Estimating Thermodynamic and Equilibrium Quantities of Exothermic Reversible Processes

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ABSTRACT: It is sometimes difficult to obtain physically meaningful parameters from experimental data for a chemical system when the mathematical model describing the system involves nonlinear functions. A simple method has been developed for the prediction of heat of reaction and equilibrium constants from experimental temperature−time data of exothermic reversible processes in adiabatic conditions. The success of this new technique is demonstrated by predicting the heat of reaction and equilibrium constant as a function of temperature for ethanol−acetic acid and propanol−acetic acid systems at temperatures between 283 and 295 K and 285 and 297 K, respectively. This technique may be useful in the estimation of heats of reaction and equilibrium constants for exothermic reversible processes at higher temperatures.

INTRODUCTION

The temperature−time history of a chemical process is of great importance for chemist and chemical engineers as it provides a great deal of information about the nature of the process. A lot of methods have been developed to extract kinetic and thermodynamic information of processes from temperature−time history. Some of the techniques used are temperature measurements from flow reactors1−4 and differential thermal analysis.5,6 These techniques either require complicated experimental procedures or the evaluation of the kinetic information which is obtained from a limited number of data points on the temperature−time curve. Simple experimentation at the expense of fairly complex data analysis has been achieved by Becker and Maelicke7 using an analogue computer and Williams and Glasser8 using a digital computer. Scott et al.9 developed an experimentally and computationally simple but accurate technique for obtaining kinetic and thermodynamic parameters from temperature−time curves. In this work, the experimental techniques developed by Williams and Glasser8 and Scott et al.9 were adopted for the study of the esterification processes, to estimate heats of reaction and equilibrium as a function of temperature using the dewer thermos-flask as an adiabatic batch reactor. This is a new technique for determining equilibrium information of equilibrium limited processes using the thermos-flask.

THEORETICAL DEVELOPMENTS

Equilibrium Information from Thermos-Flask Measurements. Consider the Gibbs −Helmholtz equation:

$$\frac{d}{dT} \left( \frac{\Delta G}{T} \right) = \frac{-\Delta H_r}{T}$$  \hspace{1cm} (1)

But

$$\frac{\Delta G}{T} = -R \ln K_{eq}$$  \hspace{1cm} (2)

Plugging eq 2 into eq 1 gives eq 3 as

$$\frac{d}{dT} \left( \ln K_{eq} \right) = \frac{\Delta H_r}{RT^2}$$  \hspace{1cm} (3)

Assuming $\Delta H_r$ is independent of temperature or only varies a small amount of some range of temperature ($T$), integrating eq 3 gives

$$\ln K_{eq} = -\frac{\Delta H_r}{RT} + C$$  \hspace{1cm} (4)

Given $T = T_0$ at $K_{eq} = K_{eq}^0$, one can write eq 4 as

$$\ln K_{eq}^0 = -\frac{\Delta H_r}{RT_0} + C$$  \hspace{1cm} (5)

Combining eqs 4 and 5, the constant of integration ($C$) can be eliminated to give eq 6 as

$$\ln \left( \frac{K_{eq}}{K_{eq}^0} \right) = -\frac{\Delta H_r}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)$$  \hspace{1cm} (6)

Equation 6 can be rewritten as:

$$K_{eq} = K_{eq}^0 \exp \left\{ \frac{(\Delta H_r)}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right\}$$  \hspace{1cm} (7)

Energy Balance of the Thermos-Flask. For a constant-volume batch reactor, one can write

$$-r_A = \frac{1}{V} \frac{dN_A}{dt} = -\frac{dC_A}{dt}$$  \hspace{1cm} (8)

The energy balance equation can be established as

Heat generated = Heat absorbed by reactor contents

+ Heat transferred through reactor walls

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Eq 9 can be written as follows:

\[ H = H_0 + (\Delta H_f)x + UA \int_0^\infty (T - T_{\text{amb}}) \, dt \]
\[ + mC_P(T - T_0) \]  

at \( T_0, \) \( H_0 = mC_P(T - T_{\text{amb}}) \)  

Combining eqs 10 and 11, one can write the total energy balance equation as follows:

\[ mC_P(T - T_{\text{amb}}) + mC_P(T - T_0) + UA \int_0^\infty (T - T_{\text{amb}}) \, dt \]
\[ + (\Delta H_f)x = 0 \]  

