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Technical Note

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RAPID DETERMINATION OF THE ORDER OF CHEMICAL REACTIONS FROM TIME-RATIO TABLES



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Joseph H. Flynn

A table of ratios of reaction times corresponding to 15%/5%, 20%/10%, ..., 95%/85% reaction for orders of chemical reaction from -10 to +10 is presented. Use of this table allows the rapid calculation of the order of chemical reactions that are kinetically simple and involves only one subjective step. Methods are discussed for interpreting deviations from constant order resulting from errors in the initial times and concentrations, from errors in stoichiometry, and from the reaction following a more complicated rate expression.

INTRODUCTION

The various methods of fitting chemical kinetic data to rate equations may be divided into two categories-- "differential" methods in which the data are fitted directly to a differential equation expressing the rate, dx/dt , as a function of the degree of advancement or extent of reaction, x , and "integral" methods in which the data are fitted to an integrated equation. (1, 2).

Integral methods are more commonly used than differential methods despite the fact that the latter permit a better interpretation of deviations from constant order, and can be used to fit data to equations of non-integral order and to determine initial rates. (1, 2). This situation results to some extent from the tedious determinations of tangents to the curves, $x(t)$, required in the differential method.

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This paper presents a rapid, simple, incremental method for determining the order of chemical reactions and may be utilized to detect erroneous assumptions concerning initial conditions and stoichiometry. In many cases it provides clues as to the form of complicated kinetic expressions that may be necessary to fit the data. Also, it minimizes personal bias, as the only subjective step involved in the method is the fitting of a smooth curve to a plot of x with respect to time.

This time-ratio table should be a particularly valuable tool for a chemist with a not too highly developed mathematical background, as its use, consisting of the application of a set of simple, rapid, non-subjective steps to a time as a function of concentration curve for a single kinetic run, can result in considerable information regarding the form of the kinetic equations describing the reaction. Also, the detailed discussion of the use of this table brings out several features concerning the treatment of kinetic data that are not apparent in the usual "differential" and "integral" methods of analyses.

If the rate of a chemical reaction is proportional to powers of the concentrations of a single reactant, or several reactants present in stoichiometric concentrations, it may be described by the equation

$$\frac{dx}{dt} = k(1 - x)^n \quad (1)$$

where k is a constant that may include stoichiometric coefficients and initial concentrations, and n is defined as the order. Many other reactions may be represented by equation (1) by means of Ostwald's "Isolation" method. (3).

Equation (1) can be integrated to obtain

$$\ln(1 - x) = -kt \quad (n = 1) \quad 0 \leq t \leq \infty \quad (2)$$

$$\frac{(1 - x)^{1-n} - 1}{1 - n} = -kt \quad (n \neq 1) \quad 0 \leq t \leq t_{x=1} \quad (3)$$

It can be seen from these equations that the ratio of times for two different percentages of reaction will have a constant numerical value for a particular value of n . For example, for $n = 3$ and t_{60} and t_{20} , the times for 60 and 20% completion, respectively,

$$\frac{-kt_{60}}{-kt_{20}} = \frac{t_{60}}{t_{20}} = \frac{.4^{1-3} - 1}{.8^{1-3} - 1} = 9.333.$$

This method of time-ratios has been used to determine integral orders (1) and recently several time-ratios have been plotted as a function of order to allow an interpolation of fractional orders (4). The method has also been used to determine rate constants of simultaneous reactions (5).

Overlapping ratios of successive 10% reaction times, t_{15}/t_5 , t_{20}/t_{10} , ..., t_{95}/t_{85} for a number of orders are tabulated in this paper and have been found to be useful, not only for determining fractional orders, but also for detecting and interpreting changes in apparent order.

TIME-RATIO TABLES

Values of t_x were calculated for $x = 0.05, 0.10, 0.15, \dots, 0.90, 0.95$ and for values of $n = -10.0, -5.0, -4.0, -3.0, -2.0, -1.5, -1.4, \dots, -0.1, 0, +0.1, \dots, +3.1, 3.3, 3.5, 3.7, 4.0, 4.5, \dots, 9.5, 10.0$. Time-ratios were then calculated. Tables of Natural Logarithms, Tables of Fractional Powers, and Tables of First Ten Powers (6) were used in these calculations. The values were checked to five significant figures by differencing tests, though only four significant figures are used in Table I. This is probably sufficient for the most accurate kinetic data.

USE OF THE TIME-RATIO TABLES

The degree of advancement, x , of a chemical reaction is obtained from the quantitative measurement of some physical or chemical property which is a known function of the concentration of a reactant or product. The times for various degrees of advancement can be obtained from a smooth curve drawn through the points of a plot of x as a function of t . (If the initial time is unknown, x may be calculated from any arbitrary zero time on a curve representing the concentration as a function of time.) The ratios of the t_x values can be compared with those in Table I and the order thus obtained. If the reaction follows equation (1), and accurate initial concentrations and time are used, the values for the order, n , determined from successive time-ratios should remain constant.

Table I is represented in graphical form in Figure 1.

The sensitivity of the time-ratios to the order may be defined by

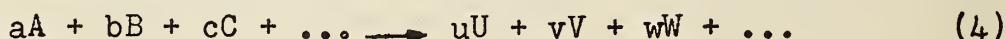
$$\frac{1}{(\text{time ratio value})_{\text{ave}}} \cdot \frac{\Delta(\text{time-ratio value})}{\Delta n}$$

where Δ indicates an incremental value. It can be seen from Figure 1 that if all time-ratios are determined with equal relative precision, the sensitivity of these ratios increases with increasing order and degree of advancement.

DISCUSSION

The greatest value of the time-ratio table lies in its applicability to kinetic expressions more complex than equation (1), and the discussion of this table will involve the analysis of some of the more easily interpretable causes of deviation from constant order. The effect on the order of errors in the times, concentrations, and stoichiometric relations will be discussed, and some consideration will be given to the deviations caused by the reaction rate following a more complicated kinetic law than equation (1).

A stoichiometrically pure chemical reaction may be represented by the equation



where small letters represent stoichiometric coefficients and capital letters represent concentrations of molecular species. For such a system the stoichiometric coefficients are independent of the time. The combination of the time derivatives of the relationships expressing the conservation of each elementary species gives

$$-\frac{1}{a} \frac{dA}{dt} = -\frac{1}{b} \frac{dB}{dt} = -\frac{1}{c} \frac{dC}{dt} = \dots = \frac{1}{u} \frac{dU}{dt} = \frac{1}{v} \frac{dV}{dt} = \frac{1}{w} \frac{dW}{dt} = \dots \quad (5)$$

whenever the concentrations of all intermediates are negligible or their concentrations change slowly with time (steady state).

Here we are interested only in the case where the reactants that contribute to the order of the reaction are present in stoichiometric amounts, the coefficients satisfy the relation

$$\frac{1}{a} A = \frac{1}{b} B = \frac{1}{c} C = \dots \quad (6)$$

Then, if the rate of disappearance of a reactant, A, is proportional only to powers of the concentrations of one or more reactants,

$$-\frac{1}{a} \frac{dA}{dt} = K \left(\frac{b}{a}\right)^q \left(\frac{c}{a}\right)^r \dots A^p + q + r + \dots \quad (7)$$

In terms of the concentration of a product, U, equation (7) will have the form

$$\frac{1}{u} \frac{dU}{dt} = K \left(\frac{b}{a}\right)^q \left(\frac{c}{a}\right)^r \dots \left(A_0 - \frac{a}{u} U\right)^{p + q + r + \dots} \quad (8)$$

where the subscript, o, indicates an initial concentration.

