

THEORETICAL EVALUATION AND LIMITATIONS OF THE EXTRAPOLATION METHOD FOR MEASURING REACTION ENTHALPY BY TITRATION CALORIMETRY

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(Received September 29th, 1971)

ABSTRACT

The extrapolation method of evaluating reaction enthalpies in thermometric titrations is examined by computing theoretical curves from the fundamental equations and simulating the extrapolation by means of a least-square best fit to the temperature-time curve. The accuracy of the method is dependent upon the magnitude of the heat transfer modulus of the calorimeter, the rate of change of heat capacity due to titrant addition, and the details of the extrapolation procedure. Computed results show that the complex equations can be accurately simulated by a simple algorithm. Use of this mathematical device leads to an accurate (0.1–0.5%) method of data evaluation which does not require measurement of the heat transfer characteristics of the calorimeter.

SYMBOLS USED

- T = temperature of the dewar contents
 T^0 = T when recording is initiated
 T_0 = T when buret is turned on
 T_E = temperature of the dewars' environment and the temperature of the titrant
 T^* = temperature of the dewar contents at time t^*
 ΔT = $T - T_0$
 $\overline{\Delta T}$ = a normalized temperature change
= $-C_p^0 / \Delta H_R \bar{\rho} t^*$
 C_p^0 = initial heat capacity of the dewar and its contents (cal/°C)
 ΔH_R = enthalpy (cal/mole) of the titration reaction
 ΔH_D = enthalpy (cal/mole) of dilution of the titrant
 $\bar{\rho}$ = rate of titrant addition (mole/sec)
 t = real time (sec)
 t^* = equivalence point time (sec)
 f = t/t^* a normalized time
 k = Newtonian heat transfer modulus (sec⁻¹)
 κ = kt^* a dimensionless heat transfer modulus
 c_p = heat capacity of the titrant (cal/°C g)
 \dot{m} = rate of addition of the titrant (g/sec)

$$\phi = \frac{c_p \bar{m} t^*}{C_p^0} \text{ a dimensionless heat capacity}$$

w = heating rate (cal/sec) due to stirring and other constant processes

Ω = $w/\Delta H_R \bar{\rho} t^*$ a dimensionless form of w

INTRODUCTION

Essentially, three independent methods of evaluating reaction enthalpies from thermometric titration curves have been proposed¹⁻³. These include two graphical methods: an extrapolation technique¹, and an initial slope procedure². The most rigorous approach³ is a mathematical method which permits simultaneous measurement of both the reaction free energy and enthalpy.

The last method is applicable only when the reaction is quite rapid and when the equilibria involved lend themselves to exact description. In those instances where the overall heat generating process is complex, *e.g.* acid-base reactions in non-aqueous solvents, the initial slope method has been used quite successfully^{2,4}.

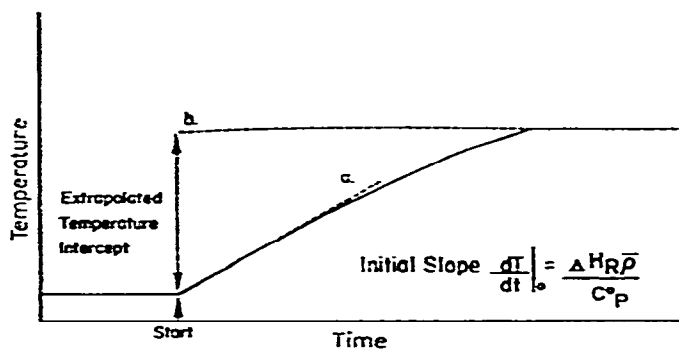


Fig. 1. Schematic plot of temperature *vs.* time; a, the initial slope method; b, the extrapolation method.

The slope method (see Fig. 1, curve a) however, relies upon a rapid reaction between the titrant species and the other reactants. Consequently, it can not be used to determine enthalpies in systems where the kinetics during the initial phase of the experiment are slow. Under these conditions the graphical extrapolation method can be used since the extrapolation is made from regions of the curve where the process is complete^{5,6}.

