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Note

COMPENSATION EFFECT IN THE PYROLYSIS OF CELLULOSIC MATERIALS

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The Arrhenius equation has been popularly used in the pyrolysis studies of cellulosic materials to present the rate data as a function of temperature. The Arrhenius equation is expressed as

$$k = A\exp(-E/RT) \tag{1}$$

where k is the rate constant, A is the pre-exponential factor and E is the apparent activation energy. The terms pre-exponential factor and apparent activation energy should be used to describe A and E, respectively, since, unlike homogeneous gas phase kinetics, they have little physical significance in case of solid-state reactions.

The Arrhenius equation may be linearized and rewritten as

$$\ln A = \ln k_{\text{iso}} + \frac{E}{RT_{\text{iso}}} \tag{2}$$

where k_{iso} represents the isokinetic rate constant and T_{iso} is the characteristic isokinetic temperature. For a series of related reactions, a relation between ln A and E as suggested by eqn. (2) is referred to as the "compensation effect", "isokinetic effect", or the θ rule. Such an effect has been widely reported in heterogeneous catalysis, evaporation of metals, and decomposition of solids such as clays and other carbonaceous materials [1–3]. Recently, the compensation effect has been reported in the pyrolysis of cellulosic materials [4–6]. Since pyrolysis of cellulosic materials is complex [7–11] it is of interest to investigate whether the compensation effect provides further insight into the reaction mechanism.

Chornet and Roy [6] reported the existence of a compensation effect based on a detailed statistical analysis of non-isothermal data reported in the literature. Table 1 summarizes the data used by Chornet and Roy [6]. Their plot of ln A vs. E, which suggests the existence of a compensation effect, is sketched in Fig. 1. Fitting the data by a linear least-squares regression

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TABLE 1

Data used by Chornet and Roy [6] in establishing the compensation effect for pyrolysis of cellulosic materials

Material	T range (°C)	E (kcal mol^{-1})	A (min^{-1})	k_{iso}	Symbols in Figs.
Wood	280–325	23.0	1.9×10^{7}	0.153	a
Wood	325–350	54.0	3.9×10^{18}	0.385	b
Lignin	280–344	21.0	9.9×10^{5}	0.04	c
Lignin	344–435	9.0	5.6×10	0.038	d
Lignin	280–300	34.8	4.3×10^{12}	2.43	e
Lignin	360–500	33.8	7.6×10^{9}	0.0097	f
Cellulose	300–420	54.3	1.8×10^{18}	0.139	g
Cellulose	280–360	39.8	2.4×10^{13}	0.236	h
Cellulose	250–1000	33.4	4.0×10^{11}	0.702	i
Cellulose	230–400	30.0	4.2×10^{9}	0.116	j
Cellulose	275–360	56.0	2.4×10^{19}	0.468	k
Hemicellulose	240–350	29.6	8.7×10^{10}	3.325	l
Hemicellulose	220–280	28.5	2.9×10^{10}	2.7	m
α-Cellulose	240–308	35.0	3.9×10^{11}	0.187	n
α-Cellulose	308–360	56.0	2.4×10^{19}	0.468	k
α-Cellulose	230–560	13.3	1.1×10^{4}	0.229	o
α-Cellulose	240–580	11.5	1.1×10^{4}	0.986	p
α-Cellulose	280–700	19.0	1.0×10^{6}	0.206	q
Filter paper	160–380	39.1	1.4×10^{13}	0.242	r
Filter paper	280–400	10.8	1.1×10^{4}	1.739	s
Peat	100–800	26.0	1.1×10^{10}	7.77	t

analysis results in the following expression

$$\ln A = -1.0484(\pm1.8287) + 0.8106(\pm0.0530)E \qquad (3)$$

with a correlation coefficient of 0.982. The figures in parentheses represent error limits at the 95% confidence level. Chornet and Roy [6] claim that these results imply the existence of compensation behavior as $\sigma_{\mathrm{slope}} < 0.03E$. These results were based on the results of Galwey [1] who suggested the existence of a compensation effect when $\sigma_{\mathrm{slope}} < 0.1E$. However, an examination of eqn. (3) suggests that $\ln k_{\mathrm{iso}}$ cannot be determined within the accuracy of these results, i.e., $\ln k_{\mathrm{iso}}$ is not significantly different from zero. Since $\ln k_{\mathrm{iso}}$ is negligible, this data set shows a false compensation effect and has no physical significance.

