NOTES

Specific Heats of Acetaldehyde and Acetaldehyde Dibutyl Acetal

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In studying the reaction

$$CH_3CHO + 2C_4H_9OH{=}CH_3CH(OC_4H_9)_2 + H_2O$$

it was necessary to know the specific heats of the compounds involved at various temperatures. Although values for water[3] and *n*-butanol[4] can be found in the literature, no values for the specific heats of liquid acetaldehyde or of acetaldehyde dibutyl acetal could be found. Accordingly, the specific heats of the latter two compounds were measured on redistilled samples of acetaldehyde (boiling at 20° at 760 mm. of mercury) and of acetaldehyde dibutyl acetal (boiling at 90° at 30 mm.); the purity of the two compounds based on physical constants and chemical analysis was not less than 99 mole per cent.

A calorimeter, similar to that described in Weissberger,[5] was employed, consisting of a silvered Dewar flask closed by a stopper through which were introduced a Beckmann thermometer, an ordinary mercury thermometer, a propeller stirrer, and a manganin coil heater. The calorimeter was almost completely immersed in a bath capable of maintaining the temperature within ±1° of the temperature of the calorimeter. The heat input was measured electrically as described in Weissberger,[6] and the time was measured by means of a stop watch.

The duration of the run was chosen to give approximately a one-degree rise in temperature. For ease of calculation and uniformity of conditions, two-minute runs were used in the determinations on both of the compounds. This time was of necessity increased to three minutes when water was used in the calibration of the calorimeter.

Due to the extremely small thermal head between calorimeter and bath, the conduction, convection and radiation losses were assumed to be negligible. In order, however, to correct for possible evaporation losses and to determine which portion of the heat input was utilized in the resultant temperature rise, a plot of calorimeter temperature *versus* time was made for each run. The corrected temperature rise was then obtained by the linear extrapolation of the temperature observations which constituted the "fore" and "after" periods, to the time when the temperature of the calorimeter was equal to the average of the values at the start and finish of the reaction period.[7]

The average values of the specific heats obtained by the method described are as follows

Compound	Temp., °C.	Specific heat, C_p cal./g.-degree
Acetaldehyde	0	0.522 ± 0.004
Acetaldehyde dibutyl acetal	25	.483 ± .004
	40	.484 ± .004
	60	.498 ± .005
	80	.513 ± .005

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[3] N. H. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 238 (1939).

[4] E. W. Washburn, ed., "International Critical Tables," Vol. 5, McGraw-Hill Co., New York, N. Y., 1929, p. 108.

[5] A. Weissberger, ed., "Physical Methods of Organic Chemistry," Vol. 1, Interscience Publishing Co., New York, N. Y., 1945, p. 365.

[6] Ref. 3, p. 330–332.

[7] Ref. 3, pp. 337–340.

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Recognition of Solid Solutions

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It has not generally been recognized that a complication of solid solution formation during determination of the amount of impurity by a study of melting point can frequently be detected from calorimetric melting point data on a single sample of a compound.

In the evaluation of the purity of samples used in calorimetric third law studies, Johnston and Giauque[1] pointed out that there were two ways in which the impurity might be determined. First, it is possible to determine purity from the melting point depression. Second, purity may be calculated from "premelting heat capacity." When the impurity is ideally liquid-soluble and solid-insoluble, the results of calculation by the two methods should agree. In fact, when the amount of impurity calculated from melting point depressions and from premelting heat capacities agree it may be considered as sufficient proof of the ideality of the solutions and the solid insolubility of the impurity.

A consideration of the shape of the heat-capacity-temperature curve for an ideal homogeneous solid solution near the fusion region shows that the heat capacity will break sharply at the beginning of fusion (solidus point) rather than gradually increase as in the case where no solid solution forms and the composition is far removed from that of the eutectic. Therefore, when solid solutions are studied calorimetrically in the fusion region, it will be found that the mole per cent. of impurity calculated from "premelting" heat ca-

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[1] Johnston and Giauque, This Journal, **51**, 3194 (1929).