The purpose of this work is to evaluate the graphical extrapolation technique, which has been used most extensively by Jordan and coworkers^{7,8} (see Fig. 1, curve b). A secondary objective is to determine the optimum method of correcting for incomplete adiabaticity, and the increase in heat capacity resulting from the continuous addition of reagent. As will be shown it is the above two phenomena which are responsible for non-linearities in the curve and concomitantly for the errors in the procedure.

EQUATIONS OF THE TEMPERATURE-TIME CURVE

In order to arrive at reasonably simple closed-form temperature-time equations a number of assumptions will be made. The most important of these assumptions are: (a) that Newtonian heat transfer applies³; (b) that the initial heat capacities of the system and of the titrant are additive; (c) that the heat of dilution of the titrant is constant; and (d) that thermal equilibrium is achieved very rapidly. Essentially, these same approximations have been made by all investigators. Although it is not essential to assume a complete reaction, this will be done to simplify the results.

Due to the discontinuities built into the computation by the start of the buret and the abrupt cessation of heat generation at the equivalence point, it is useful to consider the calorimetric curve in three parts. This is in accord with the work of Barthel, Becker and Schmahl¹⁰⁻¹² who were the first to carry out a complete analysis of the problem. These three regions are illustrated in Fig. 2.

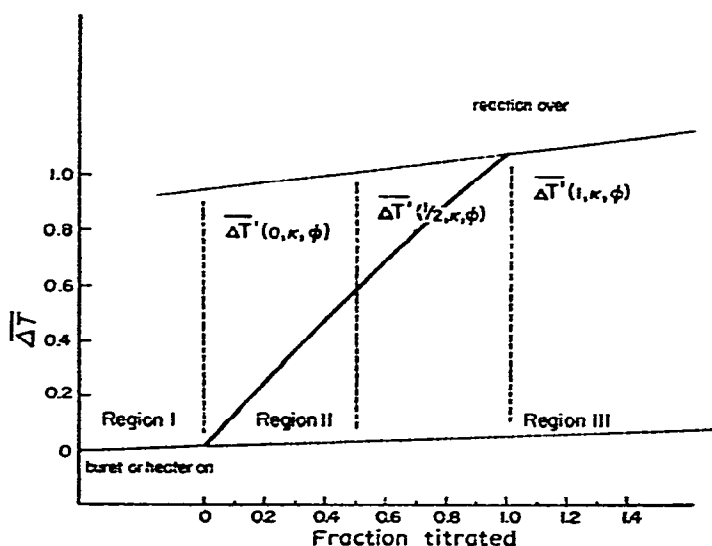


Fig. 2. Plot of $\overline{\Delta T}$ vs. fraction titrated, F , showing details of the extrapolation method and the three titration regions.

The graphical extrapolation technique is based upon the concept that such processes as heat generation due to stirring and the temperature transducer are present to exactly the same extent in all three regions of the curve, second that temperature change due to the inequality of the system and titrant temperatures cancels out by extrapolation to the point of initiation of the reaction. Last, the graphical extrapolation assumes that one can eliminate errors due to poor adiabaticity via appropriate calibration procedures. The usual method of graphical extrapolation is shown in Fig. 2. Although this technique has been used extensively there has been no previous theoretical investigation of its validity, nor have correction factors, if such are necessary, been computed.

The differential equations of the temperature-time curve have been considered previously^{2,3,11,12}. In order to carry out the present evaluation we have recast these equations in dimensionless form. The independent variable used is the fraction titrated, f , which is quite common in titration theory and is defined as the ratio of real time, t , to the stoichiometric equivalence point time t^* . In a calibration run t^* is the time duration of electrical heating.

$$f \equiv t/t^* \quad (1)$$

The dependent variable, $\overline{\Delta T}$, is a normalized temperature change defined as

$$\overline{\Delta T} \equiv \Delta T \left(\frac{-C_p^0}{\Delta H_R \bar{\rho} t^*} \right) = \Delta T \cdot \Psi \quad (2)$$

The term in parentheses in Eqn. 2 is the inverse of the total temperature change brought about by the chemical reaction under ideal circumstances. All terms in Eqns. 1, 2, and subsequent equations are defined above. After introducing Eqns. 1 and 2 into the equations which have been derived previously^{3,10-12}, one arrives at the following normalized temperature-time equations.

