

## THE ISOCONVERSIONAL METHOD FOR DETERMINATION OF ENERGY OF ACTIVATION AT CONSTANT HEATING RATES Corrections for the Doyle approximation

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The isoconversional method for the determination of energies of activation from the reciprocal temperature at which a fraction of conversion was reached in experiments at differing constant heating rates is reviewed and amplified. The error introduced into the calculation of activation energy by the use of a linear approximation of the logarithm of the temperature integral is discussed. Methods for the correction of this error are developed and a table of correction factors are given.

Since its formulation by Ozawa [1] and independently by Flynn and Wall [2], the isoconversional method has been used extensively to calculate energies of activation from thermoanalytical experiments at constant heating rate. Its popularity is due mainly to its capability of yielding activation energies without the necessity of one positing what often turn out to be incorrect models for the reaction mechanism. Such an incorrect model for the relationship between rate and conversion will give a grossly incorrect value for the activation energy since temperature and fraction conversion are changing simultaneously in nonisothermal experiments [3].

The use of Doyle's linear approximation of the temperature integral [4] often introduces a sizable error in the activation energy calculated from the isoconversional method. This was pointed out in the 1966 paper by Flynn and Wall [2], and an iterative method was given to correct for this error. It has been made obvious by a high frequency of inquiries about the above correction method that its explanation was inadequate in the original letter [2]. Therefore, we shall briefly review the isoconversional method, discuss the errors involved in the linear approximation of the logarithm of the temperature integral, and develop a method for improving the accuracy of this approximation in a more simple and comprehensible manner. With the increased sensitivity of modern thermoanalytical equipment, activation energies are often calculated to an imprecision of less than one percent. It will be demonstrated that errors in the calculation of activation energy using the Doyle approximation in many cases will be considerably greater than these experimental limits of precision.

### The isoconversional method

The most popular model for the rate of a process occurring in a condensed phase is

$$\frac{d\alpha}{dt} = f(\alpha)k(T), \quad (1)$$

where the rate of change of conversion with respect to time is  $d\alpha/dt$ , and  $f(\alpha)$  and  $k(T)$  are separable functions of conversion and temperature, respectively. At constant heating rate with  $\beta = dT/dt$ , eq. (1) may be rewritten as

$$\frac{d\alpha}{dT} = \beta^{-1}f(\alpha)k(T). \quad (2)$$

Upon integration over the variables  $\alpha$  and  $T$ , eq. (2) becomes

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \beta^{-1} \int_{T_0}^T k(T) dT. \quad (3)$$

The most successful model for  $k(T)$ , the temperature dependence of the rate, is the Arrhenius equation,

$$k(T) = A \exp\left(-\frac{E}{RT}\right), \quad (4)$$

where  $A$  is the preexponential factor,  $E$  the energy of activation and  $R$  the gas constant. The appropriateness of eq. (4) has been discussed in many papers, [5, 6]. One obtains from a combination of eqs. (3) and (4)

$$F(\alpha) = A\beta^{-1} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT. \quad (5)$$

If  $T_0$  is well below the temperature at which the rate of reaction becomes measurable, the lower limit of the temperature integral may be ignored. Defining  $x = -E/RT$  one obtains

$$F(\alpha) = \left(\frac{AE}{\beta R}\right) \left\{ -\frac{e^x}{x} + \int_{-\infty}^x \left(\frac{e^x}{x}\right) dx \right\} = \left(\frac{AE}{\beta R}\right) p(x). \quad (6)$$

The term in braces in eq. (6), symbolized by  $p(x)$  and containing the exponential integral, can not be integrated in closed form. It was first tabulated for use in non-isothermal kinetics by Akahira [7] and Vallet [8]. However, Doyle [4] was the first to point out the near linearity of the logarithm of  $p(x)$  plotted as a function of  $x$ . He proposed the approximate relationship

$$\log p(x) \cong -2.315 + 0.457x \quad (-20 > x > -60) \quad (7)$$

or, in terms of natural logarithms,

$$\ln p(x) \cong -5.3305 + 1.052x \quad (-20 > x > -60). \quad (7')$$

These are the equations upon which Ozawa and Flynn and Wall based the integral isoconversional method for calculating activation energies, for, taking the logarithm of eq. (6) and combining it with eqs. (7) and (7'), one obtains

$$\log F(\alpha) \cong \log \frac{AE}{R} - \log \beta - 2.315 + 0.457 \frac{E}{RT} \quad (8)$$

and

$$\ln F(\alpha) \cong \ln \frac{AE}{R} - \ln \beta - 5.3305 + 1.052 \frac{E}{RT} \quad (8')$$

