[CONTRIBUTION FROM THE PHOENIX PHYSICAL LABORATORIES, COLUMBIA UNIVERSITY.]

A CALORIMETRIC PROCEDURE FOR DETERMINING THE HEATS OF SLOW REACTIONS.

I. THE ANALYSIS OF PARTIALLY CONCURRENT HEAT EFFECTS.

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The reaction heats of slow chemical changes have not as yet been measured with dependable exactness. The closest approach so far made toward the satisfactory calorimetry of such processes is, without doubt, the very careful work of Brown and Pickering on the heats of mutarotation of glucose and fructose,[1] and on the heats of hydrolysis of starch and sucrose by enzymes.[2] In these investigations Brown and Pickering did not attempt the calorimetry of the whole process; but only that of a part of it, determined in each instance by the change in optical rotation which simultaneously occurred. They thus offered a method of attack which was neither completely general nor wholly calorimetric; and since, when their measurements were made, calorimetric procedure had not yet been developed beyond the stage to which Berthelot had carried it,

[1] Brown and Pickering, *J. Chem. Soc.*, **71**, 756 (1897).

[2] Brown and Pickering, *ibid.*, **71**, 783 (1897). For Berthelot's earlier but unsuccessful attempt to measure the heats of mutarotation, see *Compt. rend.*, **120**, 1019 (1895); see also Brown and Pickering's remarks upon this work (*loc. cit.*, [1] pp. 757–759); and Nelson and Beegle's criticism (THIS JOURNAL, **41**, 571 (1919)).

their work, though admirable for its ingenuity, precision and caution, must have been affected by very considerable error.[1] Their method, none the less, is clearly applicable to many, if not all, of those slow changes which do not involve an appreciable heat of mixture,[2] and their calorimetric errors could now be materially reduced. It is regrettable that their work has not been followed up. As a consequence of this and similar neglect, we still lack dependable knowledge concerning the internal energy relations of all those reactions, the speeds of which are measureable.[3] The obvious effect of such ignorance in limiting the scope and coördination of physicochemical and of physiological research points clearly to the high desirability of developing general and easily adaptable procedures adequate for the precise calorimetry of slow processes.

It was the primary purpose of this investigation to develop such a procedure, more general than that of Brown and Pickering, which should permit the calorimetric examination of complete reactions of various thermochemical character in liquid systems, whether or not these were accompanied by a heat of mixture; and which should be sufficiently exact in principle to make its gradual improvement to the limit of calorimetric precision, defined by minimal thermometric error, not impossible. In order that these conditions should be met, there was chosen for examination and experimental test a reaction of considerable complexity; that, namely, of the complete inversion of sucrose by hydrochloric acid. This reaction possessed many advantages for the purposes in view. Like the greater number of those changes which occur in liquid systems, it is always accompanied by a heat of mixture, that of dry sucrose in acid, or that of acid in sucrose solution, neither one of which can be separately determined; the heat of inversion itself requires, under safe and convenient conditions of temperature and concentration, more than 5 hours for its complete development; and the process as a whole, involves both endothermal and exothermal changes. To measure the heat of this reaction, therefore, it was necessary at the outset to devise means for overcoming the three greatest difficulties likely to be encountered in the calorimetry of

[1] For example, Brown and Pickering remark (*loc. cit.*, [2] p. 787) that in the determination of the heat of hydrolysis of starch by amylase, the most protracted measurement of which occupied 30 minutes, the correction for thermal leakage was "generally much larger than the actual rise of temperature to be measured."

[2] Brown and Pickering, in their measurements on mutarotation made correction for its progress during dissolution; but their procedure, which is not described in detail, was empirical and probably (in relation to present calorimetric precision) approximate (*loc. cit.*, [1] p. 759).

[3] The current practice of calculating these heats of reaction from heats of combustion, or otherwise by inference from thermodynamical generalizations characteristically inexact, is confessedly a makeshift procedure which yields uncertain, or at best roughly approximate results. See, for instance, the remarks of Brown and Pickering on this point (*loc. cit.*, [2] pp. 783, 784).

protracted processes, which are: the simultaneous determination of two partially concurrent heat effects; the exact maintenance of a negligible or precisely measurable thermal interchange between calorimeter and environment during a long period of time; and the facile adjustment of such control continuously for rising and falling temperatures.