Simplifying eq 12 gives eq 13:

\[ mC_P(T - T_{\text{amb}}) + UA \int_0^\infty (T - T_{\text{amb}}) \, dt + (\Delta H_f)x = 0 \]  

Consider the esterification process given below:

\[ \text{Acetic Acid} + \text{Alcohol} \leftrightarrow \text{acetate} + \text{water} \]  

For equimolar reactants we can write the equilibrium expression for eq 14 as follows:

\[ K_{\text{eq}} = \frac{x^2}{(1 - x)^2} \quad \text{or} \quad x = \frac{\sqrt{K_{\text{eq}}}}{1 + \sqrt{K_{\text{eq}}}} \]  

Combining eqs 7 and 15, \( x \) can be eliminated from eq 13 to give eq 16 below:

\[ \frac{(\Delta H_f)\sqrt{K_{\text{eq}}} \exp \left\{ \frac{(\Delta H_f)}{2R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right\}}{1 + \sqrt{K_{\text{eq}}} \exp \left\{ \frac{(\Delta H_f)}{2R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right\}} + mC_P(T - T_{\text{amb}}) 
\]
\[ + UA \int_0^\infty (T - T_{\text{amb}}) \, dt \]
\[ = 0 \]  

Let \( (T - T_{\text{amb}}) + UA \int_0^\infty (T - T_{\text{amb}}) \, dt = \alpha \) and
\[ \frac{1}{2R} \left( \frac{1}{T_0} - \frac{1}{T} \right) = \beta \]  

Eq 16 can be simplified as

\[ \frac{(\Delta H_f)\sqrt{K_{\text{eq}}} \exp ((\Delta H_f)\beta)}{1 + \sqrt{K_{\text{eq}}} \exp ((\Delta H_f)\beta)} + mC_P\alpha = 0 \]  

Equation 18 has two unknown quantities, \( \Delta H_f \) and \( K_{\text{eq}} \). If one can determine \( \alpha \) and \( \beta \), then the two unknown quantities can be determined for the process and eq 7 can be establish for the esterification process.

### EXPERIMENTAL DESCRIPTIONS

The experimental setup as shown in Figure 1 was used in all of the reactions studied. The adiabatic batch reactor used in the experiments is 18/8 stainless steel thermos-flask of total volume of 500 mL equipped with a removable magnetic stirrer. The flask is provided with a negative temperature coefficient thermistor connected online with a data-logging system. The signal from the sensor (thermistor) is fed to a measuring and a control unit amplifier and a power interface. The acquisition units are connected to a data processor. A process control engineering support was used for data management. The data acquisition system called Clarity has the following part numbers: CS0 Clarity Chromatography SW, single instrument, 3 × S5 Clarity Add-on instrument SW, 194 (INT9 quad channel A/D converter card. The hardware is INT9 PCI quad channel A/D 24 bit converters. The properties are as follows: input signal range 100 mV to 10 V, acquisition frequency 10–100 Hz, internal A/D converter (INT9–1 to 4 channel PCI A/D converter). All physically available analog inputs and outputs as well as virtual channel are all automatically monitored, and the process values are stored. The process values are transmitted in such a way that the computer screen displays profiles of voltage–time curves.
Data acquisition software was used to convert the compressed data form of the history file on the hard disk into text file format. The text files are converted to an Excel spreadsheet, and the data are then transported into Matlab 2010a for analysis.

The thermistor used in the experiments was a negative temperature coefficient with unknown thermistor constants. The calibrations involve the determination of the thermistor constants and establishment of the relationship between the thermistor’s resistance and temperature.

Figure 2. Thermos-flask cooling curve at $T(0) = 361$ K.

Figure 3. Regression line of heat transfer coefficient of reactor.
Thermistor resistance \( R_{TH} \) and temperature \( T \) in Kelvin were modeled using the empirical equation given, developed by Considine:\(^{10}\)

\[
R_{TH} = \exp\left(\frac{B}{T} + C\right)
\]

or

\[
\ln(R_{TH}) = \frac{B}{T} + C
\]

where the parameters \( B \) and \( C \) are the thermistor constants and were obtained from experimental calibration using warm water. The constants were determined by fitting the “best” least-squares straight line plot of \( \ln(R_{TH}) \) against \( 1/T \), giving the thermistor equation as

\[
\ln(R_{TH}) = -\frac{1773.8}{T} + 18.178
\]