If at $t = 0$, $A = A_0$, $U = 0$; and at $t = \infty$, $A_\infty = 0$,

$U_\infty = \frac{u}{a} A_0$, then n , k , and x of equation (1), in terms of the parameters of eqs. (7) and (8), will be given by

$$n = p + q + r + \dots \quad (9)$$

$$k = aK \left(\frac{b}{a}\right)^q \left(\frac{c}{a}\right)^r \dots A_0^{p + q + r + \dots} - 1 \quad (10)$$

$$x = 1 - \frac{A}{A_0} \quad (\text{reaction followed by change in concentration of reactant, } A, \text{ that contributes to the order}) \quad (11a)$$

$$x = \frac{a}{eA_0} (E_0 - E) \quad (\text{reaction followed by change in concentration of a reactant, } E, \text{ that does not contribute to the order}) \quad (11b)$$

$$x = \frac{a}{u} \frac{U}{A_0} \quad (\text{reaction followed by change in concentration of a product, } U) \quad (11c)$$

Errors in Initial Time and Concentration. If the reduced times, $\gamma_i = kt_i$, are in error because the initial γ differ from the correct value by an amount $\pm \epsilon_\gamma$, then instead of determining t_2/t_1 , one will actually determine n from

$$\frac{\gamma'_2}{\gamma'_1} = \frac{\gamma_2 \pm \epsilon_\gamma}{\gamma_1 \pm \epsilon_\gamma} = \frac{(1 - x_2)^{1-n} - 1 \pm (1 - n)\epsilon_\gamma}{(1 - x_1)^{1-n} - 1 \pm (1 - n)\epsilon_\gamma} .$$

If an error of $\pm \epsilon_A$ is present in the value used for the initial concentration, A_0 , then instead of $x_a = 1 - \frac{A_a}{A_0}$, (equation 11a), one will have

$$x_a' = 1 - \frac{A_a}{A_0 \pm \epsilon_A} \quad \text{and} \quad (1 - x_a') = \frac{1}{1 \pm \frac{\epsilon_A}{A_0}} (1 - x_a). \quad (12)$$

The apparent orders, n' , calculated from Table I for errors in initial time for various n , were almost identical to the n' calculated from errors in initial concentration if $-\frac{\epsilon_A}{A_0} = \epsilon_\gamma \ll 1$. The difference between the apparent and true order, $n' - n$, is found to depend only slightly on n . Deviations from the true order for $\epsilon = \epsilon_\gamma = -\frac{\epsilon_A}{A_0} = \pm 0.1, \pm 0.01, \pm 0.001$, are plotted in Figure 2 as a function of m , the percentage-reaction index in the denominator of the time-ratio $t_m + 10/t_m$. The index, m , varies from 10 to 80 and these curves represent average values for various n calculated for this interval in m .

As is to be expected, the deviations from true order resulting from errors in initial time or concentration are larger for early time-ratios. At later ratios, the deviations are relatively small.

An induction period, or an initial period of rapid reaction, which may be too short to be recognized by other methods of kinetic analysis, will appear as an error in the initial time or concentration. Therefore, an apparent error in the initial time or concentration, as shown by abnormal n , that is too large to be ascribed to experimental error, can be interpreted as evidence for initial irregularities in the rate. The calculation of a new degree of advancement from an arbitrary point on the curve representing the concentration as a function of the time should eliminate this effect, except for cases where the concentration of a product is obtained and the error in initial concentration is due to the determination of an erroneous value for the concentration of a product at infinite time.

Errors in Stoichiometric Relationships. In cases where more than one reactant contributes to the order of the reaction, the reactants must be present in stoichiometric concentrations if the kinetics are to be described by equation (1). The case where one of the contributing reactants is present in a non-stoichiometric concentration will be considered subsequently.

In cases where equation (1) is followed, errors in the determination of the degree of advancement may result from incorrect assumptions about the stoichiometry of the reaction. A similar situation could result from a stoichiometric error in the function relating the measured physical or chemical property with concentration.

If there is a constant stoichiometric error, ϵ_a , in the stoichiometric coefficient, a , in a reaction investigated by the change in concentration of a product, then the degree of advancement as defined by eq. (11c)

will have the value, $x_a' = \frac{(a + \epsilon_a) U_a}{A_0}$, and

$$(1 - x_a') = (1 - x_a) \left(1 + \frac{\epsilon_a}{a}\right) - \frac{\epsilon_a}{a} \quad (13)$$

The deviations from the true order, $n' - n$, calculated by means of equation (13), are approximately inversely proportional to n . A plot of $(n' - n)/n$ as a function of the index, m , ($m = 10, 20, \dots, 80$)

for stoichiometric errors of $\epsilon = \frac{\epsilon a}{a} = \pm 0.1$ and ± 0.01 , results in families of points that may be approximated by the curves in Figure 3.

The deviations from the true order for later time-ratios may be quite large for stoichiometric errors of this type.

If there is an error, ϵ_B , in the concentration of a reactant, B , which does not contribute to the order, and B is experimentally measured, then the degree of advancement as defined by equation (11b) will have the value

$$x_a' = \frac{a}{bA_0} (B_0 \pm \epsilon_B - B_a), \text{ and}$$

$$(1 - x_a') = (1 - x_a) - \frac{\epsilon_B a}{bA_0} \quad (14)$$

These deviations from true order are quite similar in form to those obtained for errors in A_0 (Figure 2), except for increasing positive order, the deviations change sign and become large in magnitude as m approaches 90.

Deviations from Constant Order Resulting from a More Complicated Rate Expression. A large number of chemical reactions that give a changing value for n when represented by equation (1) may be better represented by

$$\frac{dx}{dt} = \kappa (1 - x)^\mu (1 - \alpha x)^\nu \quad (15)$$

where κ , α , μ , and ν may be considered in general as arbitrary parameters.

A few examples of reactions that are well represented by equation (15) are:

- a) first order reversible reactions ($\mu = 0, \nu = 1, \alpha > 1$)
- b) parallel reactions: one zero order and one first order
($\mu = 0, \nu = 1, 1 > \alpha > 0$)
- c) parallel reactions: one first order and one second order
($\mu = 1, \nu = 1, 1 > \alpha > 0$)
- d) Hydrogen bromide formation ($\mu = 5/2, \nu = -1, \alpha > 0$)
- e) many catalytic reactions ($\nu > 0$ for positively catalyzed reactions, and $\nu < 0$ for negatively catalyzed reactions). If a reaction is catalyzed by a reactant, $\alpha > 0$; if catalyzed by an intermediate or product, $\alpha < 0$).
- f) reactions in which two or more reactants contribute to the order in proportion to powers of their respective concentrations and one of these reactants is present in a non-stoichiometric concentration.

Equation (15) was solved for values of t corresponding to $x = 0.05, 0.10, \dots, 0.90, 0.95; \alpha = 3, 2, 1.5, 1.2, 1.1, 1.0, 0.9, 0.5, 0, -0.5, -1.0, -2.0, -5.0, -10.0, -\infty$; and various combinations of $\nu = \pm 3, \pm 2, \pm 1$, and $\mu = \pm 3, \pm 2, \pm 1, 0$. These computations were performed with the Analog Computer Facility of the National Bureau of Standards for the equations involving cubics in μ and ν .

Values for n' , the apparent order as defined by equation (1), were obtained by means of Table I from the time-ratios that were calculated from these data. The

function, $\frac{n' - \mu}{\nu}$ was found to be relatively independent of μ and ν . Tables II and III demonstrate that even for large absolute values of α ($\alpha = +2.0$ and -5.0),

$\frac{n' - \mu}{\nu}$ as a function of m falls into two sets -- one for $\nu > 0$, the other for $\nu \leq 0$. The mean curves for $\nu > 0$ are shown in Figure 4 and for $\nu < 0$ in Figure 5.

