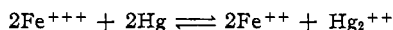


### Summary

1. The following reaction was studied chemically and found to be a truly and easily reversible reaction



2. The equilibrium constant of the reaction was calculated either from total concentration by suitable graphical and mathematical treatments or from ionic strength of dilute solutions, and was found to be  $0.0180 \pm 0.0005$ .

3. The principle of ionic strength may not be considered to hold even in solutions as low as 0.01 when there is too much acid present as compared with the other salts.

4. The oxidation-reduction potential of the ferric-ferrous electrode, calculated from the equation

$$E_{\text{Fe}} = E_{\text{Hg}} - \frac{0.05915}{2} \log K$$

was found to be  $-0.7473$  v. This value agrees very closely with  $-0.7477$  v. obtained from our former e. m. f. measurements.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## METHODS OF CALCULATING AND AVERAGING RATE CONSTANTS<sup>1</sup>

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### Introduction

In order to obtain a more probable value of the rate of a chemical reaction, for temperature coefficients, etc., it has been customary to take the simple arithmetical average of individual calculated values. Due to the nature of the rate function, such an arithmetical average may possibly be as far from the true value as that calculated from the two least accurate measurements. This applies only to the average of rate constants which are calculated from measurements made on a single sample of reacting material and not to the average of those found under identical conditions of time and concentration. Most rates of reaction have been calculated by the interval method or the method of integrating from the zero of time using the formulas:  $k = \frac{1}{t_n - t_{n-1}} \ln \left( \frac{a - x_{n-1}}{a - x_n} \right)$  and  $k = \frac{1}{t_n} \ln \frac{a}{a - x_n}$ . The arithmetical averages of the rates calculated by these methods give quite different results and both are incorrect.

<sup>1</sup> This paper was presented in preliminary form by the author before the Mid-west Regional meeting of the American Chemical Society, May 9, 1930.

### Present Incorrect Methods of Averaging

**Error of the Interval Method Average.**—It can be shown that the simple arithmetical average of the interval rate constants, when calculated for equal time intervals, is equal to the rate constant as calculated from the initial and final observed values of the concentration and is independent of all intermediate ones. If  $k_{0,1}, k_{1,2}, k_{2,3} \dots k_{n-1,n}$  are the interval rate constants for  $n$  intervals, then the arithmetical average will be:  $(1/n) (k_{0,1} + k_{2,3} + \dots k_{n-1,n})$ . For a unimolecular reaction  $k_{0,1} = (1/\Delta t) \ln (C_0/C_1)$ , where  $\Delta t$  is the time interval during which the concentration changes from  $C_0$  to  $C_1$ . If all the time intervals are the same and  $k_a$  is the arithmetical average, then

$$k_a = \frac{1}{n} \left[ \frac{1}{\Delta t} \ln \frac{C_0}{C_1} + \frac{1}{\Delta t} \ln \frac{C_1}{C_2} + \dots \frac{1}{\Delta t} \ln \frac{C_{n-1}}{C_n} \right]$$

or

$$k_a = \frac{1}{n \Delta t} \ln \left[ \frac{C_0 C_1 C_2 \dots C_{n-1}}{C_1 C_2 C_3 \dots C_n} \right]$$

All the values of  $C$  cancel out except the first and the last and since  $n \Delta t = t_n$ , then

$$k_a = \frac{1}{t_n} \ln \left( \frac{C_0}{C_n} \right)$$

$$k_a = k_{0,n}$$

Thus the arithmetical average is independent of all values except the first and last. This proof may be extended to a reaction of any order. It can be shown by very simple analytic geometry that, for points whose abscissas are equally spaced, the arithmetical average of the slopes of straight lines drawn through adjacent points is equal to the slope of the straight line drawn through the first and last points and is independent of the ordinates of the intermediate points. Wagner<sup>2</sup> showed this to be true in the case of a second order reaction.

**Error of the Second Method.**—When each value of  $k$  is calculated by integrating from the zero time, each value of  $a - x$  is combined with a single value of the initial concentration which may rest on a single measurement. Guggenheim<sup>3</sup> pointed out that this gave undue weight to the initial concentration. Even though the initial concentrations were known with absolute accuracy, this method gives too much weight to the points near the zero of time.

