

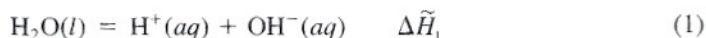
**GENERAL READING**

- J. L. Oscarson and P. A. Izatt, "Calorimetry," in B. W. Rossiter and R. C. Baetzold (eds.), *Physical Methods of Chemistry*, 2d ed., Vol. VI, chap. 7, Wiley-Interscience, New York (1992).
- L. Pauling, *Nature of the Chemical Bond*, 3d ed. Cornell Univ. Press, Ithaca, NY (1960).

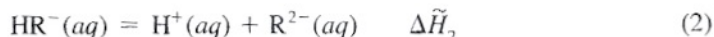
## EXPERIMENT 8

### Heats of Ionic Reaction

It is desired in this experiment to determine the heat of ionization of water:



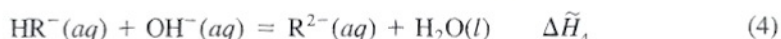
and the heat of the second ionization of malonic acid ( $\text{HOOC}-\text{CH}_2-\text{COOH}$ , hereinafter designated  $\text{H}_2\text{R}$ ):



These will be obtained by studying experimentally with a solution calorimeter the heat of reaction of an aqueous HCl solution with an aqueous NaOH solution, for which the ionic reaction is



and that of the reaction of an aqueous NaHR solution with an aqueous NaOH solution,



The last two equations can be written in the general form



where A represents the acid ion and B the basic ion.

**THEORY**

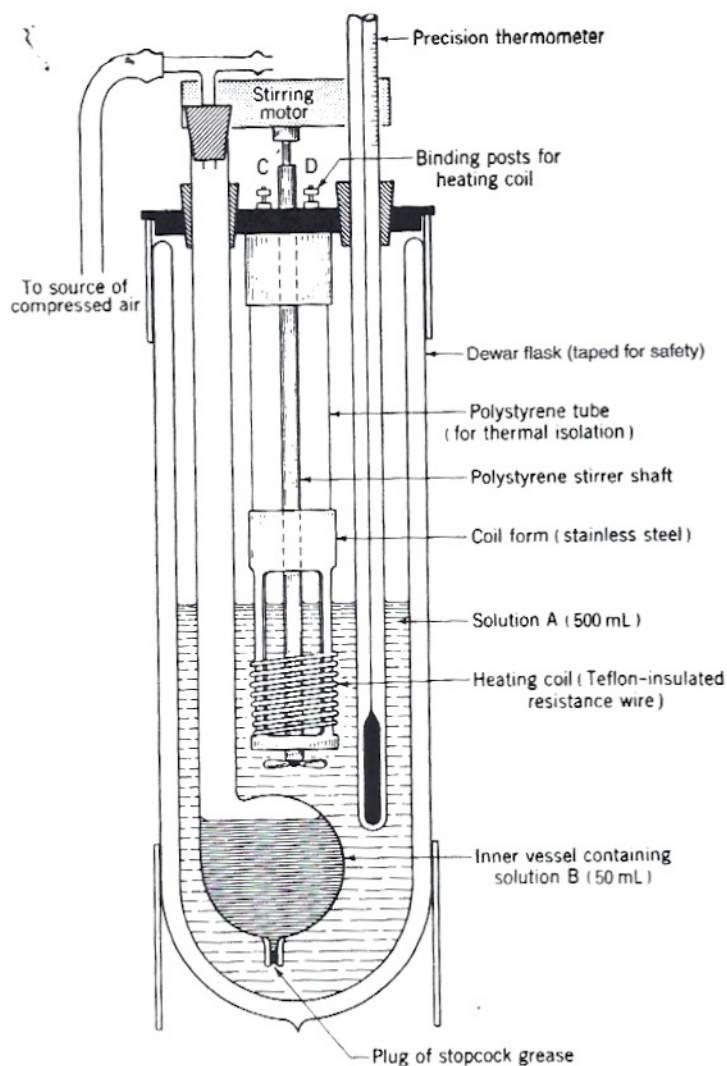
A general discussion of calorimetric measurements is presented in the section, Principles of Calorimetry, which should be reviewed in connection with this experiment. We shall not consider here the concentration dependence of these enthalpy changes. Such concentration dependence is generally a small effect, since the heats of dilution involved are usually much smaller than the heats of chemical reaction (indeed they are zero for perfect solutions). Since we are dealing here with solutions of moderate concentration, particularly in the case of the NaOH solution, it may be useful to make parallel determinations of heats of dilution of the solutions concerned by a procedure similar to that described here if time permits.