**REACTOR (THERMOS-FLASK) CALIBRATION**

The reaction vessel used was an ordinary dewer thermos-flask with removable screw cap lid. The flask has a total volume of 500 mL. The calibration involves the determination of the heat transfer coefficient of the flask and fitting the experimental data to the model described in eq 22 below:

\[
T = T_s + (T_0 - T_s) \exp\left(-\frac{UA}{mC_p} t\right)
\]

In this experiment 400.00 g of distilled water at 361 K \( (T_0) \) was injected into the reaction vessel, and the system temperature was left to fall over a period of time until the temperature–time profile reached its asymptotic state or the steady-state temperature \( (T_s) \). Figure 2 below shows the temperature–time profile of the cooling process.

From eq 22, the values of \( T_0 \) and \( T_s \) were obtained from Figure 2. Rearrangement of eq 22 gives

\[
\ln\left(\frac{T - T_s}{T_0 - T_s}\right) = \ln(\beta) = \left(-\frac{UA}{mC_p}\right) t
\]

Since \( T \) and \( t \) values are known, least-squares regression analysis was performed, and a straight plot of \( \ln(\beta) \) against time is shown in Figure 3.

The slope of the straight line of Figure 3 is given by 0.0013 \( (\text{min}^{-1}) \) which corresponds to the value of the heat transfer coefficient of the flask.

**DETERMINATION OF HEAT TRANSFER COEFFICIENT OF THE PROCESS**

For a given system (reaction vessel and content), one can write:

\[
\left(\frac{mC_p}{UA}\right)_{\text{system}} = \left(\frac{mC_p}{UA}\right)_{\text{water}} + \left(\frac{mC_p}{UA}\right)_{\text{vessel}}
\]

In this experiment different amounts of water \( (m_w) \) (200 g, 300 g, and 400 g) were injected into the reaction flask at 343.08 K, 347.77 K, and 347.85 K and allowed to cool until the temperature reached its asymptotic state or the steady-state temperature.

![Figure 4](image URL)
Figure 5. (a) Thermos-flask cooling curve $T(0) = 347.77$ K. (b) Regression line of heat transfer coefficient of reactor.

Figure 6. (a) Thermos-flask cooling curve $T(0) = 347.80$ K. (b) Regression line of heat transfer coefficient of reactor.
reaches a steady-state temperature ($T_s$). Figures 4a, 5a, and 6a of the cooling processes are shown below. The cooling process thus follows eq 22 above. A nonlinear least-squares regression analysis was performed on all the three experimental curves. Using eq 21, the value of $UA/mC_p$ for each cooling curve was obtained. Figures 4b, 5b, and 6b show the regression lines.

From Table 1, a plot of mass of water ($m$) against ($mC_p/UA$) is shown in Figure 7.

#### Table 1. Summary of the Characteristics of Figures 4–6

<table>
<thead>
<tr>
<th>mass of water (g)</th>
<th>initial temperature (K)</th>
<th>final temperature (K)</th>
<th>$UA/mC_p$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>343.08</td>
<td>292.13</td>
<td>0.00215</td>
</tr>
<tr>
<td>300</td>
<td>347.77</td>
<td>293.00</td>
<td>0.00189</td>
</tr>
<tr>
<td>400</td>
<td>347.84</td>
<td>293.38</td>
<td>0.00178</td>
</tr>
</tbody>
</table>

#### DETERMINATION OF $UA/mC_p$ FOR THE REACTION MIXTURE

Table 2 consists of some of the physical constants of the reacting species which were used in the determination of the quantity $UA/mC_p$.

Equation 25 was used to determine specific heat of the reacting mixture ($C_{p,mix}$) and the quantity $M_T C_{p,mix}$.

$$\frac{C_{p,mix}}{M_T} = \frac{m_{AA} C_{p,AA}}{M_T} + \frac{m_{AL} C_{p,W}}{M_T}$$  \hspace{1cm} (25)

$M_T$ is the total mass of the reacting mixture and $M_T C_{p,mix}$. Since the reaction is not pure water, we therefore determined its equivalent mass of water using eq 26 below.

$$m_{eqv,water} = \frac{(M_T C_{p})_{mix}}{C_{p,water}}$$  \hspace{1cm} (26)

From Figure 7 the value of the quantity ($UA/mC_p$)$_{mix}$ was determined to be 0.0025/min.