### Methods Applicable to Unimolecular Reactions

Rate measurements may be divided into two classes, depending on whether one analyzes for the concentration ( $a - x$ ) or the amount which has reacted,  $x$ .

**When  $x$  is Measured Directly.**—Guggenheim<sup>3</sup> developed a method

<sup>2</sup> C. Wagner, *Z. physik. Chem.*, 115, 132 (1925).

<sup>3</sup> E. A. Guggenheim, *Phil. Mag.*, [7] 2, 538 (1926).

which eliminates the use of the initial concentration. He plotted the common logarithm of the amounts reacting in a chosen interval of time against the time. The slope multiplied by 2.303 gave the rate constant.

The rate may also be determined analytically from three values of  $x$ , provided the time intervals between them are the same. If  $x_1$ ,  $x_2$  and  $x_3$  are the amounts which have reacted at times  $t_1$ ,  $t_2$  and  $t_3$ , then

$$k(t_2 - t_1) = \ln \frac{(a - x_1)}{(a - x_2)} \quad (1)$$

$$k(t_3 - t_2) = \ln \frac{(a - x_2)}{(a - x_3)} \quad (2)$$

If we impose the condition that  $(t_3 - t_2) = (t_2 - t_1)$ , *i. e.*, the time intervals are the same, then

$$\frac{a - x_1}{a - x_2} = \frac{a - x_2}{a - x_3}$$

and

$$a = \frac{x_1 x_3 - x_2^2}{x_1 - 2x_2 + x_3}$$

If  $t_1$  was taken as the zero of time, then this equation would reduce to that obtained by Smith<sup>4</sup> for the initial concentration in terms of the concentrations at two times, one twice the other. Substituting  $a$  from Equation 3 in either Equation 1 or 2 we obtain

$$k = \frac{1}{\tau} \ln \frac{(x_2 - x_1)}{(x_3 - x_2)} \quad (3)$$

where  $\tau$  is the time interval between the  $x_1$  and  $x_2$  as well as between the  $x_2$  and  $x_3$ . For a gaseous reaction followed by the change in volume at constant pressure or the pressure change at constant volume, the  $x$ 's may be replaced, respectively, by the volume or pressure. This method and Guggenheim's are alike in that the initial concentrations are eliminated. Even though one finds a perfectly straight line using the former method or a constant value of  $k$  using the second method, it does not follow that the reaction obeys the simple unimolecular law. A straight line and a constant value of  $k$  will be obtained when and only if the rate is given by the equation  $dx/dt = k(a - x) = k'(b - x)$ , where  $k'$  and  $b$  may or may not be zero. This expresses the rate for a reversible reaction, a side reaction, a subsequent reaction and a reaction where the product combines with the reactant making it relatively inert, as well as for a simple unimolecular reaction. The reversibility can be determined from free energies and the other exceptions by chemical analyses and by trying the effect of adding some of the product to the reacting mixture. Thus one can obtain strong but not absolute evidence of unimolecularity when the original concentration cannot be measured.

In order to best show up a trend, the time intervals should be short, but

<sup>4</sup> R. C. Smith, *Phil. Mag.*, [7] 1, 496 (1926).

to obtain the most probable value, the intervals should be longer. Since the value of  $x_3 - x_2$  can never be greater than  $x_2 - x_1$  and the probable error in  $x$  is a constant quantity independent of the time, the error in  $k$  will be due principally to the error in  $x_3 - x_2$ . Therefore, for the case when the error in determining the concentration has a greater effect on  $k$  than the error in measuring the time, the error may be considered as due to the error in  $x_3 - x_2$  alone. In this case the accuracy will be greatest when  $x_3 - x_2$  is greatest. If we let the concentration be  $a$  at  $t_1$ , then  $x_1$  will be zero and Equation 3 becomes

$$k\tau = \ln \frac{x_2}{(x_3 - x_2)} \text{ or } x_3 - x_2 = x_2 e^{-k\tau}$$

Setting the derivative with respect to  $\tau$  of  $x_3 - x_2$  equal to zero will make the latter a maximum and the error in  $k$  a minimum. Since  $e^{-k\tau}$  does not equal zero, this gives