At the isokinetic temperature, rate constants for all related reactions are equal. Hence, if a plot of $\ln k$ vs. inverse temperature is drawn, it should bring out a point of concurrence. However, Fig. 2, a plot of $\ln k$ vs. inverse temperature, shows no such point of concurrence. The calculated value of the isokinetic temperature is 621 K. Table 1 also lists the value of k_{621} calculated using eqn. (1) and individual values of A and E; k_{621} are found

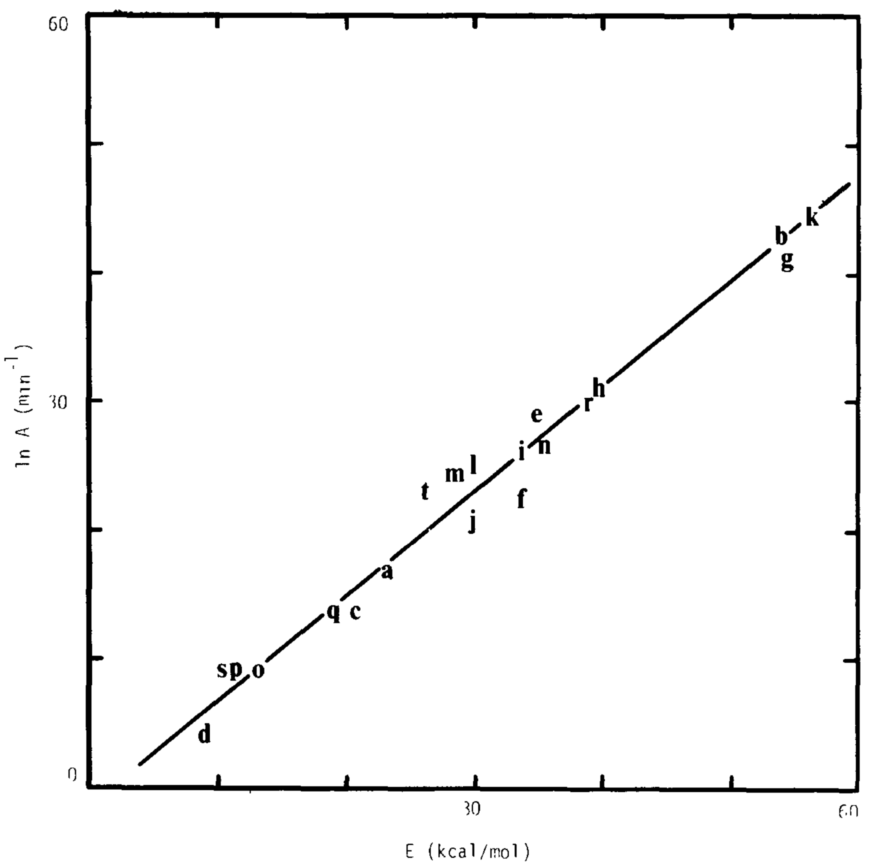

Fig. 1. A plot of ln A vs. E suggesting the occurrence of a compensation effect in the pyrolysis of cellulosic materials. Symbols are identical to those listed in Table 1.

to vary from 0.01 min^{-1} ($A = 7.6 \times 10^9$ min^{-1}, $E = 33.8$ kcal mol^{-1}) for lignin to 7.77 min^{-1} ($A = 1.1 \times 10^{10}$ min^{-1}, $E = 26.0$ kcal mol^{-1}) for peat. This again does not indicate the occurrence of a compensation effect, since the rates are not equal at the isokinetic temperature.

Since these results are derived from non-isothermal experiments, they remain of interest for studies attempting to characterize temperature gradients within the sample. From the linear regression analysis, T_{iso} is determined as 621 K with a standard deviation of 20 K. 621 K represents the average temperature and 20 K probably represents the average temperature gradient within the sample in these studies. This observation is strengthened by the results reported by Sestak [12], Blazek [13] and Antal et al. [14]. The temperature gradients reported in these studies ranged from 5 to 30 K depending on the heating rate. Antal et al. [14] in their studies with cellulose pyrolysis have reported temperature gradients of 20 to 25 K near the vicinity of the sample at a heating rate of 20°C min^{-1}.