Anticipating the results of work yet to be described, these difficulties, it is believed, have been satisfactorily met, within a margin of error largely determined by the uncertainties of mercury thermometry. The present paper describes a method devised for the analysis of the concurrent heat effects of the sucrose inversion. A second communication will describe the calorimetry of this reaction, and the application of the formulations here developed to the results of actual measurement.

The following analysis will be found applicable to many concurrent effects other than that with reference to which it is developed. The discussion must, therefore, be interpreted as illustrated by, rather than as restricted to, the phenomena of sucrose inversion.

Thermal Effects in the Inversion of Sucrose by Acid Catalysis.

For the determination of any heat of reaction which is accompanied by heat of mixture, two alternative procedures will in general be possible, since the mixture may be accomplished in two ways. For reasons that will soon be apparent,[1] it was decided in actual measurement to initiate the reaction by dissolving dry sucrose in acid, rather than to mix acid with sucrose solution.

The dissolving of sucrose in dilute acid is an endothermal process; the reaction of inversion is exothermal. When, therefore, dry sucrose is mixed with acid there is at first a considerable fall in temperature, which is succeeded almost immediately by a slow rise, the rate of which gradually diminishes as time goes on. If the temperature change in this process be plotted in rectangular coördinates against the time, we have a curve typical of this sort of reaction. Such a curve, drawn from the results of measurement, and divided for convenience into segments marked by the time intervals I, II and III, is shown in Fig. 1. During Period I the dominant effect is the negative heat of solution; in Period II, the positive
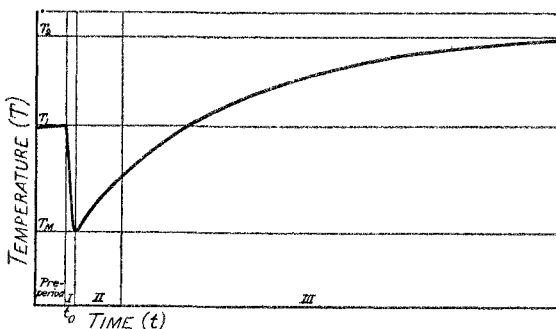
REACTION CURVE FROM DETERMINATION Nº 3

Fig. 1.

[1] See page 1302.

inversion heat at first nullifies and then overcomes the effect of solution; in Period III, solution is complete, distribution is uniform, and the heat effect is that of inversion alone. In order to determine the heat of inversion itself from a curve of this character, it is obviously necessary to extrapolate the curve of actual inversion across the entire interval, I + II. This is not altogether a simple matter. Generally speaking such a result may be accomplished by determining from the reaction curve in Period III an empirical formulation, extrapolating by this means, and modifying subsequently the extrapolated segment in accordance with the fact that during the period of concurrent effect spanned by this segment, one reacting substance is present in changing concentration. Disregarding for the present this final complication, it is clear that the first simple extrapolation itself is likely to be somewhat inexact, since it reproduces a segment of greater slope than that from which its formula was derived. The first essential precaution to be taken with respect to this procedure, therefore, would be to make the interval of concurrent effect as short as possible. In practice this would mean to effect solution as quickly as possible. One experimental necessity is thus at the outset clearly indicated. Assuming the task to have been adequately performed. there still remains the desirability of establishing a criterion of normal behavior by means of which the complete theory of extrapolation may be simply developed, and the empirical curve, insofar as it departs from the behavior thus indicated, interpreted and, if necessary, corrected. Such a criterion, in this as in other cases, will be provided by the isothermal equation of reaction speed. In the case of the inversion of sucrose this equation is well established; and for any given conditions of temperature and concentration, its constants, which are not quite invariable, may be determined with high precision by polarimetric measurement, If now, the assumptions be made: first, that in this reaction the energy release is proportional to quantity of sucrose transformed, second, that negligible external work is performed; and third, that during the change the total heat capacity remains constant within measurement error, the temperature-time curve for the isothermal condition will be sensibly of the same form as that of speed. The first of these assumptions is justifiable only if the reaction heat is that of inversion alone; since the measurements which determine the speed equation are made with reference solely to the passage of the reacting system from sucrose and water to the equilibrium mixture of hexoses. It must, however, be tentatively made; and may be so made without much danger of subsequent embarrassment, inasmuch as any superimposed effects to be anticipated are likely to be too small to affect the theory of extrapolation beyond the limit of effective correction. The assumption itself, moreover, offers a possible opportunity for the detection of superimposed heats of consecu-

tive or side reactions if these be measurable. As to the other assumptions made, the second may be granted at once; and the third also, when the heat capacities of factors and products, small in comparison with that of the whole system, are considered.[1]

On the basis of these assumptions, then, the simple theory of extrapolation may be safely developed.