$$kx_2 - dx_2/d\tau = 0 \quad (4)$$

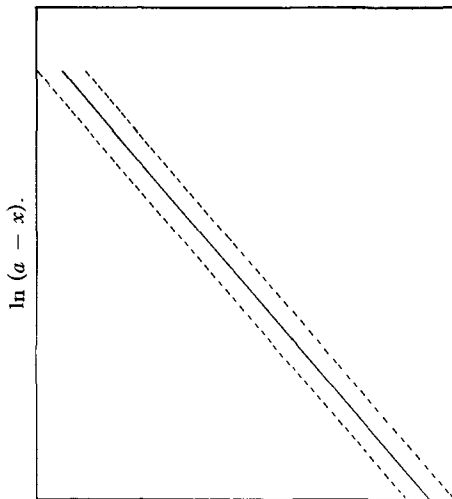
By differentiating Equation 1 with respect to  $\tau$  with  $x_1 = 0$ , one finds  $dx_2/d\tau = k(a - x_2)$ . Substituting this in Equation 4 gives  $x_2 = a/2$ , the condition for maximum accuracy in  $k$ . This means that if  $\ln(x_3 - x_2)$  is less accurately determined than  $\tau$ , then the greatest accuracy is obtained when the concentration decreases 50% during the first interval and one-half that much during the second interval.

In order to best utilize data, when the error in measurement of time is negligible and one wishes to use this method as evidence for unimolecularity, it is best to take six measurements at equal time intervals near the beginning, six with the same time intervals when about 50% has reacted, and six more when about 75% has reacted, such that the time interval between the first and seventh equals that between the seventh and thirteenth, etc. Then one can calculate a rate constant from the first three, another from the second three, etc., giving two constants for the beginning, two for the middle and two nearer the end. This will show if there is a trend not represented by  $dx/dt = k(a - x) = k'(b - x)$ . To obtain the most probable value of the rate constant one should calculate it from the first, seventh and thirteenth; the second, eighth and fourteenth, etc. These constants will all have practically the same weight and will be independent and therefore may be averaged arithmetically.

**When  $(a - x)$  Is Measured Directly.**—In this case one can calculate  $k$  from any two measurements of concentration and the time between them, but when there are more than two points, one is faced with the problem of deciding how to combine them. If the time is the least accurate measurement, then all points will have practically the same weight. On the other hand, if  $\ln(a - x)$  is least accurately determined, then each point will have a different weight since  $a - x$  and not  $\ln(a - x)$  is directly measured. The probable error in  $a - x$  in general is a constant quantity rather than a

constant percentage error. In Fig. 1a the dotted lines show the limits of error due to a constant error in time and Fig. 1b shows the limits of error for a possible error in  $(a - x)$  equal to one-tenth of the initial concentration.

The weight changes in the same way regardless of the size of the error, the very large error being used merely to facilitate graphing. If  $r_c$  is the probable error in the concentration, then by expanding  $\ln(C + r)$  in series and neglecting terms of second and higher powers, one has  $r_c/C$  as the probable error in  $\ln C$ . Letting  $r_t$  be the probable error in measurement of the time, one can see from Fig. 2 that  $r_t \tan \theta$  or  $kr_t$  is the probable error in  $\ln C$  which would produce the same probable error in  $k$  as does  $r_t$ . Therefore, one may consider the time as entirely correct and that there are



Time.

Fig. 1a.

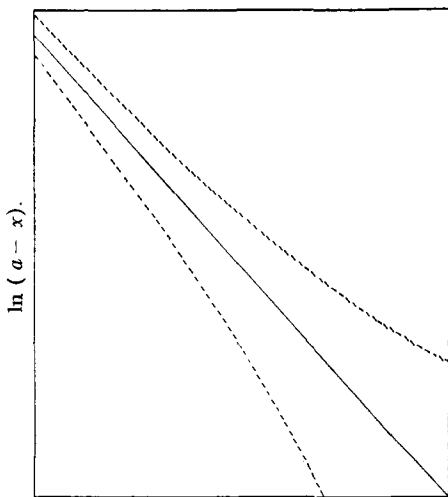
two probable errors in  $\ln C$ , one due to error in measurement of  $C$  and the other due to error in measurement of  $t$ . The effective probable error of a point in terms of  $\ln C$  will be

$\sqrt{(kr_t)^2 + (r_c/C)^2}$ . The weight  $p$  of any point will be inversely proportional to the square of its probable error, and therefore

$$p = \frac{1}{(kr_t)^2 + (r_c/C)^2} \quad (5)$$

Thus one can calculate the weight of any point. It will be seen from formula (5) that if the error was due only to the error in measuring time, all points would have the same weight. On the other hand, if the error was due only to the error in determining concentration, the weight of each point would be proportional to  $C^2$ . The weight is important in the latter case, since

if the weight at the start is taken as unity, the weight will be one-quarter when the reaction is 50% complete and one-hundredth when 90% complete.