**EXPERIMENTAL**

In this experiment 500 mL of solution A, with a precisely known concentration in the neighborhood of 0.25 M, is reacted with 50 mL of solution B at a concentration sufficient to provide a slight excess over the amount required to react with solution A. The reaction is carried out in the solution calorimeter shown in Fig. 1. The calorimeter is a vacuum Dewar

**FIGURE 1**

Solution calorimeter. The precision mercury thermometer can be replaced by a high-resolution resistance thermometer or a calibrated thermistor.



flask containing a motor-driven stirrer, a heating coil of precisely known electrical resistance, and a precision thermometer. Various methods of mixing the two solutions might be employed; here we use an inner vessel having an outlet hole plugged by stopcock grease, which can be blown out by applying air pressure at the top.

For determining the heat capacity, a dc electric current of about 1.5 A is passed through a heating coil of  $\sim 6\Omega$  resistance during a known time interval. The magnitude of the current is measured as a function of time by determining the potential difference developed across a standard resistance in series with the coil. The electrical circuit is shown in Fig. 2.

It is recommended that two complete runs be made with HCl and NaOH and two with NaHR and NaOH.

**Procedure.** It is advisable to carry out a test of the electrical heating procedure in advance of the actual runs. This will also provide a chance to check on the heating-coil resistance  $R_h$  under actual operating conditions (i.e., when the coil is hot). Place roughly



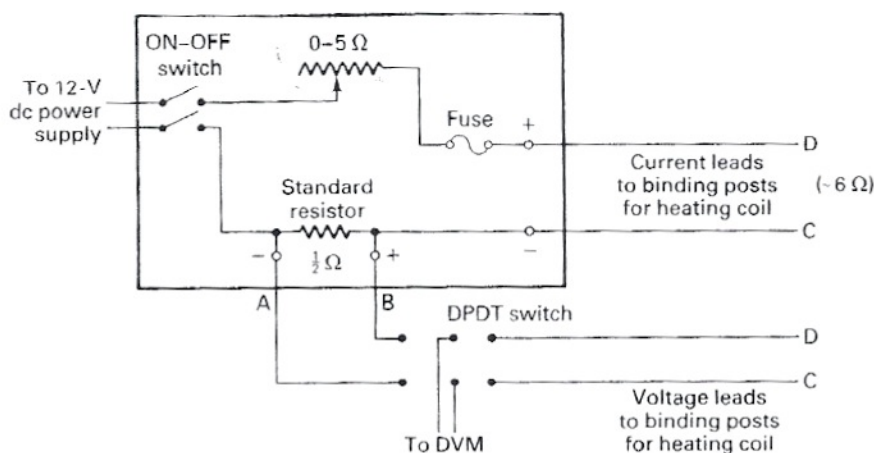


FIGURE 2

Electrical heating circuit for solution calorimeter. The standard resistor should be a wire-wound resistor with a low temperature coefficient and rated for 2 W. If a heating coil of higher resistance (say,  $\sim 60\Omega$  is to be used, the current can be reduced to  $\sim 0.5$  A and a 1- $\Omega$  standard resistor can be used.