The inversion of sucrose proceeds with negligible variation[2] after the manner of a monomolecular reaction. The familiar speed equation for this type of change,

$$\frac{dx}{dt} = k\,(a - x)$$

and its integrals

$$kt = \log \frac{a}{a - x}, \text{ and } k(t_2 - t_1) = \log \frac{a - x_1}{a - x_2} \tag{1}$$

(in which for a given weight of solvent, a is the initial weight in gram moles; x, x_1, x_2 the amounts transformed in gram moles, at the times t, t_1, t_2; and k the initial rate of transformation for unit mass) yields, on the basis of the assumption first made: namely, that temperature change under the conditions of experimentation will be proportional to quantity transformed,

$$\frac{dT}{dt} = k[(T_f - T_i) - (T - T_i)] = k(T_f - T)$$

and its integrals,

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[1] In actual determination, during the period of inversion (to which alone this analysis applies), the reacting system passed from sucrose in solution and water, to invert sugar in solution. The molecular heat of dissolved sucrose ($14°$ to $26°$) is 152.8 (Magie, *Phys. Rev.*, **16**, 381; and **17**, 105 (1903)); that of water is 18.0, and that of dissolved invert sugar is $(89.6 + 78.8) \div 2 = 84.2$ (Magie, *loc. cit.*), in gram calorie units. The change in heat capacity per mole in this reaction, is therefore, $(152.8 + 18) - 2\,(84.2) = 2.4$, and for 50 g. of sucrose, a maximal quantity in measurement, 0.35 gram caloric units. Since the heat capacity of the whole system in actual determination was closely that of 1000 g. of water, the change in that capacity due to reaction thus amounted to 0.035 per cent. of the whole, and when not corrected for, caused the same percentage error in the measurement of the reaction heat. This error is beyond the limit of possible experimental accuracy, and is quite negligible. With other reactions, of course, the corresponding values might be large enough to affect the results of measurement. If this were ever the case, the effect of change in heat capacity on the form of the reaction curve could be corrected for with sufficient exactness by modifying the curve of observed temperature change in such a way that the difference between it and the derived curve varied in an approximately exponential manner from zero at the time when the temperature was minimal to the difference defined by the total correction at the time when the reaction came to an end.

[2] That this was the case under the conditions of experimentation was shown by the results of accessory measurements of isothermal reaction speed under closely similar conditions of temperature and concentration.

$$kt = \log \frac{T_f - T_i}{T_f - T} \text{ and } k(t_2 - t_1) = \log \frac{T_f - T_1}{T_f - T_2} \qquad (2)$$

where T_i and T_f are initial and final temperatures, and T, T_1, T_2, temperatures at the times t, t_1, t_2.

Now, if in actual experience solution were instantaneous, the lowest temperature reached by heat of solution alone—identical with that at which inversion began—would be determined by the point at which the inversion curve, extrapolated from the segment in Period III by Equation 2 cut the ordinate $t = o$. It remains to consider the effect of the changing sucrose concentration during the time interval covered by the extrapolation. In this period the inversion proceeds, not in accordance with the simple formula of extrapolation discussed above, in which the term $(T_f - T_i)$, corresponding to a in the speed equation, implies maximal initial concentration and, therefore, instantaneous solution, but at all times more slowly; its speed, initially zero, gradually increasing at first with positive and toward the end with negative acceleration, until solution is complete.

The relationships involved in this behavior are graphically represented in Fig. 2, to which subsequent discussion may be conveniently referred. In this figure, the complete curve of reaction obtained by correcting the curve of observed temperatures for temperature changes due to stirring and concomitant superimposed effects, and, if necessary or desirable, for change in heat capacity and other causes of independent variation, is represented by the heavily drawn line, $\overline{abcdef}$. Of this, the branch $\overline{ab}$ represents the temperature change due to initial stirring and concomitant effects before the reaction is initiated; the very short interval $\overline{bc}$ marks the initial lag, neglected in the present discussion, the ordinate $t = o$ being drawn through c, the point from which the observed temperature fall becomes measurably significant; the initial temperature, the abscissa of c, is marked T_1; the final temperature reached, T_2; the minimal temperature, T_m. The inversion curve, extrapolated from Period III by Equation 2 (to be referred to subsequently as the simple curve of inversion), is shown by the line of dashes $\overline{er}$; the point r marking its intersection with the ordinate $t = o$ at the temperature T_3. The curve of solution, which falls sharply from the initial point c with greater slope than that of the reaction curve, and which, after sudden flexure slightly above T_o rapidly approaches and soon coincides with the abscissa of this temperature, is represented by the lightly drawn whole line $\overline{cgh}$. This curve, the form of which in measurement was not affected by the mechanism of solution, is here plotted from the results of accessory determinations of solution heats, collated in a manner yet to be described, and is very closely exponential. The curve of actual inversion, which lies at all times above