Time.

Fig. 1b.

1. **Graphical Method.**—This method of plotting  $\ln(a - x)$  against the time and drawing the best straight line through the points is well known. It has the advantage of showing trends and at present is certainly the best method for such cases. However, it has the disadvantage in that large graphs cannot be published and some data are more accurate than can be represented graphically.

2. **Arithmetical Mean.**—Where the weights of all points are nearly the same, a very convenient mean is obtained by dividing the points into two equal parts and taking a time weighted average of the slopes of pairs of points.

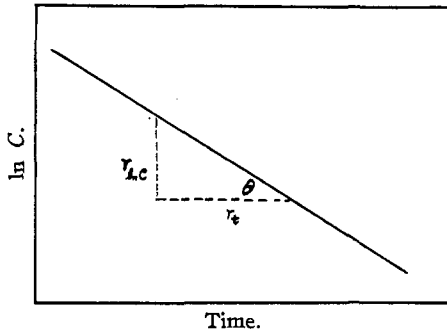


Fig. 2.

If there are six points on the plot of  $\ln C$  against  $t$ , one would take the slopes of the pairs of points 1-6, 2-5 and 3-4 and weight these according to the distance between the points. However, the distances between the points is very nearly proportional to their projection on either axis. Therefore, the weights may

be taken as the difference in  $t$  for each pair of points. The slope from points 1 and 6 is  $(\ln C_6 - \ln C_1)/(t_6 - t_1)$  and its weight will be  $(t_6 - t_1)$ . Then the weighted mean will be

$$k_m = \frac{\frac{\ln C_6 - \ln C_1}{t_6 - t_1} (t_6 - t_1) + \frac{\ln C_5 - \ln C_2}{t_5 - t_2} (t_5 - t_2) + \frac{\ln C_4 - \ln C_3}{t_4 - t_3} (t_4 - t_3)}{(t_6 - t_1) + (t_5 - t_2) + (t_4 - t_3)}$$

Since the time differences in the numerator cancel out

$$k_m = \frac{(\ln C_6 + \ln C_5 + \ln C_4) - (\ln C_3 + \ln C_2 + \ln C_1)}{(t_6 + t_5 + t_4) - (t_3 + t_2 + t_1)}$$

and in general

$$k_m = 2.303 \left[ \frac{\sum_{i=1/2n+1}^{i=n} \log C_i - \sum_{i=1}^{i=1/2n} \log C_i}{\sum_{i=1/2n+1}^{i=n} t_i - \sum_{i=1}^{i=1/2n} t_i} \right]$$

A given error in time or  $\log C$  produces the same magnitude of error in the above mean regardless of the time. Thus all points have equal weight. If there are an odd number of points, the middle one is not used, and therefore  $n$  is always even. This method should only be used for cases where the time is the least accurate measurement or for the rare case when the percentage error in analysis is a constant quantity.

**3. Method of Least Squares.**—This method of obtaining the slope of a straight line is well known, but it has rarely been used to calculate rate constants and when used has not been weighted. It has the disadvantage of requiring a great deal of arithmetical work, and weighting considerably increases the amount of work. The general formula for the slope of a straight line by the method of least squares is

$$s = \frac{\sum px \sum py - \sum p \sum pxy}{(\sum px)^2 - \sum p (\sum px^2)}$$

where  $p$  is the weight of a point whose coördinates are  $x$  and  $y$ . The rate constant of a unimolecular reaction will be

$$k = \frac{\sum pt \sum p \ln(a-x) - \sum p \sum pt \ln(a-x)}{(\sum pt)^2 - (\sum p)(\sum pt^2)}$$

The weight  $p$  of each point can be determined by the method previously given. This method has the advantage in that one can calculate the "probable error." The formula for calculating the probable error is given by Birge.<sup>5</sup> Professor Ingraham of the Mathematics Department of the University of Wisconsin pointed out to the author that the above method of least squares does not give the most probable value of the rate constant. Therefore the use of this method is questionable.

