WEBSITE DATA FOR CHAPTER 3

Sand Bath Techniques

The high sides of the crystallizing dish act to protect the apparatus from air drafts, and so the dish also operates somewhat as a hot-air bath. More uniform heating can be made by covering the crystallizing dish with aluminum foil (see Website Fig. 3.1W).

Website Figure 3.1W

Hot plate-magnetic stirrer with sand bath and reaction flask.
Metal Heat-Transfer Devices

A detailed report of the use of aluminum block systems including a number of designs has been made by Lodwig (see Lodwig, Siegfried N. J. Chem. Educ, 1989, 66, 77). Other metal systems, such as copper, have also been examined with rather promising results. To gain the advantages of both systems (sand and metal) the use of aluminum and zinc powders has been explored. Thirty-mesh zinc baths possess thermal characteristics very similar to solid aluminum blocks (see Website Fig. 3.2W).

Website Figure 3.2W

Temperature rise characteristics for several thermal devices.

Copper has nearly double the thermal conductivity of aluminum and the configuration found most attractive in this series is the **copper tube–plate device**. It requires relatively little copper, as it utilizes a 3-mm plate and 15-mm lengths of standard tubing (see Website Fig. 3.3W). The fabrication cost should be close to that of the aluminum block systems currently on the
market. As shown in Website Fig. 3.2W, compared to all other systems, the copper plate is far superior in temperature rise from room temperature. Thus, it is found at nearly 200 °C at the 5-min mark, whereas the aluminum block is barely above 100 °C at this time. It is also easier to achieve equilibrium conditions (see Website Fig. 3.4W).

An equilibrium temperature of 150 °C was reached in 9 min with copper, whereas it took 19 min with aluminum under the same conditions. The copper device also cools at nearly double the rate of the aluminum block. For example, to drop from 200 to 150 °C takes the aluminum block 8.1 min, whereas the copper system reaches the lower temperature in only 4.2 min. This characteristic is important in controlling temperature overruns.
Time to equilibrium (control set at high until the temperature reaches 85° C, then heat control adjusted to a lower setting to give 150° C at equilibrium).

A handy plot of bath temperatures versus hot plate settings for your particular hot plate system can be obtained by using a printout of Website figure 3.5W.
Plot your bath and/or vial temperature (°C) versus hot plate control setting (reference graph provided for student printout).

Of particular significance is the observation that when distilling or refluxing organic materials, the block temperatures for the copper device are measurably lower. For example, 1 mL of "p-xylene (bp 138 °C) contained in a 5-mL reaction vial refluxes at 175 °C in the copper bath. The aluminum block requires 188 °C under the same conditions and the sand bath ranks a distant third at 208 °C.

**Reflux Apparatus**

In microscale reactions, two basic types of reflux condensers are utilized: the air-cooled condenser, or air condenser (see Website Fig. 3.6W), and the water-jacketed condenser (see Website Fig. 3.7W).
Air condenser with conical vial, arranged for heating and magnetic stirring.
Water-jacketed condenser with 10-mL round-bottom flask, arranged for heating and magnetic stirring.

Distillation Apparatus

Reduced Pressure Distillation Systems

The high-performance low-cost atmospheric pressure 2.5-in. microspinning band distillation column has been modified to accommodate reduced pressure fractional distillation (see Website Fig. 3.8W) by: (a) replacing the
air condenser and suspended thermometer with a 14/10$, vacuum-tight, threaded thermometer adapter; (b) replacing the heavy-walled 3-mL conical collection vial with a thin-walled, 3-mL conical vial, which has, mounted near the bottom, a side arm with a threaded 5/5 $\varphi$ joint (a septum cap and silicone septum form a vacuum-tight seal on the side arm); and (c) a vacuum tubing
nipple replacing the Teflon stopper (7/10$\frac{3}{4}$) used to establish a vapor lock on the collection side of the system in the atmospheric still.

The system is evacuated via the vacuum tubing nipple. Fractions are efficiently collected with a gas-tight syringe and needle inserted through a septum mounted in the side arm of the 3-mL collection vial. The collection vial may be cooled externally during collection. This arrangement allows convenient collection of distillate fractions down to pressures of approximately 100 torr (successful collections have been made at pressures as low as 10 torr).

The system functions effectively under reduced pressure, even though the vapor lock present in the atmospheric still has been removed. Experimental data indicate that height equivalent/theoretical plate values remain near 0.25 in. per plate in these columns.

**Special Moisture Sensitivity Conditions**

In a few instances, reactions that are unusually moisture sensitive will be encountered. In this situation, reactions are best carried out in completely sealed systems that are scrupulously dry. The use of the Claisen head adapter with a balloon substituted for the drying tube provides a satisfactory solution to the problem (see Website Fig. 3.9W). Occasionally, it becomes
Sealed Claisen head with 3- or 5-mL conical vial, arranged for N₂ flushing, heating, and magnetic stirring.

Important to maintain dry conditions during a distillation. The Hickman stills are constructed with a 14/10$\text{f}$ joint at the top of the head that readily accepts the drying tube (or Claisen head plus drying tube, (see Website Fig. 3.10W).
Moisture-protected Hickman still head with 10-mL round-bottom flask, arranged for heating and magnetic stirring.

Collection of Gaseous Products

The collection, or trapping, of gases is conveniently carried out by using the capillary gas delivery tube. This item can be attached directly to the female 14/10$^\text{f}$ joint of a condenser connected to a reaction flask or vial (see Website Fig. 3.11W).
**Website Figure 3.11W**

Water-jacketed condenser with 3- or 5-mL conical vial and capillary gas delivery tube, arranged for heating and magnetic stirring.

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**Collection of Gas Chromatographic Effluents**

A number of the reaction products in the experimental section of the text depend on collection of gas chromatographic effluents for successful purification and isolation. The ease and efficiency of carrying out this operation is greatly facilitated by employing the 5/5$\frac{3}{4}$ collection tube and the 0.1-mL 5/5$\frac{3}{4}$ conical collection vial (see Website Fig. 3.12W).
Gas chromatographic collection tube and 0.1 mL conical vial.