that extrapolated from Equation 2, is shown by the dotted line $\overline{es}$; the initial point of which, s, lies on the abscissa T_0. Finally, points on the reaction curve are designated T_R; and those on the solution curve, the simple curve of inversion, and the curve of actual inversion, T', T'' and
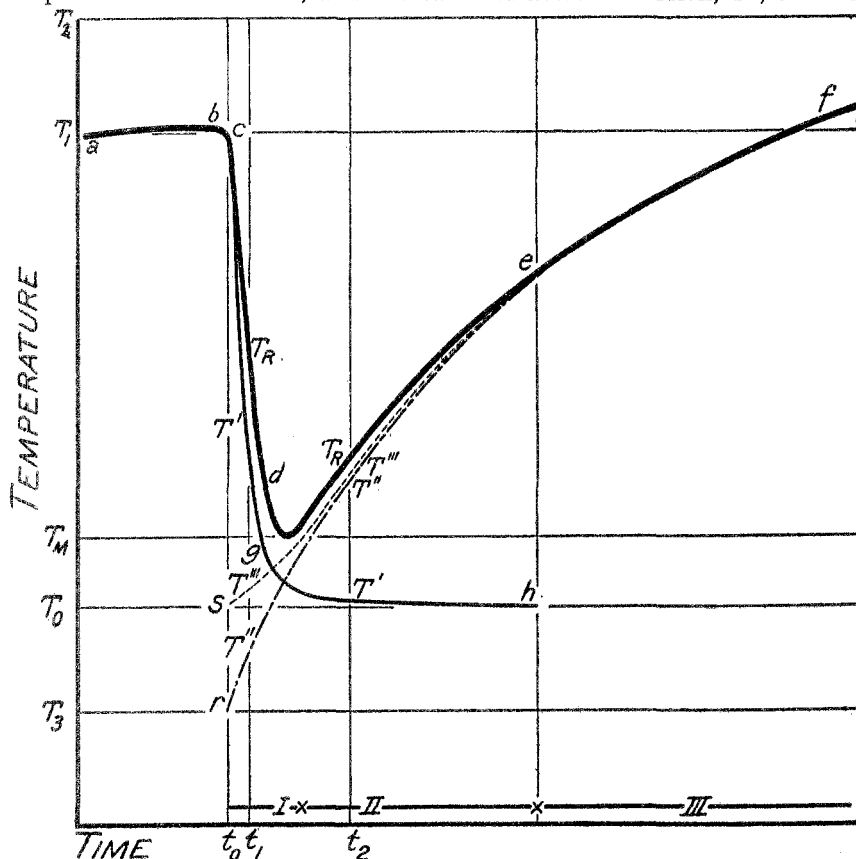
CONCURRENT HEAT EFFECTS IN INVERSION OF SUCROSE BY ACID

Fig. 2.

T''', respectively. The time at which reaction begins ($t=$o) is marked t_0. These several designations will be used in the following discussion without further remark.

The problem of extrapolation is, obviously, to determine the temperature T_0. With reference to Fig. 2, we may write the following equations. For the curve of solution,

$$T' = T_0 + (T_1 - T_0)e^{-pt} \tag{3}$$

and for the simple curve of inversion,

$$T'' = T_2 + (T_3 - T_2)e^{-kt} \tag{4}$$

The rate of actual inversion is at all times proportional to the amount of sucrose in solution.[1] This amount will be, at any instant, the amount dissolved, less the amount inverted up to that instant. That is, the slope of the curve of actual inversion may be formulated:

$$\frac{dT''}{dt} = A(x - y) \tag{5}$$

where x and y are the amounts of sucrose dissolved and inverted at the time t; and where A is a constant proportional to the constant of inversion, k.