550 mL of water in the calorimeter and introduce the stirrer-heater unit and thermometer. Make the electrical connections as shown in Fig. 2. Turn on the stirring motor and then turn on the current to the heater; **never** pass current through the heating coil when it is not immersed in a liquid, as it will overheat and may burn out. Measure the potential difference  $V_h$  across the heating coil by throwing the DPDT (double-pole, double-throw) switch to the right; i.e., measure the voltage drop between binding posts C and D on the stirrer-heater unit (see Fig. 1). Then measure  $V_s$  across the standard resistor in series with the heater by throwing the DPDT switch to the left; i.e., measure the voltage drop between A and B on the heater supply unit. The heater resistance can then be calculated from the known value of  $R_s$  and the measured ratio  $V_h/V_s$ . Also note the rate of temperature rise during heating. All of these observations will be useful during the actual runs.

Voltage measurements are best made with a good-quality digital voltmeter (DVM) having a high impedance. Such a meter, which can be read easily and rapidly, will facilitate measurements during the actual heating runs. Voltage measurements can also be made with a potentiometer; see Chapter XVI for a description of both digital multimeters and potentiometers. Either of two alternate procedures can be used to determine the electrical work dissipated inside the calorimeter during a heating run: (a) measure both  $V_h$  and  $V_s$  as a function of time and use Eq. (VI-9a); or (b) measure only  $V_h$  as a function of time, assume that  $R_h$  is constant with the value determined above, and use Eq. (VI-9b). If a DVM is used, procedure (a) is recommended. If a potentiometer is used, procedure (b) is preferable since potentiometer readings are somewhat time-consuming and, furthermore, a high-resistance potential divider would be needed in order to measure  $V_h$ . In this case, the value of  $R_h$  will be provided by the instructor.

Fill a 500-mL volumetric flask with solution A, the temperature of which should be within a few tenths of a degree of  $25.0^\circ\text{C}$ . (Adjust the temperature by swirling under running hot or cold water before the flask has been entirely filled, then make up to the mark.) Pour the solution into the clean and reasonably dry calorimeter and allow the flask to drain for a minute. Work a plug of stopcock grease into the capillary hole in the bottom of the inner vessel. The glass must be absolutely dry, or the grease will not stick. Pipette in 50 mL of solution B. Place the inner vessel in the calorimeter carefully.

Introduce the stirrer-heater unit and thermometer into the calorimeter, making sure that the thermometer bulb (or any other temperature sensor) is completely immersed (level with or just below the heating coil). The inner vessel should be held in a hole in the calorimeter cover by a split stopper so that it does not rest on the bottom of the Dewar flask.

Check the electrical connections to the heating coil. Connect the T tube to a compressed-air supply; turn on the air, adjust to a barely audible flow, and attach the T tube to the top of the inner vessel. Turn on the stirring motor.

Start temperature-time measurements. Read the thermometer every 30 s, estimating to thousandths of a degree if feasible. Tap the thermometer stem *gently* before each reading. After a slight but steady rate of temperature change due to stirring and heat leak has been observed for 5 min, initiate the reaction by blowing the contents of the inner vessel into the surrounding solution. This is done by placing a finger over the open end of the T tube. Release the pressure as soon as bubbling is heard. Record the time. After 15 s, blow out the inner vessel again to ensure thermal equilibrium throughout all the solution.