In the common case $|\nu| = 1$, a curve $n'(m)$ can be matched with a curve in Figures 4 or 5 by a displacement μ units along the ordinate. Thus the parameter, α , can be determined. For $|\nu| \neq 1$, curves $\frac{n'}{\nu}(m)$ may be tested

for various values of ν . The estimates of α , μ and ν obtained by these procedures may be used as guides for more precise curve fitting.

Thus the time-ratio method allows for a treatment of kinetic data similar to that which may be performed in the differential method of analysis (7) where the slope, n_x , determined from a plot of $\log \frac{dx}{dt}$ as a function of $\log (1 - x)$ is given by

$$n_x = \mu + \nu \frac{\alpha (1 - x)}{1 - \alpha x} \quad (16)$$

with the limiting characteristics

$$\lim_{x \rightarrow 0} n_x = \mu + \alpha \nu \quad (17)$$

$$\lim_{x \rightarrow 1} n_x = \mu \quad (\alpha < 1) \quad (18)$$

and the function $\frac{n_x - \mu}{\nu}$ vs. x for various α can be used to estimate values for α , μ , ν and .

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Table I. Time-Ratios for Various Orders

| Order | 15/5 | 20/10 | 25/15 | 30/20 | 35/25 | 40/30 | 45/35 | 50/40 | 55/45 | 60/50 | 65/55 | 70/60 | 75/65 | 80/70 | 85/75 | 90/80 | 95/85 |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| -10.0 | 1.931 | 1.332 | 1.150 | 1.072 | 1.035 | 1.017 | 1.007 | 1.003 | 1.001 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| -5.0 | 2.351 | 1.575 | 1.320 | 1.196 | 1.125 | 1.080 | 1.052 | 1.033 | 1.020 | 1.012 | 1.007 | 1.003 | 1.002 | 1.001 | 1.000 | 1.000 | 1.000 |
| -4.0 | 1.642 | 1.371 | 1.159 | 1.077 | 1.056 | 1.045 | 1.036 | 1.031 | 1.028 | 1.026 | 1.025 | 1.024 | 1.023 | 1.022 | 1.021 | 1.020 | 1.019 |
| -3.0 | 2.577 | 1.717 | 1.430 | 1.287 | 1.202 | 1.145 | 1.106 | 1.077 | 1.056 | 1.039 | 1.027 | 1.018 | 1.011 | 1.007 | 1.003 | 1.002 | 1.001 |
| -2.0 | 2.706 | 1.801 | 1.498 | 1.346 | 1.255 | 1.193 | 1.149 | 1.116 | 1.090 | 1.070 | 1.053 | 1.040 | 1.028 | 1.020 | 1.012 | 1.007 | 1.003 |
| -1.5 | 2.774 | 1.846 | 1.536 | 1.380 | 1.286 | 1.222 | 1.176 | 1.142 | 1.114 | 1.092 | 1.073 | 1.058 | 1.044 | 1.033 | 1.023 | 1.015 | 1.008 |
| -1.4 | 2.788 | 1.856 | 1.544 | 1.387 | 1.292 | 1.228 | 1.182 | 1.147 | 1.119 | 1.097 | 1.078 | 1.062 | 1.049 | 1.037 | 1.026 | 1.017 | 1.010 |
| -1.3 | 2.803 | 1.865 | 1.552 | 1.394 | 1.299 | 1.235 | 1.188 | 1.153 | 1.125 | 1.102 | 1.083 | 1.067 | 1.053 | 1.041 | 1.030 | 1.020 | 1.012 |
| -1.2 | 2.817 | 1.875 | 1.560 | 1.402 | 1.306 | 1.241 | 1.195 | 1.159 | 1.131 | 1.108 | 1.089 | 1.072 | 1.058 | 1.045 | 1.034 | 1.023 | 1.014 |
| -1.1 | 2.832 | 1.885 | 1.568 | 1.409 | 1.313 | 1.248 | 1.201 | 1.165 | 1.137 | 1.114 | 1.094 | 1.078 | 1.063 | 1.050 | 1.038 | 1.027 | 1.017 |
| -1.0 | 2.846 | 1.895 | 1.577 | 1.417 | 1.320 | 1.255 | 1.208 | 1.172 | 1.143 | 1.120 | 1.100 | 1.083 | 1.068 | 1.055 | 1.043 | 1.031 | 1.021 |
| -0.9 | 2.861 | 1.905 | 1.585 | 1.424 | 1.327 | 1.262 | 1.215 | 1.179 | 1.150 | 1.127 | 1.107 | 1.090 | 1.074 | 1.061 | 1.048 | 1.036 | 1.025 |
| -0.8 | 2.876 | 1.915 | 1.594 | 1.432 | 1.335 | 1.269 | 1.222 | 1.186 | 1.157 | 1.133 | 1.113 | 1.096 | 1.081 | 1.067 | 1.054 | 1.042 | 1.029 |
| -0.7 | 2.891 | 1.925 | 1.602 | 1.440 | 1.342 | 1.277 | 1.229 | 1.193 | 1.164 | 1.140 | 1.120 | 1.103 | 1.088 | 1.074 | 1.061 | 1.048 | 1.035 |
| -0.6 | 2.906 | 1.935 | 1.611 | 1.448 | 1.350 | 1.284 | 1.236 | 1.200 | 1.171 | 1.148 | 1.128 | 1.111 | 1.095 | 1.081 | 1.068 | 1.055 | 1.042 |
| -0.5 | 2.921 | 1.946 | 1.620 | 1.457 | 1.358 | 1.292 | 1.244 | 1.208 | 1.179 | 1.156 | 1.136 | 1.119 | 1.103 | 1.090 | 1.076 | 1.063 | 1.050 |
| -0.4 | 2.937 | 1.956 | 1.629 | 1.465 | 1.366 | 1.300 | 1.252 | 1.216 | 1.187 | 1.164 | 1.144 | 1.127 | 1.112 | 1.099 | 1.086 | 1.073 | 1.059 |
| -0.3 | 2.952 | 1.967 | 1.638 | 1.474 | 1.374 | 1.308 | 1.260 | 1.224 | 1.195 | 1.172 | 1.153 | 1.136 | 1.122 | 1.108 | 1.096 | 1.084 | 1.071 |
| -0.2 | 2.968 | 1.978 | 1.648 | 1.482 | 1.383 | 1.316 | 1.268 | 1.232 | 1.204 | 1.181 | 1.162 | 1.146 | 1.132 | 1.119 | 1.107 | 1.096 | 1.084 |
| -0.1 | 2.984 | 1.989 | 1.657 | 1.491 | 1.391 | 1.325 | 1.277 | 1.241 | 1.213 | 1.190 | 1.172 | 1.156 | 1.142 | 1.130 | 1.120 | 1.110 | 1.099 |
| 0.0 | 3.000 | 2.000 | 1.667 | 1.500 | 1.400 | 1.333 | 1.286 | 1.250 | 1.222 | 1.200 | 1.182 | 1.167 | 1.154 | 1.143 | 1.133 | 1.125 | 1.118 |
| +0.1 | 3.016 | 2.011 | 1.676 | 1.509 | 1.409 | 1.342 | 1.295 | 1.259 | 1.232 | 1.210 | 1.192 | 1.178 | 1.166 | 1.156 | 1.148 | 1.143 | 1.139 |
| +0.2 | 3.032 | 2.023 | 1.686 | 1.518 | 1.418 | 1.351 | 1.304 | 1.269 | 1.242 | 1.221 | 1.204 | 1.190 | 1.179 | 1.171 | 1.165 | 1.162 | 1.164 |
| +0.3 | 3.049 | 2.034 | 1.696 | 1.528 | 1.427 | 1.361 | 1.314 | 1.279 | 1.252 | 1.232 | 1.215 | 1.203 | 1.193 | 1.187 | 1.183 | 1.184 | 1.194 |
| +0.4 | 3.066 | 2.046 | 1.706 | 1.537 | 1.437 | 1.370 | 1.323 | 1.289 | 1.263 | 1.243 | 1.228 | 1.216 | 1.208 | 1.204 | 1.203 | 1.209 | 1.228 |
| 0.5 | 3.082 | 2.057 | 1.717 | 1.547 | 1.446 | 1.380 | 1.333 | 1.299 | 1.274 | 1.255 | 1.241 | 1.231 | 1.224 | 1.222 | 1.225 | 1.237 | 1.267 |
| 0.6 | 3.099 | 2.069 | 1.727 | 1.557 | 1.456 | 1.390 | 1.344 | 1.310 | 1.286 | 1.267 | 1.254 | 1.246 | 1.241 | 1.242 | 1.249 | 1.268 | 1.313 |
| 0.7 | 3.116 | 2.081 | 1.738 | 1.567 | 1.466 | 1.400 | 1.354 | 1.321 | 1.297 | 1.280 | 1.268 | 1.261 | 1.259 | 1.263 | 1.276 | 1.302 | 1.366 |
| 0.8 | 3.134 | 2.093 | 1.748 | 1.577 | 1.476 | 1.411 | 1.365 | 1.333 | 1.310 | 1.294 | 1.283 | 1.278 | 1.279 | 1.286 | 1.304 | 1.341 | 1.427 |
| 0.9 | 3.151 | 2.106 | 1.759 | 1.588 | 1.487 | 1.421 | 1.376 | 1.345 | 1.322 | 1.307 | 1.299 | 1.296 | 1.299 | 1.311 | 1.335 | 1.384 | 1.498 |
| 1.0 | 3.168 | 2.118 | 1.770 | 1.598 | 1.497 | 1.432 | 1.388 | 1.357 | 1.336 | 1.322 | 1.315 | 1.314 | 1.321 | 1.337 | 1.368 | 1.431 | 1.579 |
| 1.1 | 3.186 | 2.130 | 1.781 | 1.609 | 1.508 | 1.443 | 1.400 | 1.369 | 1.349 | 1.337 | 1.332 | 1.333 | 1.343 | 1.355 | 1.405 | 1.483 | 1.672 |
| 1.2 | 3.204 | 2.143 | 1.793 | 1.620 | 1.519 | 1.455 | 1.412 | 1.382 | 1.363 | 1.353 | 1.349 | 1.354 | 1.368 | 1.395 | 1.444 | 1.540 | 1.778 |
| 1.3 | 3.222 | 2.156 | 1.804 | 1.631 | 1.531 | 1.466 | 1.424 | 1.396 | 1.378 | 1.369 | 1.368 | 1.375 | 1.393 | 1.427 | 1.487 | 1.604 | 1.900 |
| 1.4 | 3.240 | 2.169 | 1.816 | 1.643 | 1.542 | 1.478 | 1.437 | 1.409 | 1.393 | 1.386 | 1.387 | 1.397 | 1.420 | 1.461 | 1.533 | 1.673 | 2.038 |