In this equation, since temperature change is assumed to be proportional to quantity transformed, the following relations obtain:

$$\frac{A}{k} = \frac{T_2 - T_0}{a}; \quad \frac{x}{a} = \frac{T_1 - T'}{T_1 - T_0}; \quad \frac{y}{a} = \frac{T'' - T_0}{T_2 - T_0};$$

so that Equation 5 may be written:

$$\frac{dT''}{dt} = k \frac{T_2 - T_0}{a} \cdot a \left(\frac{T_1 - T'}{T_1 - T_0} - \frac{T'' - T_0}{T_2 - T_0} \right)$$

$$= k \left[\frac{T_1 - T'}{T_1 - T_0} (T_2 - T_0) - (T'' - T_0) \right]$$

and, since from Equation 3,

$$\frac{T_1 - T'}{T_1 - T_0} = 1 - e^{-pt},$$

$$\frac{dT''}{dt} = k \left[(1 - e^{-pt})(T_2 - T_0) - (T'' - T_0) \right]$$

$$= k \left[T_2 - T'' - (T_2 - T_0)e^{-pt} \right].$$

From this equation, by suitable transformation and integration, we obtain:

$$T'' = T_2 + (T_2 - T_0) \, 1/k - p \, (pe^{-kt} - ke^{-pt})$$

and since, if T_R represent the observed temperature at the time t,

$$T_R = T' + (T'' - T_0),$$

we obtain finally,

$$T_R = (T_1 - T_0)e^{-pt} + T_2 + \frac{T_2 - T_0}{k - p} - (pe^{-kt} - ke^{-pt}). \tag{A}$$

In this equation, all values save T_0 are known; the temperatures, from observations made in each measurement, the constant k from available

[1] It is for this reason that in actual experiment, mixture was accomplished by dissolving dry sucrose in acid. The relation between speed of inversion and hydrogen ion concentration is too complicated to make possible a simple mathematical treatment of the alternative procedure.

data on the speed of reaction, and p from the results of accessory measurements, already referred to, on the form of the solution curve.

The equation is, nevertheless, difficult to handle. It yields, however, upon differentiation and subsequent algebraic conversion a much simpler formula which permits facile graphical solution:

$$T_2 - T_R - \frac{1}{p} \cdot \frac{dT_R}{dt} = (T_2 - T_0)e^{-kt}.[1] \qquad (B)$$

The extrapolation may now be effected graphically as follows.
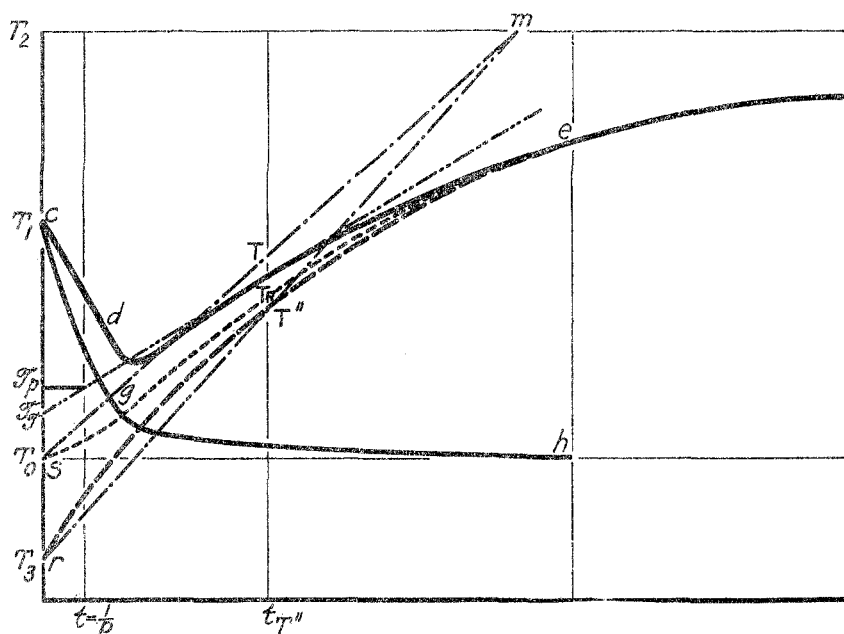
CONCURRENT REACTION HEATS IN OPPOSITE SENSES

Fig. 3.

