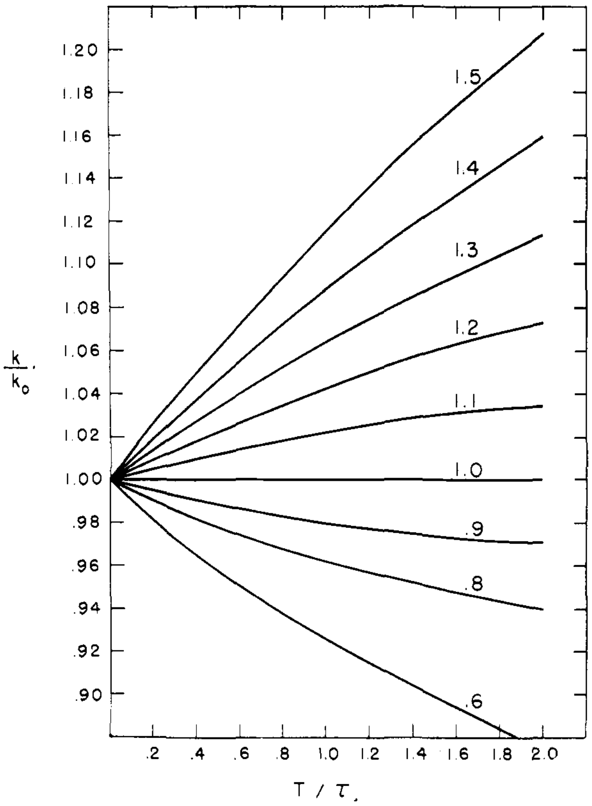

Fig. 1.—The first-order rate constant k observed by least-squares fit of the data observed from 0 to T divided by the zero time rate constant k_0 as a function of $\bar{R}$ from 0.6 to 1.5 and as a function of observation time T divided by mean life τ of the reaction.

ants and products. This error depends on three dimensionless parameters, $\bar{R}$, $[A_0]/[\mathbf{M}]$ and t/τ, where τ is the mean life of the reaction, that is, the time for $[A_0]/[A]$ to equal e. The effect of $\bar{R}$ and t/τ is presented in Fig. 1. The effect of $[A_0]/[\mathbf{M}]$ and t/τ for $\bar{R}$ = 1.41, the value found for nitryl chloride,[2] is presented in Fig. 2. For the series of studies made with nitryl chloride the observation time was the same for each foreign gas, and thus low values of $[A_0]/[\mathbf{M}]$ are coupled with high values of t/τ. Accordingly the error introduced by efficiency of products was a uniform 5%, or k/k_0 = 1.05, for all foreign gases studied. The detailed values of k/k_0 are listed in the preceding article.[2]

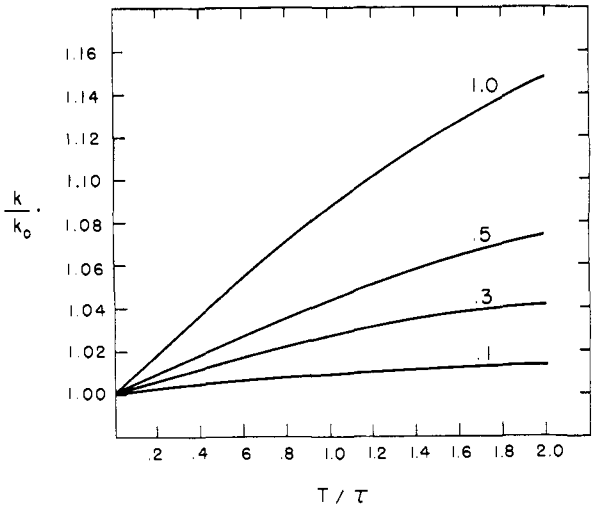

Fig. 2.—The ratio k/k_0 for various ratios of foreign gas pressure to reactant gas pressure, $[A_0]/[\mathbf{M}]$, and as a function of T/τ for $\bar{R}$ = 1.4, the value observed for nitryl chloride.

It should be emphasized that visual inspection of plots of log $[A_0]/[A]$ against t for curvature is a weak criterion for the effect of efficiency of products. For data with a slight amount of experimental error, such a plot will have a slope differing significantly from k_0 long before curvature is apparent.

Acknowledgment.—This work was supported by the Office of Naval Research, Contract N6 onr 25131, Project NR 051-246.