Therefore, if a series of experiments are performed at heating rates,  $\beta_1, \beta_2, \beta_3, \dots, \beta_j$  and  $T_{k,j}$  is the temperature at which fraction of conversion,  $\alpha_k$ , was reached at heating rate,  $\beta_j$ , then a plot of  $\log$  (or  $\ln$ )  $\beta_j$  vs  $T_{k,j}^{-1}$  for each of  $k$  fractions of conversion,  $\alpha_1, \alpha_2, \alpha_3, \dots, \alpha_k$  will yield  $k$  isoconversional lines whose slopes are, from eqs. (8) and (8'),

$$\text{(for } \log \beta_j \text{ vs } T_{k,j}^{-1}\text{); slope } \cong 0.457 \frac{E}{R} \quad (9)$$

$$\text{(for } \ln \beta_j \text{ vs } T_{k,j}^{-1}\text{); slope } \cong 1.052 \frac{E}{R} \quad (\alpha = \alpha_k). \quad (9')$$

Thus, the activation energy at any degree of conversion,  $\alpha_k$ , is calculated from a plot of  $\log$  (or  $\ln$ )  $\beta_j$  vs  $T_{k,j}^{-1}$ . The linearity of the slope for three or more values of  $\beta$  is a test of the constancy of  $E$  with respect to temperature, and any change in  $E$  with respect to conversion may be observed by comparison of slopes at various  $\alpha_k$ . More elaborate schemata for setting up grids of  $E$  as a function of  $\alpha$  and  $T$  and testing thermal history dependence of  $E$  by comparing isothermal and constant heating rate experiments are described elsewhere [6, 9].

### Corrections for Doyle's approximation

Equations (7) and (7') only approximately fit the relationship between  $\ln \rho(x)$  and  $x$ . The error in calculating  $E$  introduced by these equations will now be discussed, and the method alluded to in 1966 [2] will be clarified and described in greater detail.

As can be seen from Figure 1 where  $-\ln \rho(x)$  is plotted against  $-x$  for  $x = 1$  to 200, the Doyle linear approximation (the solid straight line) represents the correct relation between  $\ln \rho(x)$  and  $x$  (the broken line) quite well for a wide range of  $x$  values. The error resulting from the use of the approximation is less than one percent between  $x = 21$  and  $x = 81$  which encompasses a great portion of the  $x (= E/RT)$  values experienced in thermal analysis.

However, the activation energy is calculated from the slope of the  $\ln \rho(x)$  vs  $x$  curve. The correct slope of  $(\ln \rho(x) \text{ vs } x)$  is compared with the constant value

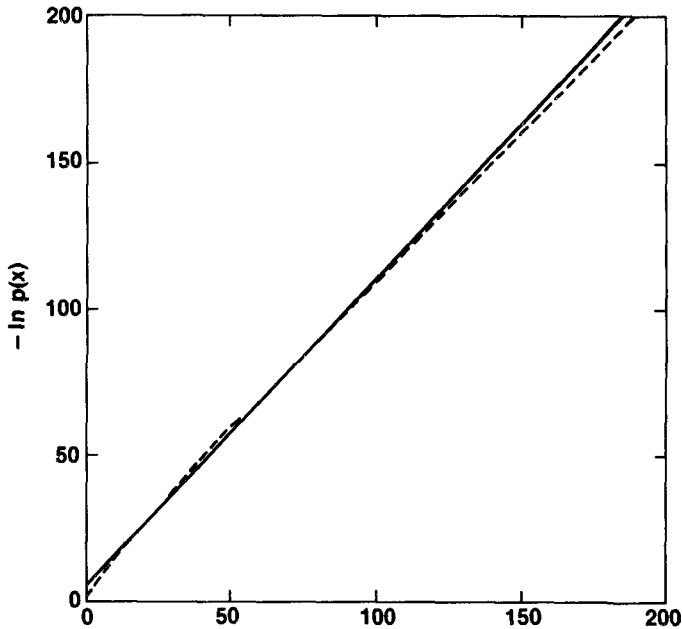


Fig. 1 Logarithm of  $p(x)$  vs  $x$ ; —  $\ln p(x) = -5.3305 + 1.052 x$  (Doyle)

$$- - - \ln p(x) = \ln \left[ -\frac{e^x}{x} + \int_{-\infty}^x \left(\frac{e^x}{x}\right) dx \right]$$

of 1.052 for the slope from the Doyle approximation in Figure 2 for  $x = 1$  to 200. The differences between the correct slope and the value from the Doyle approximation are much larger than were the differences for the integral curves in Figure 1.

