

A HANDBOOK OF  
**DECOMPOSITION  
METHODS  
IN ANALYTICAL  
CHEMISTRY**

Rudolf Bock  
translated by Iain L. Marr

# **A Handbook of Decomposition Methods in Analytical Chemistry**

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# Preface

THE GERMAN EDITION OF THIS BOOK APPEARED IN 1972, AND MANY IMPORTANT improvements in the field of decomposition methods have been made since then. Much of the stimulation for this work has been provided by the basic research of T. T. Gorsuch since 1959. The text has therefore been expanded considerably and several sections completely rewritten. The tables have been enlarged and new ones added. It is hoped that the reader will be able to use the information provided in the tables directly, without having to resort to the original publications. However, if necessary, more detailed information can be found from the extensive list of references.

I should like to thank Dr Iain Marr for his able translation of a complex German text, and for valuable additions of his own. Mr K. Beyermann has translated many Russian publications for me, and Mr H. Kürner and Mr B. Bernas have compiled information from various sources and provided descriptions of apparatus. The drawings were made by Mr W. Kelp with the help of Mrs I. Datz and Mr J. Möhner. All these people have contributed to the book, and I should like to express my gratitude. Finally, I wish to thank the authors and editors of journals who have permitted the reproduction of figures.

Appendices 1-3 are new compilations, for which many colleagues have generously supplied information from their specialized fields. Their names are given at the appropriate places, as there are too many to be mentioned here.

RUDOLF BOCK  
La Tour de Peilz

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# 1. Introduction

## 1.1 Definitions; Literature

By 'dissolution' one usually understands the dissolving of solid, liquid or gaseous substances in suitable liquids at low temperatures, with or without chemical reaction. By 'opening-out' one normally means decomposition at higher temperatures, under increased pressure if need be; when a decomposition is achieved in a molten flux, one uses only the expression 'to open out'. It is not possible to draw a clear distinction between the two terms as, for example, treatment of samples with hot concentrated sulphuric acid could be described both as dissolution and as opening-out.

There are very few comprehensive surveys of dissolution and opening-out procedures in the literature. Doležal *et al.* (1.1) have covered procedures for inorganic substances, while Gorsuch (1.2) and Grassmann (1.3) have dealt with organic substances. There are also accounts in some text-books on analytical chemistry (1.4). Harrison has surveyed the field of iron and steel analysis (1.4a).

## 1.2 The Technique of Opening-out

### 1.2.1 Opening-out by heating in a gas

Attack with a gas as reagent is achieved either in a closed vessel at normal pressures (e.g. in the oxygen flask as described by Hempel (1.5), (see section 5.1.4) or in a bomb under higher pressure (described by Berthelot (1.6), also in section 5.1.5), or in a stream of the gas, in which case the substance is usually contained in a small boat placed in a heated, horizontal tube. Decompositions in hydrogen fluoride vapour are discussed in section 4.2.1.

### 1.2.2 Dissolution and opening-out with liquids

Beakers or conical (Erlenmeyer) flasks are usually employed when the reagent selected is a liquid. When the initial reaction tends to froth or spit, long-necked pear-shaped flasks, called Kjeldahl flasks (1.7), tilted away from the vertical, are particularly advantageous. Troublesome and unpleasant vapours released during the reaction with acids can be satisfactorily

disposed of by fitting a glass bell over the flask and connecting it to a water suction pump (Figure 1.1).

Similar arrangements have been described for dealing with multi-sample decompositions in Kjeldahl flasks: up to six flasks are supported on a rack with their necks passing into openings in a slightly inclined glass manifold which is then connected to a water pump for removal of the vapours (1.8, 1.9).

More resistant substances can often be brought into solution at temperatures above the boiling point of the solvent, either in sealed glass tubes (1.10) or in small metal bombs with screw-fitting lids.

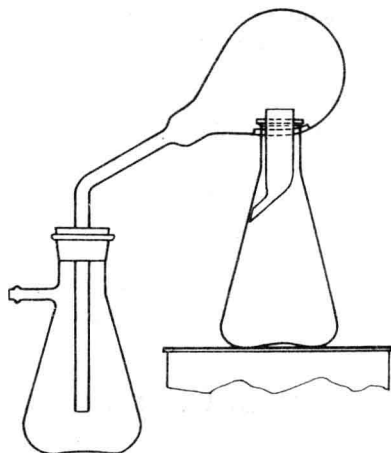


Figure 1.1 Apparatus for removal of fumes by suction during a wet-decomposition procedure  
(G. F. Smith, *Anal. Chim. Acta*, **8**, 397 (1953))

The use of sealed glass tubes goes back to Mitscherlich (1.11) and Carius (1.12). The sample and decomposition mixture are placed in a glass tube already sealed at one end to a rounded bottom of uniform thickness, and the other end is then drawn down in a flame and sealed off. The tube is then heated in an oven. It is important that there should be a sufficiently large free volume above the liquid as otherwise extremely high pressures may be reached. With two-component decomposition mixtures, such as nitric acid-water, the vapour pressure depends not only on the temperature and the composition, but also on the volume of the space over the liquid, since the composition of the remaining liquid phase depends on the amount which has been vaporized.