STANFORD, CAL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Precise Manometric Determination of Rate Data[1]

BY DELOS F. DETAR

RECEIVED JANUARY 26, 1956

Procedures are given for obtaining manometric rate data of high precision. By appropriate statistical treatment of these data it is possible to examine a reaction rigorously over its full course for compliance with a given rate expression.

Although manometric measurements have often been used for obtaining reaction rate data, most applications have been to reactions of assumed simple order. Either for want of precision of the data or more commonly for want of suitable techniques of interpretation the use of the manometric methods with complex reactions has been only moderately successful. In the course of a study of reactions of diazonium salts we have had occasion to reinvestigate methods of obtaining manometric data of high precision. In order fully to utilize this precision it has been necessary to apply statistical methods to the data. The use of such statistical methods should be helpful with rate data obtained by all techniques, for these methods make it possible to examine a reaction rigorously for compliance with a given rate expression.

---

(1) Supported in part by a grant from the National Science Foundation NSF G439 and in part by a grant from the Research Committee of the University of South Carolina.

The precision of the rate data obtained in this work may best be expressed in terms of the resolution of the manometer system. The manometers had a 500 mm. scale divided in millimeters, and readings were estimated to 0.1 mm. through a short focus telescope. Based on several hundred kinetic runs the standard deviation of a single reading of a manometer is 0.15 mm., an error estimate with over 500 D.F. In terms of rate constants this precision means potentially that one can obtain first-order rate constants with a standard deviation of 0.2%; this error estimate of the rate constant is based on the precision with which the first-order expression reproduces the pressure readings. A great many factors operate to increase the scatter of rate constants from one run to the next, and it is of course this latter estimate of rate constants that is meaningful. In the present series of papers the lowest standard deviation of rate constants based on replicate determinations and on the fit of the Arrhenius equation is about 0.5%. As work has continued various refinements in technique show promise of reducing this value. It is perhaps worth emphasizing that the error estimates given above are conservative ones computed by standard statistical techniques. Such estimates are somewhat larger than are often assigned to a given assembly of data by less impartial procedures.

In computing rate constants, the conventional methods of plotting functions of $(p_\infty - p)$ are not very satisfactory except for preliminary inspection. The observed value of p_∞ is certain to be one of the least accurate of all the values of p; in practice it has often been found to be in error by several mm. For a first-order reaction twelve half-lives are theoretically required before the p value is within one standard deviation of p_∞, but only five half-lives are needed to achieve 97% of reaction. Any sources of error that tend to affect p such as an almost insignificant leak, fluctuations of room temperature or of bath temperature which are not completely balanced out, any minor deviation of a reaction from a given order—all these will exert a disproportionate effect on the observed value of p_∞.

The useful Guggenheim[2] and Roseveare[3] procedures avoid the p_∞ error but have three disadvantages in critical work. (a) A single Roseveare value of k has a standard deviation of 0.6% with the above data (as compared with a potential 0.2%) and hence is only moderately accurate. (b) The methods can be applied only to segments of the reaction and are not very useful in determining how accurately a given reaction is following an expression of a given order. Moreover application of these methods to reactions whose order has not been independently verified can be most misleading. (c) Analogous methods cannot usually be worked out for complex reactions, and for such reactions some other procedure must be found.

Reed and Theriault[4] were the first to emphasize the value of correct statistical procedures in treating rate data. They developed procedures applicable to first-order reactions. Of more general applicability are the methods described by Deming.[5] Various examples of the application of these procedures are available.[6-8]

Experimental[9]

Apparatus.—The manometric apparatus for measuring the rate of gas evolution consisted of a reaction flask and a ballast flask attached to a differential manometer. This type of apparatus has been described previously.[10-12]

The key problems to be overcome with this type of equipment are (a) leakage, (b) adequate rate of gas-liquid equilibration, (c) erratic manometer behavior ("jumpiness"), and (d) sources of error inherent in the technique used and which must be treated properly in order to avoid biased results.

From the standpoint of eliminating leakage a completely sealed glass system would be desirable.[10] Such a system is inconvenient to load and seemed impractical for use with unstable diazonium salts. The compromise adopted was a reaction flask with a single 24/40 joint lubricated with Apiezon M grease and clamped with three springs. The ballast flask was sealed. Connections to the manometer system were made with $^{1}/_{8}''$ i.d. translucent Tygon[13] tubing with a minimum of two connections between each flask and manometer terminus, but often additional connections were convenient. By use of glass of appropriate diameter a clear seal was obtained over a 15–20 mm. length and such connections seem to be leak free. With these precautions only a very few of several hundred runs showed definite evidence of leakage, and these runs were discarded.

