

## Notes

### COMMENT ON THE REPLY BY M. D. JUDD AND M. I. POPE

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In the reply [1] to the author's comment "On the Method of Coats and Redfern for the Kinetic Analysis of Thermoanalytical Data" [2], M. D. Judd and M. I. Pope understood the comment incorrectly. As was clearly shown in the comment, the correct equation derived by A. W. Coats and J. P. Redfern [3] is as follows:

$$\log \left\{ -\frac{\ln(1-\alpha)}{T^2} \right\} = \log \frac{AR}{aE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad (1)$$

or

$$\log \left\{ -\frac{\log(1-\alpha)}{T^2} \right\} = \log \frac{AR}{2.303aE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad (2)$$

where  $\alpha$  = fraction of sample decomposed at time  $t$

$T$  = temperature (K)

$A$  = pre-exponential factor

$R$  = the gas constant

$E$  = activation energy

$a$  = conversion factor to transfer from a time scale to a temperature scale,

i.e.

$$a = \frac{dT}{dt} \quad (3)$$

However, M. D. Judd and M. I. Pope understood that

$$\log \left[ -\log \frac{(1-\alpha)}{T^2} \right] = \log \frac{AR}{aE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad (4)$$

should be replaced by

$$\log \left[ -\ln \frac{(1-\alpha)}{T^2} \right] = \log \frac{AR}{aE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad (5)$$

But both Eqs (4) and (5) are incorrect. The difference between the correct equation and the incorrect equation, misprinted and quoted, is not the difference between the natural logarithm and the common logarithm, but the difference is in the argument of the second logarithm.

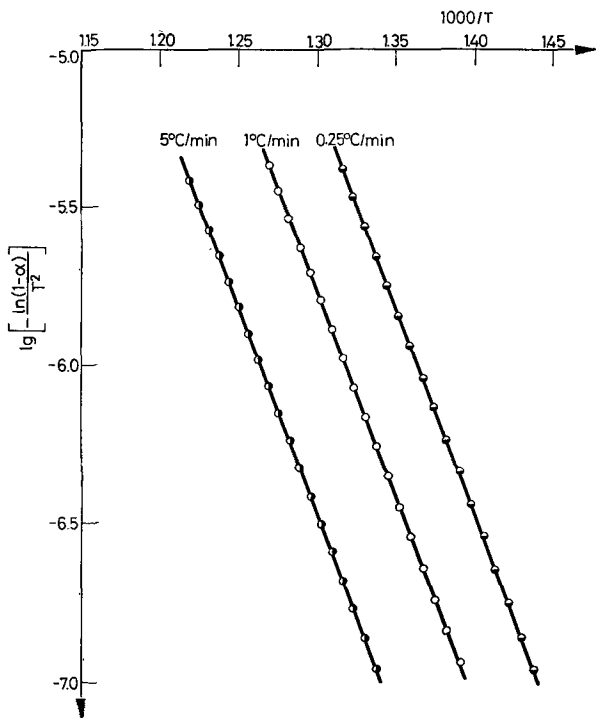


Fig. 1. Correct activation energy plots according to Eq. (1). The heating rates are indicated in the figure.

Moreover, M. D. Judd and M. I. Pope assert as follows; a simulated activation energy plot, using Eq. (4) or (5), for their some test data calculated such that the order of reaction should have a value of unity, gives a straight line, and the slope of the line has the dimension of time, though the slope should be dimensionless. The author too plotted an activation energy plot for theoretical thermoanalytical curves calculated hypothetically by the method described elsewhere [4] assuming that the order of reaction, the activation energy and the pre-exponential factor are a value of unity, 60 kcal/mole and  $1 \times 10^{14} \text{ sec}^{-1}$ , respectively. For three heating rates, the plots are shown in Figs 1 and 2. As is clearly seen, the plots, according to the correct equation (1) in Figs 1, give straight lines and the activation energies obtained from the slopes are 60.0 kcal/mole for all heating rates. The

pre-exponential factors are also obtained from the intercepts, neglecting  $2RT/E$ , and  $0.93 \times 10^{14}$ ,  $0.92 \times 10^{14}$  and  $0.92 \times 10^{14} \text{ sec}^{-1}$  for the heating rate of 0.25, 1.0 and  $5.0^\circ\text{C}/\text{min}$ , respectively. The difference in the pre-exponential factors obtained seems due to neglect of higher orders in the equation (1). On the other hand, the plots, according to the incorrect equation (4) in Fig. 2, give curved lines for all heating rates. It is clearly demonstrated that both Eqs (4) and (5) are incorrect.

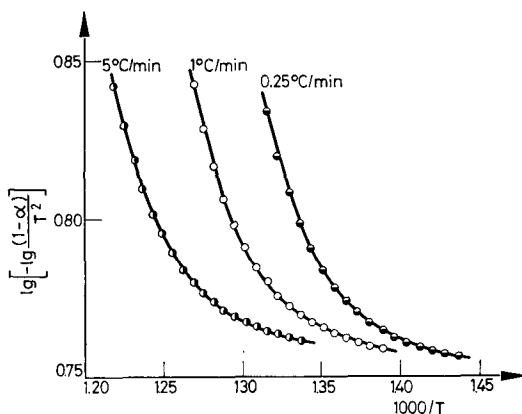


Fig. 2. Incorrect activation energy plots according to Eq.(4). The heating rates are indicated in the figure

Since M. D. Judd and M. I. Pope applied the incorrect expression to their thermoanalytical data [5], necessity of replotting their data according to the correct expression still remain. Thus, taking into account of the fact that the most plausible mechanism is deduced on the base of the most linear plot in the method of Coats and Redfern, the possibility that the revision would become necessary can not still be denied, in spite of the reply by M. D. Judd and M. I. Pope.

### References

1. M. D. JUDD and M. I. POPE, *J. Thermal Anal.*, 5 (1973) 501.
2. T. OZAWA, *J. Thermal Anal.*, 5 (1973) 499.
3. A. W. COATS and J. P. REDFERN, *Nature*, 201 (1964) 68.
4. T. OZAWA, *J. Thermal Anal.*, 2 (1970) 301.
5. M. D. JUDD and M. I. POPE, *J. Thermal Anal.*, 4 (1972) 31.