**Concentration Change for Maximum Accuracy.**—It is important to know how long to let a chemical reaction proceed in order to obtain the greatest probable accuracy in the rate constant, when the rate is calculated from the concentrations at two times. If  $r$  and  $r_0$  are the probable errors in the concentrations  $C$  and  $C_0$ , then  $r/C$  and  $r_0/C_0$  will be the corresponding errors in  $\ln C$  and  $\ln C_0$ , providing the error is small. If one assumes that the error in  $k$  is due only to the error in concentration, then the probable error in  $k$  will be

$$r_k = \frac{1}{t} \sqrt{\left(\frac{r_0}{C_0}\right)^2 + \left(\frac{r}{C}\right)^2} \quad (6)$$

If we let  $y = C/C_0$ , the fraction which has reacted at time  $t$ , then  $kt = -\ln y$ . Dividing Equation 6 by  $k$ , substituting  $C = yC_0$ , and  $kt = -\ln y$ , then the fractional error in  $k$  is

$$\frac{r_k}{k} = \frac{-1}{C_0 \ln y} \sqrt{(r_0)^2 + \left(\frac{r}{y}\right)^2} \quad (7)$$

Taking the derivative of  $r_k/k$  with respect to  $y$  and setting it equal to zero, we have

$$(r_0/r)^2 y^2 + 1 + \ln y = 0 \quad (8)$$

which is the condition that the percentage error in  $k$  shall be a minimum. Since the probable error in the concentration, instead of being a constant percentage error, is almost always a constant quantity independent of the concentration,  $r_0$  will be equal to  $r$ . Equation 8 then becomes:  $-\ln y = y^2 + 1$  or  $y = 0.33$ . Thus, for the case when the error in time is negligible,

<sup>5</sup> R. T. Birge, *Phys. Rev. Suppl.*, 1, 5 (1929).

the greatest probable accuracy in  $k$  is obtained by calculating it for the interval during which 67% of the material reacts.

In the case of fast reactions, the error in measuring the time may have a greater effect on the rate constant than the errors in measuring the concentration. One may calculate  $r'_0$ , the probable error in the initial concentration which would produce the same error in  $k$  as does the error in  $(t_n - t_0)$ . From Fig. 2 one can see that  $\tan \theta = k$  and therefore for small values of  $r_{t_0}$ ,  $r'_{\ln C_0} = kr_{t_0}$ .  $r'_{\ln C_0}$  is the probable error in  $\ln C_0$  which would produce the same probable departure from the line as does the actual probable error in  $t_0$ . The probable error  $r_t$  in reading the time is independent of time, and therefore the probable error in  $(t_n - t_0)$  will be  $\sqrt{2} r_t$ . One may consider that  $t_n$  is entirely accurate and that all the error is in  $t_0$  and equal to  $r_t \sqrt{2}$ . Since  $r'_{\ln C_0} = r'_0/C_0$ , and  $r_{t_0}$  is set equal to  $r_t \sqrt{2}$ , we have

$$r'_0 = kr_t C_0 \sqrt{2} \quad (9)$$

Therefore one may consider the time as always correct and that there is a probable error in the initial concentration  $r_0$  due to error in measurement of the concentration, and another probable error in the initial concentration  $r'_0$  or  $kr_t C_0 \sqrt{2}$  due to errors in measurement of the time. Since the probable error in concentration  $r$  is independent of time, then  $r_0$  may be replaced by  $r$  and the effective probable error expressed in terms of the initial concentration will be  $\sqrt{r^2 + (kr_t C_0 \sqrt{2})^2}$ . Substituting this for  $r_0$  in Equation 8, the general equation for optimum time will be

$$\left(\frac{kr_t C_0}{r}\right)^2 2y^2 + y^2 + 1 + \ln y = 0 \quad (10)$$

Table I gives for different ratios of  $(kr_t C_0)/r$ , the values of  $1 - y$ , the fraction which has reacted. Thus one can determine how far to let a

TABLE I

$y$	$1 - y$ (fraction changed)	Ratio ( $kr_t C_0$ )
0.33	0.67	0.0
.3	.70	0.8
.2	.8	2.7
.1	.9	8.0
.05	.95	20.0

unimolecular reaction proceed in order to obtain the greatest probable accuracy in the rate constant, regardless of the probable errors in time and concentration. The probable errors in time and concentration must be estimated by the experimenter. When applying this formula it is only necessary to know an approximate value of the rate constant  $k$ , but it must be in terms of natural logarithms and the unit of time in which  $r_t$  is expressed. It should be remembered that these probable errors are probable departures from the correct values and not percentage errors.