It is difficult to obtain evidence about leakage during the course of a reaction, for a minute constant leak or a minute continuously accelerating leak could result in a biased rate constant without causing detectable systematic variation in the p values. However, a series of observations on p_∞ after twelve half-lives or more showed that this reading remained constant (after applying the corrections described below), and that leakage was in fact absent. This test was applied to all but very slow reactions.

The problems of achieving an adequate rate of gas–liquid equilibration have been discussed by Pedersen.[14] Both shaking and magnetic stirring have been used with advantage in the present work. The shaking equipment was powered with a $^{1}/_{4}$ H.P. motor. The principal comment about the construction is that the eccentric must be rugged in order to withstand continuous operation for several days at a time. A half inch diameter rod operating in a ball bearing seems about the minimum for standing up to the thrust involved. The shaker had no convenient device for changing speed, but the available rate of 150 complete cycles per minute with a 3 cm. stroke proved adequate. The half time of carbon dioxide evolution at 25° was less than 30 sec. Several runs not in initial saturation equilibrium showed half-times for nitrogen evolution from methanol of 8–20 sec. The minimum reaction half-life used in the rate studies was 10 min.

Improvement in the equilibration rate would probably not serve any useful purpose, for nearly all runs showed up rather poorly over the first 3–5 min., there being systematic errors in p of up to 2 mm. The most probable cause has to

---

(2) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

(3) W. E. Roseveare, This Journal, **53**, 1651 (1931).

(4) L. J. Reed and E. J. Theriault, *J. Phys. Chem.*, **35**, 673, 950 (1931).

(5) W. E. Deming, "Statistical Adjustment of Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

(6) D. F. DeTar, This Journal, **77**, 2013 (1955).

(7) D. F. DeTar and D. I. Relyea, *ibid.*, **76**, 1680 (1954).

(8) See also the subsequent papers in this series.

(9) Most of the experimental work was carried out by Dr. M. N. Turetzky, by Dr. A. R. Ballentine and by Mr. B. D. Wyse; Dr. D. I. Relyea and Miss Sara Kwong also contributed. The lengthy routine calculations were performed by Mrs. M. Starr, Miss Sara Kwong and Mrs. Ellen Whiteley.

(10) J. N. Brönsted and H. C. B. Duus, *Z. physik. Chem.*, **117**, 299 (1925).

(11) E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940).

(12) M. Dixon, "Manometric Methods," 3rd ed., Cambridge University Press, New York, N. Y., 1951.

(13) Trade name for a plasticized vinyl chloride–vinyl acetate polymer.

(14) K. J. Pedersen, This Journal, **49**, 2681 (1927).

do with attainment of temperature equilibrium. With diazonium salts it is necessary to effect a compromise between achieving such equilibrium and allowing the salt to undergo premature decomposition. Even an hour in the bath with the shaker off did not seem to assure equilibration within the precision of the present work.

The magnetic stirring equipment is shown in Fig. 1. The motors were external to the oil-bath and were connected through a flexible cable. The positioning of the flasks was critical, and it was necessary to test out the operation of the stirrers before lowering the rack into the bath.

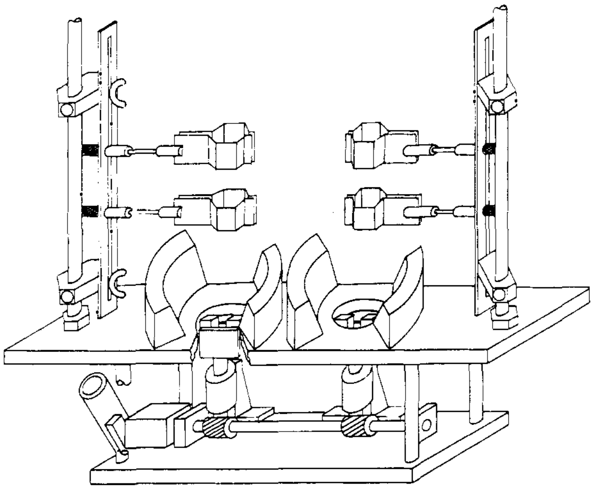

Fig. 1.—Magnetic stirring assembly.

