density ρ_i of induced fission tracks is determined. The glass piece is fractured to expose the fresh surface and etched in 20% HF for 30 seconds at room temperature. The surface density ρ of etch pits is measured and the integral neutron flux ϕ is calculated by using the calibration relation[7],

$$\phi = 2\cdot 26 \times 10^{11} \rho \qquad (5)$$

Results.—From the measured values of ρ_s, ρ_i and ϕ, the fission track ages of muscovite samples have been calculated from relation (4). The results are summarized in Table I. It is evident that the

TABLE I

Fission track ages of Bihar Mica Belt (Kodarma Muscovites)

Total neutron dose (nvt) $= 4\cdot 3 \times 10^{18}$
Radiometric age[8-10] (m.Y) $= 840$–1100

Sample No.	ρ_s (cm^{-2})	ρ_i (cm^{-2})	T Fission track age (m.Y)
1	20	5415	901 ± 212
2	19	5531	844 ± 194
3	20	5708	856 ± 196
4	23	5354	1011 ± 206
5	19	5336	865 ± 199
6	19	5460	850 ± 195
7	16	5796	679 ± 176
8	19	5681	821 ± 188
9	20	5045	957 ± 220
10	20	5768	844 ± 194
		Mean	865 ± 72

ages lie between 700–1100 m.y. The average age comes out to be 865 ± 72 million year which agrees with other age determinations made by radiometric methods[8-10].

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THERMAL DECOMPOSITION KINETICS

Part VI*. An Absolute-Rate-Theory-Based Equation for the Evaluation of Kinetic Parameters from Nonisothermal Thermogravimetry

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ABSTRACT

A new equation, taking into account the temperature-dependence of the pre-exponential factor based on the absolute rate theory of reactions, is proposed for the evaluation of kinetic parameters of solid-state reactions from nonisothermal thermogravimetric data.

THE rate equation widely used by different workers in nonisothermal thermogravimetry (TG) can be put in the form[6]

$$d\alpha/dT = (A/\phi)(1 - \alpha)^n \exp(-E/RT) \qquad (1)$$

where α = fraction decomposed at temperature T, ϕ = heating rate, A = pre-exponential term. R = gas

constant and E = energy of activation. In integrating eq. (1) it has always been assumed that A is temperature-independent[7-11]. Ingraham and Marier point out that this assumption is not rigorously valid[12]. A critical review of this aspect has recently been made by Gyulai and Greenhow[13]. In this communication, we wish to present the derivation of a more accurate equation taking into account the temperature-dependence of A.

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* For Parts I to V, see references 1 to 5.

DERIVATION

According to the theory of absolute reaction rates, the temperature-dependence of A is given by the relation,

$$A = (kT/h) \exp(\triangle S/R) \qquad (2)$$

where k = Boltzmann constant, h = Planck constant, $\triangle S$ = entropy of activation. Combining eqs. (1) and (2), we get,

$$d\alpha/dT = [(k/h\phi) \exp(\triangle S/R)]$$
$$\times \left[T \exp\left(\frac{-E}{RT}\right) \right] (1 \quad \alpha)^n \qquad (3)$$

Eq. (3) will be most useful in its integrated form. The integration may be done as follows :

Substituting

$$y = (k/h\phi) \exp\left(\frac{\triangle S}{R}\right)$$

and

$$x = E/RT$$

in eq. (3), rearranging it and putting in the integral form (limits for α and T being 0 to α and 0 to T respectively), we get

$$\int_0^\alpha d\alpha/(1-\alpha)^n = (YE^2/R^2) \int_x^\infty x^{-3} e^{-x} dx \qquad (4)$$

The R.H.S. of eq.(4) is a special case of the most general form of the incomplete gamma function[14]. Eq. (4) on integration gives

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{YE^2}{R^2} e^{-x} x^{-3} \left(1 - \frac{3}{x}\right) \qquad (5)$$

Here the series term in R.H.S. has been terminated with the second term. Putting the L.H.S. as $g(\alpha)$ and re-introducing the values of x and Y eq. (5)

$$g(\alpha) = (k/h\phi) \exp(\triangle S/R) \frac{RT^3}{E} \left(1 - \frac{3RT}{E}\right)$$
$$\times \exp\left(\frac{-E}{RT}\right) \qquad (6)$$

Taking logarithms,

$$\log\left(\frac{g(\alpha)}{T^3}\right) = \log\left[\frac{kR}{h\phi E}\left(1 - \frac{3RT}{E}\right)\right]$$
$$+ \frac{\triangle S}{2 \cdot 303 R} - \frac{E}{2 \cdot 303 RT} \qquad (7)$$

Graphical Evaluation of E and $\triangle S$ from Eq. (7)

Two approaches are possible here :

(a) As in the Coats-Redfern equation, where 2RT/E is assumed to be negligible[7] compared to unity, one may assume that the same holds good for the term 3RT/E. Then, eq. (7) reduces to :

$$\log\left[\frac{g(\alpha)}{T^3}\right] = \log\left(\frac{kR}{h\phi E}\right) + \frac{\triangle S}{2 \cdot 303 R} - \frac{E}{2 \cdot 303 RT} \qquad (8)$$

A plot of L.H.S. *versus* 1/T would now be linear, with slope equal to $-E/2 \cdot 303$ R. The value of $\triangle S$ may be got from the intercept.