$$\overline{\Delta T}_1 = \left[(T_E - T_0) \Psi + \frac{\Omega}{\kappa} \right] [1 - \exp(\kappa f)] \quad (3)$$

$$\overline{\Delta T}_2 = \left[(T_E - T_0) \Psi + \frac{\Omega + 1 + \Delta H_D \Psi}{\kappa + \phi} \right] [1 - (1 + \phi f)^{-(1 + \kappa/\phi)}] \quad (4)$$

$$\overline{\Delta T}_3 = (T^* - T_0) \Psi + \left[(T_E - T^*) \Psi + \frac{\Omega + \Delta H_D \Psi}{\kappa + \phi} \right] \times \left[1 - \left(\frac{1 + \phi f}{1 + \phi} \right)^{-(1 + \kappa/\phi)} \right] \quad (5)$$

Eqn. 3 is utilized from some arbitrary initial time up to the start of the buret or the calibration heater, and does not describe the enthalpogram during the rising part of the curve. Fig. 2 illustrates the reason for normalization, *i.e.*, the x and y axes always have the same range regardless of the values of the experimental parameters, consequently these parameters may be varied widely without need for scale adjustment.

The experimental evaluation process employed in graphical extrapolation is simulated by fitting $\overline{\Delta T}_1$ and $\overline{\Delta T}_3$ to a straight line using an unweighted least-squares computation. The analysis results in two linear equations

$$\overline{\Delta T}_1 = m_1 f + b_1 \quad (6)$$

$$\overline{\Delta T}_3 = m_3 f + b_3 \quad (7)$$

The extrapolation method utilizes the predicted difference in $\overline{\Delta T}_3 - \overline{\Delta T}_1$ as a measure of the reaction enthalpy. Thus,

$$\overline{\Delta T}' \equiv \overline{\Delta T}_3 - \overline{\Delta T}_1 = b_3 - b_1 - (m_3 - m_1)f \quad (8)$$

Only when $m_3 = m_1$ will $\overline{\Delta T}'$ be independent of f .

In order to carry out a complete analysis, three types of curves were computed. First, heater calibration was simulated by assuming no change in heat capacity, *i.e.* $\phi = 0$, and studying the effect of κ , the dimensionless heat transfer modulus, of $(T_E - T_0)$, of the total temperature change due to reaction, Ψ , and of mechanical and electrical heating, Ω . These results are summarized in Table I. Second, the effect of increased heat capacity, ϕ , in a perfect calorimeter ($\kappa = 0$) was similarly examined (see Table II). Third, simulated experimental runs in which both ϕ and κ are finite were computed (see Table III).

TABLE I

EFFECT^a OF FINITE HEAT TRANSFER MODULUS ON THE EXTRAPOLATED TEMPERATURE CHANGE

κ	$\Psi(^{\circ}\text{C}^{-1})$	Ω	$T_E - T_0(^{\circ}\text{C})$	$\overline{\Delta T}'(f=0)$	$\overline{\Delta T}'(f=1/2)$	$\overline{\Delta T}'(f=1)$
1	+10	0	0	1.1184	0.8704	0.6225
3.16×10^{-1}	+10	0	0	1.1064	0.9812	0.9459
1.00×10^{-1}	+10	0	0	1.0443	0.9979	0.9519
3.16×10^{-2}	+10	0	0	1.0152	0.9998	0.9843
1.00×10^{-2}	+10	0	0	1.0049	0.9999	0.9950
3.16×10^{-3}	+10	0	0	1.0016	1.0000	0.9984
1.00×10^{-3}	+10	0	0	1.0005	1.0000	0.9995
3.16×10^{-4}	+10	0	0	1.0002	1.0000	0.9998
3.16×10^{-4}	+10	+0.01	0	1.0154	0.9998	0.9841
3.16×10^{-2}	+10	+0.10	0	1.0176	0.9998	0.9821
3.16×10^{-2}	+10	0	-1	1.0077	0.9997	0.9916
3.16×10^{-2}	+10	0	-0.2	1.0137	0.9998	0.9858
3.16×10^{-2}	+10	0	-0.1	1.0145	0.9998	0.9851
3.16×10^{-2}	+10	0	+0.1	1.0160	0.9998	0.9836
3.16×10^{-2}	+10	0	+0.2	1.0167	0.9998	0.9829
3.16×10^{-2}	+10	0	+0.5	1.0189	0.9998	0.9807
3.16×10^{-2}	+1	+0.1	-0.10	1.0175	0.9998	0.9821
3.16×10^{-2}	+1	+0.1	+0.10	1.0176	0.9998	0.9820
3.16×10^{-2}	+10	+0.1	-0.10	1.0168	0.9998	0.9819
3.16×10^{-2}	+10	+0.1	+0.10	1.0183	0.9998	0.9813