Let us consider a case for speculating results from a typical non-isother-

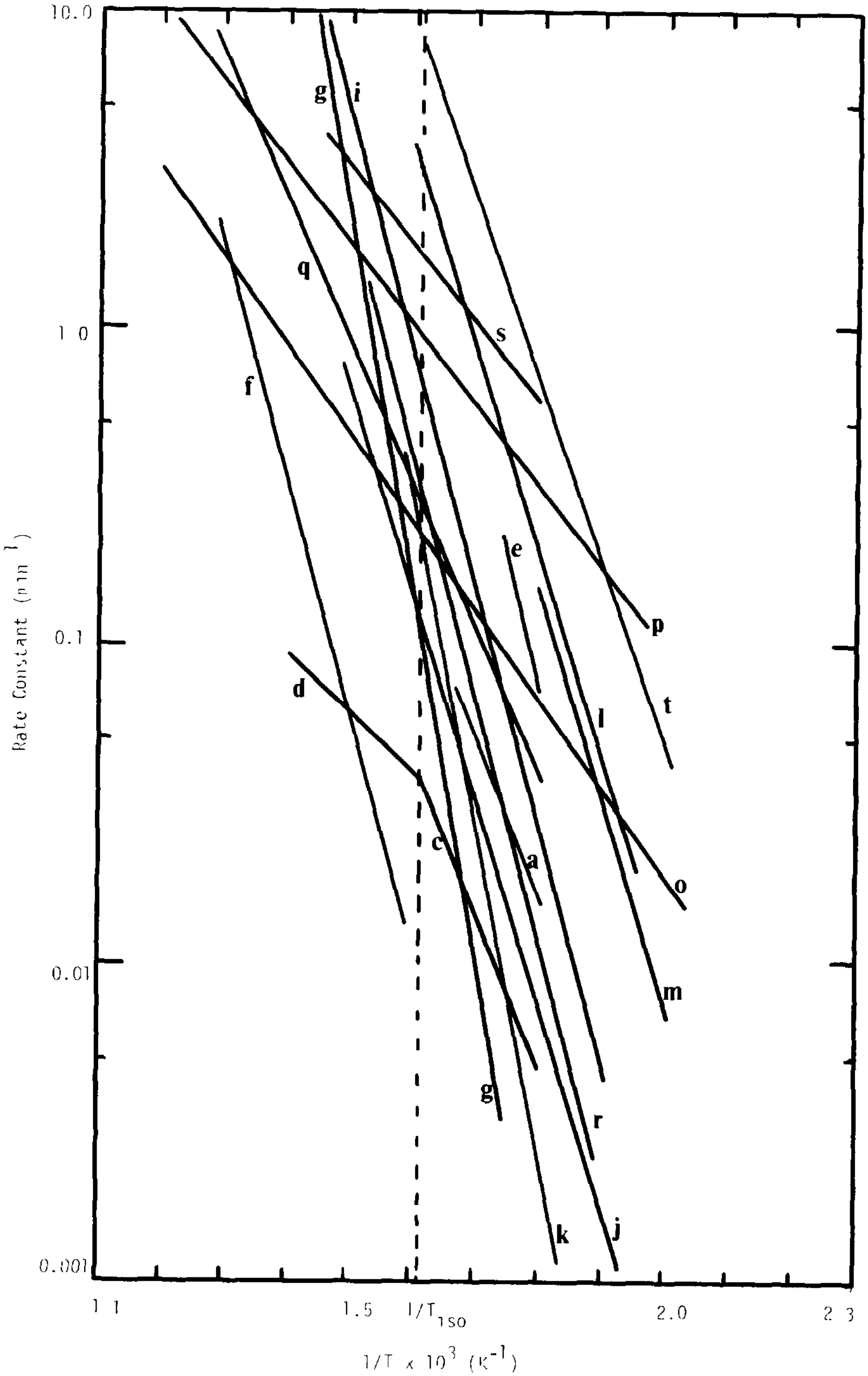

Fig. 2. Arrhenius plot showing no single point of concurrence for the pyrolysis of cellulosic materials. Line k overlaps with lines b and h (not shown) and line r overlaps with n (not shown). Such a plot shows no occurrence of a compensation effect. Symbols are identical to those listed in Table 1.

mal study. For the pyrolysis of cellulosic material, A is about 4×10^9 min^{-1} and E is about 30.0 kcal mol^{-1}. If we assume a temperature gradient of 20 K within the sample at an average temperature of 621 K, the value of k varies by as much as 80%. This error is large and the results are unreliable. Hence, these studies are unsuitable for the kinetic analysis of a complex pyrolysis mechanism. Precise control of temperature and minimizing the temperature gradient are desirable if any useful data are to be obtained.

These results strongly suggest that the compensation behavior for the pyrolysis of cellulosic materials reported by Chornet and Roy [6] is primarily due to inaccurate temperature measurement and large temperature gradients within the sample. The linear relation between ln A and E, at least in this case, has no physical significance.

REFERENCES

1 A. K. Galwey, Adv. Catal., 26 (1977) 247.
2 G. C. Bond, Catalysis by Metals, Academic Press, New York, 1962.
3 Z. Adonyi and G. Korosi, Thermochim. Acta, 60 (1983) 651.
4 C. Fairbridge, R. A. Ross and P. Spooner, Wood Sci. Technol., 9 (1975) 257.
5 C. Kala, I. S. Gur and H. L. Bhatnagar, Indian J. Chem., 19A (1980) 641.
6 E. Chornet and C. Roy, Thermochim. Acta, 35 (1980) 389.
7 R. K. Agrawal, Ph.D. Thesis, Clarkson University, New York, 1984.
8 R. K. Agrawal and R. J. McCluskey, J. Appl. Polym. Sci., 27 (1983) 367.
9 R. K. Agrawal, F. Gandhi and R. J. McCluskey, J. Anal. Appl. Pyrol., 6 (1984) 325.
10 F. Shafizadeh, J. Anal. Appl. Pyrol., 3 (1982) 283.
11 M. J. Antal, Jr., Adv. Sol. Energy, 2 (1983) 61.
12 J. Sestak, Talanta, 13 (1966) 567.
13 A. Blazek, Thermal Analysis (translated by J. F. Tyson), Van Nostrand Reinhold, New York, 1973.
14 M. J. Antal, Jr., H. L. Friedman and F. E. Rogers, Combust. Sci. Technol., 21 (1980) 141.