A. **Exact Tangent Construction.**—In Fig. 3 let a secant to the simple inversion curve be drawn through r and any other point on this curve within the time interval II, such as T''; this will intersect the abscissa of T_2 at some point, m. Draw the line $\overline{ms}$; and let the intersections of the ordinate of T'' ($t_{T''}$), with this line and with the reaction curve be T and T_R, respectively. Then

$$\frac{T_2 - T_0}{T_2 - T} = \frac{T_2 - T_3}{T_2 - T''} = \frac{1}{e^{-kt}} \text{ by Equation 4}$$

[1] NOTE.—For this equation and for invaluable collaboration in its development, the writer is indebted to Professor H. W. Webb of Columbia University.

or,

$$T_2 - T_0 = \frac{T_2 - T}{e^{-kt}}.$$

Substituting this value of $T_2 - T_0$ in Equation B, we have

$$\frac{T_2 - T_R - 1/p \cdot dT_R/dt}{e^{-kt}} = \frac{T_2 - T}{e^{-kt}}$$

or,

$$T = T_R + \frac{1}{p} \cdot \frac{dT_R}{dt}.$$

The point T is thus determined: For the temperature increment $1/p \cdot dT_R/dt$ may be found by constructing a tangent to the reaction curve at T_R, intersecting the ordinate $t = 0$ at T_T and the ordinate $t = 1/p$ at T_p. The temperature interval $T_T - T_p$ then equals $1/p \cdot dT_R/dt$.

Some uncertainty is involved in this construction, on account of the difficulty of drawing the tangent precisely. This uncertainty will be least when the ratio of the time interval $t_{T''} - t_0$ to the temperature interval $T_2 - T_T$ is smallest, and when the curvature of the reaction curve in the neighborhood of T_R is most nearly uniform. The ordinate $t_{T''}$ should, therefore, be taken on an arc of sensibly uniform curvature as near as is practicable to the minimum temperature of the reaction curve. The approximate magnitude of the uncertainty in any case will be indicated, of course, by the discrepancies shown by independent constructions on the same curve.

B. Approximate Tangent Construction.—An alternative procedure, however, yields a much neater construction, the precision of which, in

Fig. 4.

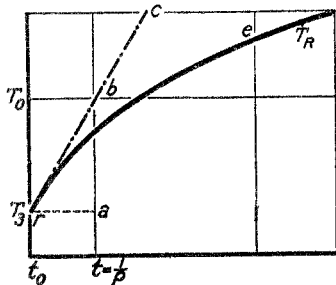practise, largely, if not wholly, compensates for the approximation which it involves. In Fig. 4, let the point T_R, taken as common to the reaction curve and the curves of inversion, be chosen for reference: let the line $\overline{rc}$ be drawn tangent to the simple inversion curve at r, intersecting the ordinate $t = 1/p$ at b; and let the intersection of the abscissa T_3 with this ordinate be a. Then, with reference to the inversion curve (since the slope at any point on an exponential curve is proportional to its distance from the asymptote)

$$\overline{ab} = \frac{1}{p} \times \text{(slope of inversion curve at } T_3) = \frac{1}{p} \cdot \frac{dT_R}{dt} \cdot \frac{T_2 - T_3}{T_2 - T_R}.$$

From Equation B, $\dfrac{1}{p} \cdot \dfrac{dT_R}{dt} = -(T_2 - T_0)e^{-kt} + T_2 - T_R$

whence

$$\overline{ab} = -(T_2 - T_0)e^{-kt} \cdot \frac{T_2 - T_3}{T_2 - T_R} + \frac{T_2 - T_R}{T_2 - T_R}(T_2 - T_3)$$

and since, on the inversion curve, $T_2 - T_R = (T_2 - T_3)e^{-kt}$

$$\overline{ab} = T_0 - T_3$$

Thus T_0 is determined, and with precision, since the slope at T_3 may be measured in terms of accurately known values; that is, at $t = 0$,

$$\frac{dT''}{dt} = k(T_2 - T_3).$$

In drawing the tangent, advantage may be taken of the fact that, as its equation $T = T_3 + kt(T_2 - T_3)$ shows, the point of its intersection with the abscissa T_2 is defined by the condition $t = 1/k$. Since, also, when $t = 1/k$ the equation of the simple inversion curve (Equation 4) becomes

$$T'' = T_2 + (T_3 - T_2)1/e,$$

whence

$$T'' - T_3 = (T_2 - T_3)(1 - 1/e) = 0.63 \ (T_2 - T_3).$$

we have in these relations an opportunity of testing both the precision of the construction, and, in some degree, the legitimacy of the premises (see pages 1298 to 1302) which it involves.