Four styles of flask head were used in this work. Two of these are pictured in Fig. 2. The anti-splash device in the heads used on the shaker apparatus proved to be very valuable in reducing "jumpiness" in the pressure readings. The crystalline diazonium salt was placed in a small bucket which was suspended from the hook. When the shaker started, the bucket fell into the flask and the reaction started. In the initial work all-glass buckets were used. Since these caused relatively rapid grinding of the insides of the flasks, Teflon[15] or Kel-F[16] buckets with platinum bails were used in most of the later work. The excellent agreement between rate constants for the decomposition of the benzenediazonium ion obtained with this apparatus and the rates obtained by Moelwyn-Hughes and Johnson[11] show that none of the materials used had any detectable effect on the rate of the ionic reactions.

The head with the high-vacuum stopcock and the spherical joint was used in preparing oxygen-free reaction mixtures as described later. The head shown is a recent modification.

A flask with creases was used with the head shown on the right in Fig. 2 in connection with the magnetic stirrers (constant temperature oil-bath up to 80°). The design shown was the result of stepwise evolution from a simpler form. Various types of magnetic stirring bars were tried. Glass coatings were rapidly ground to a powder, if they happened not to be thrown through the side of the flask. A machined Kel-F[16] capsule worked moderately well. The best type of stirrer was one with a Teflon[15] exterior. A capsule was machined with a screw type plug. The magnet bar was placed in the capsule, this was filled with styrene monomer, and the plug screwed in place. The styrene was polymerized by heating the unit at 100° for several days. Even the waxy-feeling Teflon bars show signs of wear after twenty or thirty runs.

The creases in the flask were not conventional, but instead were slanted at an angle and directed toward a point on the axis above the neck of the flask. Conventional creases, which are parallel to the axis, interfere with the magnetic stirrers. Using speeds ranging from 500 to 600 r.p.m., the contents of the flask appeared to boil, and the rate of nitrogen evolution was satisfactory.

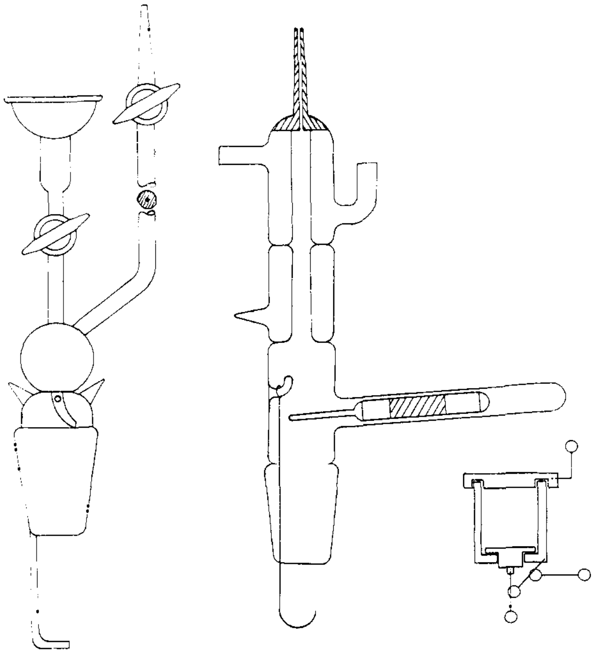

Fig. 2.—Examples of heads used on reaction flasks. On the left is the head used in loading the reaction flask on the vacuum train. On the right is the head used with the creased flasks and the magnetic stirring assembly of Fig. 1. Two other types of heads have been used: one is a simple head for use in the shaker equipment with hook and anti-splash device like the head on the left, but without side arm or stopcocks; the other is a similar head for use with a shaker at higher temperatures which includes a vacuum jacket and reflux jacket like the head on the right, but with a bucket hook in place of the plunger release shown. The bucket at the lower right was developed for use with the head on the right. The platinum wire loops on the bucket slide over the long platinum wire hook on the head, the object of which is to keep the bucket from falling to the bottom of the flask where it would interfere with the operation of the magnetic stirrer.