Table I. Time-Ratios for Various Orders - Continued.

| Time-Ratio Index | 15/15 | 20/10 | 25/15 | 30/20 | 35/25 | 40/30 | 45/35 | 50/40 | 55/45 | 60/50 | 65/55 | 70/60 | 75/65 | 80/70 | 85/75 | 90/80 | 95/85 |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| 1.5 | 3.259 | 2.182 | 1.828 | 1.654 | 1.554 | 1.491 | 1.450 | 1.423 | 1.408 | 1.403 | 1.407 | 1.421 | 1.449 | 1.497 | 1.582 | 1.749 | 2.195 |
| 1.6 | 3.277 | 2.195 | 1.839 | 1.666 | 1.566 | 1.503 | 1.463 | 1.438 | 1.424 | 1.421 | 1.428 | 1.445 | 1.479 | 1.535 | 1.635 | 1.833 | 2.373 |
| 1.7 | 3.296 | 2.209 | 1.852 | 1.678 | 1.578 | 1.516 | 1.477 | 1.453 | 1.441 | 1.440 | 1.449 | 1.471 | 1.510 | 1.576 | 1.692 | 1.924 | 2.575 |
| 1.8 | 3.315 | 2.222 | 1.864 | 1.690 | 1.590 | 1.529 | 1.490 | 1.468 | 1.458 | 1.459 | 1.472 | 1.498 | 1.544 | 1.620 | 1.753 | 2.024 | 2.804 |
| 1.9 | 3.334 | 2.236 | 1.876 | 1.702 | 1.603 | 1.542 | 1.505 | 1.484 | 1.476 | 1.479 | 1.495 | 1.526 | 1.579 | 1.666 | 1.819 | 2.132 | 3.062 |
| 2.0 | 3.353 | 2.250 | 1.889 | 1.714 | 1.615 | 1.556 | 1.519 | 1.500 | 1.494 | 1.500 | 1.519 | 1.556 | 1.615 | 1.714 | 1.889 | 2.250 | 3.353 |
| 2.1 | 3.372 | 2.264 | 1.902 | 1.727 | 1.628 | 1.569 | 1.535 | 1.517 | 1.513 | 1.521 | 1.545 | 1.586 | 1.654 | 1.766 | 1.964 | 2.373 | 3.661 |
| 2.2 | 3.392 | 2.278 | 1.915 | 1.740 | 1.642 | 1.584 | 1.550 | 1.534 | 1.532 | 1.541 | 1.571 | 1.618 | 1.694 | 1.820 | 2.074 | 2.517 | 4.050 |
| 2.3 | 3.412 | 2.293 | 1.928 | 1.753 | 1.655 | 1.598 | 1.566 | 1.551 | 1.552 | 1.567 | 1.597 | 1.651 | 1.737 | 1.877 | 2.129 | 2.668 | 4.465 |
| 2.4 | 3.432 | 2.307 | 1.941 | 1.766 | 1.669 | 1.613 | 1.582 | 1.569 | 1.572 | 1.590 | 1.627 | 1.686 | 1.781 | 1.938 | 2.220 | 2.831 | 4.932 |
| 2.5 | 3.452 | 2.322 | 1.955 | 1.780 | 1.683 | 1.628 | 1.598 | 1.588 | 1.593 | 1.615 | 1.656 | 1.722 | 1.828 | 2.002 | 2.316 | 3.008 | 5.455 |
| 2.6 | 3.472 | 2.337 | 1.968 | 1.793 | 1.697 | 1.643 | 1.615 | 1.607 | 1.615 | 1.640 | 1.686 | 1.760 | 1.877 | 2.069 | 2.419 | 3.199 | 6.042 |
| 2.7 | 3.493 | 2.352 | 1.982 | 1.807 | 1.712 | 1.659 | 1.633 | 1.626 | 1.637 | 1.666 | 1.718 | 1.799 | 1.927 | 2.139 | 2.528 | 3.405 | 6.700 |
| 2.8 | 3.513 | 2.367 | 1.996 | 1.821 | 1.727 | 1.675 | 1.650 | 1.646 | 1.660 | 1.693 | 1.750 | 1.840 | 1.981 | 2.244 | 2.644 | 3.627 | 7.436 |
| 2.9 | 3.534 | 2.382 | 2.011 | 1.836 | 1.742 | 1.691 | 1.668 | 1.666 | 1.684 | 1.721 | 1.784 | 1.882 | 2.036 | 2.362 | 2.766 | 3.867 | 8.261 |
| 3.0 | 3.555 | 2.398 | 2.025 | 1.850 | 1.757 | 1.708 | 1.687 | 1.688 | 1.708 | 1.750 | 1.819 | 1.926 | 2.091 | 2.374 | 2.896 | 4.125 | 9.184 |
| 3.1 | 3.577 | 2.414 | 2.040 | 1.865 | 1.773 | 1.725 | 1.706 | 1.709 | 1.733 | 1.780 | 1.855 | 1.971 | 2.151 | 2.460 | 3.034 | 4.403 | 10.22 |
| 3.2 | 3.600 | 2.430 | 2.056 | 1.880 | 1.789 | 1.740 | 1.725 | 1.724 | 1.755 | 1.804 | 1.881 | 2.008 | 2.203 | 2.544 | 3.184 | 4.694 | 11.364 |
| 3.3 | 3.624 | 2.446 | 2.070 | 1.896 | 1.805 | 1.760 | 1.745 | 1.745 | 1.785 | 1.842 | 1.931 | 2.068 | 2.283 | 2.644 | 3.344 | 5.024 | 12.66 |
| 3.4 | 3.648 | 2.479 | 2.100 | 1.927 | 1.839 | 1.797 | 1.786 | 1.801 | 1.840 | 1.907 | 2.012 | 2.171 | 2.422 | 2.847 | 3.670 | 5.412 | 15.72 |
