PHYSICAL METHODS of Organic Chemistry

SECOND EDITION

PART I

TECHNIQUE OF ORGANIC CHEMISTRY

Volume I — Part I

PHYSICAL METHODS of Organic Chemistry

Second Completely Revised and Augmented Edition

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PART ONE

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***Volume VII*. Organic Solvents (*Second Edition*).** A. Weissberger, E. S. Proskauer, and J. A. Riddick

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The chemist, in order to acquaint himself with a certain physical method, has in the past been compelled to search through periodicals and specialized books. The present work has been compiled with the hope of relieving him of much of this burden. It has been the object of the authors to provide a description of tested methods, the theoretical background for understanding and handling them, and the information necessary for a critical evaluation of the experimental results.

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CONTENTS

Part One

Part Two

CHAPTER I

TEMPERATURE MEASUREMENT

JULIAN M. STURTEVANT

Yale University

I. INTRODUCTION

Temperature measurement and, to a lesser extent, temperature control are fundamental to nearly all experimental work in the natural sciences.

Very few of the important attributes of material substances are even approximately independent of temperature, and this is particularly true of those properties which are of significance in organic chemistry.

Organic chemists until recent years were able to make truly remarkable progress in developing an understanding of the behavior of the compounds of carbon largely on the basis of essentially qualitative observations, and much further progress will undoubtedly be made using the well-tried methods of classical organic chemistry. However, in many branches of the subject it has become increasingly necessary to adopt more refined methods of observation in order to achieve continued progress. This extension of quantitative methods to organic chemistry nearly always involves an improvement in either temperature measurement or temperature control, or both. It is therefore a matter of some importance to organic chemists to be familiar with modern developments in these two fields, even though these developments may seem now to go beyond the needs of the moment in most phases of organic chemical work.

In the present chapter we discuss the principles and methods of temperature measurement. Particular attention is given to methods which are applicable in the relatively narrow temperature region where organic compounds are stable. Chapter II will be concerned with temperature control.

II. DEFINITION OF A TEMPERATURE SCALE[1]

1. International Temperature Scale

Temperatures in scientific work are expressed in terms of the International Temperature Scale, adopted in 1927 by the Seventh General Conference on Weights and Measures, and revised in 1948 by the Ninth General Conference. At the time of its adoption, this scale conformed to the thermodynamic scale as closely as possible in view of the experimental knowledge available at that time. The International Scale is defined by several fixed points, each point being given with a number of significant figures consistent with its reproducibility, and by means for interpolating between the fixed points.

A. FIXED POINTS

The basic fixed points of the International Temperature Scale are the temperatures of the following equilibria at a pressure of one standard atmosphere; (*a*) liquid and gaseous oxygen,[2] −182.97°. (*b*) ice and air-

[1] H. T. Wensel, in *Temperature, Its Measurement and Control in Science and Industry*. Reinhold, New York, 1941, p. 3.

[2] Unless otherwise specified, temperatures are given in centigrade degrees.

saturated water, 0.000°; (*c*) liquid water and steam, 100.00°; (*d*) liquid and gaseous sulfur, 444.60°; (*e*) solid and liquid silver, 960.8°; and (*f*) solid and liquid gold, 1063°.

B. INTERPOLATION

From the ice point to 630°, the temperature, t, is deduced from the resistance, R_t, of a standard platinum resistance thermometer by means of the formula:

$$R_t = R_0(1 + At + Bt^2) \tag{1}$$

The constants, R_0, A, and B, are determined by calibration at the ice, steam, and sulfur points. The purity and physical condition of the thermometer should be such that $R_{100}/R_0 > 1.3920$, and $4.2165 < (R_{444.6} - R_0)/(R_{100} - R_0) < 4.2180$.

From −183° to the ice point, the temperature is deduced from the resistance of a standard resistance thermometer by means of the formula:

$$R_t = R_0[1 + At + Bt^2 + C(t - 100)t^3] \tag{2}$$

where the constants are determined by calibration at the oxygen, ice, steam, and sulfur points.

From 630° to the gold point, interpolation is accomplished by means of a standard platinum *vs.* platinum–rhodium thermocouple, one junction of which is at 0°. Above the gold point, temperatures are defined in terms of Planck's radiation formula.

The chief value of the International Temperature Scale lies in the fact that its practically universal acceptance has removed the ambiguities formerly present in the specification of temperatures.

2. Secondary Temperature Standards

For many applications it is convenient to have reference temperatures more closely spaced than those provided by the International Temperature Scale. Temperatures defined by the equilibria between the liquid and solid forms of pure substances are usually preferable to those defined by the equilibria between the liquid and gaseous forms because of the difficulty of avoiding errors due to superheating and pressure effects in boiling-point determinations.

One of the best-defined and most reproducible secondary standard temperatures is the freezing point of benzoic acid. Schwab and Wichers[3] have shown that pure benzoic acid (supplied by the National Bureau of

[3] F. W. Schwab and E. Wichers, *J. Research Natl. Bur. Standards*, **34**, 333 (1945).