At reaction temperatures above about 50° moisture tends to condense in the capillary tubes, and this results in erratic pressure readings. The reflux condenser prevents such a difficulty, but due to the sensitivity of the apparatus, it was necessary to circulate constant temperature water through the jackets. The vacuum jacket provides a smooth transition between bath temperature and jacket temperature. The release device for the bucket is a conventional magnetically controlled rod. It was soon discovered that the bucket interfered with the operation of the magnetic stirrer, and it was necessary to provide a device to keep the bucket off the bottom of the flask; this is the purpose of the platinum wire hook. In preliminary runs there was a considerable amount of trouble concerning erratic pressure readings ("jumpiness"); adoption of the various measures mentioned above gradually brought this problem under control. Since the apparatus is very sensitive, temperature inequalities such as drafts or inadequate stirring must be avoided. A constant temperature room would have been most beneficial. One possibly unnecessary refinement was the construction of buckets with a drop-out bottom, since at one time it was suspected that some of the "jumpiness" was due to air trapped in the inverted bucket.

The manometer system consisted of a capillary arm joined to a large reservoir. The assembly was enclosed in a wooden box with a plate glass window. The diameter and uniformity of the 2 mm. capillary tube was determined by measuring a mercury slug. The scale was a 50 cm. Keuffel

---

[15] Polytetrafluoroethylene, Trade-mark of E. I. du Pont de Nemours and Co.

[16] Polychlorotrifluoroethylene, Trade-mark of M. J. Kellogg Co.

[17] D. F. DeTar and A. R. Ballentine, THIS JOURNAL, 78, 3916 (1956).

and Esser scale divided into mm. on one side and into half mm. on the other. The manometer fluid was *p*-xylene colored with azobenzene. The manometer was read through a simple telescope to eliminate parallax.

Procedure.—Before starting a run the reaction and ballast flasks were brought to near temperature equilibrium by shaking or by stirring for 30 minutes or more. The bucket containing the sample was then introduced, and the flasks allowed to stand for some time longer before dropping the bucket.

Readings were taken according to a systematic time sequence to permit Roseveare calculations. Furthermore readings were made at a series of equal time intervals, since various analyses of unknown rate functions are thereby simplified. It was convenient to obtain the time signal audibly from the Bureau of Standards Radio Station WWV, for it is difficult to try to observe a clock dial and a manometer simultaneously. Readings were estimated to the nearest 0.1 mm.

Computation.—A series of from four to six independent Roseveare computations was made to obtain an approximate value of the rate constant. Even with the precise data available in this work, these values showed considerable scatter and oftentimes seemed to depend on the extent of reaction concerned in the calculation. For a first-order reaction followed manometrically, the explicit function for the pressure is $p = a + be^{-kt}$ where k is the first-order rate constant, $a = p_\infty$, the final pressure reading, and $b = (p_0 - p_\infty)$ where p_0 is the initial pressure reading. Since p_0 and p_∞ are subject to much greater error than p values obtained during a run, it is best to treat a and b as disposable parameters. The best values of a, b and k are obtained by a statistical procedure which minimizes $\Sigma(p_{\text{obsd.}} - p_{\text{calcd.}})^2$ since the error in p is scalar.[4-6,8]

This statistical computation makes it possible to examine a reaction critically for deviations from a given rate law, for the whole reaction from 0 to 100% can be tested as continuously as the data are available.[18]

For some runs an abbreviated procedure was adopted. In the computation of the first-order rate constants the Roseveare method was used to obtain an initial estimate of k. This estimate was used to compute the values of e^{-kt} for the first-order rate expression $p = a + be^{-kt}$ for a series of ten to fifteen values of t. By using two selected points (or more commonly averages of two sets of several points) at about 10 and 90% of reaction, estimates of a and b were obtained on solving the simple linear equations. From these estimated values of a, b and $-k$ the value of the residuals $(p_{\text{obsd.}} - p_{\text{calcd.}}) = F_0$ was calculated for each value of t. If the best value of k were used, then the F_0 values would show only random fluctuations, but if the estimate of k were too small, then the F_0 values showed a trend: the values between the 10 and 90% selected points tended to be positive, those values outside the selected points tended to be negative. In the case of a trend, an empirical correction was made in k and the procedure was repeated.