(b) The R.H.S. of eq. (7) may be rearranged in the form

$$\log\left(\frac{kR}{h\phi E}\right) + \frac{\triangle S}{2 \cdot 303 R} + \left[\log\left(1 - \frac{3RT}{E}\right)\right.$$
$$\left. - \frac{E}{2 \cdot 303 RT}\right] \qquad (9)$$

where the terms involving variable T have been segregated into the expression within the square bracket. This expression can be put in the form (here $x = E/RT$):

$$\left[\log\left(1 - \frac{3}{x}\right) - \frac{x}{2 \cdot 303} \right] \qquad (10)$$

This may be linearised by using the method of least squares, giving various values for x ranging[16] from 20 to 100. This gives

$$\log\left(1 - \frac{3}{x}\right) - \frac{x}{2 \cdot 303} = -0 \cdot 0629 - 0 \cdot 4337x \qquad (11)$$

Resubstituting for x, we may now rewrite eq. (7) as

$$\log\frac{g(\alpha)}{T^3} = \log\frac{kR}{h\phi E} + \frac{\triangle S}{2 \cdot 303 R} - 0 \cdot 0629 - \frac{0 \cdot 4337E}{RT} \qquad (12)$$

A plot of L.H.S. *versus* 1/T would now be linear, from whose slope and intercept, E and $\triangle S$ respectively may be evaluated. A further mathematical simplification may, if desired, be effected by taking over the T^3 term also to the R.H.S. of eq. (7) and linearising, to give

$$\log g(\alpha) = \log\frac{kE^2}{h\phi R^2} + \frac{\triangle S}{2 \cdot 303 R} - 3 \cdot 7958$$
$$- \frac{0 \cdot 4582E}{RT} \qquad (13)$$

Comparison with the Coats-Redfern Equation

It is interesting to compare eq. (7) with the equation developed earlier by Coats and Redfern[7], who did not take into account the temperature-dependence of A. The Coats-Redfern equation can be put in the following form :

$$\log\left(\frac{g(\alpha)}{T^2}\right) = \log\left[\frac{AR}{\phi E}\left(1 - \frac{2RT_s}{E}\right)\right] - \frac{E}{2 \cdot 303 RT}$$
$$\qquad (14)$$

or

$$\log\left(\frac{g(\alpha)}{T^2}\right) = \log\left[\frac{kRT_s}{h\phi E}\left(1 - \frac{2RT_s}{E}\right)\right]$$
$$+ \frac{\triangle S}{2 \cdot 303 R} - \frac{E}{2 \cdot 303 RT} \qquad (15)$$

It may be seen that equations (15) and (7) are generally of the same form. But, eq. (7) has the following advantages over eq. (15).

1. Eq. (7) has a more rigorous treatment and takes account of the temperature-dependence of A. At the same time, it involves just the same type of computational work as eq. (15).

2. Eq. (7) avoids the arbitrariness with which eq. (15) introduces the temperature term in the expression for

$$A = \frac{kT}{h} e^{\Delta S/R}$$

the T in this expression has been variously and arbitrarily chosen as T_s (the DTG peak temperature)[2] or $\overline{T}$ (the average temperature)[16].

The improvement effected by the present equation may be illustrated by considering a theoretical TG curve. Such a procedure has been suggested by Sestak in a different context[17]. A theoretical TG curve with an assumed value of $E = 120$ kJ mole^{-1} was used for this purpose. Here, the Coats-Redfern equation gives a value $E = 123\cdot3$ kJ mole^{-1} whereas the present equation gives a value $E = 119\cdot8$ kJ mole^{-1}. The improvement is obvious.

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TWO UNUSUAL FLAVONES (ARTEMETIN AND 7-DESMETHYL ARTEMETIN) FROM THE LEAVES OF *VITEX TRIFOLIA*

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ABSTRACT

Adsorption chromatography on silica gel of the chloroform extract of dry leaves of *Vitex trifolia* (Verbenaceae) has yielded two methylated flavones of rare occurrence. Based on chemical as well as UV, IR, PMR and Mass spectral data, the major compound has been characterised as 5, 7-dihydroxy-3, 3′, 4′, 6-tetra methoxy flavone (3, 3′, 4′, 6-tetra methyl quercetagetin) and the minor as artemetin (5-hydroxy-3, 3′, 4′, 6, 7-penta methoxy flavone) by direct comparison with authentic sample. The earlier observation regarding the variation of flavonoid pattern with reference to plant geography in *Vitex* is further supported by our results.

THE distribution of flavonoids in the genus *Vitex*[1] under the family Verbenaceae and the Natural Order Tubiflorae is interesting especially with reference to the glycoflavones (atypical in this family) and the unusual flavones like casticin (3, 4′, 6, 7-tetra methyl quercetagetin), and certain variations in the flavonoid patterns relating to plant geography have been observed. Some significance is also attached to these flavonoids in the classification of plants of this family.

In continuation of our work on the flavone glucuronides of the Verbenaceae[2], we have made a detailed chemical examination of the flavonoids of the leaves of *Vitex trifolia* Linn. earlier recorded to contain casticin[3] and vitexin[4], and our results are recorded here.

The dry leaves of *V. trifolia* were first extracted with hot $CHCl_3$ and then with MeOH. The concentrated $CHCl_3$ extract was chromatographed on a column of silica gel using petroleum ether, benzene and $CHCl_3$ as eluting solvents. No crystalline flavonoid was obtained from petrol eluates.

The residue from the benzene fraction on recrystallisation from Me_2CO–MeOH yielded a small