^a $\phi = 0$ for all calculations in this table.

RESULTS AND CONCLUSIONS

Table I summarizes the results for the heater calibration ($\phi = 0$) experiment. A number of important conclusions can be stated:

(1) To achieve maximum accuracy in establishing the calorimetric sensitivity, *e.g.* to determine specific heats, the mid-point of the temperature rise ($\overline{\Delta T}_1$ at $f = 0.5$) should be used. With $\kappa = 0.10$ an error of less than 0.3% results. In terms of available

equipment the dewar of Christensen, Izatt and Hansen⁹ has a heat transfer modulus of $1.1 \times 10^{-3} \text{ min}^{-1}$, consequently the experimental heating period must exceed 90 min to produce an error greater than 0.3%. For less refined equipment, one could achieve the same level of accuracy by reducing the duration of the experiment to several minutes¹.

(2) The errors are *essentially* independent of the temperature difference between the dewar and the environment. Further, the error is perfectly independent of the difference when $\kappa = 0$.

(3) As might be expected for a first order process, the error is *essentially* independent of the total temperature change (Ψ^{-1}). This produces a simplification in experimental procedure since there is no need to match the temperature change in the calibration run to the temperature change in the measurement run. All that is required is that κ be the same for both experiments. This is easily achieved.

TABLE II

EFFECT^a OF TITRANT HEAT CAPACITY ON THE EXTRAPOLATED TEMPERATURE CHANGE

ϕ	$\Psi(^{\circ}\text{C}^{-1})$	Ω	$T_E - T_0(^{\circ}\text{C}^{-1})$	$\overline{\Delta T}'(f=0)$	$\overline{\Delta T}'(f=1/2)$	$\overline{\Delta T}'(f=1)$
0.516	10	0	0	0.92121	0.83983	0.75845
0.100	10	0	0	0.98786	0.94805	0.90825
3.16×10^{-2}	10	0	0	0.99858	0.98396	0.96933
1.0×10^{-2}	10	0	0	0.99985	0.99497	0.99009
3.16×10^{-3}	10	0	0	0.99998	0.99842	0.99685
1.0×10^{-3}	10	0	0	0.99999	0.99995	0.99990
0.01	10	0	-0.50	0.99910	0.97284	0.94057
0.01	10	0	-0.20	0.99955	0.98292	0.97028
0.01	10	0	-0.10	0.99970	0.98995	0.98019
0.01	10	0	+0.10	1.00000	1.00000	1.00000
0.01	10	0	+0.20	1.00010	1.00503	1.00990
0.01	10	0	+0.50	1.0006	1.02011	1.03962
0.01	1	0	-0.50	0.99977	0.99246	0.98514
0.01	1	0	+0.50	0.99992	0.99749	0.99505
0.01	10	0.10	0	1.00135	0.99525	0.98914
0.01	10	0.20	0	1.00280	0.99547	0.98814
0.01	1	0.10	0	1.00135	0.99525	0.98914

^a $\kappa = 0$ for all calculations in this table.

Table II presents the results for the case in which $\kappa = 0$. The major conclusions are:

(1) In order to eliminate or minimize temperature effects related to the titrant including the increase in heat capacity, the mismatch in the temperature of the titrant and initial temperature of the calorimeter, and the heat of dilution of the titrant, the measurement of $\overline{\Delta T}'$ must be made at $f = 0$; *i.e.* region III must be extrapolated to the start of region II (see Fig. 2).