Table 1 contains values for the slopes of a)  $\log_{10} p(x)$  vs  $x$  and b)  $\ln p(x)$  vs  $x$  for the values of  $x$  from 2 to 200. The correction factor with which to multiply the Doyle approximation of the slope for a) 0.457, and for b) 1.052, is given in the final column. It can be seen from Figure 2 and Table 1 that the error in  $E$  from using the approximation is less than one percent only for the narrow range  $-45 < x < -32$ , while for  $x = -20$  the error is 4%, and it is much greater for  $x > -20$ .

Activation energies of less than 100 kJ/mol occur frequently. Some examples of processes which have low activation energies are heterogeneous catalysis, biological reactions, and reactions where the rate limiting step is the diffusion of small molecules through or their evaporation from a condensed phase. At a temperature of 600 K and  $E = 100$  kJ/mol,  $X (= E/RT)$  is less than 20. The improvement of thermoanalytical equipment and techniques often permits the determination of  $E$  to less than one percent imprecision. Therefore, corrections to the Doyle approximation should be applied to such activation energy determinations.

**Table 1** Slopes of a)  $\log_{10}\rho(x)$  vs  $x$  b)  $\ln \rho(x)$  vs  $x$  for various values of  $x (= E/RT)$

$$\rho(x) = -\left(\frac{e^x}{x}\right) + \int_{-\infty}^x \left(\frac{e^x}{x}\right) dx$$

$-x$	a)	b)	Correction factor for Doyle approximation	$-x$	a)	b)	Correction factor for Doyle approximation
2	0.7832	1.8034	1.714	50	0.4513	1.0393	0.988
3	0.6773	1.5596	1.482	51	0.4510	1.0385	0.987
4	0.6218	1.4318	1.361	52	0.4507	1.0378	0.986
5	0.5873	1.3524	1.285	53	0.4504	1.0371	0.986
6	0.5638	1.2981	1.234	54	0.4501	1.0364	0.985
7	0.5466	1.2585	1.196	55	0.4498	1.0358	0.984
8	0.5335	1.2284	1.167	56	0.4495	1.0351	0.984
9	0.5231	1.2046	1.145	57	0.4493	1.0345	0.983
10	0.5148	1.1853	1.126	58	0.4490	1.0339	0.983
11	0.5079	1.1694	1.111	59	0.4488	1.0334	0.982
12	0.5021	1.1560	1.099	60	0.4485	1.0328	0.981
13	0.4971	1.1446	1.088	61	0.4483	1.0323	0.981
14	0.4928	1.1348	1.078	62	0.4481	1.0318	0.981
15	0.4891	1.1262	1.070	63	0.4479	1.0313	0.980
16	0.4858	1.1187	1.063	64	0.4477	1.0308	0.980
17	0.4829	1.1120	1.057	65	0.4475	1.0303	0.979
18	0.4803	1.1060	1.051	66	0.4473	1.0299	0.979
19	0.4780	1.1006	1.046	67	0.4471	1.0294	0.978
20	0.4759	1.0958	1.041	68	0.4469	1.0290	0.978
21	0.4740	1.0914	1.037	69	0.4467	1.0286	0.977
22	0.4722	1.0874	1.033	70	0.4465	1.0282	0.977
23	0.4707	1.0837	1.030	75	0.4457	1.0263	0.975
24	0.4692	1.0803	1.027	80	0.4450	1.0247	0.974
25	0.4678	1.0772	1.024	85	0.4444	1.0233	0.972
26	0.4666	1.0742	1.021	90	0.4438	1.0220	0.971
27	0.4654	1.0717	1.018	95	0.4433	1.0208	0.970
28	0.4643	1.0692	1.016	100	0.4429	1.0198	0.969
29	0.4633	1.0669	1.014	105	0.4425	1.0189	0.968
30	0.4624	1.0647	1.012	110	0.4421	1.0180	0.967
31	0.4615	1.0627	1.010	115	0.4418	1.0172	0.967
32	0.4607	1.0608	1.008	120	0.4415	1.0165	0.966
33	0.4599	1.0590	1.006	125	0.4412	1.0159	0.965
34	0.4592	1.0573	1.005	130	0.4409	1.0152	0.965
35	0.4585	1.0557	1.003	135	0.4407	1.0147	0.964
36	0.4578	1.0542	1.002	140	0.4405	1.0142	0.964
37	0.4572	1.0527	1.000	145	0.4402	1.0137	0.963
38	0.4566	1.0514	0.999	150	0.4400	1.0132	0.963
39	0.4561	1.0501	0.998	155	0.4399	1.0128	0.963
40	0.4555	1.0489	0.997	160	0.4397	1.0124	0.962
41	0.4550	1.0477	0.996	165	0.4395	1.0121	0.962
42	0.4545	1.0466	0.995	170	0.4394	1.0117	0.961
43	0.4541	1.0455	0.994	175	0.4392	1.0114	0.961
44	0.4536	1.0445	0.993	180	0.4391	1.0111	0.961
45	0.4532	1.0435	0.992	185	0.4390	1.0108	0.961
46	0.4528	1.0426	0.991	190	0.4388	1.0105	0.960
47	0.4524	1.0417	0.990	195	0.4387	1.0102	0.960
48	0.4520	1.0409	0.989	200	0.4386	1.0100	0.960
49	0.4517	1.0400	0.988	$\infty$	0.4343	1.0000	0.950