   C. **Approximate Curve Construction.**—The preceding discussion leads, finally, to a very rapid, though less closely approximate, solution. If the speed of solution is much greater than that of concurrent inversion the simple curve of inversion in the construction shown in Fig. 4 may be taken as coincident with its tangent within the time interval $t = 0$ to $t = 1/p$; itself intersecting the ordinate $t = 1/p$ at T_0. The temperature T_0 will then be determined with sufficient accuracy merely by extrapolating the simple inversion curve, and constructing the ordinate $t = 1/p$ to its point of intersection with this curve. The constant p, however, is the least dependable of all the experimental data. In order to avoid using it, advantage may be taken of the following relations.

   Under the above conditions, the curve of reaction, during the short time interval $1/p$, will be sensibly coincident with the curve of solution and may, therefore, be written (compare Equation 4)

$$T_R = T_0 + (T_1 - T_0)e^{-pt}.$$

From this equation, when $t = 1/p$ (and when therefore $T'' = T_0$)

$$T_R = T_0 + (T_1 - T_0)1/e$$

or

$$T_R = T'' + (T_1 - T'')1/e;$$

whence

$$T_1 - T_R = (T_1 - T'')(1 - 1/e), = 0.63 \ (T_1 - T'').$$

The temperature T_0 may, therefore, be determined with the same degree of precision as in the previous case by finding an ordinate ($\equiv [t = 1/p]$) such that measured upon it the distances of the reaction and simple inversion curves from the abscissa T_1 are to each other as 0.63 is to 1. Inasmuch as this can be done very easily by the application of a transparent diagram of converging lines, this approximate solution will be most conveniently rapid. Its adequacy of course depends wholly upon the ratio of the speed of solution to that of inversion within the time interval $1/p$. As this becomes greater, the error of approximation decreases, but more rapidly.

The foregoing analysis, though developed with reference to the sucrose inversion, will apply without essential modification to any partial concurrence between two reactions of the first order. It will have been noted that throughout the discussion no limitation was placed upon the
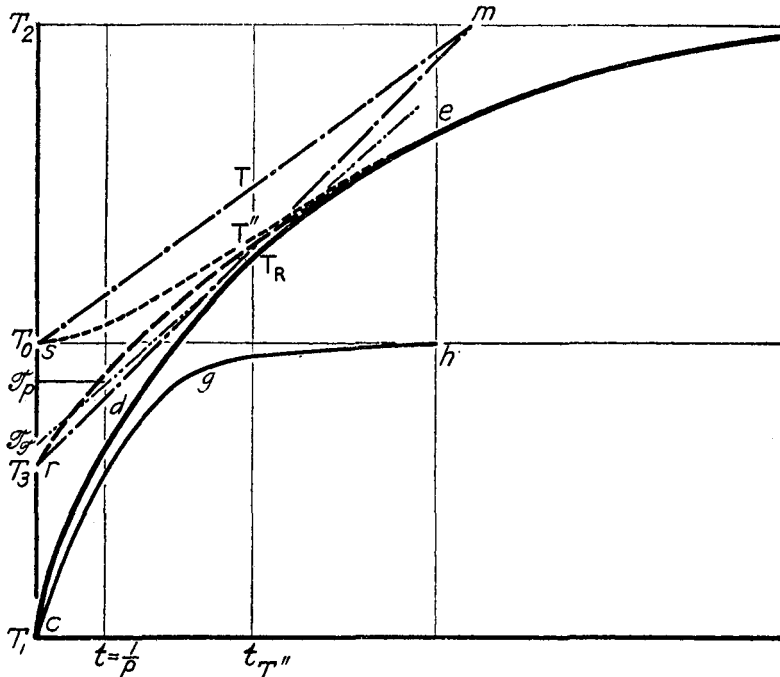
CONCURRENT REACTION HEATS IN THE SAME SENSE
Fig. 5.

general notion of such concurrence; the formulations apply not only to the case under immediate consideration, in which the heats of reaction

are opposed, but also to those in which these heats reinforce each other. The geometrical relations in this latter case are shown in Fig. 5, which thus completes the demonstration. It is likewise clear that similar analysis will be applicable to diverse phenomena involving such concurrence; and the procedure suggests, at any rate, one way in which the analysis of concurrent reactions of the same type not so simply interdependent, or of concurrent reactions of higher order, may be attempted.

