value is probably reliable to within 1.0 e. u. in an absolute sense and to 0.5 e. u. for comparative purposes.

The molal entropy of the corresponding paraffin, 2,2-dimethylbutane, has been reported recently by Stull[4] as 64.4 (±1.8) e. u. Thus the paraffin–olefin difference here is apparently 3.1 e. u., which is a somewhat greater effect than that (2.2 e. u.) found by Parks, Todd and Shomate[5] in the case of 2,4,4-trimethylpentane and 2,4,4-trimethylpentene-1.

Free Energy of Dehydrogenation of 2,2-Dimethylbutane

The data are now available for the estimation of the free energy change in the dehydrogenation process

$$t\text{-butylethane (l)} \longrightarrow t\text{-butylethylene (l)} + H_2\text{ (g)}$$

For the gas-phase reaction Kistiakowsky and coworkers[1b] have found $\Delta H_{355} = 30{,}340$ (±60) cal. Reducing this value by 250 cal. for the temperature change from 355 to 298°K. and assuming that the heats of vaporization of the paraffin and olefin are practically the same, we now find $\Delta H_{298} = 30{,}090$ (±200) cal. In the preceding section we found the entropy difference between the liquid paraffin and olefin to be 3.1 e. u. and in view of the similarities in the extrapolations we now estimate the probable error in this figure as under 1.5 e. u. Accordingly, taking 31.23 e. u.[6] for the molal entropy of hydrogen, we have $\Delta S_{298} = 28.1$ (±1.5) e. u. Hence, $\Delta F^\circ_{298} = 30{,}090 - (298.1)(28.1) = 21{,}700$ (±500) cal. for the process in question.

This result is in good agreement with the figure 21,000 (±400) cal. reported by Parks, Todd and Shomate[5] for several other cases involving the dehydrogenation of paraffins to yield monosubstituted ethylenes.

(4) Stull, THIS JOURNAL, **59**, 2727 (1937).
(5) Parks, Todd and Shomate, *ibid.*, **58**, 2505 (1936).
(6) Giauque, *ibid.*, **52**, 4825 (1930).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIF.

RECEIVED APRIL 8, 1938

A Semi-Micro Sublimation Apparatus

BY C. M. MARBERG[1]

In the course of some work on the isolation and identification of lipoids undertaken in this Laboratory, it became necessary to submit certain fractions to high-vacuum sublimation. The theory, technique, and several designs of apparatus for this procedure are contained in an article by Hickman and Sandford.[2] The apparatus of Werner,[3] which utilizes a ground joint and a water-cooled condenser is useful only with minute quantities of material, which are condensed on a cover glass. When used with larger quantities of material, omitting the cover-glass, the sublimate may become contaminated with grease upon withdrawal of the condenser, due to accidentally touching the ground joint. Finally, when sealed to the high-vacuum line, it is necessary to break the apparatus loose after each time it is used. Carothers and Hill[4] devised a molecular still which overcame the possibility of contamination of the distillate with grease, by using a large, flat-ground joint. Their apparatus was improved by Strain and Allen[5] who simplified the heating arrangement, sealed the water-cooled condenser into the upper dome, and added a ground joint by means of which the apparatus could be attached to the high-vacuum line. Since we desired to cool our condenser below temperatures possible with water or circulating fluid, none of this apparatus, which utilizes water-cooled condensers, was suitable for our work.

The apparatus devised for our work,[6] shown in the accompanying diagram, has the advantages that (1) low temperatures may be used for the condensing surface, since the condenser may be cooled with carbon dioxide, liquid ammonia, or liquid air, (2) the ground joints, including the stopcock, are all interchangeable, and (3) the section carrying the stopcock can be sealed to the high-vacuum line (we use a mercury pump backed by a Cenco Hyvac) and may be left in place, since it does not come into contact with either the crude material or the sublimate.

A solution of the crude substance is placed in the unattached lower vessel, the design of which may be modified to suit the particular experiment and the solvent is evaporated on a water-bath or *in vacuo*, leaving the crude material in a ring in the bottom of the container. Then, after placing a light ring of grease along the upper edge of the

(1) The Otho S. A. Sprague Memorial Institute and the Department of Pathology, The University of Chicago.
(2) K. C. D. Hickman and C. R. Sandford, *J. Phys. Chem.*, **34**, 637 (1930).
(3) Othmar Werner, *Mikrochemie*, **1**, 33 (1923).
(4) W. H. Carothers and J. W. Hill, THIS JOURNAL, **54**, 1557 (1932).
(5) W. H. Strain and W. M. Allen, *Ind. Eng. Chem., Anal. Ed.*, **7**, 443 (1935).
(6) The Scientific Glass Apparatus Co., of Bloomfield, N. J., have satisfactorily made it for us.