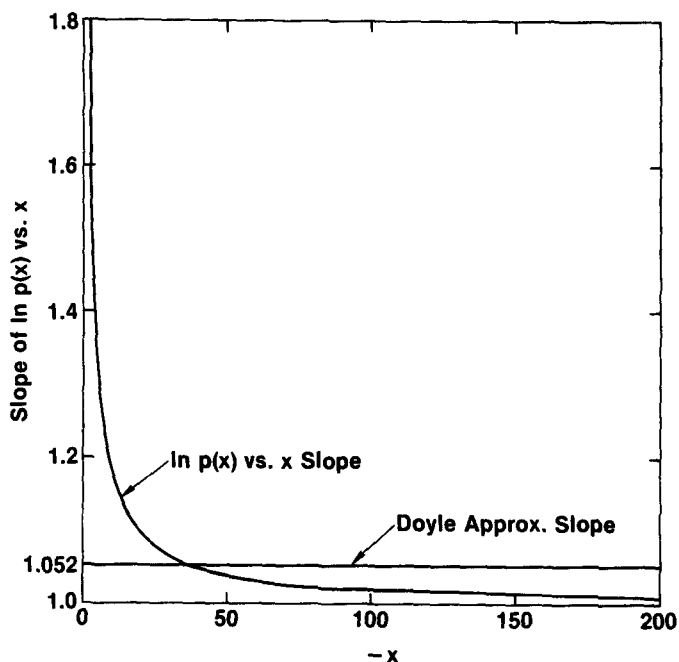


Fig. 2 Slope of  $\{\ln p(x) \text{ vs } x\}$  vs  $-x$ . Doyle approximation compared with correct slope

To summarize the problem, the activation energy is determined from equations (9) or (9') from the slope of a plot of the logarithm of the heating rate vs the reciprocal absolute temperatures at which a fraction conversion,  $\alpha$ , was reached at the various heating rates. The slope is divided by 0.457 (or 1.052) to obtain  $E/R$ . As we see from Table 1 this value for  $E/R$  may be in considerable error if  $x (= E/RT)$  differs greatly from  $-37$ , the value at which the Doyle approximation fits the slope of  $\log p(x)$  vs  $x$ .

If  $E/R$  is constant for the process of interest, then  $x$  changes only slowly with change in temperature. The first step of the correction procedure is the determination of an average value for  $x$  in the temperature range of the calculation. Then the value a) or b) in Table 1 for this average  $x$  is substituted for the Doyle value in eq. (9) or (9') to calculate a new value for  $E/R$ . Thus, one is defining a new Doyle relationship which has the correct slope near the midpoint of the  $x$  range of the experimental data.