| 3.5 | 3.708 | 2.512 | 2.132 | 1.959 | 1.873 | 1.835 | 1.829 | 1.850 | 1.898 | 1.977 | 2.098 | 2.282 | 2.573 | 3.069 | 4.044 | 6.570 | 19.53 |
| 4.0 | 3.777 | 2.564 | 2.181 | 2.010 | 1.927 | 1.895 | 1.897 | 1.929 | 1.991 | 2.089 | 2.238 | 2.464 | 2.822 | 3.441 | 4.687 | 8.056 | 27.09 |
| 4.5 | 3.836 | 2.634 | 2.267 | 2.099 | 2.024 | 2.003 | 2.020 | 2.072 | 2.162 | 2.298 | 2.502 | 2.810 | 3.305 | 3.841 | 4.616 | 11.35 | 46.83 |
| 5.0 | 4.021 | 2.750 | 2.359 | 2.196 | 2.130 | 2.122 | 2.157 | 2.233 | 2.356 | 2.538 | 2.807 | 3.217 | 3.885 | 5.096 | 7.742 | 16.02 | 81.04 |
| 5.5 | 4.151 | 2.851 | 2.458 | 2.300 | 2.245 | 2.253 | 2.309 | 2.413 | 2.574 | 2.810 | 3.158 | 3.693 | 4.577 | 6.223 | 9.979 | 22.64 | 140.3 |
| 6.0 | 4.288 | 2.959 | 2.564 | 2.413 | 2.370 | 2.396 | 2.477 | 2.614 | 2.819 | 3.118 | 3.561 | 4.247 | 5.401 | 7.610 | 12.87 | 32.01 | 243.0 |
| 6.5 | 4.432 | 3.072 | 2.676 | 2.534 | 2.507 | 2.553 | 2.662 | 2.836 | 3.093 | 3.466 | 4.021 | 4.891 | 6.380 | 9.311 | 16.61 | 45.26 | 420.9 |
| 7.0 | 4.583 | 3.192 | 2.797 | 2.665 | 2.654 | 2.725 | 2.865 | 3.083 | 3.400 | 3.859 | 4.547 | 5.638 | 7.542 | 11.40 | 21.44 | 64.00 | 729.0 |
| 7.5 | 4.741 | 3.320 | 2.925 | 2.805 | 2.815 | 2.912 | 3.089 | 3.356 | 3.742 | 4.301 | 5.145 | 6.502 | 8.912 | 13.96 | 27.67 | 90.51 | 1263. |
| 8.0 | 4.906 | 3.455 | 3.063 | 2.957 | 2.988 | 3.116 | 3.334 | 3.658 | 4.122 | 4.798 | 5.826 | 7.502 | 10.55 | 17.09 | 35.72 | 128.0 | 2187. |
| 8.5 | 5.080 | 3.598 | 3.210 | 3.120 | 3.176 | 3.339 | 3.603 | 3.990 | 4.544 | 5.355 | 6.599 | 8.658 | 12.48 | 20.93 | 46.12 | 181.0 | 3782. |
| 9.0 | 5.262 | 3.749 | 3.367 | 3.295 | 3.380 | 3.581 | 3.898 | 4.356 | 5.013 | 5.980 | 7.478 | 9.995 | 14.76 | 25.63 | 59.54 | 256.0 | 6561. |
| 9.5 | 5.454 | 3.910 | 3.534 | 3.484 | 3.600 | 3.844 | 4.220 | 4.759 | 5.533 | 6.680 | 8.475 | 11.54 | 17.46 | 31.39 | 76.86 | 362.0 | 11364. |
| 10.0 | 5.655 | 4.080 | 3.713 | 3.687 | 3.838 | 4.131 | 4.571 | 5.202 | 6.110 | 7.463 | 9.607 | 13.32 | 20.66 | 38.44 | 99.23 | 512.0 | 19683. |

Table II

$$\frac{n^* - \mu}{v} \text{ as a function of } m \text{ for } \alpha = + 2.0 \text{ and various } v \text{ and } \mu$$

| μ | $\frac{n^* - \mu}{v}$ | 10 | 20 | 30 | 40 | 50 |
|-----------------|-----------------------|------|------|------|--------|----|
| -2 | +2 | 2.28 | 2.59 | 3.33 | - | |
| 0 | 1 | 2.28 | 2.60 | 3.28 | - | |
| 0 | 2 | 2.28 | 2.63 | 3.42 | - | |
| 0 | 3 | 2.29 | 2.66 | 3.42 | - | |
| +1 | 1 | 2.28 | 2.61 | 3.32 | - | |
| 1 | 2 | 2.28 | 2.64 | 3.46 | - | |
| 2 | 1 | 2.28 | 2.62 | 3.36 | - | |
| Avg ($v > 0$) | | 2.28 | 2.62 | 3.37 | - | |
| -1 | -1 | 2.28 | 2.56 | 3.12 | 4.71 | - |
| 0 | -1 | 2.27 | 2.56 | 3.07 | 4.49 | - |
| 0 | -2 | 2.26 | 2.54 | 3.31 | 4.58 | - |
| 0 | -3 | 2.30 | 2.66 | 3.12 | > 3.33 | - |
| +1 | -1 | 2.28 | 2.56 | 3.10 | 4.60 | - |
| +2 | -1 | 2.27 | 2.56 | 3.12 | 4.71 | - |
| +2 | -2 | 2.27 | 2.55 | 3.04 | 4.73 | - |
| Avg ($v < 0$) | | 2.28 | 2.57 | 3.12 | 4.64 | |

Table III

$\frac{n^* - \mu}{v}$ as a function of m for $\alpha = +2.0$ ^{-5.0} and various v and μ .

