

Note

COMPENSATION EFFECT IN THE THERMAL DECOMPOSITION OF
CELLULOSIC MATERIALS

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The pyrolysis of cellulosic materials and peat is a complex process. Attempts to describe the extent of reaction during the pyrolysis of these materials result in rate equations of the form

$$-dw/dt = A \exp(-E/RT)w^\alpha = k w^\alpha \quad (1)$$

where w is the weight or mass of pyrolyzing sample at any time t ; A is the frequency factor; E is the activation energy; α is the reaction order, and k is the rate constant.

Our analysis of substantial and diversified amounts of data has established a clear linear relationship between the variables $\log A$ and E , as shall be shown later. Such dependence is known as a compensation effect, expressed by the following equation

$$\ln A = mE + \ln k_0 \quad (2)$$

where the parameters m and k_0 become characteristic of the group of reactions for which the compensation effect applies.

The main analytical feature of the compensation effect, also called the isokinetic effect or θ rule, is that any variation in the experimental conditions that causes E to change will induce a compensating change in A .

The constant, m , in eqn. (2) is related to the isokinetic temperature T_i — the temperature at which all the pyrolytic reactions within a given group proceed at the same rate k_0 — through the following expression

$$T_i = R^{-1} m^{-1} \quad (3)$$

where R is the gas constant.

Instances of compensation behavior during the thermal decomposition of pure solid compounds have been reported [1,2]. In this note, we give evidence of a compensation effect during the pyrolytic decomposition of a number of highly oxygenated solid fuels, namely wood, peat, lignin, cellulose, hemicellulose and α -cellulose.

The available data stem from a review of the available literature on the non-isothermal pyrolysis of the fuels considered. The reactions were carried out under diversified pressure conditions and temperature ranges and using different reaction equipment; no added catalyst was used in any of the pyrolytic reactions reported. Low-weight samples were used in all the experi-

ments. In these investigations, the activation energy and frequency factor were determined from a first-order model which assumes that the reaction rate depends only on the amount of reactant present in the reactor. Furthermore, the activation energy was assumed to be constant throughout the reaction. The first-order models were those proposed by the different authors and should represent best fits of their experimental data points.

Some available data from the published literature have been excluded from our analysis because they involve either a non-first-order treatment of the data or because they included mathematical treatment which involves parameter estimation from derivative data and further curve fitting, to accommodate elegant models which are difficult to verify from an error-analysis standpoint.

The results are presented in Table 1 and Fig. 1. The frequency factors and activation energies varied from 5.6×10 to $2.4 \times 10^{19} \text{ min}^{-1}$ and from 9.0 to 56.0 kcal mol⁻¹, respectively, and exhibited a marked compensation effect. Changes in rate of temperature rise, in pressure or in fuel type each seemed to cause log *A* and *E* to vary in a linear manner.

Since the calculated value of *E* is dependent upon the accuracy and precision of the experimental work, we must consider whether the linear relation between *E* and *A* might have been due to experimental errors rather than to a true compensation effect. Exmer [11,12] used a statistical approach, based on comparison of residual sum of squares, in testing the significance of the linear relation between the rate constant and the temper-

TABLE 1

Data values used in establishing the compensation effect shown in Fig. 1

Material	<i>E</i> (kcal/mol)	<i>A</i> (min ⁻¹)	Key in Fig. 1	Ref.
Wood	23	1.9×10^7	a	3
Wood	54	3.9×10^{18}	b	3
Lignin	21.0	9.9×10^5	d	3
Lignin	9.0	5.6×10	e	3
Lignin	34.8	4.3×10^{12}	c	4
Lignin	33.8	7.6×10^9	f	5
Cellulose	54.3	1.8×10^{18}	g	5
Cellulose	39.8	2.4×10^{13}	h	5
Cellulose	33.4	4.0×10^{11}	i	6
Cellulose	30.0	4.2×10^9	j	7
Cellulose	56.0	2.4×10^{19}	k	7
Hemicellulose	29.6	8.7×10^{10}	l	5
Hemicellulose	28.5	2.9×10^{10}	m	4
α-Cellulose	35.0	3.9×10^{11}	n	3
α-Cellulose	56.0	2.4×10^{19}	k	3
α-Cellulose	13.3	1.1×10^4	o	8
α-Cellulose	11.5	1.1×10^4	p	8
α-Cellulose	19.0	1.0×10^6	q	9
Filter paper	39.1	1.4×10^{13}	r	5
Filter paper	10.8	1.1×10^4	s	5
Peat	26.0	1.1×10^{10}	t	10

