

CRITICAL VALUES
OF MAXIMUM CONVERSIONS FOR THE APPROXIMATE SOLUTION
OF SECOND-ORDER COMPETITIVE REACTIONS

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In case of two competitive reactions of the second order corresponding to the scheme

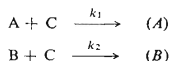


TABLE I

Critical Values of Maximum Conversions in Case of the 3 per cent Relative Error in k_{rel}

k_{rel}	k_{rel}^a	Max. conversion x/a	Max. conversion y/b
1.10	1.13	43.0	39.1
1.20	1.24	28.0	23.3
1.30	1.34	22.0	16.9
1.40	1.44	18.0	12.9
1.50	1.55	16.0	10.7
1.60	1.65	14.0	8.7
1.70	1.75	13.0	7.6
1.80	1.85	12.0	6.7
1.90	1.95	11.0	5.8
2.00	2.06	11.0	5.5
2.50	2.57	9.0	3.6
3.00	3.08	8.0	2.7
3.50	3.61	8.0	2.3
4.00	4.11	7.0	1.7
4.50	4.63	7.0	1.6
5.00	5.15	7.0	1.4
6.00	6.18	7.0	1.2
8.00	8.22	6.0	0.7
10.00	10.28	6.0	0.6
15.00	15.44	6.0	0.4
20.00	20.59	6.0	0.3
25.00	25.75	6.0	0.2
50.00	51.53	6.0	0.1
100.00	102.56	5.0	0.0
250.00	256.44	5.0	0.0
500.00	512.92	5.0	0.0

^a Calculated from Eq. (1).

it is possible to derive¹ the relation (1) for calculating the relative rate constant k_{rel} ,

$$k_{rel} = k_1/k_2 = \ln(1 - x/a)/\ln(1 - y/b), \quad (1)$$

where a, b are initial concentrations of substances A, B and x, y are concentrations of products formed. Keeping in the region of low conversions ($x, y \ll a, b$), the relation (1) is to be simplified into

$$k_{rel} = k_1/k_2 \approx (x/a)/(y/b). \quad (2)$$

This expression is obtained either by solving the differential equation of the above-mentioned scheme with the concentrations a, b considered as constants, or by expanding the expression (1) into the Taylor series and neglecting the higher-order terms. The error resulting from the ap-

TABLE II
Critical Values of Maximum Conversions in Case of the 5 per cent Relative Error in k_{rel}

k_{rel}	k_{rel}^a	Max. conversion x/a	Max. conversion a/b
1.10	1.16	58.0	52.7
1.20	1.26	41.0	34.2
1.30	1.37	33.0	25.4
1.40	1.47	28.0	20.0
1.50	1.58	25.0	16.7
1.60	1.68	23.0	14.4
1.70	1.79	21.0	12.4
1.80	1.89	20.0	11.1
1.90	2.00	19.0	10.0
2.00	2.10	18.0	9.0
2.50	2.63	15.0	6.0
3.00	3.16	14.0	4.7
3.50	3.68	13.0	3.7
4.00	4.20	12.0	3.0
4.50	4.73	12.0	2.7
5.00	5.26	12.0	2.4
6.00	6.30	11.0	1.8
8.00	8.42	11.0	1.4
10.00	10.48	10.0	1.0
15.00	15.75	10.0	0.7
20.00	21.02	10.0	0.5
25.00	26.29	10.0	0.4
50.00	52.63	10.0	0.2
100.00	104.74	9.0	0.1
250.00	261.93	9.0	0.0
500.00	523.91	9.0	0.0

^a Calculated from Eq. (1).

TABLE III
Critical Values of Maximum Conversions in Case of the 10 per cent Relative Error in k_{rel}

k_{rel}	k_{rel}^a	Max. conversion x/a	Max. conversion y/b
1.10	1.22	77.0	70.0
1.20	1.33	62.0	51.7
1.30	1.44	53.0	40.8
1.40	1.55	47.0	33.6
1.50	1.66	43.0	28.7
1.60	1.78	40.0	25.0
1.70	1.88	37.0	21.8
1.80	2.00	36.0	20.0
1.90	2.11	34.0	17.9
2.00	2.22	33.0	16.5
2.50	2.78	29.0	11.6
3.00	3.32	26.0	8.7
3.50	3.88	25.0	7.1
4.00	4.44	24.0	6.0
4.50	4.98	23.0	5.1
5.00	5.55	23.0	4.6
6.00	6.65	22.0	3.7
8.00	8.86	21.0	2.6
10.00	11.11	21.0	2.1
15.00	16.62	20.0	1.3
20.00	22.20	20.0	1.0
25.00	27.62	19.0	0.8
50.00	55.35	19.0	0.4
100.00	110.80	19.0	0.2
250.00	277.16	19.0	0.1
500.00	554.43	19.0	0.0

^a Calculated from Eq. (1).

plication of the relation (2) depends not only on the separate degrees of conversions, as it has been stated²⁻⁴ so far, but much more on their proportion, *i. e.* on the value of the relative rate constant k_{rel} . By critical values of conversions are to be called the maximum admissible conversions, for which the error does not exceed a fixed value. The dependence of these critical values of conversions (in per cent) on the quantity of the relative rate constant for the case of the relative error of 3, 5, and 10 per cent is listed in Tables I—III.

The relative error was calculated using the formula (3),

$$[(u - v)/u] 100 \leq 3, 5, \text{ or } 10, \quad (3)$$

where u , v are the right-hand sides of the relations (1) and (2).

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**THEORY OF INFORMATION
AS APPLIED TO ANALYTICAL CHEMISTRY. I.
THE AMOUNT OF INFORMATION OBTAINED BY ANALYSIS**

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The point of chemical analyses is to obtain information on the composition of an analyzed sample¹, the greatest amount of information being tried to be obtained most effectively.

The amount of information obtained by observations and measurements is defined by Brillouin² as the ratio before the observation to that after the observation. When applying this definition to the results of analyses, the uncertainty before the observation is, of course, given by our preliminary knowledge of the composition of a sample, and uncertainty after the observation is in the qualitative analysis limited by selectivity of the proof used and in the quantitative analysis it is essentially limited by precision of the result.

The amount of information² obtained in the experiment is generally given by

$$I = k \cdot \log_z(P_0/P), \quad (1)$$

where P_0 is the uncertainty before the observation, P is the uncertainty after the observation, k denotes the constant that enables us to imply, for example, the time effectiveness of analytical method in the amount of information, and \log_z is the logarithm of base z . The base of the logarithm determines units in which the amount of information is expressed: for example, for $z = e$ the natural digits ("nit") are used, for $z = 2$ the binary digits ("bit"), and for $z = 10$ decadic information digits ("dit"), sometimes also denoted as "hartley". For conversion of information units see Table I.

The uncertainty after the observation P may be defined by the Shannon³ relationship

$$P = n(x) \quad (2)$$