#### EXPERIMENTAL PROCEDURES AND RESULTS

**Acetic Acid–Ethanol Reactions.** These liquid phase esterification reactions have the general reaction model given by
Analytical reagent grade acetic acid was used in all the experiments. In all experiments about 1.0 mol of acetic acid was poured into the reaction vessel followed by 1.0 mol of the ethanol. A total of 10 mL of 98% concentrated sulphuric acid (18 M) of density 1.84 g/cm³ was added to the reactant mixture as a catalyst to initiate the reaction. These volumes were used so that at least 60% of the length of the sensor (thermistor) would be submerged in the resulting mixture. Reactants were brought to a steady-state temperature before starting the stirrer. In the course of the reaction the stirrer speed was set 100 rev/min, and the resulting voltage–time profiles were captured as described above and the corresponding temperature–time curve was determined using the thermistor equation derived in eq 21 above. Runs were carried out adiabatically at the following initial temperatures: 283 K, 289 K, and 298 K. The temperature–time profiles of the above experiments are shown in Figures 8, 9, and 10.

Acetic Acid–Propanol Reactions. These liquid phase esterification reactions have a general reaction model given by

$$\text{CH}_3\text{COOH}_{(aq)} + \text{CH}_3\text{CH}_2\text{OH}_{(aq)} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3\text{COOCH}_3_{(aq)} + \text{H}_2\text{O}$$

$\Delta H_{\text{f.o.}}(298 \text{ K}) = -6.12 \text{ kJ/mol}$

was poured into the reaction vessel followed by 1.0 mol of the propanol. A total of 10 mL of 98% concentration sulphuric acid (18 M) of density 1.84 g/cm³ was added to the reactant mixture as a catalyst to initiate the reaction. These volumes were used so that at least 60% of the length of the sensor (thermistor) would be submerged in the resulting mixture. Reactants were brought to a steady-state temperature before starting the stirrer. During the course of the reaction the stirrer speed was set 100 rev/min, and the resulting voltage–time profiles were captured as described above and the corresponding temperature–time curve was determined using the thermistor equation derive in eq 21 above. Runs were carried out adiabatically at the following initial temperatures: 285 K, 290 K, and 298 K. The temperature–time profiles of the above experiments are shown in Figures 11, 12, and 13.

**ANALYSIS OF EXPERIMENTAL RESULTS**

Consider model eqs 16–18 as stated below:

$$\int \Delta H_2 \sqrt{K_{\text{eq}}^2} \exp \left( \frac{\Delta H_2}{2R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right) \, dt = mC_p(T - T_{\text{amb}})$$

$$1 + \sqrt{K_{\text{eq}}^2} \exp \left( \frac{H_2}{2R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right) + UA \int_0^\infty (T - T_{\text{amb}}) \, dt = 0$$

(27)
Let \((T - T_{\text{amb}}) \cdot \frac{UA}{mc_p} \int_0^\infty (T - T_{\text{amb}}) \, dt = \alpha\) and
\[
\frac{1}{2R} \left( \frac{1}{T_0} - \frac{1}{T} \right) = \beta
\]  

Eq 16 can be simplified as
\[
(\Delta H_t) \sqrt{K_{eq}^\circ} \exp((\Delta H_t)\beta) \quad + \quad \text{amC}_p = 0
\]

Equation 29 has two unknown quantities \((\Delta H_t)\) and \(K_{eq}^\circ\). If one can determine \(\alpha\) and \(\beta\), using the experimental results, then the two unknown thermodynamic quantities can be determined for the process and eq 7 can be established for the esterification process.

**MODEL SOLUTION**

At a given temperatures \((T_1)\) and \((T_2)\) from experimental results, corresponding \((\alpha_1), (\beta_1)\) and \((\alpha_2), (\beta_2)\) can be determined from the experimental data for a given \((T_0)\). Then one can modify eq 18 as follows:

\[
(\Delta H_t) \sqrt{K_{eq}^\circ} \exp((\Delta H_t)\beta_1) + \alpha_1 mC_p + \sqrt{K_{eq}^\circ} \exp(\Delta H_t\beta_1)\alpha_1 mC_p = 0
\]