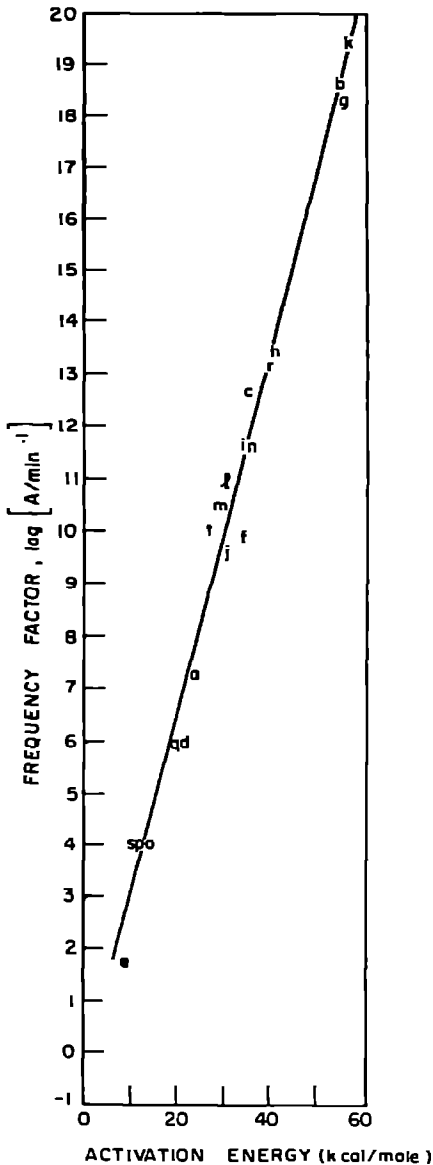


Fig. 1. Compensation behavior in pyrolytic reactions of cellulosic materials.

ature, instead of the usual parameters A and E . More conveniently, Galwey [13] concluded that there is evidence for the existence of a compensation relation when $\sigma_m < 0.1 m$ in measurements extending over $\Delta E \approx 100 \text{ kcal mol}^{-1}$; the most satisfactory examples of compensation behavior would be found when $\sigma_m < 0.03 m$. Here σ_m stands for the standard deviation of slope and m is the slope in the linear relation (2). This criterion has been applied for our results and it has been found that $\sigma_m/m = 0.03$, with a coefficient of determination of 0.98 which indicates genuine and significant compensation behavior. The calculated value of the isokinetic temperature is 621 K.

Such behavior is not without interest and could be used in practical applications to predict pyrolysis yields or to facilitate reactor operating condi-

tions for the group of materials for which the correlation applies. Recently, Ranganathan et al. [14] have made use of the compensation relation in catalyst correlations aimed at establishing criteria for catalyst selection in real applications.

The very existence of a compensation effect during the pyrolysis of cellulosic materials requires a tentative explanation beyond the simple correlation derived from the experimental data. The first point to be considered is that the existence of a compensation effect in the pyrolytic decomposition of a specific group of carbonaceous materials like those considered suggest that there may be similar reaction sequences for all the materials considered.

In pyrolysis, it is commonly admitted that the elementary steps of the overall stoichiometric reaction proceed via free-radical mechanisms. Thus, it is highly unlikely that thermodynamic relationships (enthalpies are linear functions of entropies in the significant elementary steps) could provide an explanation for the observed results.

Drawing on the analysis made by Galwey [13] of the existing theoretical hypothesis for the compensation effect for heterogeneous catalysis, one might assume that in the pyrolysis of related materials there might be a distribution of active sites which, although energetically different from one another, may vary within restricted limits for a specific group of materials (cellulosic in the present case). An exponential-energy site distribution is needed, furthermore, to explain the appearance of a compensation effect in the overall reaction. This explanation, although plausible, has to be taken with some caution in the present case, since it is difficult to visualize a structural arrangement which leads to the exponentially varying energy sites which would in turn induce a whole spectrum of free radicals.

An alternate explanation could be based on the availability of surface reactive species, as Galwey also suggested. Applied to pyrolysis, the explanation would focus on the possible systematic and continuous variation of the frequency of occurrence of the precursor state for the rate-limiting step in the overall pyrolytic reaction, either due to structural surface differences for a series of related materials or to definite yet regular changes in the porosity of these materials limiting in some way the molecular-transfer processes needed for the stabilization of free radicals and subsequent bond breaking leading to pyrolytic products. As indicated by Galwey, the concentration and mobility of active species are both important in establishing the compensation effect.

The last two approaches lower the mechanistic significance of the Arrhenius parameters, as they are strongly influenced by either a change in energy distribution of sites or by structural constraints in the different materials.

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