   D. Minimum Construction.—In the particular case of opposed heats of reaction, for instance, in the inversion of sucrose, it may often be useful to effect an independent extrapolation, by taking advantage of the fact that the reaction curve in this case shows a critical point, that of minimum temperature, at which the slopes of the curves of solution and of actual inversion are equal; and those of reaction and actual inversion very closely so. For this condition, $dT_R/dt = 0$. We have then from the general Equation B,

$$T_2 - T_m = (T_2 - T_0)e^{-kt},$$

where $T_m \equiv T_R$ at the minimum point; whence

$$\frac{T_2 - T_0}{T_2 - T_m} = \frac{1}{e^{-kt}}.$$

   In the general construction shown in Fig. 3, we have the relation:

$$\frac{T_2 - T_0}{T_2 - T} = \frac{1}{e^{-kt}}$$

   It follows, therefore, that for the case of opposed heats of reaction, $T_m = T$; so that in the construction shown in Fig. 3 as applied to this case, T_0 is known from observation and need not be calculated. This procedure is obviously questionable unless the minimum point be sharply defined in the curve of reaction, and is uncertain insofar as the observed minimum differs from the actual in consequence of thermometric lag, which at this point exhibits its most marked effect.

   The entire preceding analysis applies, of course, only to the isothermal condition. In the adiabatic condition, the observed heat of reaction, Q, or with negligible error in this case as in the case of any reaction in a condensed system, the actual change of internal energy, U, at any time equals that of the isothermal reaction, U, plus the increment in U due to change of temperature; which we may call ΔU. Now, by Kirchoff's law:

$$\Delta U = \Delta C(T_2 - T_1),$$

where ΔU is the increment mentioned, $T_2 - T_1$ the observed temperature change, and ΔC the difference between the specific heats of factors and products. Therefore,

$$\mathbf{U} = U + \Delta U = U + \Delta C (T_2 - T_1)$$

or,

$$U = \mathbf{U} - \Delta C(\mathbf{T_2} - \mathbf{T_1});$$

and similarly,

$$T = \mathbf{T} - \Delta C/H\ (\mathbf{T_2} - \mathbf{T_1}) \tag{7}$$

where H is the heat capacity of the system. If the value of T given in Equation 7 be substituted for T in Equation 2, the resulting equation will be that of the temperature-time curve in terms of the data obtained for the adiabatic condition. In this equation, however, the terms of correction are very small in comparison with the values which they affect,[1] so that, for the purpose of measurement Equations 1 and 2, from which the constant k can be determined and checked, and the curve of inversion simply extrapolated, may be used as applicable to the adiabatic condition without sensible error. Thus, in practice the equations given will be applicable, so far as the heat of reaction alone is concerned, for the separation of concurrent heat effects in the case of any reaction which does not develop an altogether unusual quantity of heat, whatever be the calorimetric method employed.

On the other hand, the form of the sucrose inversion curve is considerably altered even by a small rise of temperature during reaction; and such also will be the case for all reactions for which the temperature coefficient of the velocity constant is correspondingly great. Whenever the coefficient is known for the conditions of experimentation, the reaction curve may, obviously, be corrected for this influence, so that its extrapolation across the short period of concurrent effect will be as precise as necessary. If it be not known in advance, it may always be derived from the reaction curve itself, extrapolated to its value at the time reaction begins, and applied as before.

A more extended discussion of the experimental application of the equations here presented will find its natural place in the record of actual measurement. It is sufficient for present purposes that its general character is thus indicated.

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[1] From the data given in a preceding footnote (p. 1299), $\Delta C = (152.8 + 18.0) \div 360 - (84.2 \div 180) = 0.0069$, $\mathbf{T_2} - \mathbf{T_1}$ will always be less than $0.4°$; so that in Equation 7, $\Delta C(\mathbf{T_2} - \mathbf{T_1})$ will always be less than 0.0027 gram calorie units. In the same experiments, the heat capacity will always be greater than 1000 gram calorie units; and $T = \mathbf{T} - \dfrac{\Delta C}{H}(\mathbf{T_2} - \mathbf{T_1})$ will, therefore, differ from $\mathbf{T}$ by less than one part in 300,000. This discrepancy will be far beyond the limit of measurement accuracy, not only in these determinations, but in the case of all others of similar character, and may be disregarded.