### Methods Applicable to Bimolecular Reactions

**When  $x$  Is Measured Directly.**—When the concentrations of the reacting substances are the same, one can calculate the rate constant from the amount reacting during two equal consecutive time intervals. For these intervals

$$k(t_2 - t_1) = \frac{1}{a - x_2} - \frac{1}{a - x_1} \quad (11)$$

$$k(t_3 - t_2) = \frac{1}{a - x_3} - \frac{1}{a - x_2} \quad (12)$$

If  $t_2 - t_1 = t_3 - t_2$  then

$$\frac{1}{a - x_2} - \frac{1}{a - x_1} = \frac{1}{a - x_3} - \frac{1}{a - x_2} \quad (13)$$

and

$$a = \frac{2x_1x_3 - x_1x_2 - x_2x_3}{x_1 - 2x_2 + x_3} \quad (14)$$

Substituting this value of  $a$  in either equation (11) or (12), one obtains

$$k = \frac{1}{2\tau} \frac{[(x_2 - x_1) - (x_3 - x_2)]^2}{(x_3 - x_1)(x_2 - x_1)(x_3 - x_2)} \quad (15)$$

where  $\tau$  is the time interval between  $x_1$  and  $x_2$  as well as between  $x_2$  and  $x_3$ . If  $\Delta C_1$  and  $\Delta C_2$  are the changes in concentration during two equal and consecutive time intervals, Equation 15 may be written

$$k = \frac{1(\Delta C_1 - \Delta C_2)^2}{2\tau(\Delta C_1 + \Delta C_2)\Delta C_1\Delta C_2} \quad (16)$$

Equation 15 may also be written

$$k = \frac{1}{2\tau(x_3 - x_1)} \left[ \frac{x_2 - x_1}{x_3 - x_2} - 1 \right] \left[ 1 - \frac{x_3 - x_2}{x_3 - x_1} \right] \quad (17)$$

Since  $(x_3 - x_2)$  is always smaller than  $(x_2 - x_1)$ , which is smaller than  $(x_3 - x_1)$ , one can see from equation (17) that when  $\tau$  is more accurately known than  $(x_3 - x_2)$ , the error in  $k$  will always be largely due to the error in  $(x_3 - x_2)$ . The probable accuracy in  $k$  will be very nearly a maximum when  $(x_3 - x_2)$  is a maximum. Letting  $t_1 = 0$ , then  $x_1 = 0$  and equation (13) becomes

$$\frac{2}{a - x_2} = \frac{1}{a} - \frac{1}{a - x_3} \quad (18)$$

or

$$(x_3 - x_2) = \frac{x_2(a - x_2)}{(a + x_2)} \quad (19)$$

In order that  $x_3 - x_2$  shall be a maximum, its derivative is set equal to zero.

$$\frac{d(x_3 - x_2)}{dx_2} = \frac{-x_2}{a + x_2} - \frac{x_2(a - x_2)}{(a + x_2)^2} + \frac{a - x_2}{a + x_2} = 0 \quad (20)$$

This reduces to  $x_2 = 0.414a$ . Thus, when the rate is calculated from Formula 15 and the time interval is more accurately known than  $x_3 - x_2$ , the probable error in  $k$  will be smallest when about 41% reacts during the first time interval.

When  $(a - x)$  is Measured Directly.—The integrated equation for a bimolecular reaction, when the concentrations of the reactants are the same, may be written

$$k = \frac{1}{t} \left[ \frac{1}{C} - \frac{1}{C_0} \right]$$

The probable error in concentration  $r$  is small compared to the concentration, and therefore one may use the series expansion  $1/(c - r) = 1/C - r/C^2 + r^2/C^3 - \dots$  and neglect all terms except the first two. The error in  $1/C$  will then be  $r/C^2$  and the probable error in  $k$  due to errors in concentration will be

$$r_k = \frac{1}{t} \sqrt{\left(\frac{r_0}{C_0^2}\right)^2 + \left(\frac{r}{C^2}\right)^2} \quad (21)$$