The steps described for the abbreviated procedure are actually the same as those for the least squares adjustment up through the calculation of the F_0 values. In the least squares method it is necessary to calculate and solve the normal equations for corrections A, B and K for a, b and k. The complete least squares calculation requires about four hours with a modern desk calculator and an experienced operator; the computation of the F_0 values alone requires about three quarters of an hour.[18]

Appendix

Quantitative Characteristics of the Apparatus[12]

Definition of Terms.—Note that the subscript r refers to the reaction system and b to the ballast system; 1 refers to the liquid phase and g to the gas phase.

h' = manometer scale reading (in mm.)
h_0' = scale reading with equal pressures in reaction and ballast systems
h = $h' - h_0'$ = height of manometer fluid in capillary arm
h_0 = value of h at start of reaction (usually not quite equal to h_0')
d_r = diameter of the manometer reservoir arm (in mm.)
d_b = diameter of manometer capillary arm (in mm.)
V_r' = vol. of reaction flask (in cc.)
v_r = vol. of concentrating tubes including free space over manometric fluid
V_{1r} = vol. of liquid in reaction flask
V_r = $V_r' + v_r - V_{1r}$ = total free gas vol. of reaction system
V_{r0} = V_r when $h = h_0$
V_b', v_b, V_{1b}, V_b and V_{b0} are similar terms for the ballast system
T = temp. (°K.) of constant temp. bath in which the reaction and ballast flasks are immersed
D = density of manometric fluid
D_{Hg} = density of mercury at 0°
p_r = total pressure in reaction system (in mm. of mercury)
p_{r0} = total pressure in reaction system when $h = h_0$
p_b = total pressure in ballast system
p_{b0} = total pressure in ballast system when $h = h_0$
p_{1r} = vapor pressure of liquid present in reaction flask
p_{1b} = vapor pressure of liquid present in ballast flask
k_{1r} = Ostwald coefficient of solubility for reaction system gas in reaction liquid at temp. T
k_{1b} = Ostwald coefficient of solubility for ballast system gas in ballast liquid at temp. T

The number of moles of gas present in the reaction system at the start of the reaction, n_{r0}, is given by eq. 1. This use of the simple form of the gas

$$n_{r0} = (p_{r0} - p_{1r})(V_{r0} + k_{1r}V_{1r})/RT \qquad (1)$$

law is justified by the fact that for the evolution of 1 mmole of nitrogen the van der Waals correction amounts to only about 0.05% and for carbon dioxide to about 0.15% in the apparatus used. The use of the Ostwald solubility coefficient for the solubility of a gas in a liquid in effect replaces a given volume of liquid by its equivalent in terms of additional gas volume. The number of moles of gas present in the reaction system at any time t is given by eq. 2. The number of moles of gas evolved is given by eq. 3, in which $\Delta V = V_r - V_{r0}$

$$n_r = (p_r - p_{1r})(V_r + k_{1r}V_{1r})/RT \qquad (2)$$

$$\Delta n_r = n_r - n_{10} = (p_{r0} - p_{1r})\Delta V/RT + (V_{r0} + k_{1r}V_{1r} + \Delta V)\Delta p_r/RT \qquad (3)$$

is the volume increase due to movement of the manometric fluid and $\Delta p_r = p_r - p_{r0}$ is the pressure increase. This pressure increase is given by eq. 4; it is equal to the pressure difference between

$$\Delta p_r = \Delta p_h + \Delta p_b \qquad (4)$$

reaction and ballast systems as given by the manometer (Δp_h) plus the pressure increase in the ballast system due to compression resulting from movement of the manometric fluid. The value of the term Δp_b is obtained from eq. 5; this equation is analogous to eq. 3, but $\Delta n_b = 0_0$ since no gas is

$$\Delta n_b = 0 = -(p_{b0} - p_{1b})\Delta V/RT + (V_{b0} + k_{1b}V_{1b} - \Delta V)\,\Delta p_b/RT \qquad (5)$$

evolved and the ΔV term has a negative sign since $\Delta V_r = -\Delta V_b$.

Substituting the values Δp_b from eq. 5 into eq. 4 and then into eq. 3 gives eq. 6, in which Δn_r is expressed as a function of reaction and ballast system parameters and of ΔV and Δp_h, which are directly determined by the manometer reading h.