| μ | $v \backslash m$ | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |
|-------|------------------|-------|-------|-------|-------|--------|--------|-------|-------|
| 0 | +1 | (3.5) | (2.5) | 1.90 | 1.54 | 1.24 | .97 | .76 | .55 |
| 0 | 2 | (3.3) | 2.45 | 1.96 | 1.60 | 1.32 | 1.06 | .83 | .61 |
| 0 | 3 | (3.3) | 2.66 | 2.25 | 1.65 | 1.36 | 1.13 | .91 | .67 |
| +1 | 1 | (3.3) | (2.4) | 1.87 | 1.48 | 1.18 | .92 | .69 | .47 |
| 1 | 2 | 3.15 | 2.57 | 1.91 | 1.59 | 1.25 | .99 | .76 | .54 |
| 2 | 1 | 3.06 | 2.35 | 1.84 | 1.44 | 1.12 | .85 | .61 | .38 |
| +3 | +3 | (3.5) | (2.5) | (2.0) | (1.6) | (1.29) | (1.03) | (.81) | (.70) |
| Avg | ($v > 0$) | (3.3) | 2.49 | 1.96 | 1.55 | 1.25 | .99 | .76 | .54 |
| -3 | -3 | (3.2) | (1.8) | (1.6) | (1.3) | (1.08) | (.83) | (.68) | - |
| -2 | -1 | 3.04 | 2.32 | 1.82 | 1.46 | 1.17 | .94 | .73 | .55 |
| -1 | -2 | 2.99 | 2.25 | 1.73 | 1.33 | 1.08 | .83 | .63 | .45 |
| -1 | -1 | 3.02 | 2.30 | 1.79 | 1.42 | 1.12 | .89 | .68 | .50 |
| 0 | -3 | 2.94 | 2.17 | 1.64 | 1.25 | .95 | .72 | .52 | .36 |
| 0 | -2 | 2.98 | 2.23 | 1.70 | 1.31 | 1.01 | .77 | .57 | .39 |
| 0 | -1 | 3.01 | 2.28 | 1.76 | 1.38 | 1.08 | .83 | .62 | .43 |
| +1 | -1 | 3.00 | 2.26 | 1.73 | 1.34 | 1.03 | .77 | .56 | .36 |
| +2 | -2 | 2.95 | 2.18 | 1.64 | 1.24 | .92 | .67 | .46 | .27 |
| +2 | -1 | 2.99 | 2.23 | 1.70 | 1.30 | .98 | .72 | .50 | .23 |
| Avg | ($v < 0$) | 2.99 | 2.25 | 1.72 | 1.34 | 1.04 | .79 | .59 | .39 |

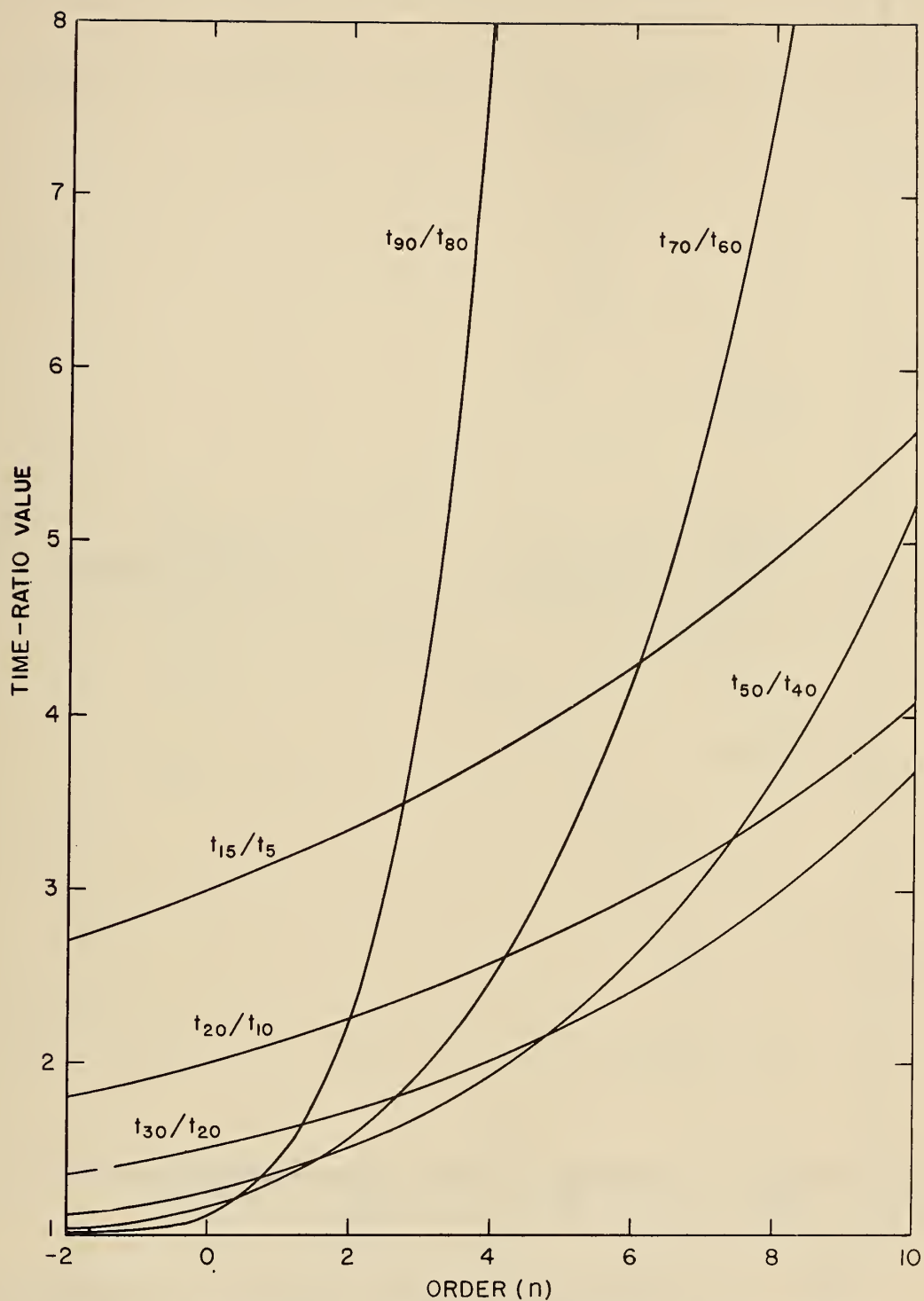


Fig. 1. A family of curves representing the dependence of time-ratios on the order and extent of reaction.

