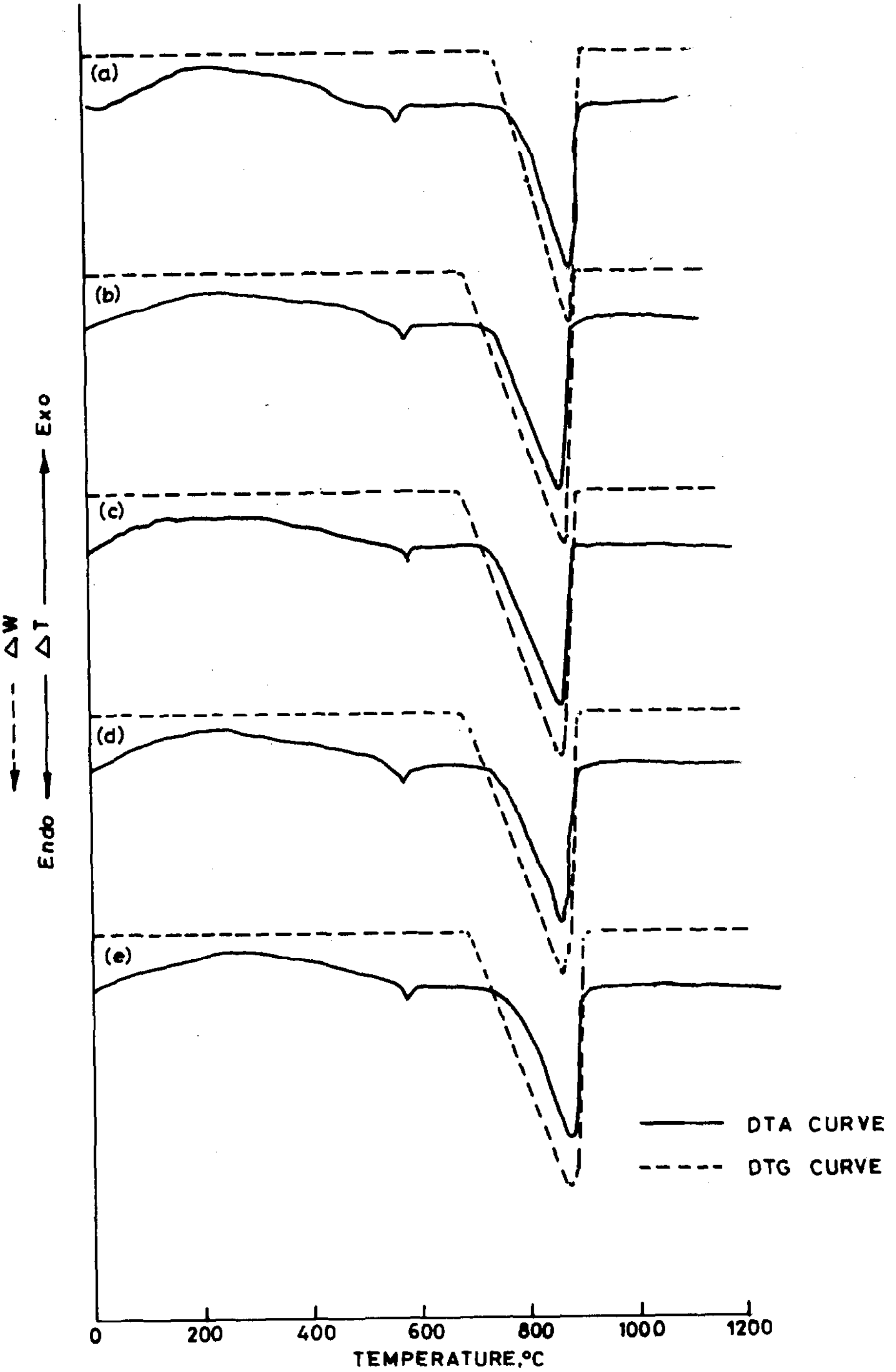


Fig. 3. Thermal curves of (a) 2 $CaCO_3:SiO_2$, (b) 2 $CaCO_3:SiO_2+0.1\%$ $BaCO_3$, (c) 2 $CaCO_3:SiO_2+0.5\%$ $BaCO_3$, (d) 2 $CaCO_3:SiO_2+1\%$ $BaCO_3$, (e) 2 $CaCO_3:SiO_2+5\%$ $BaCO_3$.