---

(18) Examples of the statistical computations of rate parameters for reactions of first-order, half-order, or mixed first plus half order have been deposited as Document number 4818 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm by check or money order payable to Chief, Photoduplication Service, Library of Congress.

$$\begin{aligned}\Delta n_{\mathrm{r}} = {} & \underbrace{(V_{\mathrm{r0}} + k_{1\mathrm{r}}V_{1\mathrm{r}})\Delta p_{\mathrm{h}}/RT}_{\text{I}} + \underbrace{(p_{\mathrm{r0}} - p_{1\mathrm{r}})\Delta V/RT}_{\text{II}} \qquad (6)\\ & + \underbrace{(p_{\mathrm{b0}} - p_{1\mathrm{b}})(V_{\mathrm{r0}} + k_{1\mathrm{r}}V_{1\mathrm{r}})\Delta V/(V_{\mathrm{b0}} + k_{1\mathrm{b}}V_{1\mathrm{b}} - \Delta V)RT}_{\text{III}}\\ & + \underbrace{\Delta V\Delta p_{\mathrm{h}}/RT}_{\text{IV}} + \underbrace{(p_{\mathrm{b0}} - p_{1\mathrm{b}})(\Delta V)^2/(V_{\mathrm{b0}} + k_{1\mathrm{b}}V_{1\mathrm{b}} - \Delta V)RT}_{\text{V}}\end{aligned}$$

Term I would express the quantity of gas evolved if the system were truly a constant volume one; term II gives the correction for the increase in volume of the reaction system due to movement of the manometric fluid while term III gives the correction due to the pressure increment caused by this movement. Terms IV and V are higher order correction terms. Equation 7 gives ΔV in cc. with h and d_{b} given in mm. Equation 8 gives Δp_{h}

$$\Delta V = h\pi d_{\mathrm{b}}^2/4000 \qquad (7)$$

$$\Delta p_{\mathrm{h}} = h(1 + d_{\mathrm{b}}^2/d_{\mathrm{r}}^2)D/D_{\mathrm{Hg}} \qquad (8)$$

in terms of mm. of mercury at 0°; the ratio of the squares of the manometer arm diameters comes from the fact that the reservoir level goes down slightly as the manometric fluid rises in the capillary.

The substitution of eq. 7 and 8 into eq. 6 is routine except for the fact that terms III and V contain ΔV in the denominator. It is to be noted that eq. 6 is exact (within the assumption of the perfect gas law); although ΔV represents only a small correction term in the denominator, it is undesirable that it should be simply neglected. It is possible to carry out a series expansion of these terms according to the relationship given in eq. 9. This leads to eq. 10; the terms are numbered as in eq. 6, and IIIa and IIIb represent the first two terms of the series expansion of III.

$$1/(a + b) = 1/a - b/a^2 + b^2/a^3 \ldots \qquad (9)$$

$$\begin{aligned}\Delta n_{\mathrm{r}} = {} & \{\underbrace{(V_{\mathrm{r0}} + k_{1\mathrm{r}}V_{1\mathrm{r}})(1 + d_{\mathrm{b}}^2/d_{\mathrm{r}}^2)D/D_{\mathrm{Hg}}}_{\text{I}} + [\underbrace{(p_{\mathrm{r0}} - p_{1\mathrm{r}})}_{\text{II}} +\\ & \underbrace{(p_{\mathrm{b0}} - p_{1\mathrm{b}})(V_{\mathrm{r0}} + k_{1\mathrm{r}}V_{1\mathrm{r}})/(V_{\mathrm{b0}} + k_{1\mathrm{b}}V_{1\mathrm{b}})}_{\text{IIIa}}]\pi d_{\mathrm{b}}^2/4000\} \times \qquad (10)\\ & h/RT + \{\underbrace{(1 + d_{\mathrm{r}}^2/d_{\mathrm{b}}^2)\pi d_{\mathrm{r}}^2 D/4000D_{\mathrm{Hg}}}_{\text{IV}} + \underbrace{(p_{\mathrm{b0}} - p_{1\mathrm{b}}) \times \pi^2 d_{\mathrm{r}}^4/16 \times 10^6(V_{\mathrm{b0}} + k_{1\mathrm{b}}V_{1\mathrm{b}})}_{\text{Va}} +\\ & \underbrace{(V_{\mathrm{r0}} + k_{1\mathrm{r}}V_{1\mathrm{r}})(p_{\mathrm{b0}} - p_{1\mathrm{b}}) \times \pi^2 d_{\mathrm{r}}^4/16 \times 10^6(V_{\mathrm{b0}} + k_{1\mathrm{b}}V_{1\mathrm{b}})^2}_{\text{IIIb}}\}\ h^2/RT +\end{aligned}$$

terms in higher powers of h.