Similarly for a given \((T_2)\), one can write
\[
(\Delta H_t) \sqrt{K_{eq}^\circ} \exp((\Delta H_t)\beta_2) + \alpha_2 mC_p + \sqrt{K_{eq}^\circ} \exp(\Delta H_t\beta_2)\alpha_2 mC_p = 0
\]
For \((T_1)\) and \((T_2)\), at a given \((T_0)\), eliminating \((K^o_{eq})^{1/2}\) using eqs 30 and 31, one can write eq 32 as follows:

\[
-\alpha_1(\Delta H_t)\exp\left[\left(\frac{\Delta H_t}{\beta_1}\right)T_1\right] + \alpha_2(\Delta H_t)\exp\left[\left(\frac{\Delta H_t}{\beta_2}\right)T_2\right]
- \alpha_3\alpha_4mC_p\exp\left[\left(\frac{\Delta H_t}{\beta_3}\right)T_1\right] + \alpha_5\alpha_6mC_p\exp\left[\left(\frac{\Delta H_t}{\beta_5}\right)T_2\right] = 0
\]

Similarly, for a given \((T_1)\) and \((T_3)\), at a given \((T_0)\), one can also write eq 33 as follows:

\[
-\alpha_1(\Delta H_t)\exp\left[\left(\frac{\Delta H_t}{\beta_1}\right)T_1\right] + \alpha_3(\Delta H_t)\exp\left[\left(\frac{\Delta H_t}{\beta_3}\right)T_3\right]
- \alpha_4\alpha_5mC_p\exp\left[\left(\frac{\Delta H_t}{\beta_4}\right)T_1\right] + \alpha_6\alpha_7mC_p\exp\left[\left(\frac{\Delta H_t}{\beta_6}\right)T_3\right] = 0
\]

Hence, for a given \((T_2)\) and \((T_3)\), at a given \((T_0)\), one can also write eq 34 as follows:

\[
-\alpha_2(\Delta H_t)\exp\left[\left(\frac{\Delta H_t}{\beta_2}\right)T_2\right] + \alpha_3(\Delta H_t)\exp\left[\left(\frac{\Delta H_t}{\beta_3}\right)T_3\right]
- \alpha_4\alpha_5mC_p\exp\left[\left(\frac{\Delta H_t}{\beta_4}\right)T_2\right] + \alpha_6\alpha_7mC_p\exp\left[\left(\frac{\Delta H_t}{\beta_6}\right)T_3\right] = 0
\]

By selecting temperatures \((T_1, T_2, \text{and} T_3)\) as maximum temperatures for the processes, Tables 3 and 4 below were developed which consist of parameters deduced from the experimental results which were used in solving for \((\Delta H_{eq})\) in eqs 32–34 for the two processes. The \((\alpha)\) and \((\beta)\) values were obtained using eq 17.

![Figure 13. Acetic acid–propanol reaction: temperature–time profile at 297.8 K.](image)

### Table 3. Parameters for Ethyl Acetate Process

| experiment \((n)\) | \(T_0\) (K) | \(T_n\) (K) | \(\alpha\) | \(\beta\)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>283.3</td>
<td>293.7</td>
<td>14.639</td>
<td>0.000097731</td>
</tr>
<tr>
<td>2</td>
<td>288.7</td>
<td>297.7</td>
<td>13.559</td>
<td>0.00006107</td>
</tr>
<tr>
<td>3</td>
<td>295.6</td>
<td>299.8</td>
<td>9.836</td>
<td>0.0000285</td>
</tr>
</tbody>
</table>

### Table 4. Parameters for propyl acetate process

| experiment \((n)\) | \(T_0\) (K) | \(T_n\) (K) | \(\alpha\) | \(\beta\)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>285.1</td>
<td>294.2</td>
<td>15.940</td>
<td>0.00006524</td>
</tr>
<tr>
<td>2</td>
<td>290.4</td>
<td>296.0</td>
<td>15.510</td>
<td>0.00003917</td>
</tr>
<tr>
<td>3</td>
<td>297.8</td>
<td>300.0</td>
<td>9.764</td>
<td>0.0000148</td>
</tr>
</tbody>
</table>

Solving for \((\Delta H_{eq})\) using eqs 32–34 combinations \([T_1–T_2], [T_1–T_3], \text{and} [T_2–T_3]\), the following values obtained for the two processes are shown in Tables 5 and 6 below.