TABLE 1

Thermal analysis data of calcium carbonate decomposition (2 $CaCO_3:SiO_2$) in the presence of MgO

Sample	Decomposition temp. (°C)			Activation energy, E_a, by DTG (kJ mol^{-1})	Activation energy, E_a, by DTA (kJ mol^{-1})	ΔH (kJ mol^{-1})	Shape index
	Threshold	Peak	Termination				
2 $CaCO_3:SiO_2$	740	885	910	247	259	160	0.143
2 $CaCO_3:SiO_2$ + 0.1% MgO	695	870	900	213	213	142	0.174
2 $CaCO_3:SiO_2$ + 0.5% MgO	685	870	910	180	190	138	0.178
2 $CaCO_3:SiO_2$ + 1% MgO	665	870	900	163	176	135	0.182
2 $CaCO_3:SiO_2$ + 5% MgO	690	870	890	180	184	152	0.196

index of DTA peaks and the thermodynamic parameters obtained from the curves (Figs. 1–3) for various concentrations of dopants have been calculated (Tables 1–3). The calculated activation energy of pure calcium carbonate in the presence of silica in a 2 : 1 molar ratio is 247 kJ mol^{-1}. This value is in fair agreement with the value reported in ref. 5. This value gradually decreases to 163 kJ mol^{-1}, through 213 kJ mol^{-1}, as the amount of MgO increases from 0.1 to 1%, but rises with 5% MgO (180 kJ mol^{-1}). The activation energies calculated by the DTA technique are slightly higher than those from DTG but are within permissible limits as reported by Rao and

TABLE 2

Thermal analysis of calcium carbonate decomposition (2 $CaCO_3:SiO_2$) in the presence of $SrCO_3$

Sample	Decomposition temp. (°C)			Activation energy, E_a, by DTG (kJ mol^{-1})	Activation energy, E_a, by DTA (kJ mol^{-1})	ΔH (kJ mol^{-1})	Shape index
	Threshold	Peak	Termination				
2 $CaCO_3:SiO_2$	740	885	910	247	259	160	0.143
2 $CaCO_3:SiO_2$ + 0.1% $SrCO_3$	670	865	895	201	218	150	0.169
2 $CaCO_3:SiO_2$ + 0.5% $SrCO_3$	660	860	890	196	210	144	0.172
2 $CaCO_3:SiO_2$ + 1% $SrCO_3$	660	875	890	184	201	140	0.176
2 $CaCO_3:SiO_2$ + 5% $SrCO_3$	670	875	890	188	205	150	0.183

co-workers [2]. The threshold decomposition temperature of the pure system (2 $CaCO_3:SiO_2$) is 740°C, which is lowered by 45°C with 0.1% MgO and further lowered by 75°C with 1% MgO, but it rises on increasing MgO to 5%. Thus, the trend in variations of activation energy and the threshold temperature are similar. The peak decomposition temperature has been observed to be uniformly lower by 15°C.

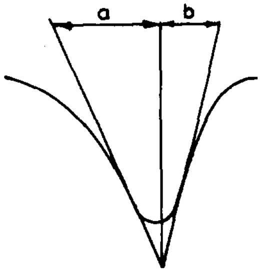
The effect of calcium carbonate decomposition is more pronounced with $SrCO_3$ as dopant compared with MgO (Table 2). The threshold temperature with 0.1% $SrCO_3$ decreases by 70°C and then further decreases by 80°C with 1% $SrCO_3$. No significant lowering of the threshold temperature was observed with further increasing the amount of $SrCO_3$. The peak decomposition temperature is also reduced by 20°C with 0.1 and 5% $SrCO_3$, which further decreases by 25°C with 1% $SrCO_3$. The peak temperature of decomposition with 5% $SrCO_3$ is, however, 15°C lower. The activation energy continues to decrease with up to a 1% addition of $SrCO_3$ and then starts increasing.