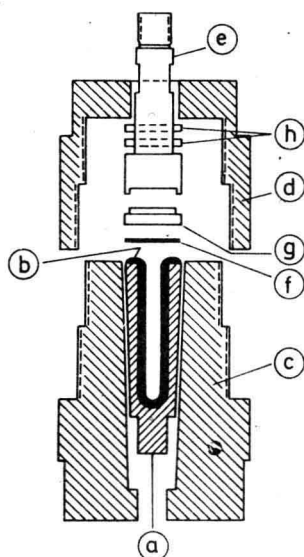


Figure 1.2 Platinum-lined crucible and bomb for decompositions with hydrofluoric acid

(E. May and J. J. Rowe, *Anal. Chim. Acta*, 33, 648 (1965))

(a) tapered nichrome crucible; (b) platinum liner; (c) Hasteloy body; (d) steel screw cap; (e) plunger; (f) copper washer; (g) platinum disc; (h) spacers

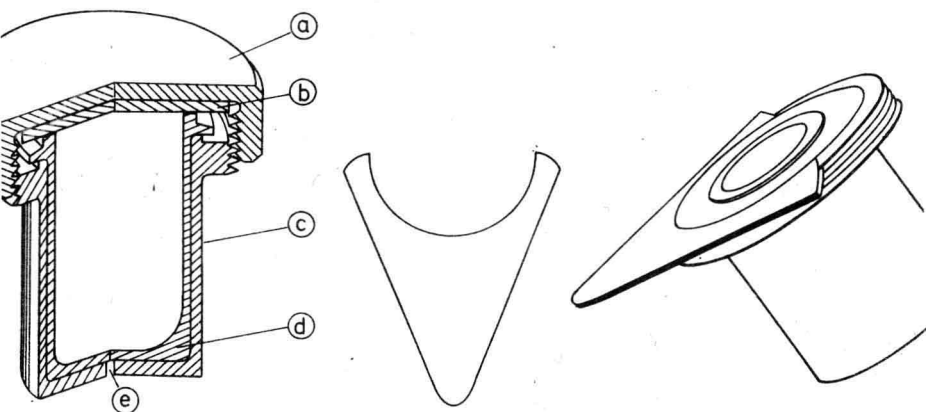


Figure 1.3 Steel bomb with polytetrafluoroethylene lining for decompositions with hydrofluoric acid

(B. Bernas, *Anal. Chem.*, 40, 1682 (1968)); NASA Tech. Brief 68-10104 (1968))

left: complete bomb, (a) screw-on lid; (b) gasket; (c) steel bomb; (d) polytetrafluoroethylene lining; (e) air-hole  
centre: pouring spout (polytetrafluoroethylene)  
right: pouring position

Opening-out mixtures in sealed glass tubes are as a rule only heated to 200-300°C, and occasionally as high as 400°C, because of the explosion risk, but as this risk can never be eliminated, the tubes are best placed in strong steel protective sheaths in a specially designed oven. After the tubes have been cooled down, they are opened by applying a very small flame to a spot on one side of the drawn-out section in order that any remaining positive

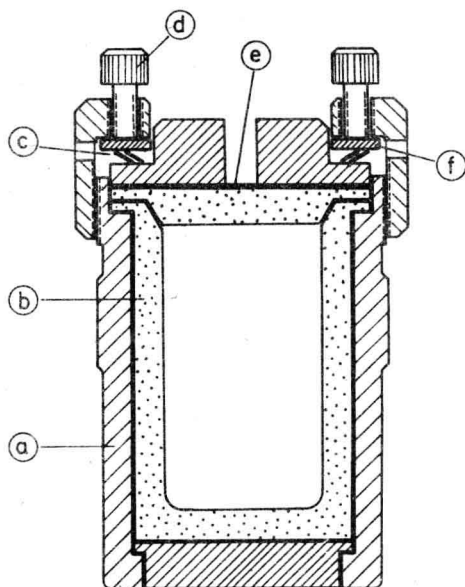


Figure 1.4 Bomb for pressure decompositions with acids  
(From Bulletin 4745 of Parr Instrument Co.)