Letting  $y = C/C_0$ , dividing by  $k$  and letting  $kt = 1/C - 1/C_0$ , one obtains

$$\frac{r_k}{k} = \frac{\sqrt{r_0^2 + \frac{r^2}{y^4}}}{C_0(1/y - 1)} \quad (22)$$

The probable error will be a minimum when the derivative of  $r_k/k$  with respect to  $y$  is zero.

$$\frac{d(r_k/k)}{dy} = \frac{1}{C_0} \left[ \left(\frac{1}{y} - 1\right) \left(\frac{-2r^2}{y^5}\right) \left(r_0^2 + \frac{r^2}{y^4}\right)^{-1/2} + \frac{1}{y^2} \left(r_0^2 + \frac{r^2}{y^4}\right)^{1/2} \right] \left[\frac{1}{y} - 1\right]^{-2} \quad (23)$$

Setting this equal to zero, we have

$$\left(\frac{r_0}{r}\right)^2 y^4 + 2y = 1 \quad (24)$$

One may calculate the probable error in the initial concentration  $r'_0$  that would produce the same probable error in  $k$ , as does the actual probable error in time  $r_t$ . By the same procedure that was used for the unimolecular reaction, one obtains  $r'_0 = kr_t C_0^2 \sqrt{2}$ , the effective probable error in the initial concentration will be  $\sqrt{(kr_t C_0^2 \sqrt{2})^2 + r^2}$  and the general equation for optimum accuracy will be

$$\left(\frac{kr_t C_0^2}{r}\right)^2 2y^4 + y^4 + 2y = 1. \quad (25)$$

Table II gives the values of  $(1 - y)$  for different values of the ratio  $kr_t C_0^2/r$ . Thus for the case when the concentrations of the reactants are the same,

TABLE II  
OPTIMUM CONCENTRATION CHANGE FOR BIMOLECULAR REACTION

Fraction changed $(1 - y)$	0.53	0.6	0.7	0.8	0.9	0.95
Ratio $kr_t C_0^2/r$	0	1.8	5	14	63	268

one may determine how much should react in order to obtain the maximum accuracy in  $k$ . In order to do this, one needs to know an approximate value of  $k$  and one has to estimate the probable error in measuring the time and concentration.

### Summary and Conclusions

The rate constants of both unimolecular and bimolecular reactions can be calculated analytically when the initial concentration or time cannot be determined. This method, however, is not to be recommended when it is possible to determine the initial concentration accurately by direct means, since it has greater probable error.

The commonly used simple arithmetical average of rate constants is entirely incorrect and should never be used except for averaging rate constants calculated from entirely independent data, and then only when the probable errors are nearly alike. The method of least squares should be used with caution. The graphical method may be used in all cases where each point on the graph represents entirely independent data.

The author recommends that one should first determine whether the rate law holds within experimental error. Then, in case it does, one should take more data in such a manner that a number of values of  $k$  can be calculated from entirely independent data for approximately the optimum concentration change. These values of  $k$  may be averaged graphically or by taking the simple arithmetical average.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MANITOBA]

## THE PHYSICAL IDENTITY OF ENANTIOMERS. THE CAMPHORIC ACIDS

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In a recent paper<sup>1</sup> the author in collaboration with another was able to produce evidence that the *d*- and *l*-mandelic acids are not absolutely identical in their physical properties. Private criticism made at that time rested upon the contention that the *d*-form was not quite pure, despite the facts that the rotation of *d*-form was normal, and that the rotatory dispersions or rather differences in rotation for the two lines used, were the same, which would not be the case if one form were impure. Nevertheless, in view of this contention, it was thought advisable to prepare the next pair of enantiomers from independent optically active sources of opposite rotation. I am indebted to Dr. Kenyon for the suggestion that I should use the *d*- and *l*-camphors, or rather the camphoric acids obtainable from them. I have been exclusively occupied for the past fifteen months with this work, most of the time being spent on preparation and purification. As I surmise that criticism will, as usual, be directed rather to this question of purity than to ability to determine physical constants, I give a detailed statement of the methods of preparation and purification.

<sup>1</sup> Campbell and Garrow, *Trans. Faraday Soc.*, **26**, 560 (1930).