The relative importance of the terms for the apparatus used in the present work can be estimated with the following values of the parameters and constants

$V_{\mathrm{r0}} = V_{\mathrm{b0}} = 400$ cc., $V_{1\mathrm{r}} = V_{1\mathrm{b}} = 100$ cc., $k_{1\mathrm{r}} = k_{1\mathrm{b}} = 0.15$, $d_{\mathrm{b}} = 2$ mm., $d_{\mathrm{r}} = 20$ mm., $D = 0.8$, $(p_{\mathrm{b0}} - p_{1\mathrm{b}}) = (p_{\mathrm{r0}} - p_{1\mathrm{r}}) = 700$ mm., $h = 500$ mm.

$$\begin{aligned}n_{\mathrm{r}} = {} & (\underbrace{24.6}_{\text{I}} + \underbrace{2.2}_{\text{II}} + \underbrace{2.2}_{\text{IIIa}})h/RT +\\ & (\underbrace{0.093}_{\text{IV}} + \underbrace{0.0086}_{\text{Va}} + \underbrace{0.0086}_{\text{IIIb}})h/RT \qquad (11)\end{aligned}$$

The calculation is presented in eq. 11 from which it can be seem that the term in h^2 represents only about 0.4% of the term in h even at the maximum value of h. The term in h^3 is of the order of $10^{-4}h/RT$ and is thus entirely negligible.

The absolute accuracy of nitrogen yields calculated from eq. 10 is only moderate, the standard deviation being 0.7–1.5% relative with the apparatus used. The largest sources of uncertainty are h, V_{r0}, and for non-aqueous solutions $k_{1\mathrm{r}}$. The uncertainty in h (about 0.5%) stems from the fact that it is not possible to achieve complete saturation equilibrium before starting the reaction with the equipment used, for shaking the flask either caused liquid to splash into the diazonium sample bucket or else caused the bucket to fall off prematurely; that in V_{r0} from difficulty of accurate estimation of the volumes of connecting tubes and manometer free space, and in V_1 in runs made up on the vacuum train; the uncertainty in $k_{1\mathrm{r}}$ is due to lack of data on the methanolic solutions used.

On the other hand the relative precision of a series of h values from a kinetic run is exceptionally good. The standard deviation of a series of values is about 0.15 mm., *i.e.*, within the limit of reading of h. With regard to precision the following factors were given careful consideration:

a. **Taper in capillary**: gives linear result if taper is linear. The error caused by an irregular capillary is largely due to variation in the capillary rise from place to place. The 2 mm. diameter was chosen as a compromise between minimizing volume change (the smaller, the better) and minimizing surface tension effects (the larger, the better). The Tru–Bore capillaries were tested for uniformity using mercury slugs.

b. **Taper in reservoir**: no problem if linear. The fluid level was kept well below the curved shoulder.

c. **Manometer temperature**: since the coefficient of expansion of *p*-xylene is 0.08% per degree, manometer temperature corrections of 0.5–2.0 mm. can arise from this source. In addition if the void space above the reaction flask side of the manometer is larger than that above the ballast flask side. there is a correction for gas expansion. The expression for the manometer temperature correction Δh is

$$\Delta h = \alpha h\Delta T + \beta\Delta T$$

in which $\alpha = 0.0008$ (the coefficient of expansion of *p*-xylene), ΔT is the difference between the manometer temperature for a given reading and the manometer temperature, T_{M}, chosen as a standard and .

$$\beta = T(p_{\mathrm{r}}v_{\mathrm{r}}/V_{\mathrm{r}} - p_{\mathrm{b}}v_{\mathrm{b}}/V_{\mathrm{b}})D_{\mathrm{Hg}}/DT_{\mathrm{M}}^2$$

d. **Connecting tube temperature**: for a connecting tube volume of 1.5 cc. (1/8″ i.d. tubing) a difference of 1° in the temperature of the two tubes will lead to a difference of about 0.2 mm. in the manometer reading for the typical conditions given above.

e. **Non-linear relation between the manometer height and the number of millimoles of nitrogen evolved**: the maximum correction was under 0.5% (2.5 mm.) for the flasks used. Failure to apply the correction will cause a slight bias in rate constants calculated for runs which use the full manometer range. The correction may be expressed as

$$h_{\mathrm{cor}} = h_{\mathrm{obsd}}(1 + \alpha' h_{\mathrm{obsd}})$$

$$\alpha' = \pi d_{\mathrm{b}}^2/4000(V_{\mathrm{r0}} + k_{\mathrm{s}}V_{\mathrm{sr}})$$

Examples of calculations are given elsewhere.[18]

COLUMBIA, S. C.