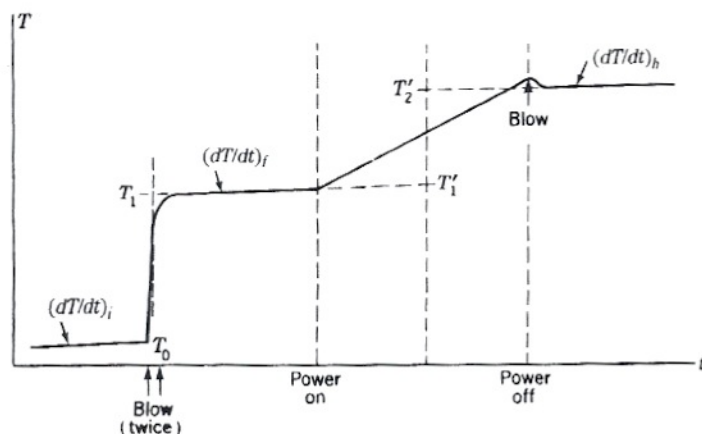
After a plateau with a slight, steady rate of temperature change has prevailed for 5 min, turn on the current to the heater and *record the exact time*. Immediately measure the potential difference across the standard resistor in series with the heater. Continue to make voltage measurements approximately every 30 s, alternating between readings of  $V_s$  and  $V_h$  (or readings of  $V_s$  at least once every minute if a potentiometer is being used, in which case the potentiometer should be standardized and set at the expected potential before the current is turned on). Note the time at which each voltage reading is taken.

When a temperature rise of about  $1.5^\circ\text{C}$  has been obtained by electrical heating, turn off the current, again noting the exact time. Simultaneously blow out the inner vessel again to mix the contents with the surrounding solution. After a final plateau with a slight, steady rate of temperature change has been achieved for about 7 min, the run may be terminated.

### CALCULATIONS

For each run, plot temperature versus time using a greatly expanded temperature scale with an interrupted temperature axis (see Fig. VI-1*b*). Determine the drift rates  $(dT/dt)_i$  and  $(dT/dt)_f$  before and after the chemical reaction took place and the rate  $(dT/dt)_h$  after electrical heating was completed. Carry out appropriate extrapolations to determine the temperature differences  $(T_1 - T_0)$  and  $(T'_2 - T'_1)$  shown in Fig. 3. In the case of  $(T_1 - T_0)$  associated with the adiabatic reaction, use the method described in the section Principles of Calorimetry and illustrated in Fig. VI-3*b*. If  $(dT/dt)_f$  and  $(dT/dt)_h$  have reasonably

**FIGURE 3**  
Schematic plot of temperature versus time: heat of ionic reaction.





similar values, one can simplify the determination of  $(T_2' - T_1')$  by choosing  $t_d$  as the midpoint of the electrical heating period as illustrated in Fig. 3.

The heat capacity is determined from Eqs. (VI-9) and (VI-13a). The integral in either Eq. (VI-9a) or (VI-9b) should be evaluated graphically unless the integrand is essentially constant during the heating period. The enthalpy change of the ionic reaction is calculated from Eq. (VI-12a). Calculate the number of moles of reaction from the number of moles of A (the limiting reactant) present and calculate the molar enthalpy change  $\Delta\tilde{H}_3$  or  $\Delta\tilde{H}_4$ .

From the average values of  $\Delta\tilde{H}_3$  and  $\Delta\tilde{H}_4$  obtained above, calculate  $\Delta\tilde{H}_1$  and  $\Delta\tilde{H}_2$ .

## DISCUSSION

Using literature data for the appropriate heats of formation,<sup>1</sup> estimate the difference between the  $\Delta\tilde{H}_3$  value for the concentrations employed in this experiment and the value that would apply at infinite dilution. Compare this effect with a qualitative estimate of the experimental uncertainty in the measured  $\Delta\tilde{H}_3$ . Indicate why there should be a large percentage error in  $\Delta\tilde{H}_4$  as determined here.

## SAFETY ISSUES

Use a pipetting bulb; do not pipette by mouth.

## APPARATUS

Solution calorimeter (1-L Dewar); stirrer-heater unit complete with motor and power cord; inner vessel; precision calorimeter thermometer covering range from 19 to 35°C with magnifying thermometer reader (can be replaced by either a resistance thermometer or a calibrated thermistor with a resolution of  $\pm 0.003^\circ\text{C}$ ); 0 to 30°C thermometer; two split rubber stoppers; glass T tube with stopper and rubber tubing; timer; dc power-supply unit for heater (see Fig. 2); double-pole, double-throw switch; digital multimeter or potentiometer setup (see Chapter XVI); 15 electrical leads with lugs attached; 250-mL beaker; 500-mL volumetric flask; 50-mL pipette; 100-mL beaker; rubber pipetting bulb.