(2) The effect of ϕ on the measurement is much more serious than the effect of κ . For example with $\phi = 0.10$, representing a 10% change in heat capacity, an error of 1.2% results at $f = 0.0$. Contrast this with the 0.3% error when $\kappa = 0.10$. Consequently, one should employ a titrant which is as concentrated as possible. Fortunately the parameter ϕ is easily estimated from measurement of the heat capacity of the system and the rate of addition of titrant.

(3) The results also indicate that the error at $f = 0.0$ is *essentially* independent of the total temperature change, the heat of dilution, and temperature mismatch. In the limit as ϕ approaches zero, this becomes exactly true.

TABLE III
SIMULTANEOUS EFFECT^a OF ϕ AND κ ON EXTRAPOLATION ACCURACY

ϕ	κ	$\overline{\Delta T}'(f=0)$	$\overline{\Delta T}'(f=1/2)$	$\overline{\Delta T}'(f=1)$
0.316	0.0316	0.92411	0.83625	0.74839
0.100	0.0316	0.99713	0.94624	0.89535
3.16×10^{-2}	0.0316	1.01158	0.98301	0.95443
1.00×10^{-2}	0.0316	1.01432	0.99450	0.97468
3.16×10^{-3}	0.0316	1.01496	0.99811	0.98127
1.00×10^{-3}	0.0316	1.01513	0.99925	0.98337
0.10	0.10	1.01461	0.94082	0.86702
0.01	0.10	1.04194	0.99211	0.95228
0.10	0.01	0.99088	0.94761	0.90454
0.01	0.01	1.00455	0.99487	0.98519
0.10	0.001	0.98817	0.9483	0.90840
0.01	0.001	1.00032	0.99496	0.98960

^a $T_E - T_0 = 0$, $\Omega = 0$, $\Delta H_D = 0$, and $\Psi = 10$ for all calculations in this table.

Table III indicates that when ϕ and κ are both finite there is no *trivial extrapolation method* which minimizes or eliminates errors; *i.e.* $\overline{\Delta T}'$ is never exactly, or even approximately unity, within a few tenths percent, at any fixed value of f . This is an extremely unfortunate circumstance since it limits the accuracy of a simple extrapolation procedure to several percent, depending upon the value of ϕ and κ . If ϕ and κ were available then one could compute the normalized curve and use it to estimate the error and correct the results. However, this defeats the major virtue of the extrapolation method *i.e.*, its simplicity.

In order to circumvent this problem we examined a number of algorithms, *e.g.* weighted linear combinations of functions which would permit computations of $\overline{\Delta T}'(f, \kappa, \phi)$ from a table of $\overline{\Delta T}'(f, 0, \phi)$ and a table of $\overline{\Delta T}'(f, \kappa, 0)$. The most efficient algorithm was a simple product

$$\overline{\Delta T}'(f, \kappa, \phi) \cong \overline{\Delta T}'(f, 0, \phi) \cdot \overline{\Delta T}'(f, \kappa, 0) \quad (9)$$

The accuracy of this approximation is illustrated in Table IV. As can be seen it is most accurate when both κ and ϕ are small, and when $f = 0.5$. However, in order to

TABLE IV

ACCURACY OF THE APPROXIMATION METHOD FOR COMPUTING $\overline{\Delta T}'(\phi, \kappa, f)^*$

ϕ	κ	$\overline{\Delta T}'(f=0)$	$\overline{\Delta T}'(f=1/2)$	$\overline{\Delta T}'(f=1)$
0.316	3.16×10^{-2}	0.93522	0.83964	0.74659
0.100	3.16×10^{-2}	1.0028	0.94784	0.89403
3.16×10^{-2}	3.16×10^{-2}	1.01377	0.98374	0.94515
1.00×10^{-2}	3.16×10^{-2}	1.01505	0.99475	0.97459
3.16×10^{-3}	3.16×10^{-2}	1.01519	0.99820	0.98125
1.00×10^{-3}	3.16×10^{-2}	1.01518	0.99975	0.98420
0.10	0.10	0.99270	0.94148	0.86420
0.01	0.10	1.00475	0.98949	0.94207
0.10	0.01	0.99270	0.94796	0.90370
0.01	0.01	1.004751	0.99487	0.98514
0.10	0.001	0.98835	0.94805	0.90779
0.01	0.001	1.00034	0.99497	0.98959