The effect of $BaCO_3$ on the thermal decomposition of $CaCO_3$ is given in Table 3, which shows that there is a steep fall in the threshold temperature by 50, 65 and 70°C with 0.1, 0.5 and 1% $BaCO_3$, respectively. The peak decomposition temperature of calcium carbonate is also decreased by 15°C with 0.1% $BaCO_3$, 25°C with 0.5% $BaCO_3$ and 30°C with 1% $BaCO_3$. A further increase in the concentration of $BaCO_3$ does not lead to any beneficial effect in lowering of threshold temperatures, as is evident from Table 3. The temperature at the termination point remains the same. The activation energy also shows the same trend as is seen in the case of MgO and $SrCO_3$.

TABLE 3

Thermal analysis data of calcium carbonate decomposition (2 $CaCO_3:SiO_2$) in the presence of $BaCO_3$

Sample	Decomposition temp. (°C)			Activation energy, E_a, by DTG (kJ mol^{-1})	Activation energy, E_a, by DTA (kJ mol^{-1})	ΔH (kJ mol^{-1})	Shape index
	Threshold	Peak	Termination				
2 $CaCO_3:SiO_2$	740	885	910	247	259	160	0.143
2 $CaCO_3:SiO_2$ + 0.1% $BaCO_3$	690	870	900	209	213	148	0.162
2 $CaCO_3:SiO_2$ + 0.5% $BaCO_3$	675	860	900	192	196	136	0.168
2 $CaCO_3:SiO_2$ + 1% $BaCO_3$	670	855	890	176	179	135	0.173
2 $CaCO_3:SiO_2$ + 5% $BaCO_3$	690	865	900	180	191	145	0.186



Shape Index $= \frac{b}{a}$

Fig. 4. Shape index of decomposition peak.

The enthalpies (ΔH) of the decomposition reaction of calcium carbonate in the presence of MgO, $SrCO_3$ and $BaCO_3$ have been calculated by the standard method [8] and the results are given in Tables 1–3. The enthalpy tends to decrease with up to 1% of the dopants studied and then starts rising. However, there is no remarkable change in the enthalpy of the system as a whole.

The value of the shape index (Fig. 4) of the DTA curves in Figs. 1–3 shows an increasing trend with increasing percentage of dopants. Thus, according to Kissinger [9], the values indicate that the order of reaction for the decomposition of calcium carbonate and silica (2 : 1 molar ratio) is one and it increases with increasing percentage of dopants.

CONCLUSION

These investigations have led to the conclusion that the addition of alkaline earth metal carbonates to the calcium carbonate–silica system (2 : 1 molar ratio) results in a considerable lowering of the decomposition temperature and activation energy of calcium carbonate leading to a lowering of the energy required for the formation of the dicalcium silicate phase in the clinker.

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REFERENCES

1 B.D. Chattaraj, S.N. Dutta and M.S. Iyengar, J. Therm. Anal., 5 (1973) 43.
2 G.V. Subbarao, M. Natrajan and C.N.R. Rao, J. Am. Ceram. Soc., 51 (1968) 179.
3 H. Lehmann and M. Schmidt, Tonindustrie, 85 (1961) 73.
4 I. Masood, N.G. Dave and R.S. Gupta, Indian Ceram., 24 (1981) 9.
5 W.U. Malik, D.R. Gupta, H.O. Gupta and R.S. Gupta, Indian Ceram., 25 (1982) 63.
6 G.O. Piloyan, I.D. Ryabchikov and O.S. Novikova, Nature (London), 50 (1966) 1229.
7 N.G. Dave and S.K. Chopra, Z. Phys. Chem., Neue Folge, 48 (1966) 257.
8 T.R. Ingraham and P. Marier, Can. J. Chem. Eng., 41 (1963) 170.
9 H.E. Kissinger, Anal. Chem., 29 (1959) 1702.