**Solutions.** NaOH, concentration slightly greater than 2.5 M (0.4 L); 0.25 M HCl (1.5 L); 0.25 M  $\text{NaHC}_3\text{H}_2\text{O}_4$  (1.5 L; the sodium acid malonate solution can be prepared by neutralizing malonic acid with sodium hydroxide to a point just past the  $\text{NaHC}_3\text{H}_2\text{O}_4$  end point); stopcock grease; source of compressed air.

## REFERENCE

1. D. D. Wagman et al., "The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and  $\text{C}_1$  and  $\text{C}_2$  Organic Substances in SI Units," *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).

# EXPERIMENTS IN PHYSICAL CHEMISTRY

EIGHTH EDITION

---

CARL W. GARLAND

*Massachusetts Institute of Technology*

JOSEPH W. NIBLER

*Oregon State University*

DAVID P. SHOEMAKER

*(deceased)*

*Oregon State University*

 **McGraw-Hill**  
**Higher Education**

Boston Burr Ridge, IL Dubuque, IA New York San Francisco St. Louis  
Bangkok Bogotá Caracas Kuala Lumpur Lisbon London Madrid Mexico City  
Milan Montreal New Delhi Santiago Seoul Singapore Sydney Taipei Toronto



EXPERIMENTS IN PHYSICAL CHEMISTRY, EIGHTH EDITION

Published by McGraw-Hill, a business unit of The McGraw-Hill Companies, Inc., 1221 Avenue of the Americas, New York, NY 10020. Copyright © 2009 by The McGraw-Hill Companies, Inc. All rights reserved. Previous editions © 2003, 1996, 1989, 1981, 1974, 1967, 1962. No part of this publication may be reproduced or distributed in any form or by any means, or stored in a database or retrieval system, without the prior written consent of The McGraw-Hill Companies, Inc., including, but not limited to, in any network or other electronic storage or transmission, or broadcast for distance learning.

Some ancillaries, including electronic and print components, may not be available to customers outside the United States.

♻️ This book is printed on recycled, acid-free paper containing 10% postconsumer waste.

1 2 3 4 5 6 7 8 9 0 QPD/QPD 0 9 8

ISBN 978-0-07-282842-9  
MHID 0-07-282842-0

Publisher: *Thomas Timp*  
Senior Sponsoring Editor: *Tamara L. Hodge*  
Director of Development: *Kristine Tibbetts*  
Senior Developmental Editor: *Shirley R. Oberbroeckling*  
Marketing Manager: *Todd L. Turner*  
Senior Project Manager: *Kay J. Brimeyer*  
Senior Production Supervisor: *Kara Kudronowicz*  
Associate Design Coordinator: *Brenda A. Rolwes*  
Cover Designer: *Studio Montage, St. Louis, Missouri*  
Compositor: *Laserwords Private Limited*  
Typeface: *10/12 Times Roman*  
Printer: *Quebecor World Dubuque, IA*

Cover description: The figure depicts the absorption and emission spectra of CdSe nanocrystals, whose color is a sensitive function of size. The figure is based on spectral data provided by NN-Labs. The authors thank both NN-Labs and Evident Technologies for CdSe samples used in the development of the quantum dot experiment.

Library of Congress Cataloging-in-Publication Data

Garland, Carl W.  
Experiments in physical chemistry.—8th ed. / Carl W. Garland, Joseph W. Nibler, David P. Shoemaker.  
p. cm.  
Includes index.  
ISBN 978-0-07-282842-9—ISBN 0-07-282842-0 (hard copy : acid-free paper)  
I. Chemistry, Physical and theoretical—Laboratory manuals. I. Nibler, Joseph W.  
II. Shoemaker, David P. III. Title.  
QD457 .S56 2009  
541.078—dc22

2007043492