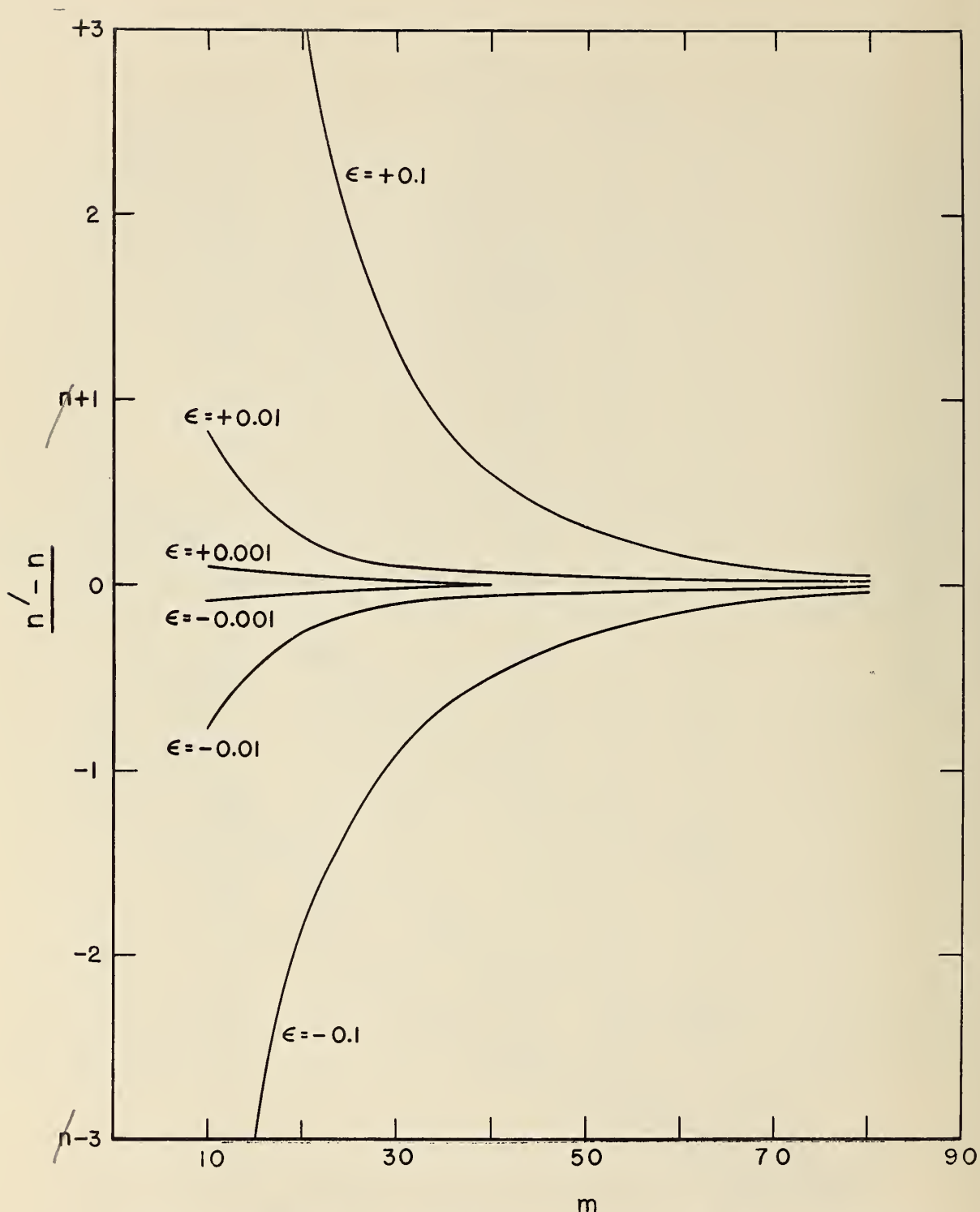


Fig. 2. Effects of errors in initial time or concentration on the apparent order of reaction. Deviations from true order, $n' - n$, are plotted as a function of time-ratio index, m . The error in reduced time

$$\text{or concentration is } \epsilon = k \epsilon_t = - \frac{\epsilon A}{A_0}.$$

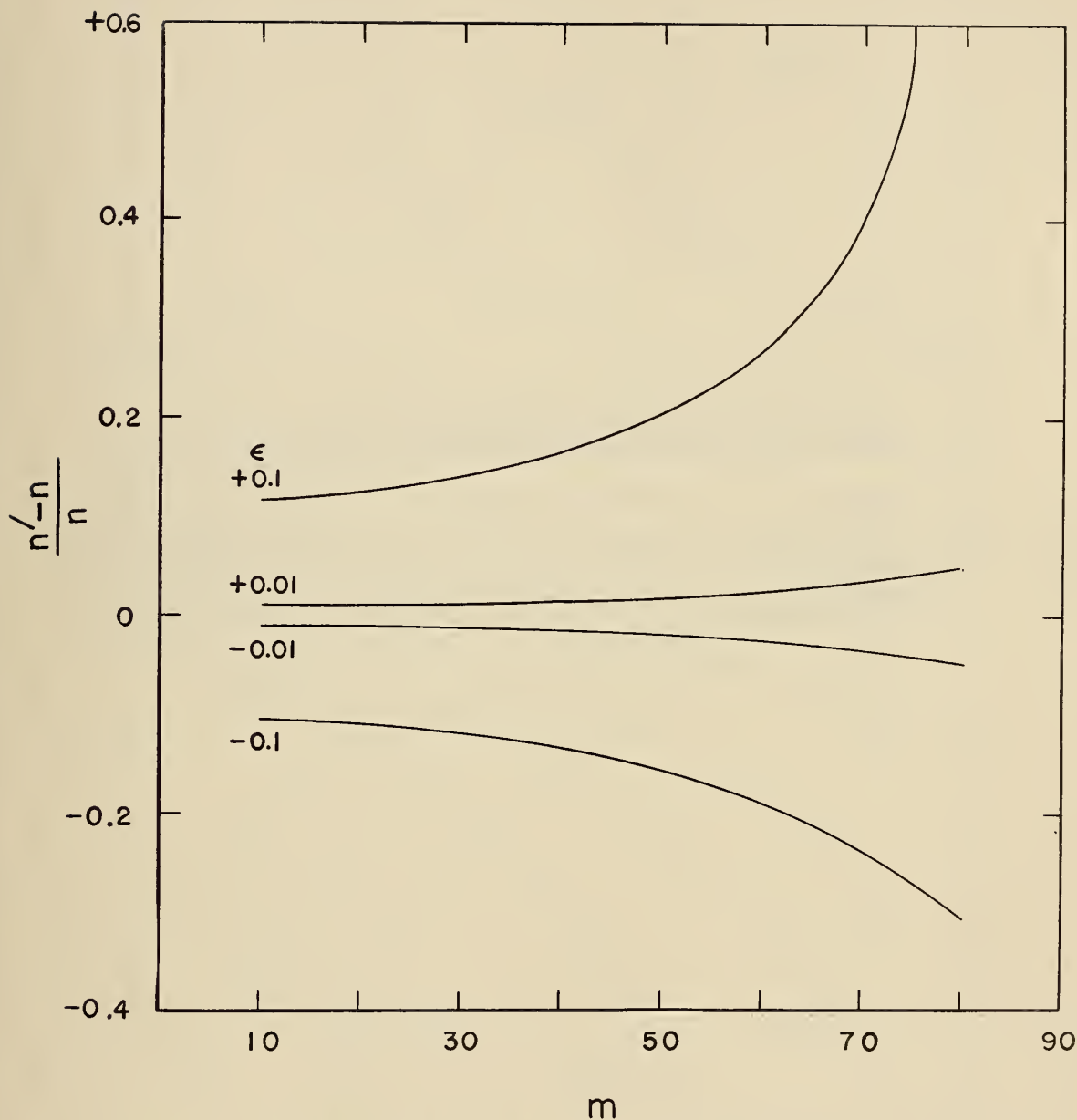


Fig. 3. Effects of constant stoichiometric errors (product measured) for an n th order reaction. The function $(n' - n)/n$ is plotted as a function of the time-ratio index, m . The error in the stoichiometric

coefficient, a , is $\epsilon = \frac{\epsilon a}{a}$.