### The correction method

A corrected value for  $E/R$  may be obtained by either of two procedures:

1. Equation (9) or (9'), containing Doyle's approximate values of 0.457 or 1.052, is used to obtain a first estimate of  $E/R$ . This value of  $E/R$  is divided by  $\bar{T}$ , the average

temperature of the calculation interval, to give an estimate of  $X$ . Division of the first estimate of  $E/R$  by the correction factor in Table 1 for the estimated  $X$  value yields a corrected value for  $E/R$ .

2. An estimate of  $E/R$  is made a priori from previous experience or by analogy to other processes and an estimate of  $X$  is obtained by division by  $\bar{T}$ . A corrected value for  $E/R$  is obtained by substituting the value of a) or b) in Table 1 for the estimated  $X$  in place of 0.457 or 1.052 in eqs. (9) or (9') respectively.

In either procedure, a new  $X$  value is obtained by division of the corrected value of  $E/R$  by  $\bar{T}$ . If the new  $X$  value differs substantially from the first estimate of  $X$ , then the value of a) or b) in Table 1 for the new  $X$  value is substituted for 0.457 or 1.052 in eqs. (9) or (9') and a more accurate  $E/R$  value obtained. This procedure may be repeated.

In either case, these calculations may be set up as a simple computer routine.

## Discussion

The attractiveness of the isoconversional method is that  $A$  and  $f(\alpha)$  which are difficult to separate and model are unneeded for the calculation of  $E/R$ . However, after  $E/R$  is calculated, if a model for  $f(\alpha)$  is assumed, then  $A$  is also easily calculated.

The extrapolation of the rate for service lifetime prediction or other purposes needs only the parameter,  $E/R$ . If the rate of reaction  $\nu_1$  at temperature  $T_1$  is known, the rate  $\nu_2$  at any other temperature  $T_2$  may be calculated from

$$\ln \nu_2 = \frac{E(T_1 - T_2)}{RT_1T_2} \ln \nu_1 \quad (\alpha = \alpha_k). \quad (10)$$

Two other methods exist which are very similar to the one described in this paper and do not require approximation or iteration.

If accurate values for rate,  $(d\alpha/dt)_j$ , are obtainable from  $\alpha$  and  $T$  data, Friedman's differential method [10] may be used to calculate  $E/R$  from the slope of a plot of  $\ln (d\alpha/dt)_{k,j}$  vs  $1/T_{k,j}$  where  $T_{k,j}$  is the temperature at which fraction of conversion  $\alpha_k$  was reached in an experiment at heating rate  $\beta_j$  since

$$\frac{E}{R} = \frac{d \ln \left( \frac{d\alpha}{dt} \right)_{k,j}}{d \left( \frac{1}{T_{k,j}} \right)} \quad (\alpha = \alpha_k). \quad (11)$$

Programming of the heating rate so that  $\beta' = cT^2$ , permits calculation of  $E/R$  from integral data without approximation because the temperature integral

$$\int_{T_0}^T T^{-2} \exp \left( -\frac{E}{RT} \right) dT$$

is easily integrated, and from a series of experiments at heating rates  $\beta' = c_j T^2$  the slope a plot of  $\ln c_j$  vs  $1/T_{k,j}$  will yield  $E/R$  directly for fractional conversion  $\alpha_k$ . The effect of this "parabolic" heating rate on the equations for calculating kinetic parameters for the isoconversional and many other methods was discussed in considerable detail on pp 517–519 of the 1966 paper by Flynn and Wall [3].

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**Zusammenfassung** — Es wird eine Literaturübersicht über die und eine ausführliche Darstellung der Isokonversionsmethode zur Bestimmung von Aktivierungsenergien aus den Reziprokwerten derjenigen Temperaturen gegeben, bei denen ein bestimmter Konversionsgrad in Experimenten mit verschiedener Aufheizgeschwindigkeit erreicht wird. Der in die Berechnung der Aktivierungsenergie durch lineare Näherung des Logarithmus des Temperaturintegrals eingehende Fehler wird diskutiert. Es werden Methoden zur Korrektur dieses Fehlers entwickelt und Korrekturfaktoren in Tabellenform angegeben.

**Резюме** — Сделан обзор и расширен изоконверсионный метод определения энергий активации из обратной температуры, при которой достигается фракция конверсии в эксперименте при различающихся постоянных скоростях нагрева. Обсуждена ошибка вычисления энергии активации, обусловленная использованием линейного приближения логарифма температурного интеграла. Развита методика исправления этой ошибки и приведена таблица корректировочных коэффициентов.