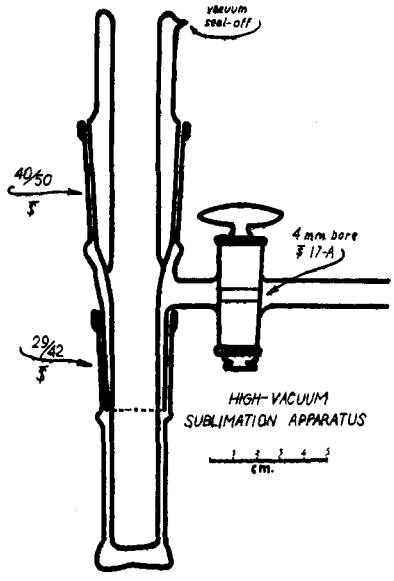

Fig 1.

ground joint, the cup is slipped into place. The condenser is similarly greased and inserted. After evacuation of the apparatus the refrigerant is added. Water may be used, if desired, by inserting a stopper carrying one long and one short tube, and passing the water through these tubes. We have found that any of the low-temperature refrigerants, including liquid nitrogen, has been satisfactory. The lower cup is warmed by insertion into a bath at the desired temperature, and sublimation proceeds. When the process is completed, the sublimate can be washed from the condenser with a few drops of solvent, and worked up in any way desired.

CHICAGO, ILLINOIS RECEIVED MARCH 12, 1938

The Effect of β-Aminopyridine in Experimental Blacktongue

BY Y. SUBBAROW, W. J. DANN AND E. MEILMAN

β-Aminopyridine was isolated from liver extracts by the following method.

Eight liters of solution (Cohn fraction D)[1] representing one ton of fresh liver was diluted to 20 liters with water and treated with 3 kg. of charcoal. The charcoal adsorbate was filtered and was eluted with hot 60% ethyl alcohol. The elute was concentrated to four liters. The concentrate was made strongly alkaline with potassium hydroxide and extracted three times with four liters of normal butyl alcohol each time.

The butyl alcohol was removed from the extract by vacuum distillation, and the residue was taken up with one liter of water. There was some insoluble residue which was discarded.

The clear solution was made strongly alkaline with potassium hydroxide and was extracted eight times with one liter of ether each time. The ether extract was dried with anhydrous potassium carbonate and concentrated to a sirup. The sirup was extracted with 500 cc. of hot benzene. The benzene extract was concentrated to a small volume (30–40 cc.) and dry petroleum ether was added till a precipitate began to appear. After standing at 0° for forty-eight hours, a crystalline precipitate was obtained.

The crystals were filtered, and recrystallized from hot benzene and dried over sulfuric acid; yield 150 mg. The analysis agreed with the formula $C_5H_6N_2$.

The substance was hygroscopic and melted at 65°. Synthetic β-aminopyridine melted at 64°. There was no depression of mixed melting point. It gave an intense diazo reaction and was partially precipitated with cuprous oxide. It reduced phenol reagent (Folin). A gold salt formed readily by the addition of gold chloride in the presence of dilute hydrochloric acid, of composition $C_5H_6N_2 \cdot HAuCl_4$, m. p. 218°. The substance gave a flavianate. The crystals were rectangular plates. They began to char at 212° and melted with decomposition and evolution of gas at 241°. The flavianate of synthetic β-aminopyridine behaved in the same way. The picrate melted at 188–190°. There was no depression of mixed melting point with β-aminopyridine picrate. With concentrated hydrochloric acid, the substance gave transparent plates: β-aminopyridine dihydrochloride, $C_5H_6N_2 \cdot 2HCl$, m. p. 175°.

Six adult dogs weighing, respectively, 9.15, 12.3, 7.75, 15.1, 11.2 and 11.0 kg. were housed in individual cages and fed on Goldberger's blacktongue-producing diet No. 123[2] modified by substituting a more complete salt mixture for the sodium chloride and calcium carbonate used in this diet. The dogs were allowed to develop blacktongue, as judged by inflammation and necrosis of the mucous membranes of the mouth and throat, excessive salivation, listlessness, loss of appetite and loss of weight. After the onset of acute blacktongue each was given daily doses of a solution of β-aminopyridine dihydrochloride in distilled water for five days; administration was by subcutaneous injection. The daily dose for each of the six dogs was 20, 20, 20, 20, 15 and 15 mg., respectively. The dihydrochloride contains 56.5% of the free base.

All the dogs quickly made complete recoveries, as shown by return of the mucous membranes to normal, cessation of the abnormal salivation, and restoration of appetite, body weight and normal activity.

The rapidity and completeness of cure were at least equal to the rapidity and completeness of cure of other dogs to which we have given 20 mg. of nicotinic acid daily for five days, showing that β-aminopyridine is, weight for weight, at least as active in curing blacktongue as nicotinic acid. Further experiments are in progress to determine whether smaller doses of β-aminopyridine will be completely effective in curing an attack of acute blacktongue, as there are indications from a preliminary trial that they may be.

(1) E. J. Cohn, G. R. Minot, G. A. Allen and W. T. Salter, *J. Biol. Chem.*, **77**, 331 (1928).

(2) J. Goldberger, G. A. Wheeler, R. D. Lillie and L. M. Rogers, *U. S. Pub. Health Rep.*, **41**, 297 (1926).