* All data are computed with $T_E = 25^\circ\text{C}$, $\Omega = 0$, $\Delta H_D = 0$, $\Psi = 10$. Data were obtained from Eq. 9 and Tables I and II.

eliminate the effect of heats of dilution and titrant temperature mismatch, it is essential to carry out the extrapolation to $f = 0.0$. This analysis implies that the optimum experimental procedure is to first calibrate the dewar and its contents by a heater calibration run using a heating time within 10–20% of the experimental end point time. The calorimetric constant (cal/cm) is determined by extrapolation to $f = 0.0$. The reaction is then carried out and the temperature–time curve extrapolated to $f = 0.0$. The heat (Q) generated in the reaction step is computed as

$$Q_{\text{Exp}} = Q_{\text{H.C.}} \frac{\overline{\Delta T}'_{\text{Exp}}}{\overline{\Delta T}'_{\text{H.C.}}} \quad (10)$$

where any number proportional to the true temperature change, such as a voltage or recorder deflection, may be used in Eqn. 10 instead of $\overline{\Delta T}'_{\text{Exp}}$ and $\overline{\Delta T}'_{\text{H.C.}}$. Q_{Exp} , as defined in Eqn. 10, is an accurate measure of the heat generated by the reaction only to the extent that Eqn. 9 is accurate, and to the extent that heat capacity effects are negligible. The results are easily corrected for finite values of ϕ through Table II. As stated previously, ϕ is readily computed. The true, (within the accuracy of Eqn. 9), reaction heat may then be computed as

$$Q_{\text{Reaction}} \equiv Q_{\text{Exp}} / \overline{\Delta T}'(f, 0, \phi) \quad (11)$$

Q_{Reaction} as defined by Eqn. 11 becomes a more accurate measure of the real heat evolved by the chemical reaction as ϕ and κ approach zero.

The procedure discussed in this paper has been used by us in previous work⁶ to measure the heat of neutralization of a strong acid and strong base. The results were, within experimental precision ($\pm 0.3\%$) in agreement with the best available data³.

ACKNOWLEDGEMENT

The author would like to thank the University of Georgia Computer Center for computational time used in this work and the National Institute of Health for grant GM 17913-02.

REFERENCES

- 1 J. Jordan, *Thermometric Enthalpy Titration*, in I. M. Kolthoff and P. J. Elving (Eds.), *Treatise on Analytical Chemistry*, Vol. 8, Interscience Publishers, New York, 1968, Chap. 91, p. 5210.
 - 2 H. J. Keily and D. N. Hume, *Anal. Chem.*, 28 (1956) 1294.
 - 3 J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, *J. Phys. Chem.*, 70 (1966) 2003.
 - 4 H. J. Keily and D. N. Hume, *Anal. Chem.*, 36 (1964) 543.
 - 5 J. Jordan and P. W. Carr, *Enthalpimetric Analysis*, in R. S. Porter and J. Johnson (Eds.), *Analytical Calorimetry*, Plenum Press, New York, 1968, p. 203.
 - 6 P. W. Carr, *Thermochim. Acta*, 2 (1971) 505.
 - 7 J. Jordan and W. H. Dumbaugh, *Bull. Chem. Thermodyn.*, 2 (1959) 9.
 - 8 J. Jordan, *Chimia*, 17 (1963) 101.
 - 9 J. J. Christensen, R. M. Izatt, and L. D. Hansen, *Rev. Sci. Instrum.*, 36 (1965) 779.
 - 10 J. Barthel, F. Becker, and N. G. Schmahl, *Z. Phys. Chem. (Frankfurt am Main)*, 29 (1961) 58.
 - 11 J. Barthel, F. Becker, and N. G. Schmahl, *Z. Phys. Chem. (Frankfurt am Main)*, 35 (1963) 3.
 - 12 J. Barthel, F. Becker, and N. G. Schmahl, *Z. Phys. Chem. (Frankfurt am Main)*, 37 (1963) 52.
- Thermochim. Acta*, 3 (1972) 427-435