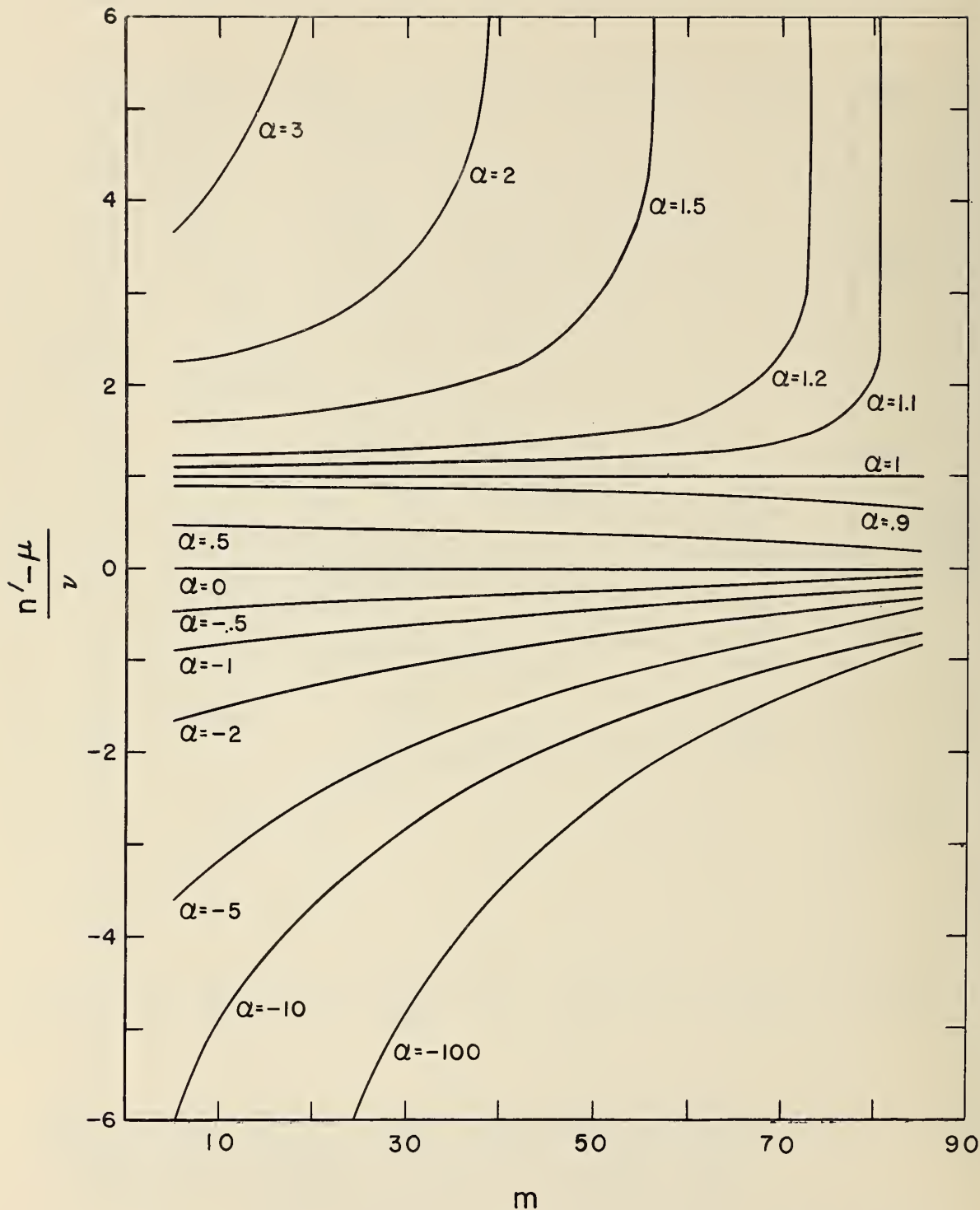


Fig. 4. A family of curves showing the dependence of the function $\frac{n' - \mu}{\nu}$ on the time-ratio index, m . Curves for $0 \leq \nu \leq 3$, $|\mu| \leq 3$ almost coincide.

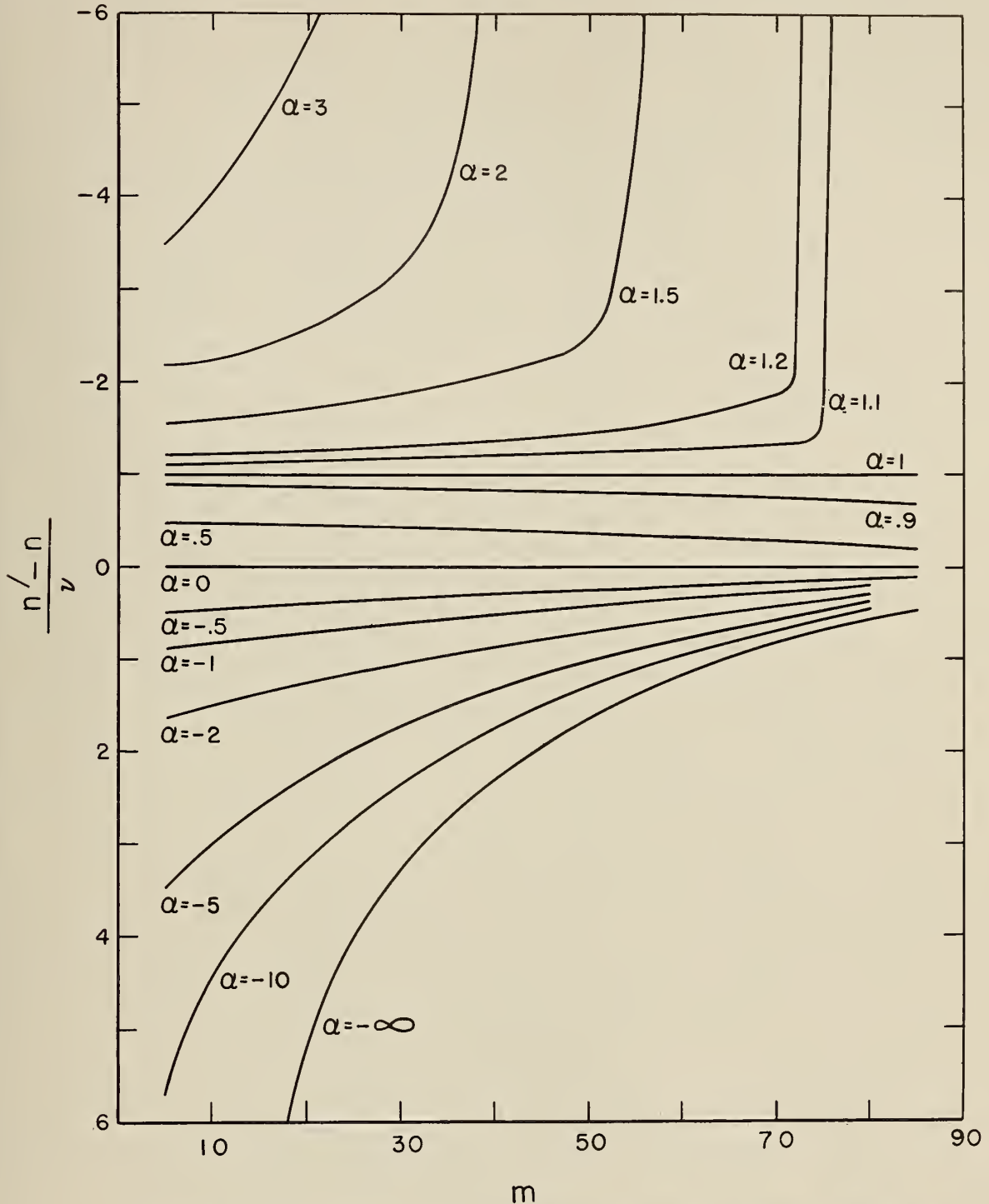


Fig. 5. A family of curves showing the dependence of the function $\frac{n' - \mu}{\nu}$ on the time-ratio index, m . Curves for $-3 \leq \nu \leq 0$, $|\mu| \leq 3$ almost coincide.

U.S. DEPARTMENT OF COMMERCE

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NATIONAL BUREAU OF STANDARDS

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