(a) bomb body; (b) polytetrafluoroethylene cup with cover; (c) spring; (d) compression screw; (e) rupture disc; (f) compression ring

pressure may be vented conveniently and safely through the small hole resulting when the glass softens. The whole of the drawn-out part of the tube is then broken off after making a scratch with a glass-knife, and the contents are rinsed out of the tube. Details of the size and shape of the tubes are to be found in section 5.3.3.

Liebig suggested (1.13) that the risk of shattering could be lessened if the sealed glass tube were placed in a rather wider steel tube, the space between being partly filled with ether or petroleum ether, and the whole vessel bearing a gas-tight seal. On heating, a substantial pressure develops in the surrounding space which to some extent equalizes the internal pressure.

One attempt at avoiding the inconvenience of opening the sealed glass

tubes involved using a thick-walled end to the tube which was then ground flat and sealed with a gasket compressed against it (1.14). More recently, however, small steel bombs with screw caps containing a platinum or a polytetrafluoroethylene lining are generally preferred. The latter lining material is suitable for use up to about 250°C, though only up to 150°C or so if it is to be used repeatedly under compression. Platinum linings must be used for higher temperatures. Reaction times can be shortened by stirring the contents (1.15) (using an external magnet and internal follower) or by rotating the bomb itself (1.16). Figures 1.2 to 1.4 show some of the many variations which have been described in the literature.

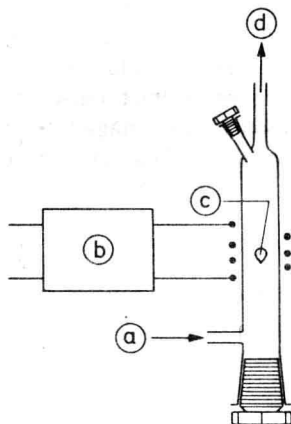


Figure 1.5 Levitation melting  
(G. Tölg, *Talanta*, 21, 327 (1974))  
(a) oxygen inlet; (b) H.F. generator; (c) sample; (d) gas outlet

Bomb decompositions offer the great advantage that many substances which are inert towards the usual reagents at lower temperatures may be attacked successfully at higher temperatures, and also an additional bonus in that the loss of volatile reaction products is avoided, unless of course there is an escape of gases when the bomb is opened after cooling. One should also consider the disadvantages which include the risk factor with sealed tubes, the generally inconvenient procedure, and the often rather serious attack by the reagents on the vessel, with the consequent introduction of contaminants into the sample solution.

### 1.2.3 Opening-out in melts

Decomposition in a melt is usually achieved in a small crucible, made from some material which offers as high a resistance as possible to the particular

flux being used. In order to minimize loss from the crucible it can be placed in a metal vessel fitted with a cold finger (Figure 1.9); occasionally melts are used in sealed glass tubes (Figure 6.4) or in screw-topped metal bombs (Figure 5.25).

Special forms have been designed for micro and ultramicro scales of working. One can carry out the decomposition in one drop of melt on a flat piece of platinum foil (1.17), on a platinum sling (1.18), or in a loop of platinum wire (1.19). Extremely small amounts of material have been opened out by attack in a melt supported in a 200  $\mu\text{m}$ -diameter hole in a sheet of platinum (1.20). One procedure which avoids the sample coming into contact with the container material employs a cooled aluminium support (1.21); this is coated with a layer of calcium oxide, which in turn supports the sample mixed with more calcium oxide. The sample can be heated to very high temperatures in a solar furnace. The so-called levitation melting (1.22) also eliminates contact between sample and container; metallic samples can be supported by a magnetic field and heated at the same time by radio-frequency induction heating (Figure 1.5).

## 1.3 Container Materials

Vessels for use in analytical work are constructed largely from borosilicate glasses or porcelain, and sometimes silica, alumina or other oxides, metals (mainly platinum but also silver, nickel, iron, gold, zirconium, etc.), graphite, and nowadays also a number of plastics.

### 1.3.1 Glass

Laboratory glass-ware is generally fabricated from borosilicate glasses of one sort or another, which all contain the highest possible silica content compatible with the production processes (see Table 1.1). The types known as Vycor (1.23) are prepared by leaching a two-phase solidified melt and sintering what is left (1.24). The resulting composition and properties are not very different from those of fused silica.

Jena apparatus glass G 20 (1.25) has a particularly high chemical resistance, but as its resistance to temperature changes is not so good it can only be used for thin-walled vessels. Duran glass (1.25) on the other hand can be used for thick-walled vessels, which offer greater mechanical strength, as its thermal expansion coefficient is lower. It is slightly less resistant to chemical attack than the G 20 glass. Pyrex glass has properties close to those of the G 20 glass (1.23).

Extensive investigations, following standardized procedures, have been carried out which make it possible to compare the chemical resistances of