### Table 5. Heats of Reaction for the Ethyl Acetate Process

<table>
<thead>
<tr>
<th>combination</th>
<th>([T_1–T_2])</th>
<th>([T_1–T_3])</th>
<th>([T_2–T_3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat of reaction (J/mol)</td>
<td>(4.01 \times 10^1)</td>
<td>(8.15 \times 10^1)</td>
<td>(9.85 \times 10^1)</td>
</tr>
</tbody>
</table>

### Table 6. Heats of Reaction for the Propyl Acetate Process

<table>
<thead>
<tr>
<th>combination</th>
<th>([T_1–T_2])</th>
<th>([T_1–T_3])</th>
<th>([T_2–T_3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat of reaction (J/mol)</td>
<td>(1.90 \times 10^1)</td>
<td>(1.11 \times 10^1)</td>
<td>(9.97 \times 10^1)</td>
</tr>
</tbody>
</table>

By modifying eqs 30 or 31, the equilibrium constant \((K^o)\) values of the various temperature combinations were computed. Tables 7 and 8 show the equilibrium constant values for the two processes.

### Table 7. Equilibrium Constants \((K^o)\) for the Ethyl Acetate Process

<table>
<thead>
<tr>
<th>combination</th>
<th>([T_1–T_2])</th>
<th>([T_1–T_3])</th>
<th>([T_2–T_3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>equilibrium constant ((K^o_{eq}))</td>
<td>1.209</td>
<td>0.0018</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

### Table 8. Equilibrium Constants \((K^o)\) for the Propyl Acetate Process

<table>
<thead>
<tr>
<th>combination</th>
<th>([T_1–T_2])</th>
<th>([T_1–T_3])</th>
<th>([T_2–T_3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>equilibrium constant ((K^o_{eq}))</td>
<td>0.00033</td>
<td>0.1567</td>
<td>0.0024</td>
</tr>
</tbody>
</table>

From the values in Table 9 and with the help of eq 7 above, the equilibrium values can then be estimated at temperature ranges within which \((\Delta H_{eq})\) and \(K^o_{eq}\) values were evaluated.

### Table 9. Mean Values of the Heat of Reaction \((\Delta H_t)\) and the Equilibrium Constants \((K^o_{eq})\) of the Two Processes

<table>
<thead>
<tr>
<th>process</th>
<th>((\Delta H_{eq}))</th>
<th>((K^o_{eq}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl acetate</td>
<td>(7.343 \times 10^4)</td>
<td>0.404</td>
</tr>
<tr>
<td>propyl acetate</td>
<td>(9.93 \times 10^4)</td>
<td>0.053</td>
</tr>
</tbody>
</table>

#### CONCLUSIONS

A new technique has been proposed and demonstrated for the determination of thermodynamic quantities (heats of reaction and equilibrium constants) for exothermic reversible processes.
by utilizing experimental temperature–time information under adiabatic conditions. The proposed method used simple algebraic equations and does not involve derivatives of any function(s). Although the demonstration did not cover higher temperatures, it is possible to apply the method to estimate heats of reactions and equilibrium constants at higher temperatures.

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Notes

The authors declare no competing financial interest.

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■ LIST OF SYMBOLS

\( \Delta H_{\text{rxn}} \) = heat of reaction (KJ/mol)
\( B, C \) = thermistor constants
\( C_A \) = concentration of A (mol/L)
\( C_p \) = specific heat capacity (KJ/(mol-K))
\( C_{p,AA} \) = specific heat capacity of acetic anhydride (KJ/(mol-K))
\( C_{p,mix} \) = constant heat capacity of reaction mixture (KJ/(mol-K))
\( C_{p,W} \) = specific heat capacity of water (KJ/(mol-K))
\( K^\circ_{\text{eqm}} \) = equilibrium constant
\( m \) = mass (g)
\( M_{AA} \) = mass of acetic anhydride (g)
\( M_{AL} \) = mass of alcohol (g)
\( M_{eqv} \) = equivalent amount of water (g)
\( N_A \) = mole of A (mol)
\( R \) = molar gas constant (J/(mol-k))
\( -r_A \) = rate of reaction of (A) (mol/L·s)
\( R_{\text{TH}} \) = thermistor resistance (ohm)
\( t \) = time (min)
\( T_{\text{amb}} \) = ambient temperature (K)
\( T_{\text{max}} \) = maximum temperature (K)
\( T_0 \) = initial temperature (K)
\( T_r \) = reactor temperature (K)
\( T_s \) = steady state temperature (K)
\( U \) = heat transfer coefficient (J/(m²·s·K))
\( V \) = volume of vessel (mL)
\( x \) = equilibrium conversion
\( \alpha, \beta \) = constants

■ REFERENCES